Master thesis

Solid-Phase Extraction of Rare Earth Elements from Phosphoric Acid Solutions

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Date(29/06/2022)

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Declaration of Authorship

„I declare in lieu of oath that this thesis is entirely my own work except where otherwise indicated. The presence of quoted or paraphrased material has been clearly signaled and all sources have been referred. The thesis has not been submitted for a degree at any other institution and has not been published yet.”

Abstract

The master's thesis is devoted to the rare earth elements obtaining from phosphoric acid solutions as by-products of apatite concentrate sulfuric acid leaching, which will increase its processing depth.

The paper gives an analysis of global achievements in the field of rare earth elements obtaining, presents the technological and chemical bases of producing phosphoric acid, and outlines rare earth elements properties, main sources and applications. The purpose of the paper is to explore the solid-phase method of rare earth elements extraction using polymer-based materials impregnated or immobilized with di-2-ethylhexylphosphoric acid as an extractant.

The results of the research revealed thermodynamic and technological features of the process, as well as the possibility of effective multiple use of the resins, regenerated with sulfuric acid.

Zusammenfassung

Die Masterarbeit widmet sich den Seltenerdelementen, die aus Phosphorsäurelösungen als Nebenprodukte der Apatitkonzentrat-Schwefelsäurelaugung gewonnen werden, wodurch die Verarbeitungstiefe erhöht wird.

Das Papier gibt eine Analyse der globalen Errungenschaften auf dem Gebiet der Gewinnung von Seltenerdelementen, stellt die technologischen und chemischen Grundlagen der Herstellung von Phosphorsäure vor und skizziert die Eigenschaften, Hauptquellen und Anwendungen von Seltenerdelementen. Der Zweck des Papiers ist es, die Festphasenmethode der Extraktion von Seltenerdelementen unter Verwendung von Materialien auf Polymerbasis zu untersuchen, die mit Di-2-Ethylhexylphosphorsäure als Extraktionsmittel imprägniert oder immobilisiert sind.

Die Forschungsergebnisse zeigten thermodynamische und technologische Merkmale des Verfahrens sowie die Möglichkeit einer effektiven Mehrfachverwendung der mit Natriumcitrat regenerierten Harze.

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1 Introduction

Rare earth elements (REE) are a group of seventeen metals that possess a complex of unique optical, magnetic and electrical properties, which made them the basis for the creation of high-tech products. Thus, the majority of priority directions in the development of science, technologies and engineering are simply impossible without REE.

Nevertheless, despite the steady growth of rare earth elements consumption due to ongoing technological progress, the share of the Russian Federation in world production is extremely small, which is due to the lack of technological development of the country in this area. This entails a high dependence on imports and necessitates the creation of domestic industries.

Most of the reserves of Russian REE are contained in apatite-nepheline ores of the Khibiny group deposits, which have a huge potential for the introduction of their production as by-products due to the higher content of the most valuable heavy and medium groups of elements. Apatite has already found wide application: for many decades it has been used as a raw material for the production of phosphoric acid, which, in turn, serves as a raw material for the production of phosphorus-containing fertilizers and feed phosphates. Such phosphoric acid contains about 0.1% of rare earth elements that at the moment are practically not extracted on an industrial scale.

The extraction of rare earth elements is associated with a number of difficulties: occurring in ores as often as metals like zinc, lead and nickel, they are difficult to extract due to their extremely low content, which is often insufficient for economically feasible development. Also, the separation of REE into individual metals is not an easy task due to the similarity of their chemical behavior.

Currently, there are several main methods of obtaining REE, including precipitation, extraction and sorption methods. The choice of the method is determined by the characteristics of the raw materials containing the extracted metals, the process conditions and the general technological scheme. The most widely used extraction methods are divided into solvent and solid-phase extraction.

Solid-phase extraction has significant technological advantages, such as simplicity and the possibility of eliminating toxic solvents. The use of flammable organic solvents in solvent extraction has a negative environmental effect due to their ability to form fire-explosive mixtures.

Thus, the aim of the paper is to identify the thermodynamic and technological features of solid-phase extraction of REE from phosphoric acid solutions using polymer materials that contain impregnated or immobilized di-2-ethylhexylphosphoric acid.

2 Properties and Consumption of Rare Earth Elements

The rare earth elements are a group of seventeen metals with similar physical and chemical properties. The group includes the lanthanides (metals from lanthanum to lutetium with an atomic weight ranging from 57 to 70), yttrium, and scandium. REE are divided into light (lanthanum, cerium, praseodymium, neodymium, samarium, europium) and heavy (gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, yttrium) ones. Sometimes REE are classified into three groups, distinguishing in addition to heavy and light a medium one, including metals from samarium to dysprosium.

Yttrium, which is not a lanthanide, is considered a heavy REE because of the similar ionic radius, which leads to similar chemical properties. The properties of scandium, in turn, are very different, and therefore it is considered neither heavy nor light, but is classified as REE because it is usually present with them in rare-metal ores.

