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Chapter 6

Investigation of Sorption and Separation of Lanthanides on the Ion Exchangers of Various Types

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Additional information is available at the end of the chapter

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1. Introduction

Rare earth elements of high purity play a significant role in many areas of contemporary techniques. They also have many scientific applications. For example, their compounds are used as catalysts in the production of petroleum and synthetic products, lanthanides are used in lamps, lasers, magnets, phosphors, motion picture projectors, and X-ray intensifying screens. The addition of the pyrophoric mixed rare-earth alloy called Mischmetal or lanthanide silicates improves the strength and workability of low alloy steels. Therefore, the preparation of high purity rare earth elements is very important for such technologies.

Mainly cation exchangers and elution by complexing agents are used for separation of rare earth elements using ion exchange methods. In this process the order of elution of individual rare earth(III) elements depends on the values of stability constants of formed complexes. They generally increase from light lanthanides(III) to heavy lanthanides(III). Ion exchange of rare earth elements in the presence of chelating ligands on anion exchangers is still a poorly studied field. However, the papers published during the last few years show particular applicability of anion exchangers to this end. The anion exchangers have been used so far for separation of thorium(IV) and uranium(IV,VI) from lanthanides(III) with mineral acid solutions and for the studies of chromatographic separation of rare earth(III) elements. As for isotopes of these elements separation processes were mainly of analytical or physicochemical character. For separation of rare earth elements the impregnating resins are also used.

In separation of rare earth(III) element complexes with chelating organic ligands strongly basic, gel polystyrene anion exchangers of quaternary ammonium groups proved to be the most effective. The research carried out dealt mainly with application of such complexing

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agents as: ethylenediaminetetraacetic acid (EDTA), iminodiacetic acid (IDA), N′-(2-hydroxoethyl)ethylenediamine-N,N,N′-triacetic acid (HEDTA) and *trans*-1,2-cyklohexanediaminetetraacetic acid (CDTA) in lanthanides separation.

Particular attention is also paid to separation and removal of rare earth(III) elements nitrate complexes by means of frontal analysis from the polar organic solvent-H_2O-HNO_3 on anion exchangers of various types. The affinity series of rare earth(III) elements nitrate complexes depends on the kind of functional groups, kind of the skeleton, porosity of skeleton, cross linking degree of anion exchanger skeleton as well as kind and concentration of polar organic solvent, concentration of nitric acid, addition of another organic solvent and concentration of rare earth(III) elements.

In the paper the research on the applicability of different types of anion exchangers for the separation of rare earth elements in the presence of the complexing agents IDA, HEDTA and CDTA will be presented. The effect of the addition of a polar organic solvent (methanol, ethanol, acetone, 1-propanol, 2-propanol) on separation of rare earth(III) elements in such system will be also discussed. The examples of the removal of rare earth(III) elements nitrate complexes from the polar organic solvent-H_2O-HNO_3 will also be presented in detail.

2. Rare earth elements occurrence

The rare earth elements (REE) are an unusual group of metallic elements with unique properties: chemical, catalytic, magnetic, metallurgical and phosphorescent which consists of seventeen elements belonging to lanthanides. The lanthanide group includes rare earth elements with the atomic number (Z) from 57 to 71 which are: 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). Yttrium (Y) and scandium (Sc) belonging to the scandium subgroup are grouped with rare earth elements because of their similar physicochemical properties (Spedding & Daane, 1961; Powell, 1964; Gschneidner, 1981; Stasicka, 1990)

Generally, lanthanide elements with low atomic numbers are more abundant in the earth crust than those with high atomic numbers. Those with even atomic numbers are two to seven times more abundant than the adjacent lanthanides with odd atomic numbers. The lanthanide elements traditionally have been divided into two groups: the light rare earth elements group (LREEs) which contains elements from lanthanum to europium (Z from 57 to 63) and the heavy rare earth elements group (HREEs) which contains elements from gadolinium to lutetium (Z from 64 to 71). Although yttrium is the lightest rare earth element, it is usually grouped with the HREEs to which it is chemically and physically similar (Kumar, 1994; Robards et al. 1998; Moustafa & Abdelfattah, 2010).

The geochemical studies have revealed that rare earth elements are actually not rare at all. Rare earth elements as the lithophilous ones occur mainly as phosphates and silicates. Due to their chemical similarity, lanthanides occur side by side in the scattered form in about 200 own minerals or as admixtures in the minerals of other elements. They occur in the crust of the earth in higher concentrations than Bi, I and Ag. For example, cerium, which is the most

abundant and its average amount is equal to $6.0 \cdot 10^{-3}$% occurs in higher concentrations than Sn, Pb, Co and Mo. Thulium the least abundant of them ($4.8 \cdot 10^{-5}$%) is still more abundant than the platinum group metals (PGM). As for spread in the earth crust scandium occupies position 31 ($2.2 \cdot 10^{-3}$%) and occurs in higher concentrations than Pb, Cu and Ag, whereas the average content of yttrium is $3.3 \cdot 10^{-3}$%.

There are known abort 250 rare earth element minerals of which 10-20 are found to be useful and only 5 practically applicable. Over 90% of the world's economically recoverable rare earth elements are found in primary mineral deposits i.e. in bastnaesite ores which are located in China and at Mountain Pass in California (USA) (Fig.1). Monazite deposits in Australia, South Africa, China, Brazil, Malaysia, India and Russia are the second largest concentrations of rare earth elements. Concerns over radioactive hazards associated with monazites because of thorium presence and high costs associated with its disposal have nearly eliminated it as a rare earth element source in the USA. Additional rare earth elements reserves and resources are found in Colorado, Idaho, Montana, Missouri and Utah. HREEs dominate in the Quebec-Labrador (Strange Lake) and Northwest Territories (Thor Lake) areas of Canada. There are high-grade deposits in Bayan Obo, Inner Mongolia, China and lower-grade deposits in South China provinces providing a major source of the HREEs. The areas considered to be attractive for rare earth elements development include also Karonga, Burundi and Wigu Hill in Southern Tanzania.



1 Mountain Pass, USA; 2 Pajarito Mountain, USA; 3 Gallinas Mountains, USA; 4 Iron Hill, USA; 5 Bald Mountain, USA; 6 Bear Lodge, USA; 7 Pea Ridge, USA; 8 Green Cove Springs, USA; 9 Carolina placers, USA; 10 Lemhi Pass, USA; 11 Snowbird, USA; 12 Rock Canyon Creek, Canada; 13 Hoidas Lake, Canada; 14 Thor Lake, Canada; 15 Elliot Lake, Canada; 16 Strange Lake, Canada; 17 IIimaussaq complex, Greenland; 18 Araxa, Brazil; 19. Barro do Itapirapua, Brazil; 20 Lovozero and Khibina complexes, Russia; 21 Tamazeght complex, Morocco; 22 Bou Naga, Mauritania; 23 Nile Delta and Rosetta, Egypt; 24 Etaner, Nambia; 25 Okorous, Namibia; 26 Steenkampskraal , South Africa; 27 Zandkopsdrif, South Africa; 28 Plinesberg Complex, South Africa; 29 Naboomspruit, South Africa; 30 Palabora, South Africa; 31 Richards Bay, South Africa; 32 Kangankunde, Malawi; 33 Congolone, Mozambique; 34 Karonge, Burundi; 35 Chavara, India; 36 Amba Dongar, India; 37 Orrisa, India; 38 Perak, Malaysia; 39 Maoniuping/Dalucao, China; 40 Bayan Obo, China; 41 Weishan, China; 42 Xunwu/Longnan, China; 43 Dong Pao, Vietnam; 44 Eneabba, Australia; 45 Jangardup, Australia; 46 Mount Weld, Australia; 47 Brockman, Australia; 48 Nolans Bore, Australia; 49 Mary Kathleen, Australia; 50 Olympic Dam, Australia; 51 WIM 150, Australia; 52 Dubbo Zirconia, Australia; 53 Fraser Island, Australia.

Figure 1. The rare earth deposits (http://www.bgs.ac.uk/research/highlights/2010 /rare _earth_elements.html).

As for their distribution in the environment and in living organisms it should be stressed that they are found, as mentioned above, in the earth crust in a relatively wide range (Hedrick, 1993; Hedrick, 1995). Moreover, they are found in the North Atlantic Ocean waters in very low concentrations. The predominant species are carbonates, such as $La_2(CO_3)_3$ with the concentration 0.002-0.005 ppb in the case of La(III), Ce(III) and Nd(III) and from 4 to 20 times less in the case of other lanthanides. The studies of the pathways of La(III), Ce(III), Th(IV) and Sm(III) from the soil to plants and farm animals show that sorption and soil abundance decrease in the following order: Ce(III) > La(III) > Th(IV) > Sm(III) (Linsalata, et al. 1986). The levels of lanthanides in healthy human tissues have been reported as follows: liver 0.005 μg/g of ash, kidney 0.002 μg/g, lung 0.004 μg/g, bones 0.2-1.0 μg/g (Goering, et al. 1991).

In the paper by Du & Graedel (2011) the first quantitative life cycles (for the year 2007) for ten rare earth elements: La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III) and Y(III) were presented. In the charts it was shown that after extraction from ores using different separation processes the mixed rare earth element concentrates are produced. Thereafter, they are separated from each other into individual rare earth element compounds (i.e., oxides, chlorides, fluorides). The compounds are converted into pure metals or alloys and further transformed into intermediate products. Purification of metals is by electrolysis or vacuum reduction. Production of alloys is either by direct co-reduction of the rare earth element compounds or by melting and casting of metals. The intermediate products are manufactured into final goods. When the products containing rare earth elements are discarded at the end-of-life (EOL), the quantity of rare earth element material in use is lost unless recycling occurs. The idea of generic scheme for the REE cycle is presented in Fig.2. Losses of rare earth elements occur at five points in the cycles: mining, separation, fabrication, manufacturing, and waste management. The authors also emphasize that recycling of rare earth elements is challenging and it appears possible for metallurgical applications, automobile catalysts, magnets in wind turbines and automobiles, in which REEs are used in fairly large quantities.

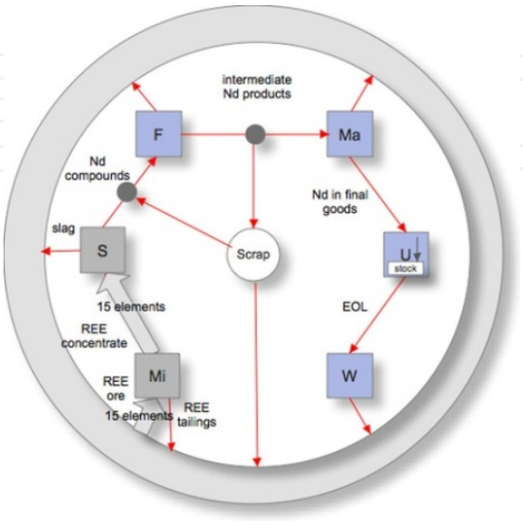


Figure 2. The generic scheme of REE cycle (Du & Graedel, 2011)

3. Rare earth elements – physicochemical properties

Lanthanides are characterized by great similarity with respect to chemical properties. This similarity is considered by approximate electron structure of exterior coating and ionic radii. Generally, the electron configuration of scandium, yttrium and lanthanum can be written as $(n\text{-}1)d^1ns^2$. The elements occurring after lanthanum do not develop the subcoating *5d* (except gadolinium and lutetium, which possess the electrons $5d^1$) but the subcoating *4f*. Considering lanthanides as *f*-electron elements, the configuration $4f^{1\text{-}14}5d^{0\text{-}1}6s^2$ can be ascribed to them. According to some authors also lanthanum can be considered as *f*-electron element (Charewicz, 1990).

The electrons reaching the subcoating *4f* do not affect significantly chemical properties of the elements with the increasing atomic number. All lanthanides have the same oxidation number +3. Passing into the three positive ions, the lanthanide atom loses *6s* electrons and one *5d* electron (if it possesses) or *4f* electron (in the case *5d* electron does not occur). Cerium, praseodymium and terbium as well as neodymium and dysprosium can also have the oxidation number +4 but samarium, europium and ytterbium the oxidation state +2. Also cerium, neodymium and thulium form low stability compounds with the oxidation number +2.

Passing from scandium to yttrium the atomic radius increases from 164.1 pm to 180.1 pm. Also the radius of the ions of the above mentioned elements increases with the oxidation number +3 (from 88.5 pm to 104 pm). In the case of lanthanides the situation is different. The number of electron coatings does not change with the increasing atomic number.

The effect of electrons reaching the *4f* subcoating on the atom size is small. An important factor is the increasing atomic number as well as increased attraction of valency electrons by the nuclei with its charge increase. This leads to the decrease of atomic and ionic radii. This phenomenon is called *lanthanide contraction.* The atomic radius decreases from 187.7 pm (for La) to 173.4 pm (for Lu) in the lanthanide series. Europium whose atomic radius is 204.2 pm and ytterbium of the radius 194.0 pm are the exceptions (Cotton, 2006).

The contraction phenomenon is characteristic of lanthanide ions with different oxidation numbers and it is the most evident for the ions Ln^{3+}. The ionic radius decreases more quickly from lanthanum to gadolinium reaching the value from 115 pm to 107.8 pm and more slowly from gadolinium to lutetium reaching the values: 106.3 pm for terbium, 105.2 pm for dysprosium, 104.1 pm for holmium, 103 pm for erbium, 102 pm for thulium, 100.8 pm for ytterbium and 100.1 pm for lutetium. In the case of gadolinium there occurs the so called *gadolinium break.*

4. Rare earth occurrence and the market

Consumption of rare earth elements in individual countries all over the world is the measure of their technological level and modernity. This is evidenced by concurrence of intensive development of production of many new materials and possession of rare earth

elements separation and purification technology. This is also reflected in the total number of papers registered in Chemical Abstracts of American Chemical Society (CA) which gradually increases (Fig.3). In 2007 the total number of papers in CA was around 1 million and the percentage of papers related with rare earths was about 3%.

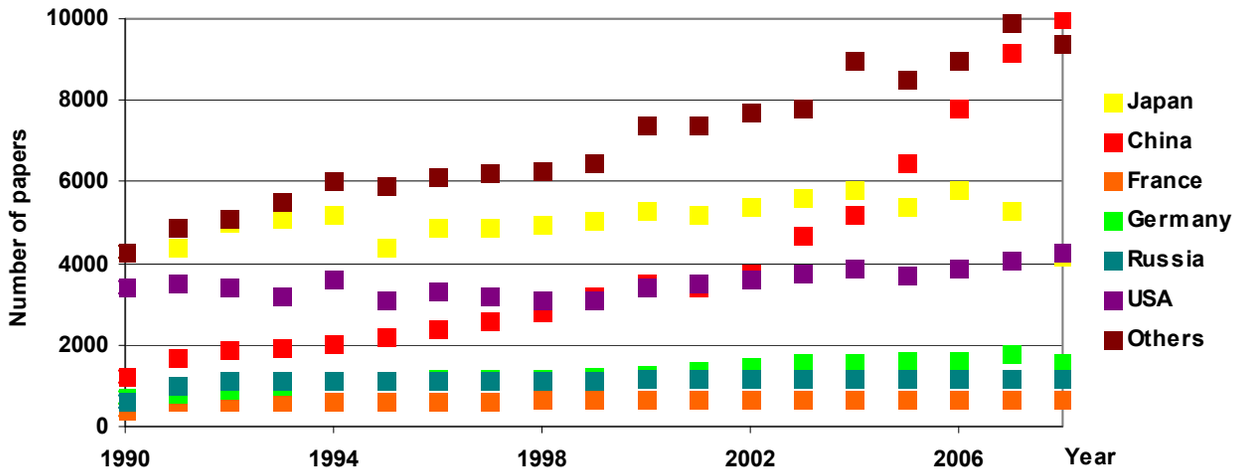


Figure 3. The number of papers related to rare earths in Chemical Abstracts of American Chemical Society (Adachi, et al. 2010).

As follows from Fig.3 there has been the high leap of increase of the number of Chinese papers and a sharp decline in the Japanese one since 2001 probably due to greater research funding and reforming of research organization systems in China such as the foundation of the State Key Laboratory of Rare Earth Materials and Application and the State Key Laboratory of Rare Earth Resource Utilization. According to Adachi et al. (2010) in 2008 in such fields of research as: separation, complexes, electrolysis, oxides, spectroscopy, RKKY interaction, Kondo effect, organometallics, magnet China, magnetism, crystal fields, superconductors, battery, hydrides, phosphors, capacitors, polishing agents, environment, recycling, catalysis and catalysts China is the leader in 16 of them (even in such sections as separation of rare earths, complexes, electrolysis, oxides and spectroscopy) and the growth is faster than in other countries (Fig.4a-d).

In recent few years China has contributed about 97% of the supply on the world market of rare earth elements, whereas according to the United States Geological Survey in 2009 the total resources were about 99 million tons of rare earth. In that China had about 37%, CIS (Commonwealth of Independence States-the former Soviet Union) had about 19% and USA about 13% (Fig.5).

This is reflected in a new supply risk index for chemical elements or element groups which are of economic value published by British Geological Survey (2011) (Table 1). The risk list highlights a group of elements where global production is concentrated in a few countries and which are at risk of supply disruption. On it rare earths (risk index 8.0, fifth position), antimony, platinum group metals, mercury, tungsten and niobium are included. The list also shows the current importance of China in production of many metals and minerals.