For most neutral lanthanide atoms the electronic configuration can be represented as $4f^{n+1}5s^{2}5p^{6}6s^{2}$. The loss of one electron from the 4f and two from the 6s orbitals leads to the formation of characteristic cations with a 3+ charge. In some cases, the energy difference between the electrons in the 4f and 5d orbitals is so insignificant that the electron transfers from the 4f to the 5d orbital, resulting in the formation of cations with a 4+ charge, such as Ce^{4+}. It is also possible for an electron to transfer from the 5d orbital to the 4f orbital, which in turn leads to the formation of cations with a 2+ charge, such as Sm^{2+}, Eu^{2+} and Yb^{2+} (Greenwood and Earnshaw 1997, p. 38).

The similarity of the rare earth elements properties is due to the similarity of their crystallochemical affinity because of close values of the ionic radii. It is explained by the important phenomenon, influencing properties of REE, namely the lanthanide contraction, characterized by essential decrease of atomic and ionic radii with increase of serial number. Thus, lanthanum has the largest radius and lutetium has the smallest one. Due to this effect, the radius of yttrium is comparable to radii of heavy REE. The outer electron layer of yttrium is also similar to that of the heavy subgroup metals, which explains their chemically similar behavior, as well as their concentration with yttrium in geochemical processes, because of which yttrium separation is a significant problem in the extraction of rare earth elements (Voncken 2016, p. 59).

The crystalline structure of the rare earth elements is mostly represented by a hexagonal close-packed lattice (Figure 1) (Kudrevatykh and Volegov 2017, p. 36; Savitskiy et al. 1963, p. 127). The structure of samarium, europium and ytterbium is different: they are represented by rhombohedral, volume-centred and face-centred cubic structures, respectively. The crystal lattice of promethium, which practically does not occur in nature, is unknown.

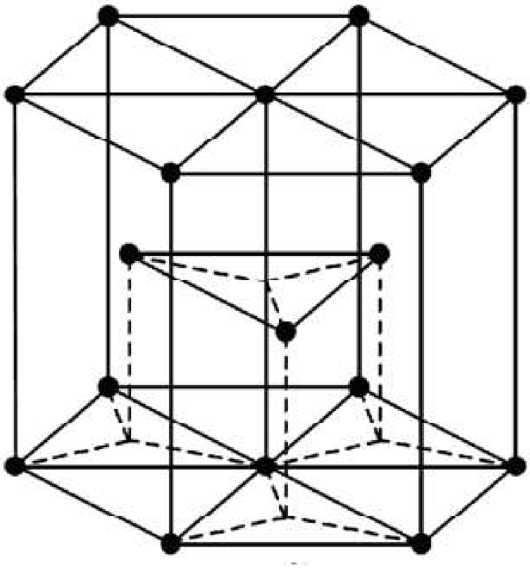


Figure 1: Hexagonal close-packed lattice (Kudrevatykh and Volegov 2017, p. 36)

The stability of the crystal lattice and the strength of the bond between the atoms cause sufficiently high melting points of rare earth elements: from 1099 K for europium to 1936 K for lutetium. Due to this feature, rare earth elements began to be used in the production of refractory ceramics, which finds application in the production of high-temperature protective coatings, refractory materials and optics. REE is also used in ceramics and enamels to increase the saturation and depth of colors. Thus, up to 5% of praseodymium is used to create yellow (“Science of Rare Earth Elements” 2020). REE additives increase the strength and brightness of ceramic products. For example, the use of yttrium oxide as an additive in zirconium oxide provides high hardness and increased abrasion resistance (Fialkovsky 2020, p. 48). It is expected that the average annual growth rate of ceramic applications from 2019 to 2025 will be 7.0%. (“Мировой рынок редкоземельных металлов будет расти на 10,4% в год / The global rare earth metals market will grow by 10.4% per year” 2021), which will also have an impact on the demand for REE.

Mostly, REE do not have good electrical conductivity, but for lanthanum and cerium a sharp increase in temperature is accompanied by superconductivity. Gadolinium, unlike other REE, is a ferromagnet, i.e. it is magnetised in the absence of an external magnetic field at temperatures below the Curie point, and is therefore used in the production of magnetic materials.

The large number of unpaired electrons allows REE to create magnetic fields and store magnetic energy. This quality is particularly strong with neodymium, dysprosium and samarium (“Science of Rare Earth Elements” 2020). Holmium, on the other hand, has the greatest magnetic strength, allowing it to be used in the manufacture of particularly powerful magnets (Balaram 2019, p. 1294).

Many rare earth elements exhibit pronounced luminescence in the ultraviolet to near-infrared range, which is why they have found use in the manufacture of phosphors and LEDs. Such metals include europium, erbium and neodymium. The ability of the ions to convert excitation energy into visible energy allows them to be used in solar cells.

Rare earth elements are of great importance in the production of catalysts, which is one of the leading uses of REE. Cerium and lanthanum are the most frequently used because of their electronic structure. Cerium, which can be easily oxidized and reduced, is needed in automotive catalytic converters to oxidize toxic carbon monoxide into carbon dioxide. Lanthanum, on the other hand, has found application in catalytic cracking, one of the most common methods of oil refining. Thus, application of REE in cracking allows increasing productivity of the unit by 20-30%.

Mechanical properties of rare earth elements, such as elasticity, plasticity and hardness, have determined their importance in alloy production both as alloying additives and as basic constructional materials. Alloys with REE elements like neodymium and yttrium allow increasing heat resistance, corrosion resistance and electrical conductivity.

Neodymium, dysprosium and praseodymium are also important components in some types of wind turbines. In 2020, 1.5 times more wind power capacity has been commissioned in the world as compared to 2019, and their total volume by the end of

2019 already met more than 7% of the global electricity demand ("Мировой рынок редкоземельных металлов будет расти на 10,4% в год / The global rare earth metals market will grow by 10.4% per year" 2021), which, in turn, will increase the demand for REM in the future.

In spite of the fact that REE exhibit similar properties, it is not always possible to replace one with another. Moreover, the use of concentrates containing several non-separated elements at once loses its relevance and amounts to no more than 30% (Gasanov et al. 2018, p. 32), while the consumption of individual REE is rapidly growing (Petrov and Naumov 2012, p. 65).

By and large, the distribution of rare earth elements by industry in the global economy is shown in Figure 2.

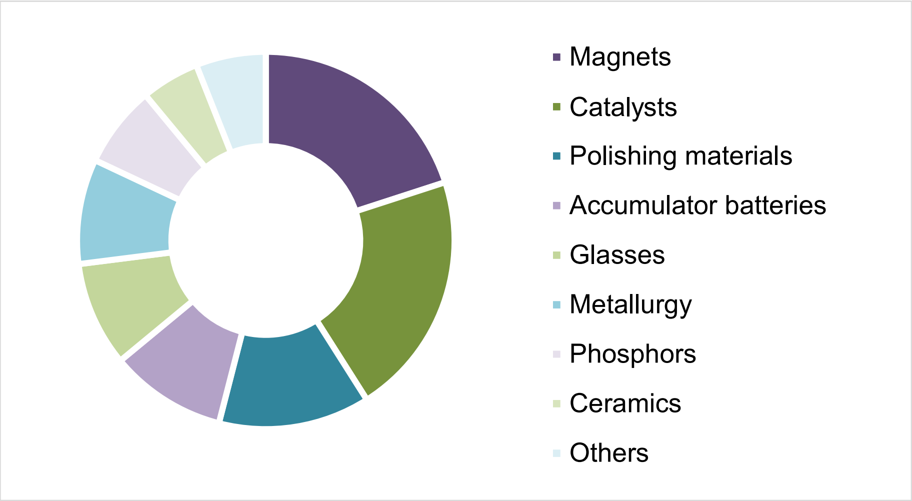


Figure 2: **Distribution of REE by industry in the world (Kondratiev 2017, p. 51)**

Examples of the rare earth elements use with specific metals used are shown in Figure 3.

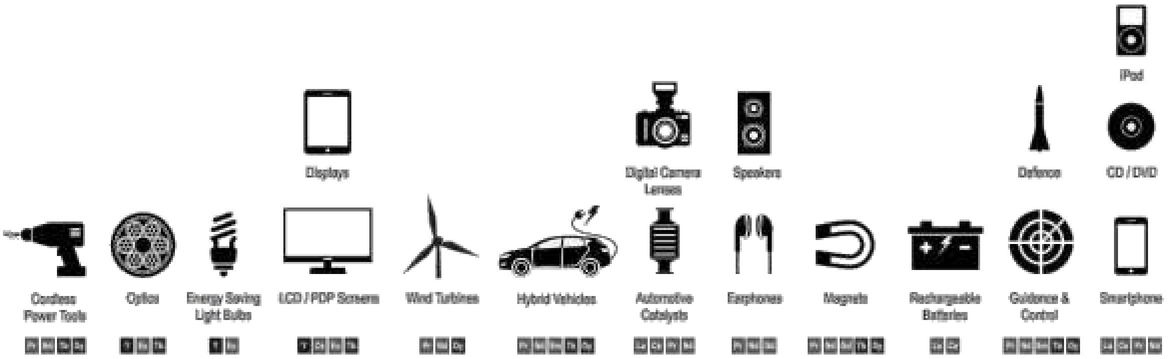


Figure 3: **Examples of REM use (Hongqiao et al. 2016, p. 12)**

Therefore, the unicity of the physical and chemical properties of rare earth elements has determined their widest application in numerous science-intensive industries. Nevertheless, the similarity of these properties determines their almost identical chemical behavior during extraction. This explains the difficulty of their extraction and separation, which requires the selection of an extraction method that provides the best selectivity based on the small differences in the structure of these elements that determine their individual characteristics in their combined presence.

3 Reserves and Production Rare Earth Elements

The increased demand for rare earth elements led to changes in market conditions and made them a critically important raw material resource for both Russia and the world.

Rare earth elements are currently classified as critical raw materials by the European Commission 2020 (Figure 4). This is mainly due to the concentration of resources in China, which is currently the uncontested monopoly in REE production and is responsible for 98% of Europe's supply (European Commission report, Study on the EU's list of Critical Raw Materials 2020, p. 3). Russia's and Europe's lack of technological sophistication in REE mining and processing reflects their weak sustainability and high dependence on imports. The economic importance of these metals is also increasing, as can be seen in their rightward shift compared to the European Commission's 2014 estimate (European Commission report, Study on the EU's list of Critical Raw Materials 2014, p. 3).