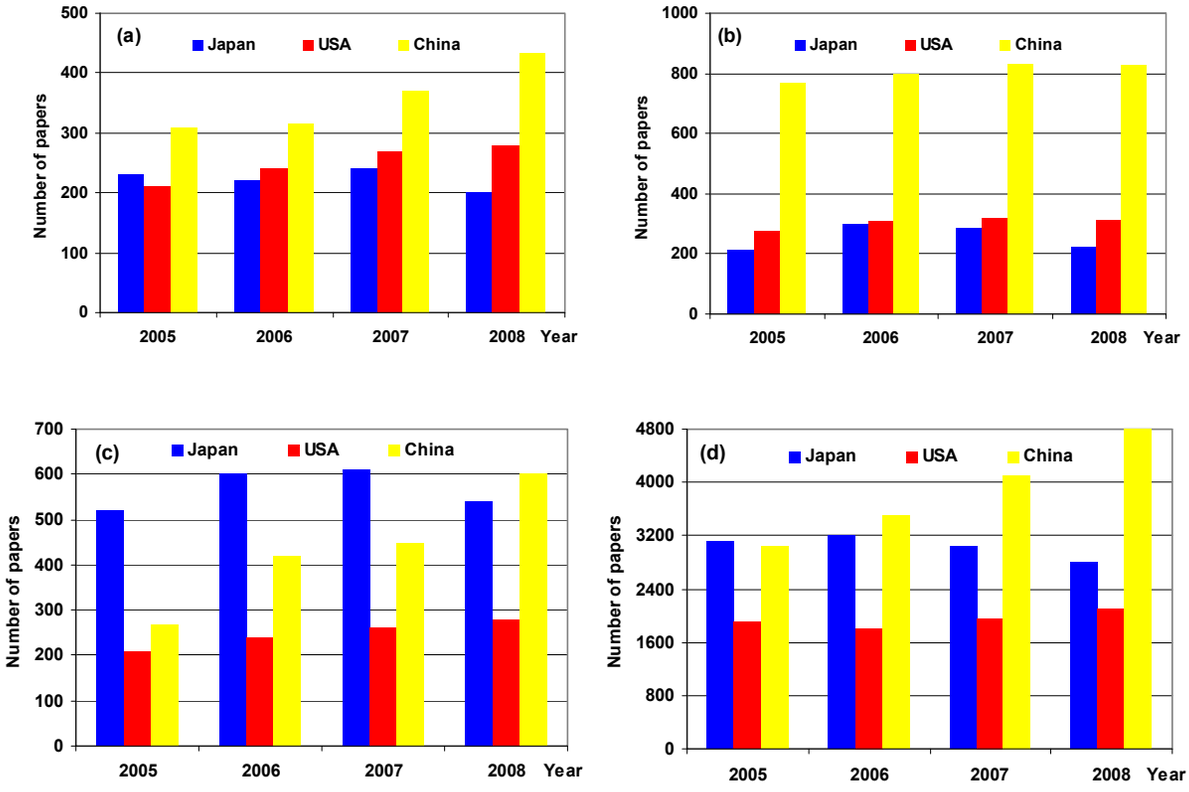


Figure 4. The number of papers related to (a) separation, (b) complexes, (c) electrolysis and (d) oxides of REEs published by Japan, USA and China (Adachi, et al. 2010).

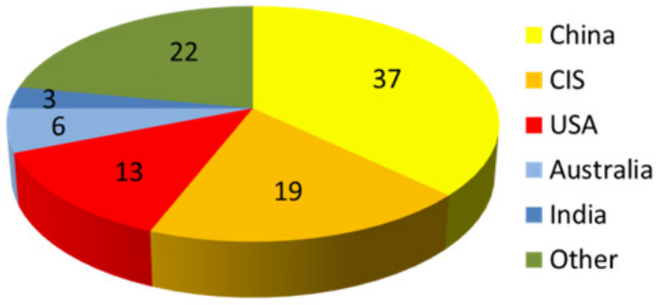


Figure 5. The global reserves of REEs (2009) (US Geological Survey, USGS).

Element or element group	**Symbol**	**Risk index**	**Leading producer**
antimony	Sb	8.5	China
platinum group elements	PGE	8.5	South Africa
mercury	Hg	8.5	China
tungsten	W	8.5	China
rare earth elements	REEs	8.0	China
niobium	Nb	8.0	Brazil

Table 1. The risk index for chemical element group which are of economic value.

It should be mentioned that the rare earth elements resources were discovered by the Chinese scientists in Bayan Obo (Inner Mongolia) in 1927. The rare earth elements production started in 1957. At present, among 21 of Chinese Provinces and Autonomous Regions possessing rare earth elements resources (Fujian, Gansu, Guangdong, Guangxi, Guizhou, Hainan, Henan, Hubei, Hunan, Jiangxi, Jilin, Liaoning, Nei Mongol, Qinghai, Shaanxi, Shandong, Shanxi, Sichuan, Xinjiang, Yunnan, and Zhejiang) the most important are *Fujian, Guangdong, Jiangxi, Sichuan and Nei Mongol Autonomous Region.*

Among North American companies with combined resources of $ 52.7 billion the following should be mentioned: *Molycorp Inc., Avalon Rare Metals Ltd., Quest Rare Minerals Ltd.* and *Rare Element Resources Ltd.*

From the mid-1960s to the 1980s, Molycorp's Mountain Pass mine was the world's dominant source of rare earth oxides. In 2002 they ceased production and in 2008 resumed it based on rare earth oxides from stockpiled concentrates derived from the rare earth ore that was previously mined at Mountain Pass. Since that they have been testing the innovative new processes on a commercial scale. Three facilities e.g. Molycorp Mountain Pass (Califorina), Molycorp Sillamae (Estonia) and Molycorp Tolleson (Arizona) produced 5,000 tons in 2011 and currently have been predicted to reach 8,000-10,000 tons in 2012. *Avalon Rare Metals Ltd.* from Canada it is a mineral developmentcompany with a primary focus on the rare metals and minerals at (Thor Lake, Ontario) which has one of the highest concentrations of heavy rare earth oxides (HREOs) in the world with 26.1% of their 4.298 million tons of total rare earth oxides (TREO) composed of more expensive HREOs. Moreover, *Quest Rare Minerals Ltd.,* Canadian based the exploration company focused on the identification and discovery of new world class rare earth deposit opportunities. Their 'Strange Lake' project in Northern Quebec is believed to hold at least 2.1 million tons of TREOs in their important new rare earth elements mineralized zone named the B Zone, of which 39% is estimated to be HREOs. They expect to start production in mid-2015 to 2016, with the output initially expected to be 12,000 tons of REO/yr. On the other hand, *Rare Element Resources Ltd.* the core project 'Bear Lodge' is believed to be one of the richest LREO deposits in the USA. And with the company expecting to begin production in 2015, with an anticipated output of 11,400 tons of REO/yr, it could be well-positioned to meet growth in demand for LREOs.

The advanced stage projects of rare earth elements production in 2012 and 2013 are also proposed by Lynas Corporation Ltd. (Mt. Weld, West Australia) based on the richest known deposit of rare earth elements in the world, and a state-of-the-art Rare Earths processing plant, the Lynas Advanced Materials Plant (LAMP), currently under construction near Kuantan (Pahang, Malaysia). At the spearhead there are also Silmet (Estonian Republic) which is one of the biggest rare metal and rare earth metal producers in Europe.

In Poland rare earth elements resources do not occur (Charewicz 1990; Paulo, 1993; Paulo 1999). Since 1987 the apatite concentrates from the deposits of Chibiński Massif on Kola Peninsula have been imported to Poland as phosphorous raw material. Apatite deposits contain about 1% of REO. Therefore, the secondary resources of rare earth elements are in

the form of phosphogypsum dump in the area of the former Chemical Plant 'Wizów' near Bolesławiec. In 1948 the firm was set up as a producer of sulphric acid. In 1969 -1979 it started to produce phosphoric acid and then phosphoric salts. Up to the 80s the plant was only producer of tripolyphosphate. In its area there is localized a dump of phosphogypsum including mainly calcium sulphate(VI) originating from the extraction of phosphoric acid (obtained from the apatite raw material) and on the average 0.5% of rare earth element oxides. At present over 5 million tons of the waste are found in the dump.

Despite the fact the Chinese resources are estimated to be 37% (Fig.5), due to intensive promotion of their exploitation and large expenditure of money on investigations, at present China is a monopolist imposing the prices of these elements. The latest policy of China – decrease of export by 40% and temporary ban of export to Japan is reflected in an immediate rise in raw materials prices (Fig.6).

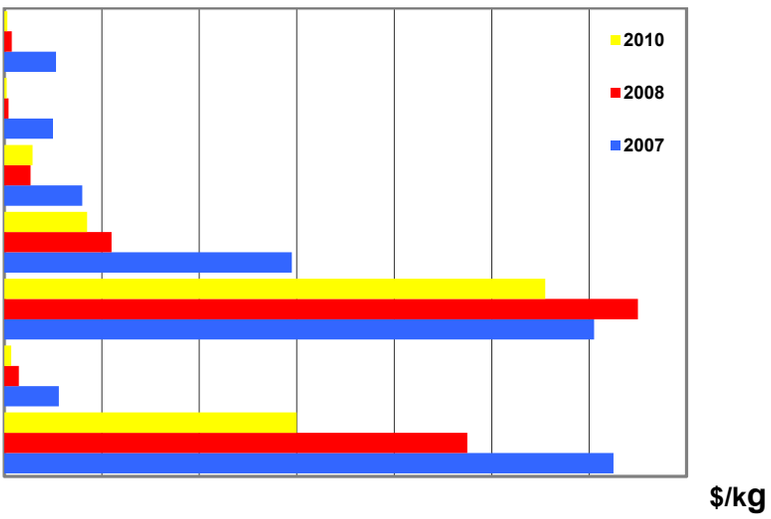


Figure 6. REO prices from 2007 to 2010 (Congressional Research Service report).

High prices mostly affected HREO. The price of terbium oxide used in production of hybrid cars or solar systems increased from $600 in the end of 2010 to $ 3200 for a kilogram at the beginning of 2011. As follows from the data of the firm Shanghai Metals Market, despite over 20% decrease in the prices in the end of 2011, temporary stoppage of production by the largest Chinese firms (among others, Inner Mongolia Baotou Steel Rare-Earth, Hi-Tech Co.) is to stabilize the market and prevent from further drop in prices. According to the China authorities the high cost of mining is connected with huge environmental cost of rare earth processing. On one hand, the mining of rare earths causes the erosion of land and water, on the other, the emission after the mining further damages the environment. Additionally, the China government will not approve of any new rare earth separation projects before 2015. To protect rare earth resources, rare earth producers will be required to have a minimum mine output capacity of 300,000 tons/yr of ore for light rare earths and 3,000 tons/yr (REO) for ion adsorption rare earths. The Chinese government will ban monazite mining if the monazite contains radioactive elements. For rare-earth separation, producers will be required to have a separation output capacity of 8,000 tons/yr (REO) of mixed rare earths, 5,000 tons/yr (REO) of bastnaesite, and 3,000 tons/yr (REO) of ion-adsorption rare earths.

Metal smelting producers must have an output capacity of 1,500 tons/yr. Rare earth producers will be required to meet the environmental emission standards; otherwise, they will be shut down (China Ministry of Environmental Protection, 2011; Tse, 2011). Therefore, the countries, which are potential miners of rare earth elements start to search for their deposits and exploitation. For example, based on the released data from USGS (2010) there is an interesting situation concerning rare earth elements sources from Brazil.

5. Application of rare earth elements

The rare earth elements export reduction introduced by China in 2009 caused anxiety among many world economies including the largest ones as these in the USA or Japan. The USA from being self-reliant in domestically produced rare earth elements over past 15 years became 100% reliant on imports, primary from China. Japan-based firms and the Japanese government made a number of joint venture agreements and potential partnerships around the world to secure supplies of rare earth elements (Sumitomo Corp. and Kazakhstan National Mining Co.; Toyota Tsusho and Sojitz with Vietnam's Dong Pao to produce LREEs, Japan's JOGMEC had also decided to seek investments in Australia's Lynas Corporation).

As follows from the market analysis for several years the exploitation of rare earth elements has been on the same level but the demand for rare earth element compounds has been growing. The total demand for rare earth elements is expected to grow from 128,000 tons in 2011 to 170,000 tons by 2015 and to 255,000 tons in 2020 and a growth rate of about 7-10%/yr is estimated according to the data presented in Table 2. According to the Chinese Rare Earth Industry Association the global demand for rare earth elements may even reach 210,000 tons/yr. However, the Industrial Minerals Company of Australia (IMCOA) estimates that the demand will be 185,000 tons in 2015. China's output may reach 140,000 tons/yr in 2015 as China's annual demand is estimated to rise from 73,000 tons. Such great demand for rare earth elements results mainly from their potential application in many fields of human life (Bünzli et al., 2007).

Application	Growth rate [% p.a.]	Demand in 2015 [tones]
Catalysts	0	25,500
Glass additive	0	10,000
Polishing powder	5-10	23-30,000
Metal alloys	4-8	36-40,000
Permanent magnets	10-15	40-45,000
Phosphors and pigments	4-8	13-15,000
Ceramics	5-8	9-10,000
Other	8-12	12-14,000
Total	**7-10**	**170-190,000**

Table 2. Probable total demand for REE in 2015.

Rare earth elements find application in many advanced materials such as high performance magnets ($Nd_2Fe_{14}B$ and $SmCo_5$, Sm_2Co_{17}) which revolutionized technology by miniaturization of hard disc drives, in fluorescent materials, chemical sensors, high temperature superconductors, magnetoptical discs and rechargeable nickel-metal hybride batteries (NiMH). The alloy used for the battery's positive pole consists of rare earth metals and this makes up 26%of the weight of the battery. Taking into account consumer products they are used in TVs, computer hard drives, plasma and LCD screens, laptop computers, cell phones, DVD players, cameras, electric motors and generators of hybrid cars (Nd-Fe-B magnets and La batteries). For example, in Toyota Prius, Chevy Volt, Nissan Leaf etc. motors and generators of hybrid auto use approximately 25-27 kilograms of rare earth elements and only Toyota plans to sell 1 million of these cars till the end of 2012. In cars, rare earth elements are also used in fuel injectors, airbags and seat belt sensors, anti-lock brakes, power steering and seat adjustment motors and even in the fuel and car catalytic converters (Kucharczyk & Zabrzeski, 2001). The next example, are new wind turbines that are 70% more efficient than the standard ones. However, each requires about two tons of rare earth magnets (Nd-Fe-B magnets). The wind power industry is experiencing explosive growth. The Chinese have spent $150 billion and they plan to install 330 GW of the additional wind powers in the next 10 years. This would require about three times the world's total annual production and as follows from the World Wind Energy Report projects, the global wind power capacity will grow by almost four times in the next 10 years. Rare earth elements are also used in catalysts that can increase the capacity of refinery equipment up to 30% and gasoline production by 5% (in the USA that is additionally 18 million gallons of production per day), commercial air conditioners, medical magnetic resonance imaging equipment, for peptide preparation as well as microfertilizers that can increase certain crop yields by 15% etc (Chegwidden & Kingsnorth, 2002; Xu et al. 2002; O'Driscoll, 2003; Fricker, 2006; Li et al. 2010).

The main groups of rare earth elements application are presented in Fig. 7.

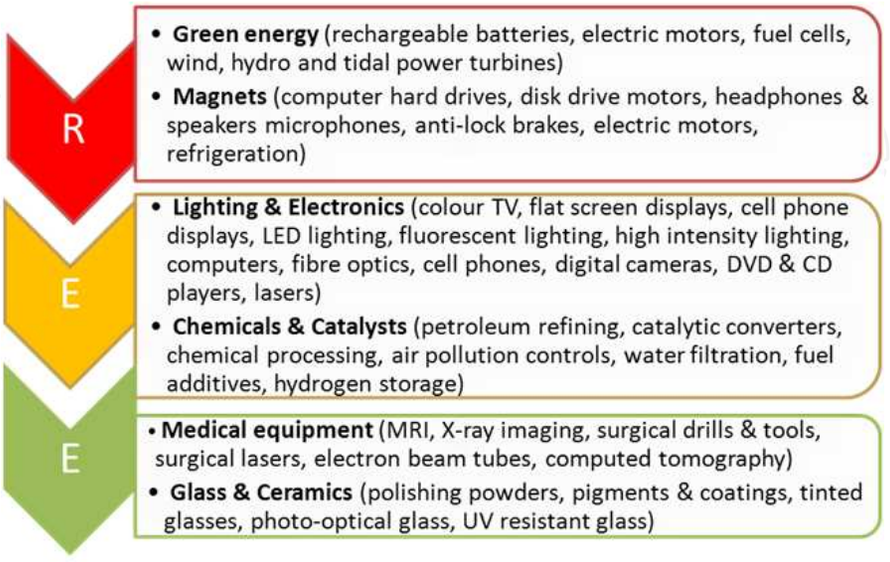


Figure 7. The uses of REEs.

6. Separation of rare earth elements

Lanthanides separation and preconcentration of high purity compounds is one of the most difficult problems in inorganic chemistry as it makes use of the subtle differences between the physicochemical properties of these elements and their compounds like solubility, basicity, volatility and possibility of occurrence with different oxidation numbers (Kowalczyk & Mazanek, 1990; Jimenez-Reyes, 1993; Uda et al. 2000).

Most frequently used methods in the separation of rare earth elements are - fractional crystallization, selective precipitation, oxidation-reduction methods, ion exchange and liquid-liquid extraction. As the rare earth ions can be substituted for readily in crystal lattices and the most precipitates consist of crystals of almost the same rare earth mixture, the fractional precipitation is used for the nitrate(V), suphate(VI) and bromate solutions. However, fractional separation for adjacent heavy rare earths is extremely slow and tedious. If the lanthanides are differentiated in terms of their atomic number, their separation is simplified. It takes only a few partial precipitations, for example, to obtain a lanthanum–cerium–praseodymium fraction completely free of erbium, thulium, ytterbium, and lutetium. The separation of La(III) and Ce(IV) is even easier. In this case only a few fractions should be enough for their separation. Consequently, fractional precipitation is used in operations of rare earth concentrate pre-treatment and pure lanthanum and cerium compounds have been commercially available for many years (Nash, 1994).

The method of crystallization of phosphorus containing lanthanides at a temperature of 150-200 ^{o}C depends on the acid concentration. This type of technology is used in the processing of apatites. The phosphate type mineral, apatite used in the production of phosphoric acid has rare earth oxide content between 0.4 and 0.9%. There are two main types of processing of apatites to phosphoric acid and fertilizers based on the decomposition of raw material with nitric(V) or sulphuric(VI) acids. In terms of recovery of rare earth elements favourable conditions occur during apatite dissolution in nitric(V) acid because this method provides a quantitative transition of lanthanides to liquid phase containing phosphoric(V) and nitric(V) acids as well as calcium nitrate(V). The concentration of lanthanide in this method can be up to 0.5% Ln_2O_3 in solution. However, with the continuous precipitation method to separate Ln(III) ions high concentrations of Ca(II) ions will result in their co-precipitation.