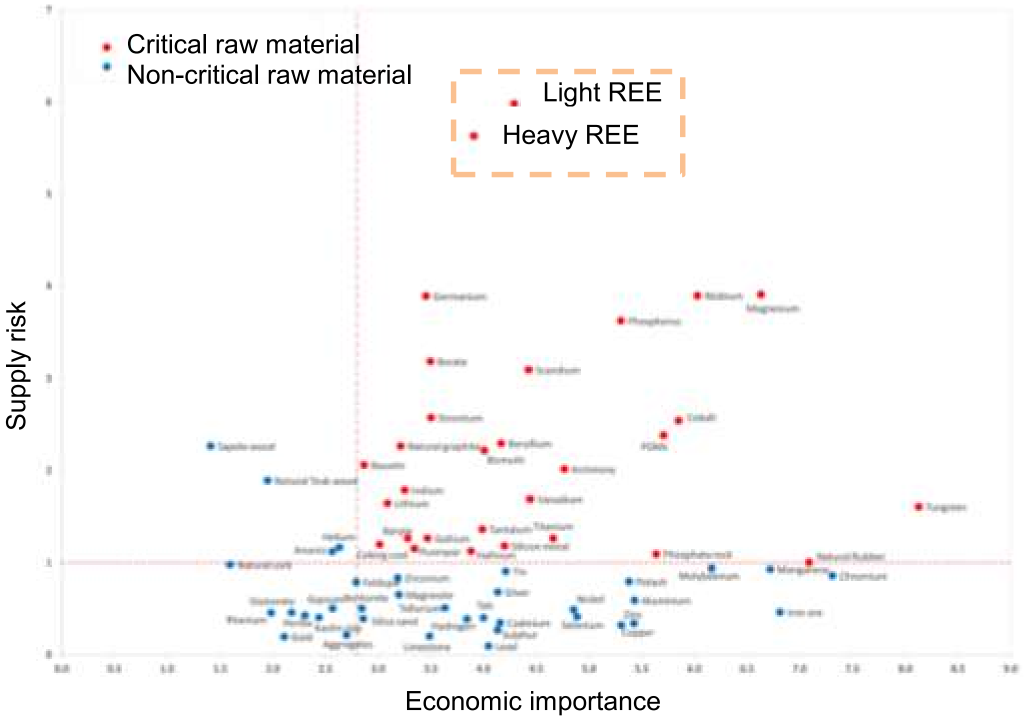


Figure 4: **European Commission report, Study on the EU's list of Critical Raw Materials 2020, p. 4**

Russia has huge resources and reserves of rare earth metals and, together with Brazil, ranks third in the world in terms of their volume. Nevertheless, very small amounts of

REE are produced within the country, amounting to no more than 1% of the world volume (U.S. Geological Survey, Mineral commodity summaries 2022: U.S. Geological Survey 2022, p. 135). The graph of the volumes of reserves and consumption of REE by the country in 2021 is shown in Figure 5.

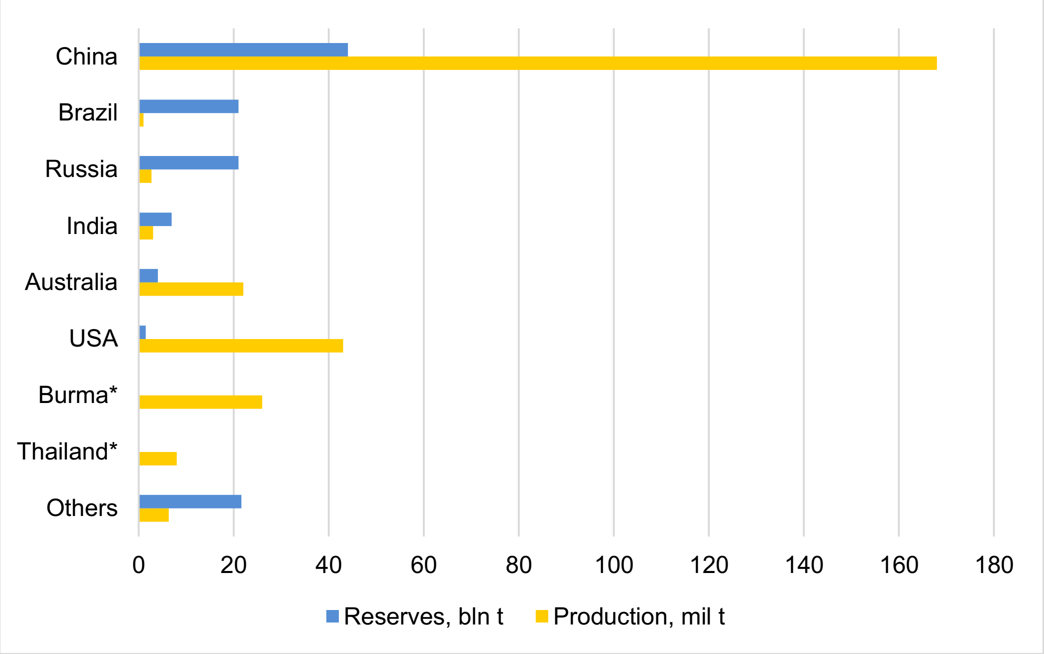


Figure 5: Reserves and production volumes in different countries in 2021 (U.S. Geological Survey, Mineral commodity summaries 2022: U.S. Geological Survey 2022, p. 135)
***Resource assessment is not available**

Despite the name, rare earth elements are very common. The most abundant in the Earth's crust, cerium has a content of 63 ppm, higher than that of copper (47 ppm) and lead (16 ppm), while the rare thulium and lutetium themselves (0.3 and 0.31 ppm respectively) exceed precious metals like silver, which is only 0.08 ppm (Dushyantha et al. 2020, 103521; Kudrevatykh and Volegov 2017, p. 11-12). However, unlike precious metals, which are often found in ores as an individual component, such as gold, REE are always present in ores together, which complicates their selective obtaining.

Total world reserves of rare earth elements in 2021 were estimated at 120 000 million tons (U.S. Geological Survey, Mineral commodity summaries 2022: U.S. Geological Survey 2022, p. 139). Rare earth elements can be found in more than 250 minerals, represented mainly by silicates, fluorocarbonates, oxides and phosphates, and only a relatively small number are suitable as REE sources. The main rare-metal minerals and their average REE content are presented in Table 1.

Mineral	Formula	REE content, %
Bastnaesite	Ln(CO$_3$)F	74.8
Gadolinite	(Ln,Y)$_2$FeBe$_2$Si$_2$O$_{10}$	48.3
Xenotime	Y(PO$_4$)	62.0
Loparite	(Na,Ce,La,Ca,Sr)(Ti,Nb)O$_3$	29.8
Monazite	(Ln,Th)PO$_4$	65.1
Parisite	CaLn$_2$(CO$_3$)$_3$F$_2$	60.3
Synchysite	CaLn(CO$_3$)$_2$F	49.6
Fergusonite	YNbO$_4$	39.9
Fluocerite	LaAl$_3$(PO$_4$)$_2$OH	83.4

Table 1: Main rare metal minerals* (Jordens et al. 2013 p. 101; U.S. Geological Survey, Mineral commodity summaries 2022: U.S. Geological Survey 2022, p. 139)
***Ln — total REE**

Due to the scarcity of raw materials, REE is often obtained as co-product or by-product, which allows increasing the depth of processing of the mineral without interfering with the main production, while at the same time providing a valuable product (Qi, D. 2018, p. 321; Wu et al. 2018a, p.112). For example, the main product of the Bayan Obo mine in China is iron ore, but the REE mined there as a by-product account for most of the REE produced globally (Philip and Anderson 2018, p. 4).

In addition to the insignificant volumes produced in Russia, the problem is also presented by the fact that the REE products obtained are often in the form of a concentrate of carbonates containing a group of REE at once. The current global production and consumption, in turn, are focused on obtaining individual rare earth elements.

The raw material base of Russian REE is localised in a small number of regions. About 70% of reserves are located in North-Western Federal Districts, of which about 40% in the form of loparite ores of the Lovozero deposit and the remaining 60% in the form of apatite-nepheline ores of Khibiny group (О состоянии и использовании минерально-сырьевых ресурсов Российской Федерации в 2019 году: Государственный доклад / On the state and use of mineral resources of the Russian Federation in 2019: State Report 2020, p. 305).

Apatite ores from deposits in the Khibiny group have great potential for the introduction of by-product production. Despite the higher percentage of REE in loparite that is traditionally used as raw material for REE obtaining, apatite contains higher amounts of particularly valuable elements of heavy and medium groups. It is also important to note that there are practically no radioactive elements in Khibiny apatite concentrate and consequently there is no need to purify separated REE from radioactive impurities.

The difficulty in creating domestic technology lies in the extremely low quality of rare metal raw materials in Russia, which is why production to obtain exclusively REE is impractical. To solve this problem, it is necessary to introduce the stage of extraction of REE as by-products into already functioning production facilities. Thus, in Russia, a promising method of rare earth elements obtaining is their associated production from phosphoric acid, which is formed during the processing of apatite into phosphoric fertilizers. Such phosphoric acid contains about 0.1% of the amount of lanthanides and yttrium.

4 Phosphoric acid as raw material

REE is present in apatite because of its ability to replace calcium in the crystal lattice (Dostal 2017, p. 6). Apatite has higher content of heavy REE, but due to low concentration of total REE (for example, apatite of Khibiny group contains only up to 1%), it is unprofitable to produce them as an independent product. However, the introduction of by-product production of rare earth elements from semi-processed products, which are then returned to the production cycle for further use, will increase the economic attractiveness of the main production at the expense of an additional valuable product. In the case of apatite, this semi-product is extractable phosphoric acid. In terms of volume production, it is the most important mineral acid after sulphuric acid, and its global production in terms of P_2O_5 exceeds 40 million tons per year, of which Russia accounts for about 3 million tons (Информационно-технический справочник по наилучшим доступным технологиям ИТС 2-2019 «Производство аммиака, минеральных удобрений и неорганических кислот» / Information and Technology Handbook on Best Available Techniques for Ammonia, Mineral Fertilizers and Inorganic Acids 2019, p. 124).