It should be also mentioned that in the case of application of sulphuric(VI) acid, depending on temperature, acid concentration, the ratio of the liquid phase to the solid phase as well as the phase contact time $CaSO_4 \cdot 2H_2O$, $CaSO_4 \cdot 0{,}5H_2O$ or $CaSO_4$ are obtained as byproducts. The concentration of lanthanides in phosphoric(V) acid is equal to 0.1%, while in the phosphogypsum exceeds 0.3%. One method of further processing consists in combining the process of hydration of $CaSO_4 \cdot 0{,}5H_2O$ to $CaSO_4 \cdot 2H_2O$ with the simultaneous process of lanthanides extraction using e.g. D2EHPA. Also application of resin in the leaching (RIL) process instead of solvent extraction eliminates the need for a costly solid/liquid separation unit operation (Padayachee et al. 1996). The authors found that hydrocycloning gypsum to concentrate the leachable rare earth elements into a smaller and finer particle size mass fraction resulted in the increasing rare earth elements concentration from about 2500 g/kg to about 9000 g/kg. Additionally, the application of ion exchange resins such as

aminophosphonic Duolite ES-467 and sulphonic Duolite C 20MB to extract rare earth elements from the cyclone gypsum shifted the equilibrium reaction and allowed to increase their leaching efficiency up to five times. The technology developed by the Institute of Chemistry and Inorganic Technology of the University of Technology in Cracow (Poland) eliminates the storage of phosphogypsum, by processing prostproduction wastes and stocks into commercial products: anhydrous calcium sulphate (anhydrite) and rare earth metal oxide concentrates of the content up to 99% recalculated into La_2O_3 (Kowalczyk & Mazanek, 1987; Kowalczyk & Mazanek, 1990). The resulting product, which is a building material, maintains parameters of the cement anhydrite produced from natural materials, and other parameters (such as strength or white colour). The resulting anhydrite, among others, can be applied for producing self-leveling floor screeds, fully meeting all requirements of this type of materials. This technology was tested on the experimental scale processing with 1ton/h phosphogypsum. The technology allows for the elimination of phosphogypsum storage and elimination of the existing waste dumps of phosphogypsum (Kowalski et al. 2006).

7. Cation exchange

Ion exchange separation of rare earth elements was initiated by Spedding and Powell to separate fission products obtained from nuclear reactors (Spedding et al. 1956; Powell, 1961, 1964). For several years the cation exchange was the primary method used to obtain individual lanthanides(III). In previous years and at present the development of extraction methods for separation of rare earth elements(III) 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 [Preston 1996; Preston et all, 1996].

In the process of cation exchange separation of rare earth elements(III) the polystyrene-sulphonic cation exchangers are most often used and rare earth cations are exchanged with H^+, ammonium ion or other cations derived from the ion exchange phase. The 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 the hydration.

In the lanthanide(III) group with the increasing atomic number decrease of the ionic radius is observed. However, due to similar values of ionic radii of individual lanthanide(III) ions there are not significant differences in their affinity for the polystyrene cation exchangers. Therefore, attempts to obtain individual rare earth elements from the solutions of mineral acids (HCl, HBr, HNO_3 and H_2SO_4) did not yield positive results (Nelson et al. 1964; Korkish, 1967; Korkish & Ahluwalia, 1967). HCl and HNO_3 can be used for the separation of lanthanide(III) from other metal ions occurring in the lower oxidation states (Strelow & Bothma, 1964). This relationship is also used for the separation of cerium(IV) from other rare earth elements using nitric acid(V). Some improvement of the separation of rare earth elements(III) can be obtained by using mineral acid solutions containing organic solvents. In this case rare earth elements(III) are much harder sorbed on cation exchangers than using aqueous solutions of these acids (Starý, 1966).

Therefore, both on a laboratory scale and in industrial separations the elution technique is usually applied. The complexing agents used as eluents form complexes with rare earth elements with different values of stability constants. Separation of rare earth elements, without the introduction of a complexing agent is not possible due to small differences in the values of the separation coefficients. In the case of the complexation of cations by the anionic ligands cation exchanger prefers a cation which forms a complex anion with the lowest average number of ligands and in a series of analogous complexes the one which forms the weakest complex.

The effectiveness of rare earth elements(III) separation on cation exchangers using complexing agents as eluents depends on both the affinity of a given element for the cation exchanger as well as on the kind of complexing agent. As the affinity of rare earths(III) elements is similar to the cation exchanger, the order of elution depends on the stability constants of complexes of individual elements. Thus the separation rate depends on the ratio of stability constants of these complexes. In this group: aminopolycarboxylic acids (EDTA, NTA, HEDTA, DTPA, CDTA), carboxylic acids (acetic acid, malonic acid, maleic acid, phtalic acid), hyroxylicacids (α-hydroxyisobutyric acid, citric acid, lactic acid), ketoacids (pyruvic acid), aldehydeacids (glyoxilic acid), tioacids (tiodiglicolic acid), phosphonic (1-hydroxyethane-1,1-diphosphonic, HEDP) and aminophosphonic acids should be mentioned. The eluent selection and elution conditions are largely dependent on the composition of the mixture of separated rare earth elements.

Among eluents used in the process of cation exchange separation of rare earth elements EDTA and NTA were of the greatest industrial application. Stability constants of the formed complexes generally increase from light to heavy lanthanides(III) because lanthanides(III) are eluted in the order of decreasing atomic numbers. Y(III) location in the elution sequence changes with the change of stability constants of its complexes, therefore, is dependent on the type of eluent, for example, yttrium(III) elutes between Dy(III)-Tb(III) with 1% EDTA solution at pH 3.5, near Nd(III) with DTPA, near Pr(III) with HEDTA, near Eu(III) with citrate 10-20^{o} C and Dy(III)-Ho(III) with citrate at 87-100^{o} C, near Ho(III)-Dy(III) with lactate, near Dy(III)-Ho(III) with thiocyanate and between Sm(III)-Nd(III) with acetate (Powell, 1964).

The advantages of EDTA, in comparison with other complexing agents, are its high efficiency separation of adjacent pairs of rare earth elements(III) with the exception of the pair Eu(III)-Gd(III) ($K_{Eu(III)}=2.24\cdot10^{17}$; $K_{Gd(III)}=2.34\cdot10^{17}$). The separation factors (β) of rare earth elements using EDTA are as follows: La(III)-Ce(III) 3.3; Ce(III)-Pr(III) 2.4; Pr(III)-Nd(III) 2.0; Nd(III)-Pm(III) 1.9; Pm(III)-Sm(III) 1.8; Sm(III)-Eu(III) 1.5; Eu(III)-Gd(III) 1.1; Gd(III)-Tb(III) 3.5; Tb(III)-Dy(III) 2.7; Dy(III)-Ho(III) 2.0; Ho(III)-Er(III) 2.0; Er(III)-Tm(III) 2.0; Tm(III)-Tb(III) 1.8 and Yb(III)-Lu(III) 1.6. EDTA is readily available, inexpensive and easy to regenerate. However, due to its low solubility elution can not be conducted in an acidic environment (pH <3) and on the cation exchanger in the hydrogen form. Using a solution of EDTA at higher pH values the separation process is carried out with a cupric-ion retaining bed. Of the ions proposed by Spedding, Krumholz and Powell the most relevant retaining ions are Cu(II) and Zn(II) (Spedding et al. 1956; Powell, 1961).

The elution can be carried out even at elevated temperatures, which creates the possibility of recovery of EDTA and increases the separation factor of the Gd(III)-Eu(III) and Eu(III)-Sm(III) pairs (Powell & Burkholder, 1967). The partial complexation method proved to be advantageous for obtaining concentrated heavy lanthanides(III) as well as for separation of lanthanum(III) from other rare earth elements(III). NTA as EDTA is available, although it is more expensive (Fitch et al. 1951, Courtney et al. 1958; Mąkowska, 1970).

Of the group of salts of aminopolycarboxylic acids used as eluents in the process of cation exchange separation of rare earth elements(III), HEDTA proved to be effective for the separation of light and heavy lanthanides(III) (exhibits high separation efficiency of a mixture containing Er(III), Tm(III), Yb(III) and Lu(III)) and for the separation of La(III) from other rare earth elements(III). However, it is completely useless for the separation of medium lanthanides (from Sm(III) to Ho(III)) (Powell, 1961). In the case of separation of rare earth elements(III) with the buffered solution of HEDTA on the cation exchanger Dowex 50 there was reported over 7-fold reduction of the number of theoretical plates with the reduction in the degree of cross linking of the cation exchanger (from 12% to 2% DVB DVB). In this system, the decrease of the number of theoretical plates as a result of the addition of neutral salt solution such as LiCl, NaCl or KCl to the eluent and with the increasing concentration of these salts (Merciny & Duyckaerts, 1966). However, so far, there has not been theoretical explanation of this phenomenon.

The other complexing agent - DTPA proved to be particularly useful for the separation of Y(III) from heavy lanthanides(III), since in a elution series with DTPA Y(III)occupies a position near the Nd(III) (Hale & Hammer, 1972). Of the group of carboxylic acids (acetic, malonic, maleic, phthalic acid) ammonium acetate is the cheapest and easily regenerated complexing agent. Elution using ammonium acetate gives good results in the separation of light lanthanides(III), yttrium(III) from the light and medium lanthanides(III). The best effects of separation were achieved using a solution of ammonium acetate at pH 6.8-6.9 and the gradient concentration 0.45-1.0 M. Yttrium(III) in the elution series occupies a position between Nd(III) and Sm(III).

In the group of hydroxyacids (α-hydroxyisobutiric (α-HIBA), citric and lactic acids) used as eluents, of significant importance are α-hydroxyisobutiric and α-hydroxy-2-methtlbutiric acids (Faris, 1967). α-HIBA is one of the most favourable eluents in this group. In comparison to citric or lactic acids, using α-HIBA high rates of separation of neighbouring pairs of rare earth elements(III) were achieved (Smith & Hoffman, 1956; Choppin & Chopoorian, 1961). This also gives good results of separation of Gd(III)-Eu(III) pair (Hubicka & Hubicki, 1982). The eluent can be applied at room temperature using the ion exchangers of low cross linking, such as Dowex 50x4 and Dowex 50x8 (Smith & Hoffman, 1956). It should be mentioned that α-hydroxyisobutiric acid is not used to on a commercial scale. The most favourable ion exchange separation of lanthanides(III), compared to the α-HIBA can be achieved using 2-hydroxy-2-methylbutyric acid.

As eluents of rare earth elements also other complexing agents such as pyruvic, glyoxylic and thiodiglycolic and 1-hydroxyethane-1,1-diphosphonic as well as aminophosphonic

acids were used (Jegorov & Makarova, 1971; Hubicka & Hubicki, 1983a; Hubicka & Hubicki, 1983b).

Of them, special attention should be paid to pyruvic acid (Hubicka & Hubicki, 1983a; Hubicka & Hubicki, 1983b). The pyruvic acid solutions at the concentration 0.15-0.4 M at pH 3.5 and 5.0 proved to be useful for separating such pairs of elements as Y(III)-Nd(III), Sm(III)-Nd(III) as well as for separation of lanthanum(III) from other light lanthanides(III), yttrium(III) from heavy lanthanides using the cation exchanger Wofatit KPS with 4 and 8% DVB. Using pyruvic acid the elution of rare earth elements proceeds in the order of decreasing atomic numbers. Yttrium becomes similar to the medium lanthanides(III).

In the case of thiodiglycolic acid application for the separation of rare earth elements, the unusual position of Y(III) in the elution series can be seen. It can be as follows: Sm(III), Eu(III), Gd(III), Nd(III), Pr(III), Dy(III), Ho(III), Er(III), Yb(III), Lu(III), Y(III), La(III). Yttrium(III) elutes after heavy lanthanides, which enables its separation from Dy(III). The thiodiglycolic acid solution at the concentration 0.15 M and pH 5.5 can be applied for the separation of Y(III) from Nd(III); Sm(III) from light lanthanides(III) and Y(III) as well as Y(III) from Sm(III), Eu(III) and Gd(III).

Using α-hydroxoethylideno-1,1-diphosphonic acid proved that Y(III) behaves as a medium lanthanide(III) and can be separated from heavy lanthanides(III) (especially from Lu(III), Yb(III) and Tm(III)) as well as from Nd(III) (Hubicka & Hubicki, 1980). Availability and low price of this acid also provides an opportunity to use it as an eluent in the purification process of lanthanum(III).

The disadvantage of ion exchange separation of mixtures of rare earth elements on the polystyrene-sulphonic cation exchangers is the lack of universal eluent, which would allow for selective separation of light, medium and heavy lanthanides(III) as well as to achieve high concentrations in the eluate.

8. Anion exchange

In the separation and preparation of rare earth elements with a high degree of purity and separation of macro quantities from micro quantities practical application of anion exchangers to this end took place much later than that of cation exchangers because the mechanism of the processes involved in anion exchangers was more complex and for a long time was not fully explained.

Rare earth elements(III) show little tendency to form anionic complexes with simple inorganic ligands and are poorly sorbed on the anion exchangers from aqueous solutions of hydrochloric and nitric(V) acids. They are also weakly sorbed from sulphuric(VI), phosphoric(V) and mixture of hydrochloric and hydrofluoric acid solutions (Jegorov & Makarova, 1971). Much better results of rare earth elements(III) sorption were obtained from the solutions of such salts as chlorides, nitrates(III), nitrates(V), sulphates(IV), sulphates(VI), thiocyanates, thiosulphates and carbonates (Marcus & Nelson, 1959), which for the chloride system was interpreted by HCl_2^- formation which as a stronger anion than

HCl acid has greater affinity for the anion exchanger than Cl^- ion (Minczewski et al. 1982). It was also shown that using the gradient elution of 6-3 M LiCl solutions at 351 K the separated elements are eluted in the order: Cs(I), Ba(II), Yb(III), Eu(III), Sm(III), Nd(III), Pr(III), Ce(III), La(III). For 3 M solution of $Mg(NO_3)_2$ there was obtained the analogous elution series: Gd(III), Eu(III), Sm(III), Nd(III), Pr(III), Ce(III), La(III) and the heavy lanthanides are poorly separated.

In practice, the anion exchangers were therefore used only for the separation of thorium(IV) and uranium(IV, VI) from rare earth elements(III) from the solutions of mineral acids (Buddery et al. 1959; Marhol, 1982). Thorium(IV) in the nitric(V) acid and uranium(VI) in hydrochloric acid medium form stable, anionic complexes and therefore their separation from rare earth elements(III) forming less stable, cationic, neutral or anionic complexes is possible. Using 7 M HNO_3 solution selective separation of thorium(IV) from rare earth elements(III) was achieved (Danon, 1960).

Significant improvement in the sorption and separation processes of nitrate(V) complexes of rare earth elements(III), due to higher rates of separation, may be obtained by the addition of methanol to the aqueous solution of nitric(V) acid (Stewart & Faris, 1956, Faris & Wharton, 1962). A similar role is also played by higher order alcohols, derivatives of ethylene glycol, dioxane, acetone and tetrahydrofurane.

In the case of such eluents as bufforic solutions of citric and α-hydroxyisobutiric acids rare earth elements from strongly basic anion exchangers are eluted in the reverse order than in the case of their elution from the cation exchangers: La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III), Lu(III). Yttrium(III) occupies the position near dysprosium(III).

The studies begun by Dybczyński (Minczewski & Dybczyński, 1962a; Minczewski & Dybczyński, 1962b) on application of complexing agents from the group of aminopolycarboxylic acids (EDTA, CDTA) for the micro quantities of rare earth elements separation reveal that their separation mechanism depends on the factors affecting differentiated anion exchange affinity in the studied system.

Determined by Dybczyński for radioactive indicators the order of elution of rare earth elements(III) using EDTA from the strongly basic anion exchanger Dowex 1x4 in the EDTA form is as follows: Lu(III), Yb(III), Tm(III), Sc(III), Er(III), Y(III), Ho(III), La(III), Dy(III), Ce(III), Tb(III), Pr(III), Nd(III), Gd(III), Pm(III), Eu(III), Sm(III). While the elution order for radioactive indicators of rare earth elements(III) with CDTA from the same anion exchanger in the CDTA form is as follows: Lu(III), Yb(III), Tm(III), Er(III), Y(III), Ho(III), Dy(III), Tb(III), Sc(III), La(III), Gd(III), Eu(III), Ce(III), Pr(III), Sm(III), Nd(III), Pm(III).

Selectivity coefficients of complexes of rare earth elements(III) with EDTA and CDTA in both systems initially grow with the increasing atomic number, pass through a maximum and then decrease (Dybczyński, 1964; Wódkiewicz & Dybczyński, 1968; Wódkiewicz & Dybczyński, 1972). The change of the maximum values of selectivity coefficients from the position of Sm(III) (when EDTA was used as the eluent) to the position of Pm(III) (when

CDTA was used as the eluent) can be conditioned by the necessity of the presence of metal ion with a larger ionic radius, in order to ensure optimal packing of ligands around the central ion. Selectivity coefficients of complexes of rare earth elements(III) with CDTA, in most cases, are lower than in the case of rare earth elements(III) complexes with EDTA. The higher values of the theoretical plates designated for the system with CDTA also demonstrated a less favorable kinetic reaction of ion exchange than in the case of EDTA.

It was also shown that not only the type of eluent used affects the quality of the separation of the above mentioned complexes of rare earth elements(III). In the selected chromatographic system, the values of the separation coefficients can also be modified by changes in temperature and the degree of cross linking of the anion exchanger (Dybczyński, 1964).

Increasing the temperature generally results in improvement of the kinetics of ion exchange (an increase of diffusion coefficients in the ion exchange phase and solution), which significantly reduces the height of the theoretical plates. The temperature rise also affects the selectivity coefficients and separation factors, for example for CDTA the selectivity coefficients increase with the increasing atomic number from La(III) to Pm(III) and then decrease with further increase in the atomic number. At higher temperatures they reach the maximum value for Nd(III). The order of elution of rare earth elements(III) at 365 K is thus as follows: Lu(III), Yb(III), Tm(III), Er(III), Y(III), Ho(III), Dy(III), Tb(III), Gd(III), La(III), Eu(III), Sm(III), Ce(III), Pm(III), Pr(III), Nd(III).