Apatite has already found wide application: for many decades it has been used as a raw material for extractable phosphoric acid, which in turn serves as a raw material for phosphate-based fertilisers and feed phosphates.

The main phosphorus-containing component of the apatite ore of the Khibiny group is fluorapatite with the formula $Ca_5(PO_4)_3F$, whose calcium ions in the crystal lattice can be replaced by rare earth metals. In order to obtain phosphoric acid, it is leached with sulphuric, nitric or hydrochloric acids. In Russia, as well as in the world, sulphuric acid is more widely used to decompose apatite, which is used in a mixture with recycled phosphoric acid, returned to the reactor for greater mobility of the suspension.

Depending on the conditions, chief among which is the temperature of the process, the resulting calcium sulphate can be released in the forms dihydrate, half-hydrate and anhydrite, having the following formulas:

- $CaSO_4 \cdot 2H_2O$ as dihydrate;
- $CaSO_4 \cdot 0.5H_2O$ as hemihydrate;
- $CaSO_4$ as anhydrite.

The most widespread of them is the dihydrate method, which treats more than 80% of phosphate rocks (Wu et al. 2018b, p. 780). During this method, the decomposition of apatite is accompanied by the formation of calcium sulfate in the form of a dihydrate, also called phosphogypsum.

The dihydrate process takes place according to the following reaction equation:

$$Ca_5(PO_4)_3F + 5H_2SO_4 + nH_3PO_4 + 2H_2O \rightarrow (n+3)H_3PO_4 + 5CaSO_4 \cdot 2H_2O + HF + Q. \quad (1)$$

The extracted phosphoric acid is used in the production of fertilizers, while phosphogypsum, a solid industrial waste, is transported to the dump and practically not used. During decomposition of apatite concentrate, about 20% of the initial amount of rare earth elements passes into solutions of phosphoric acid, including particularly valuable heavy group, and the rest part, which mainly contains light and medium elements, goes into phosphogypsum, in which final REE content reaches 0.45%. Research is being carried out in the field of REE recovery from phosphogypsum, but the essential drawback of its use as a raw material is the necessity of obligatory preliminary preparation.

Phosphoric acid as a raw material compares favourably with phosphogypsum, as there is no need for its preliminary preparation. The choice of rare earth element extraction technology is based on the requirements to keep the composition of phosphoric acid unchanged for its subsequent use in fertilizer production. Thus, it is not possible to use methods such as precipitation or evaporation due to the presence of precipitating impurities such as calcium, iron, titanium, etc.

Identical physical and chemical properties of rare earth metals and multicomponent composition of apatite processing products create additional difficulties for their extraction and separation into individual components. Technological difficulties of REE extraction are also connected with their incommensurably low content in comparison to impurity macroelements: the total concentration of REE amounts to 0.07-0.10%, which are not extracted in the current conditions and further transform into phosphoric acid during phosphoric acid application. The content of iron ions competing during extraction or sorption reaches 0.3-0.4% in recalculation to iron oxide(III).

With phosphoric acid as the object of research the choice of technology for the extraction of REE is conditioned by the need to keep the composition of phosphoric acid unchanged for its further use in fertilizer production. Thus, it is not possible to resort to methods such as precipitation and evaporation. In addition to REE, the precipitate also contains significant amounts of impurities, such as calcium, iron, titanium, etc., which makes it difficult to extract the individual components. The method of extraction, in its turn, allows to avoid changes of phosphoric acid properties and was considered in this work.

5 Rare Earth Elements Obtaining

5.1 Main Methods

Several methods have been used to obtain REE from recycling solutions, the main ones being extraction with organic solvents, sorption and precipitation.

Precipitation methods, which have significant disadvantages, have been studied in the literature in sufficient detail. One of them is that the proportion of lanthanides in the solid products usually does not exceed 20% because in addition to the target components a large number of impurities is precipitated such as calcium, iron, titanium and aluminium, which are extremely difficult to separate later. For example, in (Alemrajabi et al. 2017, p. 258) the recovery of REE from the nitric acid product of apatite processing by phosphate precipitation was studied, where the final concentration of REE in the resulting sediment was only 12.5%. An even more significant disadvantage of the method is the necessity of preliminary neutralization of phosphoric acid with ammonia, which makes it impossible to use it in production.

Because of these disadvantages, the precipitation method is nowadays increasingly preferred to the extraction method, which consists in the transfer of the target components into the extractant when the phases come into contact. Extraction is divided into solvent extraction, which involves two immiscible liquids, and solid-phase extraction, which involves a parent liquid with extractable metals and a reactive solid phase consisting of an extractant applied to an auxiliary material.

iquid extraction has become widespread due to the efficiency of extraction and separation of elements, simplicity, versatility and the ability to adapt the process to large volumes of solutions on an industrial scale. In addition, extraction remains the main method of recovery of rare earth elements from complex water-salt solutions, to which EFC belongs and which have extremely low pH values due to the specifics of acidic processing of rare metal ores.