The temperature rise does not always lead to improvement of the separation process. Distribution coefficients and the values of the theoretical plates can either increase, decrease, or remain constant with the increasing temperature, depending on the system. For elution of rare earth elements(III) with EDTA on the anion exchanger Dowex 1x4 in the EDTA form, for some pairs of elements as, for example, Pm(III)-Eu(III) and La(III)-Tb(III) reverse of selectivity takes place (Minczewski et al. 1982).

Dybczyński (1970) examined the impact of the degree of cross linking of the anion exchanger Dowex 1 on the effectiveness of separation of rare earth elements(III). He stated that the separation coefficients generally increase on a regular basis with the increasing degree of cross linking. However, for the complexes $[Ln(edta)]^-$ the change in the degree of cross linking from 4 to 16% of DVB causes increase of the value of the theoretical plate up to two orders of magnitude. This has an important impact on the separation. Resolving power, which is good for anion exchange resins with the optimal degree of cross linking (4% DVB for Dowex 1 - which corresponds to the smallest value of the theoretical plate) is less than unity for the anion exchange resins with a high degree of cross linking. This is related to the exclusion of large ions from the anion exchange phase by the 'sieve effect'.

On the basis of the thermodynamic studies of the anion exchange process with application of EDTA and CDTA it was stated that the unusual and non-monotonic affinity of the rare earth elements(III) complexes with the above mentioned complexing agents is associated with differences in the structure of these complexes and therefore with their different hydration (Surls & Choppin, 1957).

It is not bound, as in the case of cation exchange, with different values of their stability constants. Sizes of complex ions such as $[Ln(edta)]^-$ and $[Ln(cdta)]^-$ do not change on a regular basis with the change of the central ion radius. On a regular basis, the degree of hydration of these ions does also not change as evidenced by the designated value of the standard thermodynamic potential (ΔG^o). The hydration degree decreases (from La(III) to Nd(III)) and then increases (from Pm(III) to Ho(III)), then it increases but much more slowly, from Ho(III) to Lu(III) .

The papers by Dybczyński (Minczewski & Dybczyński, 1962a) confirmed the hypothesis made by Speeding and Mackey according to which, together with the decreasing ionic radius of lanthanide(III) in the yttrium group a decrease of dentate of EDTA is observed. $Edta^{4-}$ and $cdta^{4-}$ anions act as pentadentate ligands for light and heavy(III) lanthanide(III) while their hexadentate character is enhanced in the group of medium lanthanides (Fig.8).

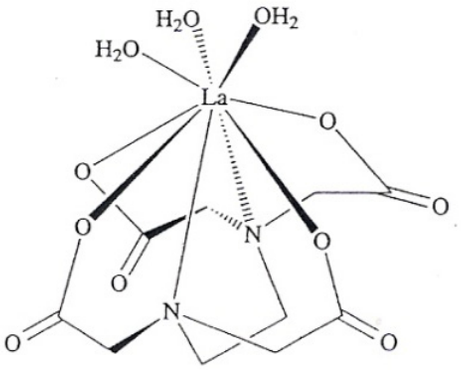


Figure 8. The structure of $[La(edta)(H_2O)_3]^-$ complex.

The proposed model is also suggested by comparing the solubility of the complex salts of [MLn(edta)] and [MLn(cdta)] types (where $M = Na^+$ or K^+) to the ion exchange affinity of the complexes $[Ln(edta)]^-$ and $[Ln(cdta)]^-$ (Minczewski & Dybczyński, 1962a). Ion affinities of these complexes are arranged in the opposite order to the solubility of the corresponding salts. The selectivity coefficients increase from lanthanum(III) to europium(III), and then decrease to lutetium(III), while the solubility of salt decreases from lanthanum(III) to samarium(III), europium(III) and then rises to lutetium(III).

Non-monotonic and different affinity of the complexes of rare earth elements(III) with EDTA and CDTA for strongly basic anion exchangers was used by Hubicka (Hubicka & Hubicki, 1986; Hubicka, 1989a) to separate the pairs of complexes of rare earth elements(III) in the macro-micro component system using the frontal analysis technique. It was shown that the efficiency of separation of rare earth elements(III) complexes with EDTA of $[Ln(edta)]^-$ type is affected by not only the type of anion functional groups, but also their form and degree of cross linking and porosity of the used anion exchanger. Good results were obtained by purification of yttrium(III) from neodymium(III), samarium(III) and terbium(III) as well as lanthanum(III) from neodymium(III) and erbium(III) from dysprosium(III). For the pair Y(III)-Nd(III), the influence of the type of functional groups, degree of cross linking and anion exchanger form as well as structure and porosity of the

skeleton was determined. Among the tested anion exchangers Dowex 2x8 and Dowex 1x8 in the form of EDTA proved to be most advantageous. Good results were also obtained for the macroporous, weakly basic anion exchanger Lewatit MP-7080 in the EDTA form.

Studies on the separation of anionic complexes of rare earth elements(III) with CDTA $[Ln(cdta)]^-$ type, which is an analogue of EDTA showed that in the macro-micro system Y(III) from Sm(III), Eu(III) and Nd(III) can be separated (Hubicka, 1989a). It was found that the process of separation of these complexes affects the degree of cross linking and the anion exchanger form. As follows the best results of separation of Y(III) from Nd(III) and Sm(III) were obtained on Dowex 1x4 in the acetate form.

Application of anion exchangers for separation of rare earth elements(III) complexes with EDTA and CDTA by the frontal analysis technique allows, in comparison with cation exchangers and elution process, to reduce the consumption of these chelating agents, obtaining higher concentrations of rare earth elements(III) in the eluate and shortening the process time which is important from the economical point of view. Additionally, alkali and alkaline earth metal ions forming unstable complexes with EDTA, and sometimes accompanying rare earth elements(III) have no effect on the separation result.

Kutun and Akseli (1999, 2000) for the separation of milligram quantities (5 mg) of rare earth elements(III) in the anion exchange process used the solution of sodium trimethaphosphate as the eluent. The elution was carried out with a gradient of 0.007-0.01 M concentration on the strongly basic polystyrene anion exchangers of types 1 and 2.

The advantage of anion exchangers over cation exchangers in the separation of rare earth elements(III) using aminopolycarboxylic acids as complexing agents is associated with their lower consumption in comparison to other eluents used, much faster process time, achieving higher concentrations in the eluate and the lack of negative impact of alkali(I), Ca(II) and Mg(II) ions on separation.

A particular attention has been paid to separation and removal of rare earth(III) elements nitrate complexes by means of frontal analysis from the polar organic solvent-H_2O-HNO_3 on anion exchangers of various types. The addition of organic solvent to an aqueous solution of rare earth complexes generally improves their ability of separation. Selection of an organic component and its concentration in the mixture is to a large extent arbitrary. The separation process is frequently carried out with the HNO_3, H_2SO_4, NH_4SCN and CH_3COOH solutions. The examples of such systems are presented in (Marcus, 1983).

9. Separation 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 beads 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 (Kunin & Gustafson, 1969).

For the separation of rare earth elements(III) and their purification from uranium(IV, VI), thorium(IV), iron(III), chromium(III), copper(II), nickel(II), cobalt(II), manganese(II) the chelating ion exchangers with the following functional groups: phosphinic -PO(OH), phosphonic-$PO(OH)_2$, phosphate -$OPO(OH)_2$, iminodiacetate -$CH_2N(CH_2COOH)_2$, iminodiacetate and aminoacetate > N-CH_2COOH, -aminophosphonic -$CH_2NHCH_2PO(OH)_2$ carboxylic -COOH, etc are used.

It is worth mentioning that the ion exchangers with the phosphonic functional groups in the medium acidic system effectively absorb the rare earth elements(III), uranium(VI) and iron(III). According to Hubicki (1989), uranium(VI) and thorium(IV) can be selectively separated from rare earth elements(III) on the phosphonic ion exchanger Duolite ES-63 by both the frontal analysis technique and elution with mineral acids. It was found that on this ion exchanger in the macro-micro component system Y(III) from Lu(III), Yb(III), Tm(III), Er(III), Dy(III) and Ho (III); La(III) from Pr(III) and Nd(III); Ce(III) from Pr(III), Nd(III), Sm(III), Eu(III), Y(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III) and Lu(III) can be separated (Hubicka & Hubicki, 1978a,b). For Duolite ES-63 the affinity series of rare earth elements(III) can be as follows: Sc(III) > Lu(III) > Yb(III) > Tm(III) > Er(III) > Ho (III) > Dy(III) > Tb(III) > Gd(III) > Eu(III) > Sm(III) > Nd(III) > Pr(III) > Ce(III) ≈ La (III).

Very interesting are the results of the studies on selective separation of micro quantities of scandium(III) on Duolite ES-63 from other rare earth elements(III) at the maximum concentration of 500 g Ln_2O_3/dm^3 (Hubicki, 1990). This ion exchanger is particularly useful for separation of micro quantity of scandium(III) and the preparation of scandium(III) with a high degree of purity. In the technology of processing of rare earth elements(III) concentrates also phosphonic ion exchanger KFP of Russia production was used for the selective removal of micro quantities of Th(IV) (Sozański, 1981).

The selectivity of phosphonic ion exchangers can be increased by connecting different substituents to the phosphorus atom, which affects its electro-donor strength. In the case of the alkylphosphonic ion exchangers affinity for rare earth elements(III) increases with the increasing atomic number of the element, which can be used for the separation of individual rare earth elements(III) by the elution using mineral acid solutions. Separation coefficients of the heavy lanthanides (Lu(III), Yb(III), Tm(III), Er(III)) for alkylphosphonic ion exchangers are from 1.3 to 1.4. The ion exchangers with the phosphine groups are characterized by stronger affinity for lanthanide(III) than the phosphonic ion exchangers. The percentage of the complexation of europium(III) and ytterbium(III) in 0.5 M HCl using the phosphonic ion exchanger is 70% and 82%, while for the ion exchanger with the phosphonic groups is equal to 25% and 50%, respectively.

Marhol (1982) which synthesized a number of ion exchange resins with the functional groups containing phosphorus found that the phosphinic ion exchangers are characterized by strong affinity for scandium(III) in agreement with the affinity series: Sc (III)> Fe (III)> In (III)> Ga (III)> Al(III) > La(III).

Szczepaniak and Siepak (1973) as a result of the cross linking reaction of (5% DVB) vinylbenzylamine with formaldehyde and phosphoric acid(III) in the hydrochloric acid medium obtained the ion exchanger containing aminomethylphosphonic groups. The obtained K-AMF ion exchanger can be defined as a phosphonic analogue of the iminodiacetic ion exchanger Dowex A-1 (Chelex 100). It can be recommended for separation of cations on the +2 and +3 oxidation states. Based on the volume distribution coefficients the affinity series of selected rare earth elements(III) for this aminophosphonic ion exchanger is as follows: La (III) > Gd (III) > Sm (III) > Nd (III) > Dy(III) > Pr(III) > Y(III). This series is not consistent with that obtained for the commercial ion exchange resins such as Duolite ES-467 and Lewatit OC-1060. These ion exchangers are used for the purification of micro quantities of lanthanum(III) from praseodymium(III) and neodymium(III) by means of both the frontal analysis technique and elution with mineral acids.

The aminophosphonic ion exchangers were used for selective purification of rare earth elements(III) from U(VI), Th(IV), Fe(III), Zn(II), Co(II) and Ni(II); purification of yttrium (III) from micro quantities of ytterbium(III), erbium(III), dysprosium(III) and holmium(III) as well as cerium(III) from rare earth elements(III). Of special interest are the values of separation coefficients determined by Van der Walt and Coetzee (1996) for the commercial ion exchanger Purolite S-950, which shows that rare earth elements(III) can be selectively separated from a number of other elements.

As for the phosphate ion exchangers cellulose phosphate is commercially produced. For cellulose phosphate, the mass distribution coefficients were determined for Cs(I), Li(I), Ba(II), Ca(II), Sr(II), Co(II), Ni(II), La(III), Pr(III), Yb(III), Cr(III) and Al(III) ions depending on the concentration of hydrochloric acid. There was made quantitative separation of rare earth elements(III) and earth metals(II); rare earth elements(III) and earth metals(II) and aluminum(III) as well as rare earth elements(III) and alkali and alkaline earth metals. High selectivity can be found in the case of cellulose phosphate ion exchangers. Passing the solution obtained from decomposition of monazite through such ion exchanger a relatively selective sorption of thorium(IV) is achieved with the capacity of the ion exchanger of about 300 g/kg with respect to Th(IV). In the four-column battery (bed height 340 cm, flow rate 15 cm^3/min) of which two columns worked in the sorption cycle and two were eluted, the recovery of thorium(IV) exceeds 99% (Brown and Coleman, 1956). The recovery of pure mixed rare earth elements as well as Th(IV) and U(VI) from the monazite concentrate is based on the reaction with sulphuric acid. Then, after adding hydrazine sulphate, Ce(IV) is reduced to Ce(III). This treatment is also based on the fact that Th(IV) ion with sulphate(VI) ions forms anionic $[(ThSO_4)_4]^{4-2n}$, that could pass freely through a cation exchange resin while the rare earth elements are completely adsorbed (Sherief & Almasy, 1968). Also the uranyl ionUO_2^{2+} forms anionic complexes of the type $[UO_2(SO4)_n]^{2-2n}$ where n=1, 2 or 3 (Preuss & Kunin, 1958).

The polyfunctional ion exchanger Diphonix Resin® is commonly used for separation of rare earth elements(III) (Fig. 9). It contains phosphonic, carboxylic and sulphonic groups. Another ion exchanger is Diphonix A with the phosphonic and ammonium or pyridine functional groups (Horwitz et al., 1993).

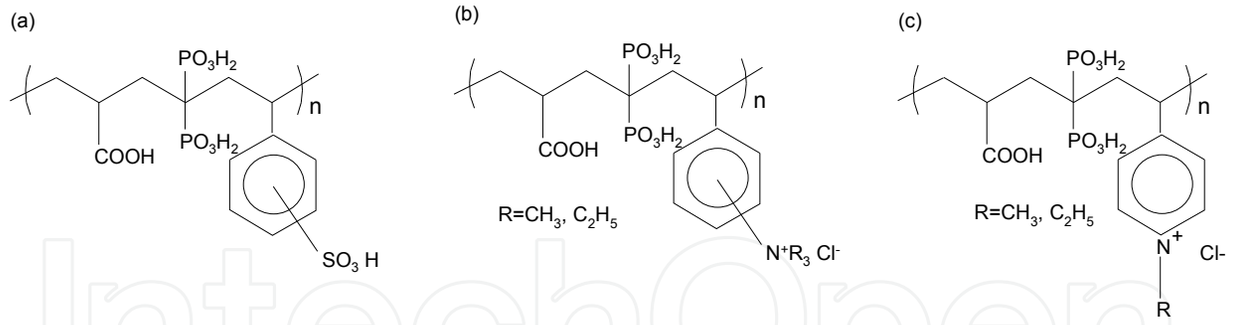


Figure 9. The structure of Diphonix®Resin, Dipxonix A (type 1) and Diphonix A (type 2).

These ion exchangers are characterized by high affinity for uranium(VI), plutonium(IV), neptunium(IV), thorium(IV), americium(III), europium(III) and a number of outside transient elements. The removal factor of europium(III) from 1 M HNO_3 solution at the phase contact time 30 min. for Diphonix®Resin is 98.3%.

An important group of chelating ion exchangers used for lanthanide separations are those with the iminodiacetate functional groups. As follows from the literature data in the pH range 2.5-3.5 with the Ln(III) ions the cationic complexes are formed and in the pH range 4.0-4.5 the anionic ones.

Christell et al. (1961) showed that the standard iminodiacetic ion exchanger Chelex 100 has stronger affinity for La(III) than Lu(III), which is opposed to the values of stability constants of iminodiacetate complexes of these elements. Affinity for Chelex 100 in a lanthanide series increases with the increasing atomic number of La(III) to Eu(III), and then decreases to Lu(III). By contrast, based on the distribution coefficient determined by Schrobilgen and Lang (1968) for the iminodiacetic ion exchanger Dowex A-1 the affinity series is as follows: La(III) < Pr(III) < Nd(III) > Sm(III) > Gd(III) > Tb(III) ≈ Dy(III) < Er(III) > Yb(III).

The gel and macroporous ion exchangers, iminodiacetate ion exchangers Amberlite IRC 718, Diaion CR-10, Duolite ES 466, Lewatit TP 207 and Lewatit 208 as well as Wofatit MC 50 were tested for separation of rare earth elements(III) by both the frontal analysis technique and elution. The results of these studies revealed their great applicability in the process of rare earth elements separation as well as for obtaining individual lanthanides with a high degree of purity. Of the group of the above mentioned ion exchangers Wofatit MC-50 proved to be the most useful. Particularly favourable results were obtained for purification of the concentrate of yttrium(III) from ytterbium(III) (Hubicka & Hubicki, 1978; Hubicka, 1989b), which is one of the most common contaminants of yttrium(III). It was also very useful for the ion exchange purification of samarium(III) from ytterbium(III); samarium(III) from europium(III); yttrium(III) from neodymium(III); lanthanum(III) from praseodymium(III) and neodymium(III); cerium (III) from praseodymium(III), neodymium(III), samarium(III), europium(III), yttrium(III), dysprosium(III), holmium(III), erbium(III), thulium(III), ytterbium(III) and lutetium(III) as well as scandium(III) from other rare earth elements. The determined affinity series for heavy lanthanides(III), neodymium(III) and yttrium(III) can be as follows: Yb(III) > Er(III) > Dy(III) > Ho(III) > Nd(III) > Y(III) and this is consistent with the values of stability constants of their complexes with iminodiacetic acid (Inczedy, 1972).

Noteworthy is the unusual position of yttrium(III). It was also found that Yb(III) has higher affinity for this ion exchanger than Er(III), Dy(III), Ho(III) and Tb(III), which is not consistent with the data obtained for Dowex A-l (Schrobilgen & Lang, 1968).