Nevertheless, solvent extraction has significant disadvantages. For example, (Xie et al. 2014, p. 17) noted the small contact area of the phases and the formation of an interfacial emulsion during extraction. Also extractants are used in mixture with flammable diluents like paraffin, heptane and benzene to reduce the viscosity and cost of the solvent, which has a negative environmental effect.

Solid-phase extraction, which combines the properties of extraction and sorption processes, is becoming increasingly popular. The equilibrium and stoichiometry in solvent and solid-phase extraction, where the same compound is used as an extractant, can be identical. However, there are differences in the kinetics of the process: solid-phase extraction is much slower than solvent extraction and the target components have a lower adsorption capacity.

5.2 Solid-Phase Extraction

The investigated method of solid-phase extraction lacks the essential deficiency inherent in the more common method of liquid extraction, where extras are used in a mixture with flammable diluents like kerosene, heptane and benzene to reduce their viscosity and cost, which imposes special requirements on storage and the process itself (Hidayah and Abidin 2017, p. 10). The use of such mixtures has the following negative environmental effects:

- isolation of volatile organic compounds;
- the appearance of toxic waste;
- risk of fire due to the ability to form fire-explosive mixtures.

Solid-phase extraction, in which the extractant is applied to a solid polymer material, allows this to be avoided.

However, such solid carriers, even under the condition of repeated use due to washing, cannot work forever. After the extractant loses its properties, the matrix can be re-impregnated, which will allow for extraction and re-extraction cycles an unlimited number of times.

Solid-phase extractants are organic compounds deposited on the solid material that are capable of coordination or ionic interaction with the target metal ion. The active component may be retained on the surface by physical adsorption through the forces of intermolecular interaction, be in a thin layer of solvent that covers the surface of the sorbent, or be distributed in the volume of the solvent that fills the pores of the solid carrier. The carriers used are synthetic organic polymers such as copolymers of styrene and divinylbenzene, natural polymers, inorganic carriers such as porous silica, etc. The sorption mechanism depends on the nature of the sorbent and can proceed as simple sorption, complexation or ion-exchange sorption. The choice of the base material of solid extractant for REE extraction must take into account the composition of the treated solution.

The classical method of solid-phase extractants production consists in immobilization of an active component in a polymer in the process of its synthesis, for example, in copolymerization of styrene and divinylbenzene. This method of synthesis provides a high content of the active component in the sorbent phase, its lower entrainment, uniform distribution in the volume of the pellet and identical behavior to the solvent extraction process (Callura et al. 2019, p. 471). The disadvantages of this method are the presence of closed micropores and the absence of macropores, which results in a slow diffusion of extractable substances deep into the grains, worsens the process kinetics compared to solvent extraction and therefore the dynamic exchange capacity.

Another approach is the modification, or impregnation, of already prepared polymers or other carriers. Two main methods are used for modification: dry and wet.

The dry method consists of impregnating the carrier with the active component or its solution in a volatile solvent and then removing this solvent as well as the excess active component by heating. In this process, the molecules of the active ingredient are physically adsorbed on the surface of the carrier. On contact with aqueous solution, they are surrounded by water molecules, i.e. their interaction with metal ions is different from that of solvent extraction.

The wet method consists in impregnating the carrier with a solution of the active component in a non-polar or low-polar solvent followed by repeated washing of the sorbent with water. Such sorbents are more predictable, the active component in them is in the organic solvent layer and therefore their behaviour should be identical to the solvent extraction processes.

A serious disadvantage of impregnated sorbents is their low stability caused by gradual washout of the active component into the mobile phase during operation, which reduces the service life of the sorbent and leads to the side effect of contamination of the liquid phase.

A new and inexpensive activated carbon impregnated with ethylenediamintriacetic acid (EDTA-AC) was synthesized by the authors of (Babu et al. 2018, p. 1488) by adding N-[(3-trimethoxysilyl)propyl]ethylenediamintriacetic acid (TMS-EDTA) to oxidized activated carbon (AC). The affinity of EDTA-AC to each of the lanthanide ions was determined, and from binary mixtures of La/Ni, Sm/Co, Eu/Y and Dy/Nd, the greatest selectivity was observed for (heavy) rare earth elements (REE). Equilibrium adsorption isotherms with a high coefficient of determination are described using the Langmuir model. The adsorbed metal ions were recovered and the adsorbent was regenerated by treatment with a dilute HCl solution, which shows the large-scale potential of the EDTA-functionalized solvent for the extraction of rare earth elements from aqueous solutions.

Silica nanoparticles and porous microparticles functionalized by a monolayer of ligands obtained from diethylenetriamine pentacetic acid are proposed as sorbents for the extraction of REE from solutions by the authors of (Ashour et al. 2018, p. 6891). The possibility of using DTPA-functionalized microarrays for chromatographic separation of rare earth elements at different sample concentrations, elution modes, eluent concentrations, eluent flow rates and process temperatures is investigated. Optimal separation of *La(III)*, *Ce(III)*, *Pr(III)*, *Nd(III)* and *Dy(III)* ions was achieved by using HNO_3 as an eluent due to a linear concentration gradient from 0 to 0.15 M for 55 minutes. The results of this study demonstrate the potential of using DTPA-functionalized silica particles in the chromatographic process of separating REE from waste as an environmentally preferable alternative to standard processes.