The selectivity of the carboxylic acid ion exchange resins in relation to the rare earth elements (III) is highly variable. Arnold and Son Hing (1967) set the separation coefficients and investigated the mechanism of sorption of lanthanides on the carboxylic ion exchangers Amberlite IRC-50 and Amberlite XE-89. They showed that with the decreasing ionic radii of rare earth elements(III) their affinity for Amberlite IRC 50 increases reverse to that in the case of polystyrene-sulphonic cation exchangers. The determined separation coefficients for the selected pairs of elements are equal to: Ce(III)-La(III) 1.86, Pr(III)-La(III) 2.40; Nd(III)-La(III) 2.60; Nd(III)-Pr(III) 1.1; Pm(III)-La(III) 3.50; Tb(III)-La(III) 5.60; Tb(III)-Ce(III) 3.00, respectively.

Both small ion exchange rate (compared to the polystyrene-sulphonic cation exchangers) and high affinity for the ion H^+ excludes practical application of the carboxylic ion exchange resins for the separation of rare earth elements(III) in the acidic media. However, carboxylic ion exchangers, especially phenol-carboxylic ion exchangers can be used for separation of uranium(VI) from rare earth elements(III).

A relatively small number of selective ion exchange resins is produced commercially. Therefore, the authors propose various modifications of ion exchangers by sulphonated aromatic chelating agents. The development of new functional resins which have chelating properties, prepared by simple immobilization of complexing organic reagents by ion exchange or adsorption onto conventional anion exchange resins or non ionic adsorbents has acquired great importance.

These modified resins can react with RRE ions by complex formation and can be used to preconcentrate their traces. For example, the research carried out by Hubicki (1989a) connected with the selective separation of micro quantities of scandium(III) from macro quantities of yttrium(III) and lanthanum(III) (50g/dm^3) on strongly basic anion exchangers with gel and macroporous skeleton modified with sulphonated organic reagents as prototypes of the new chelating ion exchange resins should be mentioned. To this end the anion exchangers were modified by alizarin S, arsenazo I, arsenazo III, beryllonite II, thymol blue, phenol red, cresol red, pyrogallol red, chrome azurol S, 8-hydroxyquinoline-5-sulphonic acid, sulphosalicilic acid, nitroso-R-soli, R-salt, SPANDS, tirone, torone as well as orange xylene. The best results of separation of Sc(III) from Y(III) and La(III) were obtained on the anion exchanger Merck MP-5080 in the chrome azurol S form. In addition, modified different types of anion exchangers were used for the purification of macro quantities of lanthanum chloride from micro quantities of Eu(III), Tb(III), Yb(III) and Lu(III). Of the anion exchangers tested for this purpose the most preferred proved to be the anion exchanger modified by 8-hydroxyquinoline-5-sulphonic acid (Hubicki, 1989a; Hubicki, 1989b).

Amberlite XAD-4 functionalized with o-vanillinsemicarbazone has been applied for the preconcentration of lanthanum, cerium, thorium and uranium ions (Jain et al., 2001). Complexing properties of the XAD-4 resin functionalized with the bicine ligand (N,N-bis(2-

hydroxyethyl) glycine) were investigated for La(III), Nd(III), Tb(III), Th(IV) and uranium(VI). Polydithiocarbamate chelating resin has been applied for the preconcentration of rare earth elements with Fe(III), Fe(II), Cr(VI), Cr(III), V(V), V(IV), Ti(IV), Mo(VI), W(VI), Th(IV) (Miyazaki & Barnes 1981). In the paper by De Vito et al. (1999) it was found that Amberlite XAD-7 resin with (o-[3,6-disulpho-2-hihydroxy-1-naphthylazo]-benzenearsonic acid) was successfully used for the separation and preconcentration of Sm(III), Eu(III) and Gd(III). The resin containing the fluorinated-β-diketone chelating group immobilized on solid support styrene divinyl benzene was applied for the simultaneous preconcentration of La(III), Ce(IV), Nd(III), Sm(III), Gd(III), Eu(III), Dy(III), Er(III), Yb(III) and Lu(III) (Rao & Kala, R. 2004; Waqar, et al. 2009). Preconcentration of La(III), Eu(III) and Yb(III) was also achieved by sorption of their 1-phenyl-3-methyl-4-benzoylpyrazol-5-one (PMBP) complexes on a silica gel column (Liang & Fa, 2005).

In the paper by Vigneau et al. (2001) the molecular imprinting resins containing DTPA and EDTA were also studied in lanthanides(III) separation. It was found that DTPA derivative monomers exhibited much higher Ga(III)-La(III) selectivity than EDTA ones. Also ionic imprinting resins can be used to this end. In the molecular imprinting process, the selectivity of a polymeric material is based on the size and shape of the template as well as the affinity between the host matrix and the guest molecule. More particularly in the case of ionic imprinting, the affinity partly depends on the number and the orientation of interaction points (ligand denticity) as well as on the counter ion. As described in the paper by (Krishna et al. (2005) ion imprinting allows significant enhancement in selectivity coefficients of neodymium(III) with respect to La(III), Ce(III), Pr(III), Sm(III) and Eu(III). The obtained selectivity coefficients are several times higher than those for the best extractant such as D2EHPA, for example selectivity coefficient for Nd(III) over Ce(III) and Pr(III) increases twentyfold, threefold over La(III) and Sm(III).

10. Separation of rare earth(III) by means of the extraction method

Ion exchange was of most significant importance in uranium production. However, success of ion exchange methods in uranium technology does not apply to that of other elements. Compared to the extraction method, rate of ion exchange and concentration of purified rare earth elements(III) salts are, as a rule, much smaller. Therefore large size of industry installations, generating large investment costs, is necessary. During extraction the elements are divided, according to the Nernst division law, into two immiscible with each other phases: organic and aqueous. Tri-n-butyl phosphate (TBP) and D2EHPA are commonly applied extracting agents in separation of rare earth elements(III) (Preston & Du Preez, 1990). Their application results mainly from their good extraction properties with a relatively law price. The advantages of this method are large concentration of elements in the organic and aqueous phases, thus large yield of multi-stage extraction. Others have discussed the use of bis(2-ethylhexyl)phosphonic acid (HDEHP) in rare earth elements separations (Jensen et al. 2001; Fontana & Pietrelli, 2009; Yin et al. 2010). HDEHP, a liquid cation exchanger that is also a chelating agent, most typically forms a tris complex with trivalent lanthanides in the organic phase, simultaneously releasing three H^+ for each

trivalent metal ion transferred into the organic phase. The distribution ratios for the extraction of the lanthanides from mineral acid solutions vary by nearly 10^5 from La(III) to Lu(III) (Nilsson & Nash, 2007, Mel'nik et al. 1999).

As follows from the literature data (Yan et al. 2006) the novel solvent extraction process and its application in industry for separating HREEs (thulium(III), ytterbium(III) and lutetium(III)), yttrium(III) and scandium(III) has been developed recently. The most popular solvent extraction method is using PC-88A (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester) or Cyanex 272 (bis(2,4,4-trimethylpentyl)phosphinic acid) as the extractant with lower equilibrium acidity. The additives of modified PC-88A were also adopted to separate Lu(III) in practice. Naphthenic acid or related carboxylic acid derivative were also used to separate the heavy rare earth elements in a very long cascade. Although the efficiency was not satisfactory, the chemical consumption was economical enough. The electrochemical method is also piloted to obtain Yb(III). This makes the separation of Tm(III), Yb(III) and Lu(III) more effective by solvent extraction.

As for the purification of Y(III) its chloride salt is separated from heavy rare earth elements using PC-88A - HCl process. The contaminants of light rare earth elements and bivalent ions such as Ca(II) were removed in PC-88A-HCl cascade and then yttrium (≥99.999%) is co-precipitated with Eu(III), Tb(III) and Zr(IV) by purified oxalic acid (Yan, et al. 2006).

Solvent extraction is also the most commonly used and effective technique in Ce(IV) separation. Cerium(III) is most likely to be oxidized to a tetravalent state either by bubbling oxygen during rare earth hydroxide precipitation or by drying the rare earth hydroxide in the presence of air. In acidic solutions, the oxidation of Ce(III) to Ce(IV) may occur by chemical oxidation with strong oxidants, such as peroxosulphates(VI), permanganates, lead oxide or silver oxide or by electrochemical oxidation or photochemical oxidation. Separation of insoluble cerium(IV) from rare earth elements can be carried out by selective dissolution of the trivalent rare earth hydroxides or through its selective precipitation from acid solution (Ura et al. 2005; Zhang et al. 2008; Luna et al. 2011). Many studies have been conducted on Ce(IV) separation using various extractants such as Cyanex 923, TBP, primary amine N1923, Aliquat 336, synergistic extractant and ionic liquids. The recovery of Ce(IV) and Th(IV) from rare earths(III) with Cyanex 923 has been applied in a industrial process. However, there are some disadvantages of solvent extraction of Ce(IV), for example such as a third phase formation.

The extraction of rare earth elements by amine and quaternary ammonium salts has been investigated in detail by many authors. As follows from the paper by Kovalancik and Galova (1992) low values of separation factors in the rare earth elements extraction with amines may be enhanced by the addition of a complexing agent. The greatest differences in the stability constant values are found in the case of CDTA and HEDTA.

In the extraction process the separation of Eu(III) from Gd(III) is exception. Similar to Zr(IV)-Hf(IV) this pair is the most difficult one to separate. Among rare earth elements, which can be reduced to divalent ions, Eu(III) has the highest standard redox potential, which makes its selective reduction and recovery from a mixture containing the other trivalent rare earth

ions possible (Morais & Ciminelli, 1998). It can be accomplished by several techniques, such as chemical reduction by Zn or Zn-Hg, photochemical reduction and electrochemical reduction (Atanasyants & Seryogin, 1995; Preston et al. 1996). The recovery is finally accomplished by precipitation with sulphate, based on the fact that the chemical properties of Eu(III) are similar to those of the alkaline earth ions. Among different sulphate sources $(NH_4)_2SO_4$, K_2SO_4, Na_2SO_4, $NaHSO_4$ and H_2SO_4 can be used as precipitating agents. As follows from the Morais and Ciminelli paper (2001) the precipitation with sulphuric(VI) acid led to higher-grade europium oxide by keeping pH in a range that does not favour gadolinium co-precipitation. The continuous addition of sulphuric(VI) acid is mainly responsible for the improvement of europium recovery. Maximum recovery was achieved within 2 h or more. Based on the experiments the product assaying 99.99% Eu_2O_3 can be obtained from the feed containing 5.0 Eu_2O_3 g/dm^3 and 138.2 Gd_2O_3 g/dm^3 in two stages of reduction–precipitation. The overall recovery is about 94%.

To overcome inconveniences of the extraction of rare earth elements there should be used various impregnating substances. Solvent impregnated resins (SIRs) were developed by Warshawsky (1981). It is now well known that the extraction of metal ions with macroporous polymeric supports impregnated by extractants is an attractive method for the separation and preconcentration of metal ions (Schmidt, 1987; Cortina & Warshawsky, 1997; Horwitz and Schulz, 1999). Solvent impregnated resins for lanthanides separation are produced by adsorbing extractants such as TBP or D2EHPA on a macroporous resin without any functional groups. Different types of highly selective resins can be obtained by adsorbing various extractants. However, it should be mentioned that SIRs are characterized by smaller adsorption capacity and shorter life compared with the common ion exchange resins (Shibata & Matsumoto, 1998). The disadvantage of impregnating substances is slow kinetics due to the limited size of interfacial area and wet ability with the aqueous solution. An essential drawback is the irreversible loss of active substances. However, using Cyanex 302 in industrial processes of scandium(III) purification should be highlighted.

In the paper by Turanov (2010) bis(diphenylphosphoryl-methylcarbamoyl)alkanes were synthesized and studied as extractants for La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III), Lu(III) and Y(III) from perchloric acid solutions. The influence of both $HClO_4$ concentration in the aqueous phase and that of the extractant in the organic phase on the extraction of metal ions was considered. The stoichiometry of the extracted complexes has also been determined. Bis(diphenylphosphoryl-methylcarbamoyl)alkanes possess a higher extraction efficiency towards Ln(III) than their monoanalogue $Ph_2P(O)CH_2C(O)NHC_9H_{19}$.

In the paper the research on the applicability of different types of anion exchangers for the separation of rare earth elements in the presence of the complexing agents IDA, HEDTA and CDTA is presented. The effect of the addition of a polar organic solvent (methanol, ethanol, acetone, 1-propanol, 2-propanol) on separation of rare earth(III) elements in such system is discussed. The examples of the removal of rare earth elements nitrate complexes from the polar organic solvent-H_2O-HNO_3 are discussed in detail.

11. Experimental

The strongly basic anion exchangers Dowex 1x1, Dowex 1x2, Dowex 1x4, Dowex 1x8 (type 1), Dowex 1x16, Dowex 2x8 (type 2) and macroporous Dowex MSA-1 produced by the Dow Chemical Company (USA) as well as Lewatit MonoPlus M 500, Lewatit MonoPlus M 600, Lewatit MonoPlus MP 500, Lewatit MonoPlus MP 64 and Lewatit MP 62 produced by Lanxess (Germany) were used in the investigations. From the group of polyacrylate anion exchangers Amberlite IRA 458, Amberlite IRA 68 and Amberlite IRA 958 (Rohm and Haas, France) were selected. Additionally, in the case of separations of rare earth elements in the polar organic solvent systems there were used the following: Zerolite FF IP 2-3%, Zerolite FF IP 3-5%, Zerolite FF IP 7-9%, Lewatit MP 5080, Purolite A 850, Permutit SK, Wofatit SBWx2%, Wofatit SBWx4%, Wofatit SBWx6%, Wofatit SBWx8%, Wofatit SBWx12%, Wofatit SBWx16%, Wofatit SBKx7%. The bead size of these anion exchangers was 0.15-0.3 mm. They were used in the appropriate form.

In the case of rare earth elements separation in the presence of complexing agents (L=IDA, HEDTA, CDTA or EDTA) 1.5 or 2.5 g of the oxides of rare earth elements with 2% excess of stoichiometric quantities of complexing agent solution (in the Ln(III):L=1:1 or Ln(III):L=1:2 systems) were mixed while heated. Moreover, in the case of the systems in the polar organic solvent the rare earth element solution of 2.5-100 g Ln_2O_3/dm^3 for separation of Y(III) from Nd(III) and 1.5-5.3 g Ln_2O_3/dm^3 for separation of Sm(III) from Y(III) were prepared by dissolving the appropriate rare earth element oxides in HNO_3 and then the organic solvent was added. In order to measure affinity series the breakthrough curves were determined using the solutions of rare earth elements at a concentration 0.01 M or 0.004 M. These solutions were passed continuously through 2 cm i.d. glass columns packed with the suitable ion exchanger keeping the flow rate 0.2 $cm^3/cm^2 \cdot min$. The breakthrough curves were normally obtained using 40-80 cm^3 of the anion exchanger in the appropriate form. The effluent was collected as fractions of 15-10 cm^3 from which oxalates were precipitated and converted to oxides.

The percentage of micro component in macro component was determined by the spectrophotometric analysis using a SPECORD M 42 spectrophotometer (Zeiss, Germany). The determination was made by a direct method using the neodymium adsorption maximum λ=793.4 nm and the praseodymium adsorption λ=444 nm. Calculations were made by using the background adsorption elimination method. In some cases the determination was made using the XRF spectrometer (Canberra Packard).

There were determined the affinity of rare earth element complexes and the effects of kind of functional groups (basicity), kind of skeleton, porosity of skeleton (microporous and macroporous), cross linking degree of anion exchanger skeleton as well as kind and concentration of complexing agent and polar organic solvent (methanol, ethanol, 1-propanol, 2-propanol, acetone, dimethylformamide, dimethylsulphoxide). The effect of the nitric acid concentration, the addition of another organic solvent and the concentration of rare earth elements(III) (up to 100 g Ln_2O_3) on effectiveness of their sorption and separation were also studied.

12. Results

As follows from the literature data little attention was paid to the purification of rare earth elements using complexing agents and separation of formed anionic complexes on strongly and weakly basic anion exchangers (Hubicka & Hubicki, 1992a; Hubicka & Hubicki, 1992b). For this aim such complexing agents as iminodiacetic acid (IDA), N′-(2-hydroxoethyl)ethylenediamine-N,N,N′-triacetic acid (HEDTA), *trans*-1,2-cyklohexane-diaminetetraacetic acid (CDTA) and ethylenediaminetetraacetic acid (EDTA) can be proposed.

It was worth mentioning that iminodiacetic acid (IDA) as the eluent is not applied in the separation of rare earth elements(III) on cation exchangers. In the aqueous solution and the solid state the following complexes of $[Ln(ida)]^+$, $[Ln(ida)_2]^-$, $[Ln(ida)OH]$, $[Ln(ida)_2OH]^{2-}$ and $[Ln(ida)_3]^{3-}$ types with IDA are formed. Based on the breakthrough curves found the affinity series in the Ln(III):IDA=1:2 system and at pH 5.07-6.0 for most rare earth element complexes was found for the anion exchanger Dowex 1 in the acetate and IMDA forms to be as follows: **Ho(III) ≈Dy(III) > Gd(III) > Eu(III) > Er(III) > Y(III) > Yb(III) > Sm(III) > Tm(III) > Nd(III) > Pr(III) >>La(III)** (Hubicka & Drobek, 1998)**.**

The affinity series for the anion exchanger in the acetate and IDA forms is the same, but for the acetate form greater differentiation in affinity of individual lanthanides was found. Additionally, it can be stated that the affinity of rare earth elements for the anion exchangers does not depend on the stability constants of Ln(III)-IDA complexes and the obtained series is different from that of rare earth element complexes with EDTA, CDTA and HEDTA. Taking into account the position of individual lanthanides in the above mentioned series the possibility of purification of La(III) from Nd(III) or Pr(III); Sm(III) from Ho(III); Nd(III) from Y(III); Y(III) from Dy(III), Ho(III) as well as Yb(III) from Ho(III) and Er(III) is possible.

As follows from the obtained data the most effective separations of La(III) from Nd(III) or Pr(III) were achieved on Dowex 2 (type 2) with 8% DVB. Using Dowex 2x8 in the acetate form with an anion exchanger bed of 1 dm^3, over 1285 g La_2O_3 was obtained, in which the Nd_2O_3 content (0.52%) was reduced to below 0.005% and 1100 g La_2O_3 in which the Pr_6O_{11} content (0.50%) was reduced to below 0.01% (Fig.10). It is also worth noting that the yield of obtained La_2O_3 is high about 96%. Comparing the earlier results of La(III) purification from Nd(III) on the anion exchanger of the same type with those obtained for EDTA, it follows that using IDA increases the amount of purified La_2O_3 by over 20 times. The analogous results were obtained on Dowex 1x8 (Hubicka & Drobek, 2000b).

Satisfactory results were also obtained on Dowex MSA-1. On 1 dm^3 of this anion exchanger in the acetate form 1100 g of La_2O_3 was purified from Nd_2O_3 and 600 g La_2O_3 from Pr_6O_{11}. Despite slightly worse performance separation of those pairs on Dowex MSA-1, in comparison with the analogous results obtained for Dowex 1x8 and Dowex 2x8, due to their favourable physicochemical properties, such as large resistance to chemical agents, well-developed surface area and availability of all ion exchange groups, it can be recommended for the use on a macro scale (Hubicka & Kołodyńska, 2000).

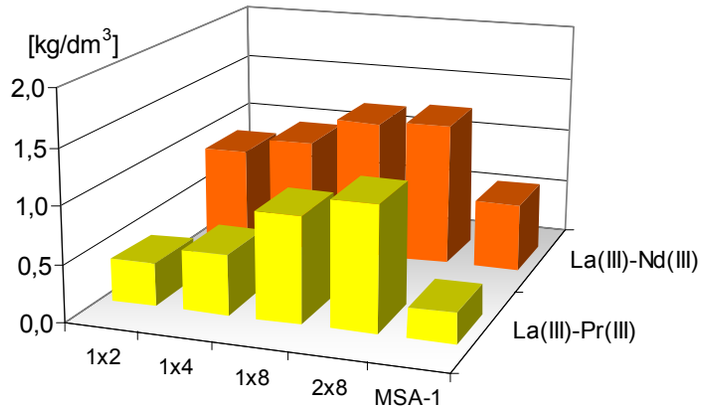


Figure 10. Separation of La(III) from Nd(III) (0.52%) and La(III) from Pr(III) (0.50%) on Dowex 1x2, Dowex 1x4, Dowex 1x8 and Dowex 2x8 as well as Dowex MSA-1 in the acetate form (1 dm^3 of anion exchanger in the Cl^- form, Ln(III):IDA=1:2, pH 6.0, 2.5g Ln_2O_3/dm^3).

In next step the optimal conditions for sorption and separation processes of Sm(III)-Ho(III) on the polystyrene anion exchangers were studied. It was found that in the Sm(III) from Ho(III) separation the most effective was Dowex 2x8 (type 2). On 1dm^3 of Dowex 2x8 about 221 g of Sm_2O_3 was purified from Ho_2O_3 (Fig.11).

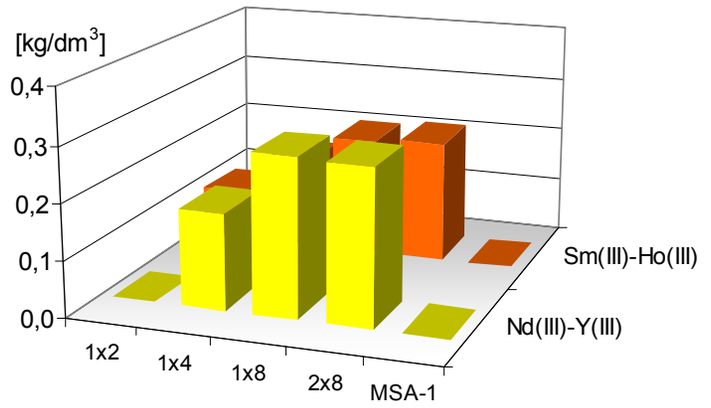


Figure 11. Separation of Nd(III) from Y(III) (0.35%) and Sm(III) from Ho(III) (0.33%) on Dowex 1x2, Dowex 1x4, Dowex 1x8 and Dowex 2x8 as well as Dowex MSA-1 in the Ac form (1 dm^3 of anion exchanger in the Cl^- form, Ln(III):IDA=1:2, pH 5.0, 1.5g Ln_2O_3/dm^3).

It was found that for Dowex 1 the effectiveness of Sm(III)-Ho(III) pair separation (as pairs of LaIII)-Nd(III) and La (III)-Pr (III)) increases with the increasing degree of cross linking from 2 to 8% DVB. The Ho(III) complexes with IDA exhibit the greatest affinity for the anion exchanger Dowex 1 in the acetate form of cross linking 8 % DVB and the smallest for Dowex 1 in the acetate form of cross linking 2 % DVB.

As for the Nd(III) separation from Y(III) it should be emphasized that in the ion exchange processes of rare earth elements(III) separation on cation exchangers using such eluents as ammonium acetate or DTPA, the yttrium(III) elutes close to neodymium(III), and partially overlaps the neodymium(III) (Fig.11). The above method obtaining high purity

neodymium(III) on Dowex 1x8 or Dowex 2x8 can be complementary to obtaining this element from the neodymium concentrates in the process of lanthanide(III) elution on the polystyrene-sulphone cation exchangers (Hubicka et al., 1998).

Due to the increasing demand for yttrium(III) in many branches of industry and technology, purification of yttrium(III) from heavy lanthanides(III) can be of significant applicative character. Its advantage is a simple method and low consumption of iminodiacetic acid. Based on the results of purification of the studied pairs of rare earth elemet(III) complexes on anion exchangers of polystyrene skeleton, it was proved that the anion exchangers Dowex 1 and Dowex 2 of the cross linking 8% DVB in the acetate form are the most effective. On 1 dm^3 of strongly basic anion exchangers Dowex 1x8 and Dowex 2x8 it can be obtained more than:

- 113 g and 116 g Y_2O_3 in which the Ho_2O_3 content can be reduced from 0.34% to 0.05%;
- 115 g and 108 g Y_2O_3 in which the Dy_2O_3 content can be reduced from 0.365% to 0.035%;
- 103 g and 91 g Y_2O_3 in which the Er_2O_3 content can be reduced from 0.35% to 0.05%.

The best results were obtained during purification of Y(III) from Ho(III) and Y(III) from Dy(III). However, the amount of Y(III) purified from Er(III) is smaller which is in accordance with the erbium position in the affinity series of rare earth element complexes with IDA compared to the strongly basic gel anion exchanger Dowex 1x4.

In the process of ion exchange separation of rare earth elements on cation exchangers, most eluents washe out ytterbium(III) in the first fractions. However, if the content of ytterbium(III) is small, it is eluted along with heavy lanthanides(III) and yttrium(III). Whereas separation of ytterbium(III) to ytterbium(II) using reduction with metallic limestone at elevated temperature in the argon atmosphere or using the reduction electrolytic method is a multi-stage expensive process (Hubicka & Drobek, 1999; Hubicka & Drobek, 2000a; Hubicka & Drobek, 2000b).

The affinity series of anionic complexes of rare earth elements(III) with IDA for the strongly basic gel anion exchanger Dowex 1 in both acetate and iminodiacetate forms indicates atypical position of ytterbium(III) in it, which creates possibility of Yb(III) purification from accompanying heavy lanthanides(III) such as e.g. Ho(III) or Er(III). The process of Yb(III) separation from Ho(III) and Yb(III) from Er(III) in the acetate form was studied using the anion exchangers Dowex 1x4 and Dowex 1x8 by means of the frontal analysis technique (Fig.12).

Assuming that 1:2 complexes are formed the sorption process of Ln(III)-IDA complexes can be written as:

$$RCH_3COO + [Ln(ida)_2]^- \rightleftarrows R[Ln(ida)\ CH_3COO] + Hida^-$$

and

$$RCH_3COO + [Ln(ida)_2]^- \rightleftarrows R[Ln(ida)_2] + CH_3COO^-$$

as well as for the IDA form

$$RHida + [Ln(ida)_2]^- \rightleftarrows R[Ln(ida)_2] + Hida^-$$

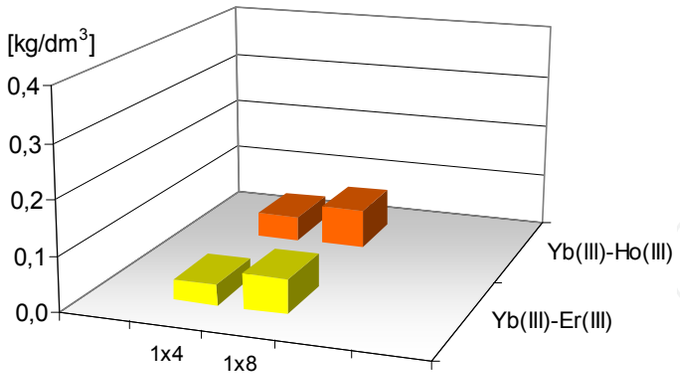


Figure 12. Separation of Yb(III) from Er(III) (0.36%) and Yb(III) from Ho(III) (0.35%) on Dowex 1x4 and Dowex 1x8 in the acetate form (1 dm^3 of anion exchanger in the Cl^- form, Ln(III):IDA=1:2, pH 5.0, 1.5g Ln_2O_3/dm^3).

The acetate form of the studied anion exchangers shows greater differentiation in the affinity of individual complexes than in the iminodiacetate form. Structure and porosity of the skeleton of the anion exchanger and cross linking degree play a significant role in the sorption process. Taking into consideration the kind of functional groups, it was shown that in the separation process the anion exchanger Dowex 2x8 proved to be a little more effective for the pair La(III)-Pr(III) whereas the results are similar for all other pairs.

HEDTA is more readily soluble in water than EDTA. It forms with rare earth element complex compounds in the ratio 1:1. For example, the following complexes are known: $[Ln(hedta(OH)]^-$, $[LnH(hedta)_2]^{2-}$ and $[Ln(hedta)_2]^{3-}$. The studies of sorption of the Ln(III) complexes with HEDTA on anion exchangers were begun by (Brücher et al. 1975). The affinity of the rare earth element complexes with HEDTA at pH 7.5 (Ln(III):HEDTA=1:1) for the anion exchanger Dowex 1x2 in the HEDTA form is: **Dy(III) > Ho(III) > Er(III) > Gd(III) > Y(III) > Tm(III) > Tb(III) > Eu(III) > Sm(III) > Yb(III) > Nd(III) > Pr(III) ≈ La(III)** (Hubicka & Drobek, 1997a) and differs from that of rare earth element complexes with EDTA and CDTA.

Based on the determined affinity the possibility of separation of Sm(III) from Ho(III) and Sm(III) from Y(III); Y(III) from Ho(III); Y(III) from Er(III); Y(III) from Dy(III); Nd(III) from Y(III) as well as Yb(III) from Ho(III) and Yb(III) from Er(III) complexes with HEDTA in the macro-micro component system by the frontal analysis technique is possible (Hubicka & Drobek, 1997b).

Separation of Sm(III) from Ho(III) (Ln(III):HEDTA=1:1, pH 4.0 and 7.5) in the HEDTA form was conducted on the strongly basic polystyrene anion exchangers Dowex 1 with cross linking 2, 4 and 8% DVB as well as Dowex MSA-1.

As follows from the comparison of the obtained data, the process of purification of Sm(III) from Ho(III) and Sm(III) from Y(III) is the most effective on the anion exchanger Dowex 1x4 in the HEDTA form at solution pH 7.5 (Fig. 13). On 1 dm^3 of this anion exchanger it is

possible to obtain about 48 g Sm_2O_3 in which Ho_2O_3 content can be reduced from 0.33% to the value below 0.05% and about 15 g Sm_2O_3 in which Y_2O_3 content can be reduced from 0.37% to the value below 0.03%. Using the macroporous Dowex MSA-1 gave less advantageous results of Sm(III) purification from Ho(III).

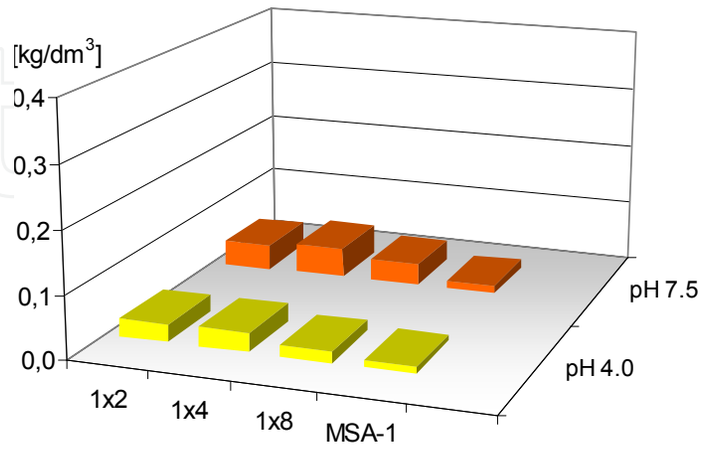


Figure 13. Separation of Sm(III) from Ho(III) (0.33%) on Dowex 1x2, Dowex 1x4, Dowex 1x8 and Dowex MSA-1 in the HEDTA form (1 dm^3 of anion exchanger in the Cl^- form, Ln(III):HEDTA=1:1, pH 4.0 and 7.5, 1.5g Ln_2O_3/dm^3).

A smaller amount of Sm(III) purified from Y(III) compared with that of Sm(III) purified from Ho(III)confirms that the Ho(III) complexes exhibit greater affinity than that of Y(III) complexes which is in agreement with the determined affinity series of the rare earth elements(III) complexes with HEDTA.

As follows from the series of rare earth elements(III) complexes with HEDTA for the anion exchanger Dowex 1x2 in the HEDTA form, also the Y(III) complexes are characterized by greater affinity for this anion exchanger than corresponding Nd(III) complexes which indicates possibility of purification of Nd(III) from Y(III) in the macro-micro component system by the frontal analysis technique. In the process of Nd(III) purification from Y(III) the best separation results were obtained using the anion exchanger Dowex 1 of the 4% DVB cross linking. The amount of neodymium(III) purified from yttrium(III) (under the same conditions) obtained using the anion exchangers Dowex 1x2 and Dowex 1x8 is comparable and lower than using the anion exchanger Dowex 1x4. However, the anion exchanger Dowex 2x8proved to be useless in the process of Nd(III) purification from Y(III) (Fig. 14).

The affinity of the complexes of the $[LnH(hedta)_2]^{2-}$ type is greater for heavy lanthanides(III) such as Dy(III), Ho(III) and Er(III) than for Y(III) which suggests possibility of purification of Y(III) macro quantities from Dy(III), Ho(III) and Er(III) micro quantities. As follows from the studies, similar to the pair Nd(III)-Y(III) the effectiveness of the pairs Y(III)-Ho(III) and Y(III)-Er(III) separation on strongly basic gel polystyrene anion exchangers is greater at solutions pH 7.5 than pH 4.0. Of all studied anion exchangers Dowex 1x4 gave the best results in purification of the above mentioned rare earth elements(III) complexes with HEDTA. The anion exchanger Dowex 1x4 was also used for separation of the pair Y(III)-

Dy(III). The obtained results show that on 1 dm^3 of this anion exchanger in the HEDTA form it is possible to obtain 16 g of yttrium(III) (counted over Y_2O_3) in which the dysprosium(III) content can be reduced over 10 times i.e. from 0.365% Dy_2O_3 to the value below 0.035%.

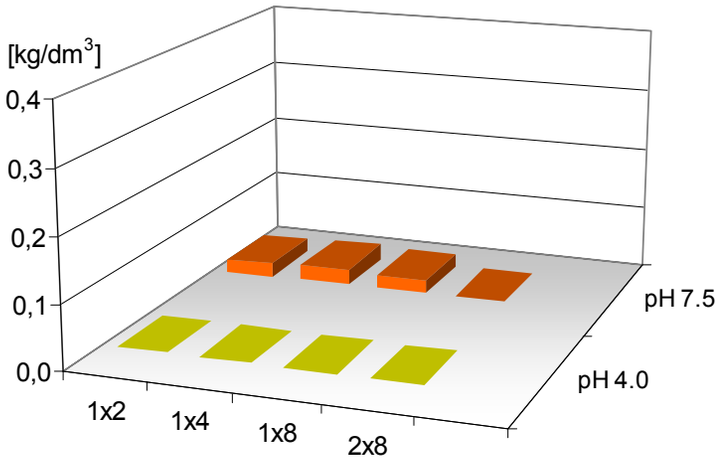


Figure 14. Separation of Nd(III) from Y(III) (0.35%) on Dowex 1x2, Dowex 1x4, Dowex 1x8 and Dowex 2x8 in the HEDTA form (1 dm^3 of anion exchanger in the Cl^- form, Ln(III):HEDTA=1:1, pH 4.0 and 7.5, 1.5g Ln_2O_3/dm^3).

In the determined affinity series of rare earth elements(III) with HEDTA for strong basic anion exchangers of the polystyrene skeleton one can see atypical position of Yb(III). Using the strongly basic anion exchanger Dowex 1 with different DVB cross linking, it was proved that for Dowex 1x2 in the HEDTA form, in the affinity series position of Yb(III) is near light rare earth: **Yb(III) > Nd(III) > Pr(III) > La(III).** However, its position is different for Dowex 1x4 in the HEDTA form: **Ho(III) > Y(III) > Sm(III) > Nd(III) > Yb(III)** and Dowex 1x8 in the HEDTA form **Ho(III) > Y(III) > Yb(III) > Sm(III) > Nd(III)**, which indicates that the purification process of Yb(III) from Ho(III) should be more effective on Dowex 1x4.

Based on the results of Yb(III) separation from Ho(III), Yb(III) purification from Er(III) as a micro component was carried out at pH 7.5 using Dowex 1x2 and Dowex 1x4 in the HEDTA form. In this case the anion exchanger Dowex 1x4 also proved to be more effective than Dowex 1x2 (Fig.15).

The obtained results of separation of the pairs Yb(III)-Ho(III) and Yb(III)-Er(III) are in agreement with the breakthrough curves and calculated values of distribution coefficients of the Yb(III), Ho(III) and Er(III) with HEDTA on the anion exchanger Dowex 1x2 in the HEDTA form (Hubicka & Drobek, 1997c). The agreement of the results in Yb(III) purification from Ho(III) and Er(III) with the affinity series of rare earth complexes with HEDTA leads to the suggestion that it is also possible to purify Yb(III) macro quantities from Dy(III), Tm(III) and Y(III) (Hubicka & Drobek, 1997c).

Non-monotonic and atypical the affinity series of anion lanthanide complexes with CDTA was also obtained for isotopes of these elements on the strongly basic anion exchanger Dowex 1x4 in the H_2cdta^{2-} form by Wódkiewicz and Dybczyński (1968): **Pm(III) > Nd(III) > Sm(III) > Pr(III) > Ce(III) > Eu(III) > Gd(III) > La(III) > Sc(III) > Tb(III) > Dy(III) > Ho(III) >**

Y(III) > Er(III) > Tm(III) > Yb(III) > Lu(III). Higher affinity of the Nd(cdta)- and Sm(cdta)-complexes for the anion exchangers than that of [Y(cdta)]- complexes was used for yttrium purification in the macro-micro component system by the frontal analysis technique on the polystyrene anion exchangers Dowex 1x2 and Dowex 1x4 (Hubicka, 1989a). Based on the obtained results it was pointed out that the affinity depends not only on the type of complexes, their structure but also on physicochemical properties of anion exchangers such as their form. The most effective form in the separation of $[Y(cdta)]^-$ from $[Nd(cdta)]^-$, $[Sm(cdta)]^-$ and $[Eu(cdta)]^-$ complexes proved to be the acetate from rather than the H_2cdta^{2-} one but the chloride form of the anion exchangers was completely useless.

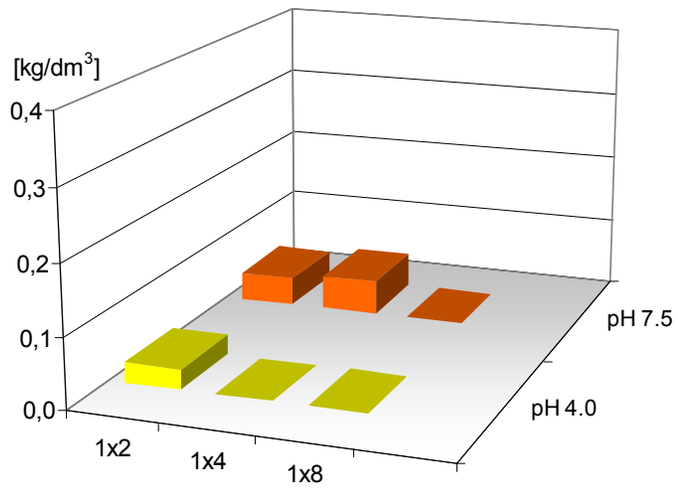


Figure 15. Separation of Yb(III) from Ho(III) (0.34%) on Dowex 1x2, Dowex 1x4 and Dowex 1x8 in the HEDTA form (1 dm^3 of anion exchanger in the Cl^- form, Ln(III):HEDTA=1:1, pH 4.0 and 7.5, 1.5g Ln_2O_3/dm^3).

Taking the above into consideration it was interesting to study applicability of the anion exchanger of the polyacrylate skeleton for separation of rare earth elements(III) complexes with CDTA (Hubicka & Kołodyńska, 2003). As follows from the breakthrough curves the Nd(III) and Sm(III) complexes with CDTA exhibit higher affinity for both strongly basic and weakly basic polyacrylate anion exchangers Amberlite IRA 458, Amberlite IRA 958 for the corresponding Y(III) complexes and their affinity is arranged in the same order as for strongly basic polystyrene anion exchangers.

Assuming that the complexes 1:1 are formed, the anion exchange reaction can be written as:

$$RCH_3COO + Ln(cdta)^- \rightleftarrows RLn(cdta) + CH_3COO^-$$

The obtained data indicate that the strongly basic, polyacrylate, gel anion exchanger Amberlite IRA 458 is more effective in purification of Y(III) from Nd(III) in comparison with the strongly basic, macroporous anion exchanger Amberlite IRA 958.

It was shown that the weakly basic polyacrylate gel anion exchanger Amberlite IRA 68 is more effective than the strongly basic, gel anion exchangers of polyacrylate and polystyrene types (Fig. 16). On 1 dm^3 of this anion exchanger it is possible to obtain about 90 g Y_2O_3 in

which the Nd_2O_3 content was reduced from 0.35% to below 0.005% and about 81 g Y_2O_3 in which the Sm_2O_3 content was reduced from 0.36% to below 0.015%. Therefore, polyacrylate anion exchangers with respect to their applicability in purification of Y(III) from Nd(III) and Sm(III) complexes with CDTA can be arranged as follows: weakly basic, gel > strongly basic, gel > strongly basic, macroporous (Hubicka & Kołodyńska, 2003; Hubicka & Kołodyńska, 2004).

The analogous results were obtained using the monodisperse anion exchangers Lewatit MonoPlus M 500, Lewatit MonoPlus M 600, Lewatit MonoPlus MP 500, Lewatit MonoPlus MP 64 and the heterodisperse anion exchanger Lewatit MP 62 (Hubicka & Kołodyńska, 2008). The data indicate that Lewatit MonoPlus M 500 (type 1) in the acetate form is more effective in purification of Y(III) from Nd(III) and Y(III) from Sm(III) in comparison with Lewatit MonoPlus M 600 (type 2).

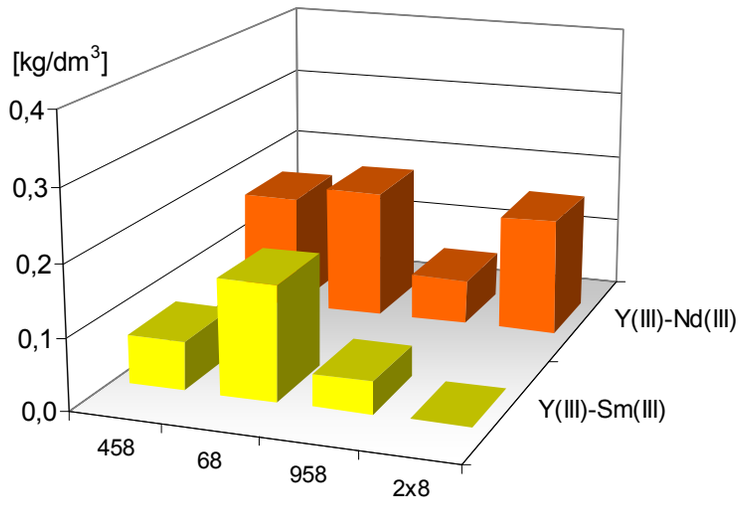


Figure 16. Separation of Y(III) from Sm(III) (0.36%) and Y(III) from Nd(III) (0.35%) on Amberlite IRA 458, Amberlite IRA 68, Amberlite IRA 958 and Dowex 2x8 in the CDTA form (1 dm^3 of anion exchanger in the Cl^- form, Ln(III):CDTA=1:1, pH 4.8, 1.5g Ln_2O_3/dm^3).

On 1 dm^3 of this anion exchanger, it is possible to obtain approximately 79 g Y_2O_3 in which the Nd_2O_3 content was reduced from 0.35% to below 0.005% and approximately 70 g Y_2O_3 in which the Sm_2O_3 content was reduced from 0.35% to below 0.015% (data not presented). It was also shown that purification of Y(III) from Nd(III) in the system with CDTA on the polystyrene anion exchangers is less effective than in the system with EDTA (Hubicka & Kołodyńska, 2007). Smaller differentiation in affinity of the $[Ln(cdta)]^-$ complexes than the $[Ln(edta)]^-$ complexes on anion exchangers can be justified by larger 'flexibility' of EDTA compared with the 'rigidity' structure of CDTA.

Ion exchange reactions proceed not only in the aqueous system but also in the non-aqueous solvents such as alcohols, ketones, glycols, etc. as well as in the mixed systems, e.g. water-alcohol, water-ketone, etc. Application of non-aqueous and mixed solvents in the anion exchange of metal complexes has increased considerably by a number of possible separations. In most cases the distribution coefficients of metal complexes in mixed media

like water-alcohol, water-acetone etc. are larger than those in pure water solutions (Moody & Thomas, 1968; Marcus, 1983). Therefore, using an unusual order of affinity series of anion lanthanide complexes with EDTA of $Ln(edta)^-$ type for the strongly basic anion exchanger in the H_2edta^{2-} form (Dybczyński, 1964; Dybczyński, 1970): **Sm(III) > Eu(III) > Gd(III) > Nd(III) > Pr(III) > Tb(III) > Ce(III) > Dy(III) > La(III) > Ho(III) > Y(III) > Er(III) > Sc(III) > Tm(III) > Yb(III) > Lu(III)** and higher affinity of the $[Nd(edta)]^-$ complexes than that of $[Y(edta)]^-$ complexes the yttrium(III) purification as a macro component from neodymium(III) by the frontal analysis technique in the solvent organic system were also carried out. The results of separation of Y(III) from Nd(III) (Nd_2O_3 0.35%) in the presence of EDTA without and with 10%(v/v) and 20%(v/v) addition of methanol, 1-propanol, 2-propanol and acetone on Lewatit MonoPlus M 500, Lewatit MonoPlus M 600, Lewatit MonoPlus MP 500, Lewatit MonoPlus MP 64 and Lewatit MP 62 are presented in Fig. 17.

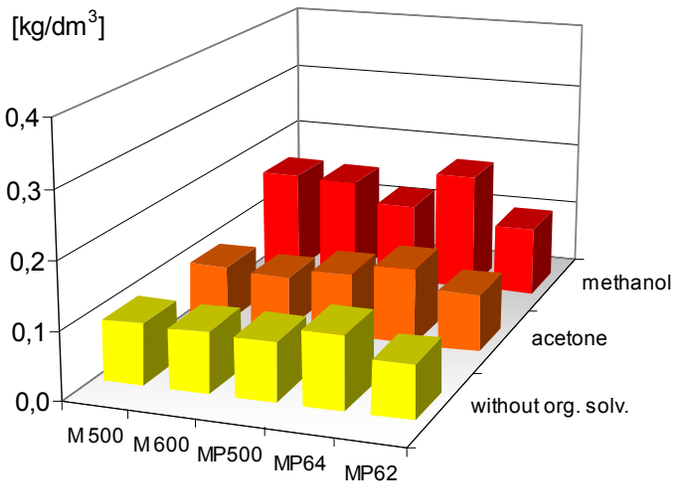


Figure 17. Separation of Y(III) from Nd(III) (0.35%) on Lewatit MonoPlus M 500, Lewatit MonoPlus M 600, Lewatit MonoPlus MP 500, Lewatit MonoPlus MP 64 and Lewatit MP 62 in the H_2O-20 % (v/v) polar organic solvent systems (1 dm^3 of anion exchanger in the Cl^- form, Ln(III):EDTA=1:1, pH 4.8, 1.5g Ln_2O_3/dm^3).

Taking into consideration the effect of the addition of polar organic solvent on the effectiveness of separation of rare earth element(III) complexes with EDTA on the above mentioned anion exchangers the best results of Y(III) from Nd(III) purification are obtained in 20% (v/v) methanol system on Lewatit MonoPlus M 500 and Lewatit MonoPlus MP 64. Taking 1 dm^3 bed of Lewatit MonoPlus M 500 it is possible to obtain above 158 g Y_2O_3 in which the Nd_2O_3 content can be reduced from 0.35% to below 0.005%, whereas 182 g Y_2O_3 for Lewatit MonoPlus MP 64. The yield obtained in these processes is above 70-100% higher than that obtained in the aqueous solutions. However, the increase of methanol addition up to 20% (v/v) increases accordingly the yield of purified Y_2O_3 only by about 15%, but the increase of methanol addition up to 50% (v/v) already affects insignificantly the yield increase in this process (Hubicka & Kołodyńska, 2005; Hubicka & Kołodyńska, 2007).

Analogous studies on the separation of Y(III)-Nd(III) with EDTA were also carried out in the presence of ethanol, 1-propanol, 2-propanol and acetone. However, only 20% (v/v) addition

of acetone to the system increases effectiveness of separation process compared to the aqueous solutions.

Moreover the analogous studies were carried out for the IDA complexing agent. The data obtained indicate that Lewatit MonoPlus M 500 and Lewatit MonoPlus M 600 in the acetate form in aqueous solutions are the most effective in separation of the $[Sm(ida)_2]^-$-$[Ho(ida)_2]^-$ pair (Fig.18).

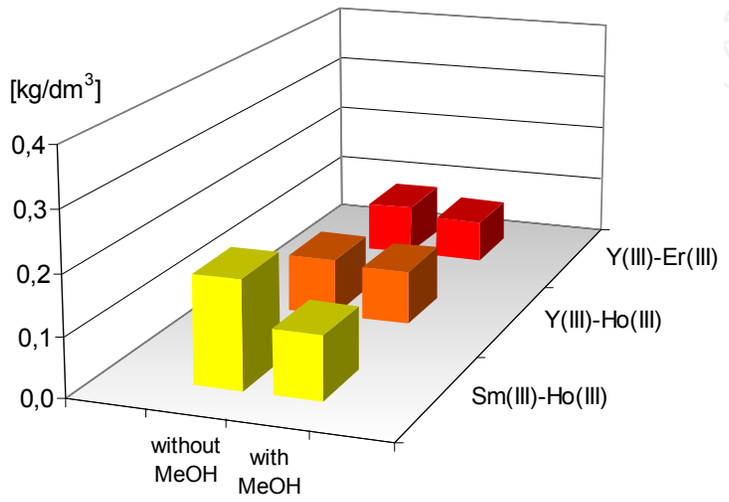


Figure 18. Fig. 18. Separation of Sm(III) from Ho(III) (0.35%), Y(III) from Ho(III) (0.36%) and Y(III) from Er(III) (0.35%) on Lewatit MonoPlus M 500 in the H_2O-20 % (v/v) CH_3OH (1 dm^3 of anion exchanger in the Cl^- form, Ln(III):IDA=1:1, pH 5.0, 1.5g Ln_2O_3/dm^3).

Taking into account the effect of types of functional groups $-N^+(CH_3)_3$ (Lewatit MonoPlus M 500) and $-N^+(CH_3)_2C_2H_4OH$ (Lewatit MonoPlus M 600) on the results of separation of rare earth element(III) complexes with IDA both for the Sm(III)-Ho(III) and Y(III)-Ho(III) pairs, the anion exchanger Lewatit MonoPlus M 500 (type 1) of slightly larger basicity of the functional group compared with the anion exchanger Lewatit MonoPlus M 600 (type 2). However, the addition of 10% (v/v) or 20% (v/v) methanol proved to be disadvantageous both for Lewatit MonoPlus M 500 and Lewatit MonoPlus M 600.

Due to the fact that the addition of polar solvent improves the efficiency of the separation of rare earth elements(III) only for the selected complexing agents, the possibility of selective separation of nitrate complexes of rare earth elements(III) in a polar organic solvent-H_2O-HNO_3 by the frontal analysis was also examined in the case of the absence of complexing agents. In the studies the following parameters were taken into account: type of the functional groups, type of the anion exchanger skeleton, the degree of cross linking, porosity and grain size as well as the effect of type and concentration of polar organic solvent, the presence of another organic solvent and the concentration of nitric(V) acid as well as the concentration of rare earth elements(III) in solution (Hubicki & Olszak, 1994; Hubicki et al. 1995; Hubicki & Olszak, 1996a; Hubicki & Olszak, 1996b; Hubicki et al. 1996).

Taking into account the obtained affinity series for the anion exchangers Wofatit SBWx4%, Wofatit SBKx7% and Wofatit SBWx6%in the systems:

90% v/v CH_3OH-10% v/v 7M HNO_3 – Wofatit SBWx4%

Nd(III) > Pr(III) > **Sm(III)** > Ce(III) > La(III) > Eu(III) > Gd(III) > Tb(III) > **Y(III)** > Dy(III) > Tm(III) ≥ Ho(III) ≥ Er(III) > Yb(III),

90% v/v CH_3OH-10% v/v 7M HNO_3 – Wofatit SBKx7%

Pr(III) ≥ **Nd(III)** > La(III) > **Sm(III)** > Eu(III) > Gd(III) > Tb(III) > Dy(III) ≥ Ho(III) = Er(IIII) = Tm(III) = Yb(III) > **Y(III),**

90% v/v C_2H_5OH-10% v/v 7M HNO_3 – Wofatit SBWx4%

Nd(III) > La(III) ≥ Pr(III) > **Sm(III)** > Eu(III) > Gd(III) > Tb(III) > Dy(III) > Ho(III) ≥ Er(III) > Yb(III) ≥ **Y(III)** ≥ Tm(III),

90% v/v C_2H_5OH-10% v/v 7M HNO_3 – Wofatit SBKx7%

Yb(III) ≥ La(III) ≥ **Y(III)** = Pr(III) = **Nd(III)** = Tb(III) = Er(III) ≥ Eu(III) = Dy(III) = Ho(III) ≥ **Sm(III)** = Gd(III) = Tm(III),

90% v/v CH_3COCH_3-10% v/v 7M HNO_3 – Wofatit SBWx4%

Nd(III) > La(III) ≥ Pr(III) > **Sm(III)** > Eu(III) > Gd(III) > Tb(III) > Er(III) > Dy(III) > Ho(III) = **Y(III)** ≥ Tm(III) > Yb(III),

90% v/v CH_3COCH_3-10% v/v 7M HNO_3 – Wofatit SBKWx7%

Nd(III) > La(III) ≥ Pr(III) > **Sm(III)** > Eu(III) > Gd(III) > Tb(III) > Dy(III) > Ho(III) ≥ Er(III) > Yb(III) ≥ **Y(III)** ≥ Tm(III),

it was found that the distribution coefficients have the largest values in the CH_3OH system.

The differences in affinity of rare earth(III) elements nitrate complexes for anion exchangers in individual systems, for example Y(III)-Nd(III), Sm(III)-Nd(III), are probably due to a different structure of complexes (degree of their solvation) or different stability or kinetics of their formation in the anion exchanger phase. Probably in the resin phase the $[Nd(NO_3)_5]^{2-}$ complexes are formed, whereas Y(III) forms the complexes of $[Y(NO_3)_4]^-$ (Korkish, 1968). It was also found that macroporous anion exchangers give better separation results whereas using strongly basic anion exchangers with the pyridine functional group Permutit SK the obtained results were worse. The analogous situation was in the case of Amberlite IRA 938 and Wofatit SBWx2% (Hubicki et al. 1996; Hubicki and Olszak, 1998a; Hubicki and Olszak, 1998b; Hubicki and Olszak, 1998c; Hubicki and Olszak, 1998d; Hubicki and Olszak, 1998e).

Additionally, it should be emphasized that these non-typical affinity series give the opportunity to obtain ion exchange separation of rare earth elements. Very interesting is the position of Y(III) in the obtained affinity series on Wofatit SBKx7%in the 90% v/v CH_3OH-10% v/v 7M HNO_3 system (Hubicki and Olszak, 1994; Hubicki et al. 1995). As follows from the theory of yttrium(III) migration in the lanthanide series, it behaves like pseudolanthanide(III) when the central ion-ligand bonding in the complex is covalently shortened and behaves like heavy lanthanides(III) when this bonding is of ionic character. In the studied system yttrium(III) behaves like heavy lanthanide(III).

Noteworthy are also the results of treatment of macro quantities of yttrium(III) from neodymium(III) in the 90% v/v CH_3OH–10% v/v 7 M HNO_3 system on the strongly basic anion exchanger Wofatit SBW with the degree of cross linking 4 and 6% DVB. On this anion exchanger, the effect of nitric(V) acid concentration in the 90% v/v CH_3OH–10% v/v 0.1-9 M HNO_3 system as well as the effect of the addition of ammonium nitrate(V) in the 90% v/v CH_3OH–10% v/v 0,1 M HNO_3 –1-5 M NH_4NO_3 system were also studied (Fig.19).

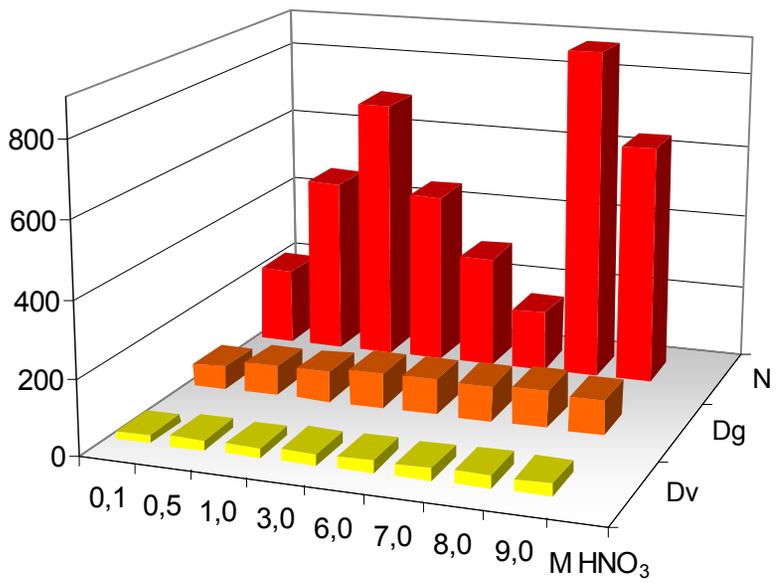


Figure 19. Mass (D_g) and volume (D_v) distribution coefficients as well as the number of the theoretical plates (N) of Wofatit SBWx6% in the dependence of HNO_3 concentration (0.1-9.0 M).

It was shown that with the increasing concentration of nitric(V) acid, the efficiency of sorption and separation of nitrate complexes of rare earth elements(III) initially increases in the systems 7-8 M HNO_3–CH_3OH, 3 M HNO_3–C_2H_5OH and 7 M HNO_3–CH_3COCH_3 and then decreases. The results of the effect of HNO_3 concentration on the efficiency of the purification process of Y(III) from Nd (III) (<0.001%Nd_2O_3) on the anion exchanger Wofatit SBWx4 with a varyingdegree of the cross linking is shown in Fig.20a. The analogous results obtained for the Sm(III)-Nd(III) pair are shown in Fig. 20b.

The type of skeleton of the used ion exchanger is also an important parameter. For the polyacrylate anion exchangers Amberlite IRA 458, Amberlite IRA 958 and Purolite A 850 the efficiency of the sorption process is low. Mass of the purified yttrium oxide(III) (<0.001%Nd_2O_3) was equal to 0.18 kg/dm^3 for Amberlite IRA 458; 0.26 kg/dm^3 for Amberlite IRA 958 and 0.09 kg/dm3 for Purolite A 850. The anion exchanger Amberlite IRA 68 proved to be completely useless. However, the best results were obtained on the strongly basic anion exchangers of type 1. For example, using Lewatit MP 5080 with the macroporous 25 skeleton structure there was achieved 1.9 kg Y_2O_3/dm^3 (<0.001%Nd_2O_3) in the methanol system while in the acetone system 2.3 kg Y_2O_3/dm^3 (<0.001%Nd_2O_3) (Fig.21).

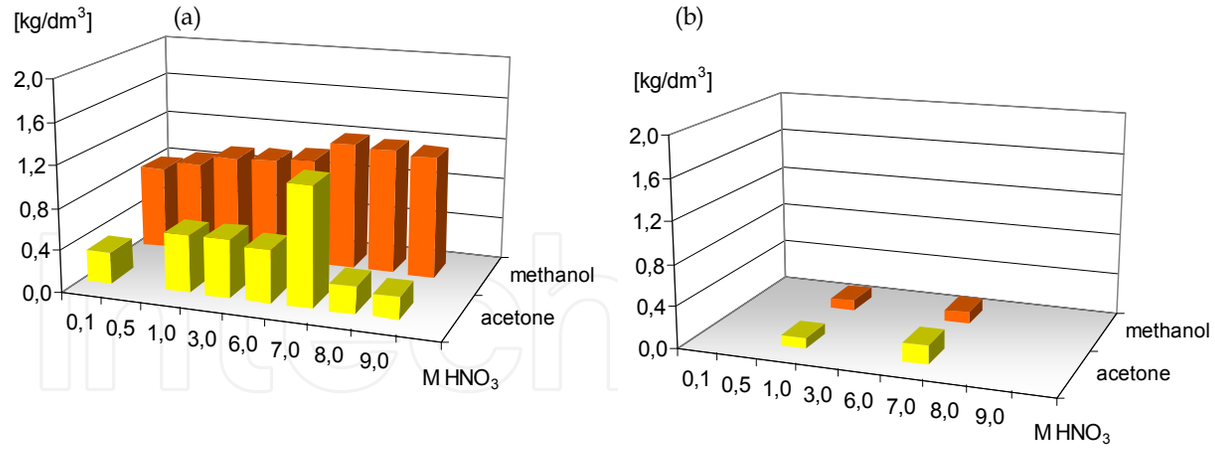


Figure 20. a-b. Effect of the HNO_3 concentration on the effectiveness of Y(III) from Nd(III) separation (<0.001%Nd_2O_3) on Wofatit SBWx4 (a) and Sm(III) from Nd(III) (<0.001%Nd_2O_3) on Wofatit SBWx6 (b) at different HNO_3 concentrations in the methanol and acetone systems.

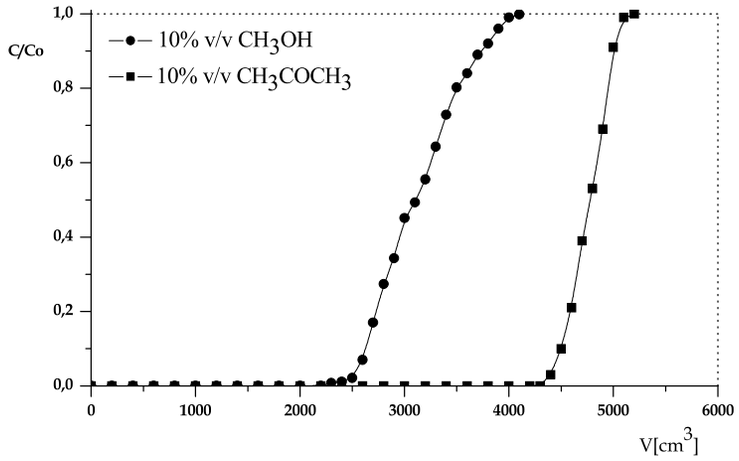


Figure 21. Separation of Y(III) fromNd(III) (<0.001%Nd_2O_3) on Lewatit MP 5080 in the 90% v/v CH_3OH–10% v/v 7 M HNO_3 and 90% v/v CH_3COCH_3–10% v/v 7 M HNO_3 systems.

Good results were also obtained on Zerolit FF IP 2-3%, Zerolit 3-5% FF IP and Wofatit SBWx6%. In in the case of Zerolit FF IP 7-9% more than two fold decrease of the efficiency of purification process of Y(III) from Nd(III) was obtained (Hubicki et a. 1994).

The influence of cross linking degree on the effectiveness of separation of Y(III)-Nd (III) pair was also studied. For the ion exchanger Dowex it increases from 2% to 6% DVB and then decreases. For the systems with methanol this effect is observed at 4% DVB. For Zerolit FF IP the highest sorption capacities were obtained at the degree of cross linking equal to 2-3%, which may be associated with the sieve effect (Hubicki & Olszak, 1996; Hubicki, et al. 1996). In comparison with the separation of yttrium(III) from neodymium(III) the effects of the purification process of samarium(III) from neodymium(III) are much lower. This is due to a smaller difference between the distribution coefficients of Sm(III)-Nd(III) in comparison with the Y(III)-Nd(III) pair. Taking into account the effectiveness of this sorption process gel and macroporous anion exchangers can be arranged as follows: in the $Ln(NO_3)_3$–90% v/v

CH_3OH–10% 7 M HNO_3 system: Lewatit MP 5080 (0.26 kg/dm^3) > Wofatit SBWx6% (0.16 kg/dm^3) > Dowex 1x4 (0.11 kg/dm^3) > Wofatit SBKx7% (0.07 kg/dm^3) > Wofatit SBWx7% (0.04 kg/dm^3) > Dowex 1x8 (0.031 kg/dm^3) > Dowex 1x2 (0.03 kg/dm^3) > Wofatit SBWx4% (0.02 kg/dm^3) > Dowex 1x10 (0.01 kg/dm^3) > Dowex 1x1 (0.009 kg/dm^3) (Hubicki & Olszak, 2000a; Hubicki & Olszak, 2001). The strongly basic anion exchanger Lewatit MP 5080 proved to be the most effective (Hubicki & Olszak, 2001). Depending on the separation system the obtained results are in the range from 0.26 to 0.24 kg of Sm_2O_3 (0.001 % Nd_2O_3) on 1 dm^3 of the ion exchanger. The smaller results were obtained on Wofat SBWx6 - 0.18 kg Sm_2O_3 (0.001% Nd_2O_3)/dm^3). Much smaller yield of Sm(III) from Nd(III) purification compared with that of Y(III) from Nd(III) is caused by a smaller difference between the distribution coefficients of Sm(III)-Nd(III) compared with Y(III)-Nd(III). Different affinities of neodymium(III) and samarium(III) nitrate complexes in the systems $Ln(NO_3)_3$–90% v/v CH_3OH–10% 1 M or 7 M HNO_3 as well as in $Ln(NO_3)_3$–90% v/v CH_3COCH_3–10% 1 M or 7 M HNO_3 are probably caused by the formation of neodymium nitrate complexes with a higher negative charge, e.g. $[Nd(NO_3)_5]^{2-}$ than that of samarium(III) complexes , e.g. $[Sm(NO_3)_4]^-$) or by their different structures (possibly by the differences in the degree of solvation) and the kinetics of formation of neodymium(III) and samarium(III) anionic nitrate complexes (Hubicki, et al. 1996; Hubicki and Olszak, 2000a; Hubicki and Olszak, 2000b; Hubicki and Olszak, 2001; Hubicki and Olszak, 2002).

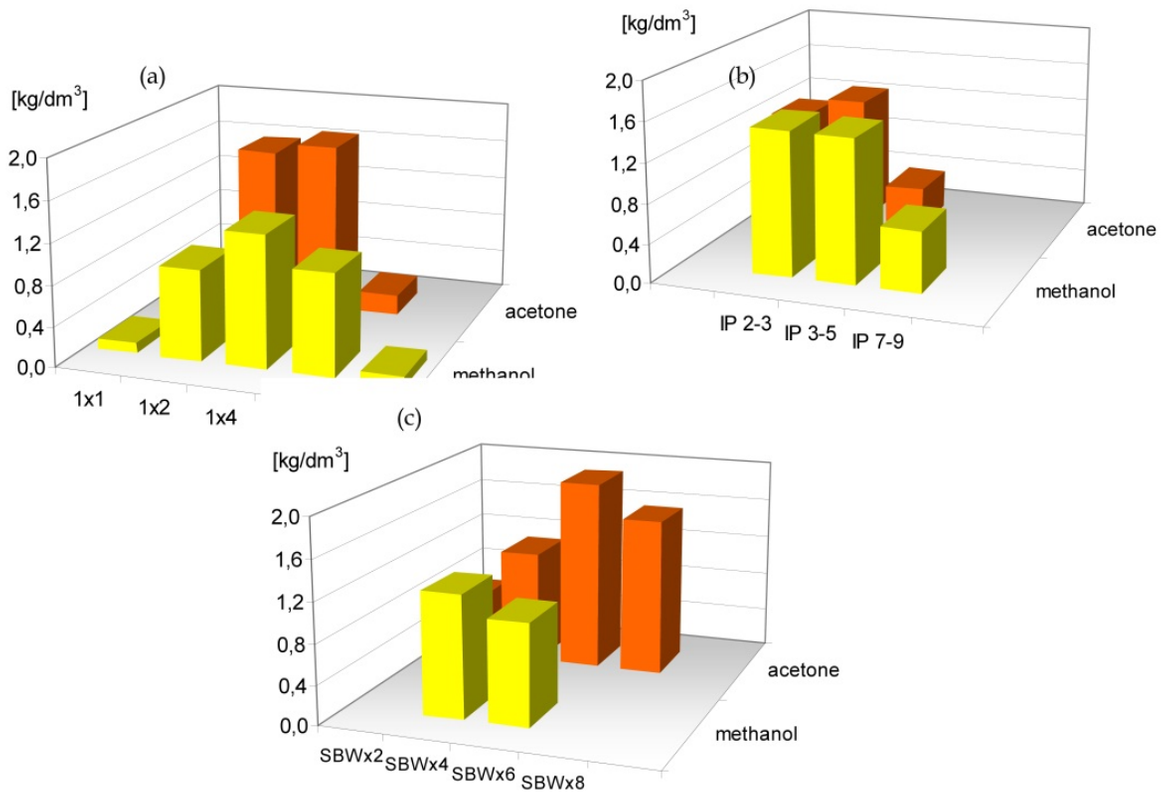


Figure 22. a-c. Separation of Y(III) from Nd(III) (<0.001%Nd_2O_3) on Dowex 1 (a), Zerolit FF IP (b) and Wofatit SBW (c) with different cross linking in the methanol and acetone systems.

Determination which of the used organic solvents possesses the best sorption properties is not possible.

However, it should be noted that using 1-propanol and 2-propanol the efficiency of the separation process is lower than for methanol and acetone (data not presented). It was also shown that for dimethylosulphoxide (DMF) in a 90% v/v DMF-10% v/v 7 M HNO_3 system separation does not occur.

In industrial processes of ion exchange separation of rare earth elements(III) on cation exchangers using aminopolycarboxylic acids or hydroxyacids as eluents, the concentration of lanthanides(III) in the eluate rarely exceeds a few grams per liter. In the present study, the effect of concentration of rare earth elements(III) on the efficiency of Y(III)-Nd(III) pair separation in the macro-micro component was investigated. It was found that in the methanol and ethanol systems the increase in the concentration of purified yttrium(III) to 50 g Ln_2O_3/dm^3 practically does not affect the efficiency of the process. However, further increase of Ln_2O_3 concentration decreases the efficiency of the ion exchange column. Very good results were obtained at a concentration of 50 g Ln_2O_3/dm^3 in the acetone system.

The effect of the percentage concentration of Nd(III) on the effectiveness of the separation process was also examined. Both, in the case of yttrium(III) and samarium(III) separation at 0.1% of neodymium(III) content the effectiveness of the process is much better.

The sorption of nitrate(V) complexes of rare earth elements(III) is also dependent not only on the type of solvent used but also on its concentration in the mixture. This fact was confirmed by the results of the separation of yttrium(III) from neodymium(III). The addition of an organic solvent such as methanol or acetone (with a lower polarity and dielectric constant than water) generally reduces the degree of dissociation of rare earth elements(III) and increases their tendency to form ion complexes. At the same time the distribution coefficients of lanthanides(III) on anion exchangers are also changed.

It should be mentioned that the anion exchangers can be regenerated with water in the amount of 2–4 bed volumes after the purification process of rare earth elements. The relatively high yield of rare earth elements purification, the low costs and the simple and cheap regeneration of the anion exchanger bed when the purification process is over, as well as the possibility of methanol recovery from the eluate by using the distillation method suggest the possibility of using this process in technologies for high purity rare earth production.

13. Conclusions

Rare earth elements(III) are extremely important for the development of economy and technology. Among others, they are used for the production of electronic equipment, in automotive, aerospace, missile, military industries and even in medical diagnostics.

Atypical affinity series create new possibilities of ion exchange separation of rare earth elements(III) which is very significant from a practical point of view. The results of rare earth elements nitrate complexes separation in the micro-macro component system as well

as in the presence of aminopolycarboxylic acids and organic solvents can be successfully applied in production of rare earth elements(III), particularly yttrium(III), ytterbium(III), samarium(III) and lanthanum(III) of a large purity degree. It is worth mentioning that regeneration of anion exchangers in these systems is very economical using distilled water as a regenerating factor.

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