The adsorption capacity of nanogoetite (NG) synthesized by co-deposition and modified by a composite formation with activated carbon and sodium alginate to increase the adsorption capacity with respect to La(III) was investigated by the authors of (Sayed et al. 2021, p. 2865). The adsorption process was carried out under optimal conditions: pH 5.0, contact time 6.0 h, sorbent dosage (0.1 g / 20 mL) and initial concentration of La^{3+} (500 ppm). The sorption capacity of goethite was 49.5 mg/g, goethite modified with activated carbon: from 44.0 mg/g to 56.8 mg/g, goethite modified with sodium alginate — from 63.9 mg/g to 77.8 mg/g.

In (Galhoum et al. 2015, p. 2590), the sorption of ions of three rare earth elements (*Yb(III), Dy(III)* and *Nd(III)*) was studied using hybrid chitosan-based particles impregnated with diethylenetriamine (DETA). The influence of pH on sorption characteristics was analyzed: an optimal initial pH value of 5 and an equilibrium value of 6.5 were established. Sorption isotherms were effectively described using the Langmuir equation: maximum sorption capacities reached 50 mg/g for each of the rare earth metals. The sorption process is characterized by an endothermic character, the negative Gibbs energy values obtained determine the spontaneous direction of adsorption.

Nevetheless, the use of sorbents modified with substances exhibiting a high ability to form complex compounds with REE from aqueous media is ineffective in phosphoric acid solutions.

Acidic and neutral organophosphorus extractants, such as tributyl phosphate (TBP), are most commonly used for the extraction of REE from strongly acidic solutions, di-2-ethylhexyl phosphoric acid (D2EHPA), mono-(2-ethylhexyl)-phosphoric acid (M2EHPA), dialkylmethylphosphonate, diisooctylmethylphosphonate, bis-2,4,4-trimethylpentylphosphonic acid (Cyanex 272). The reduction of branching in the carbon chain of the radical and the increase of the C-P bond energy has a positive effect on the efficiency of the extractants.

The authors (Morillo Martín et al. 2019) used polyacrylonitrile (PAN) nanofibres impregnated with the organic extractant Cyanex 272 to selectively extract Eu(III) and Y(III) from aqueous solutions in order to increase their chemical affinity for the rare earth metal ions. Maximum extraction capacities were 200 and 400 mg/g for Y(III) and Eu(III), respectively. In terms of thermodynamics, the equilibrium adsorption is best described by Langmuir model, in terms of kinetics - pseudo-second order model. Experiments on sorption in a continuous mode have shown that the adsorption of target elements is close to 100%.

The authors of (Mohhamedi et al. 2020, p. 26949) proposed a composite sorbent for the extraction of Eu(III). The sorbent is a mesoporous silica with a surface layer of Cyanex 272 extractant impregnated and immobilized in an alginate matrix.

The authors of (Battsengel et al. 2018, p. 522) investigated the selective separation of light and heavy REE by solvent extraction from a solution obtained by leaching apatite ore with 1 mol/L sulphuric acid. Comparison of three organophosphorus extractants, namely di-2-ethylhexylphosphoric acid, mono-2-ethylhexyl ester of 2-

ethylhexylphosphonic acid (PC88A) and tributyl phosphate, showed the highest efficiency of D2EHPA for heavy REE extraction. With respect to light REE the efficiency of extractants was equal.

On the basis of the analyzed literature data it was concluded that it is advisable to use D2EHPA as an extractant, which shows itself to be the most selective and effective. Thus, PC88A, Cyanex-272, D2EHPA were considered in (Reddy and Kumar 2016, p. 236). Of these, only D2EHPA is efficient and selective in phosphoric acid solutions with low pH and can be used for REE extraction and separation at phosphoric acid concentration in solution of 3 to 5 M. This difference of D2EHPA can be explained by the lower value of the acidity constant pKa.

The authors (Radhika et al. 2010, p. 299) also concluded that D2EHPA is preferable: among the studied acidic extractants, TOPS 99 (high purity D2EHPA) is the best in the 0.5-5.0 M acid range. The recovery of any of the REE by organophosphorus reagents decreases in the series: D2EHPA > PC88A > Cyanex 272. TOPS 99 can be used for the separation of heavy REE in the 3-5M acid range similar to phosphoric acid solutions. For the separation of heavy from light REE, TOPS 99 is only suitable in the acid range 3-5 M.

Extraction of rare earth metals from phosphoric acid solutions using alkylphosphinoxides (Cyanex 272, Cyanex 302), D2EHPA, and others were studied in works (Ashour et al. 2018, p. 6894; Babu et al. 2018, p. 1495; Burghoff et al. 2008, p. 1321; Callura et al. 2019, p. 472). The highest extraction rates were obtained using D2EHPA as an extractant. The extraction rate increases with increasing D2EHPA concentration and reaches about 80% when using an extractant with a concentration of 2 mol/L. At the same time, it was noticed that the extraction efficiency in the series from lanthanum to dysprosium and then to yttrium increases. However, increasing the concentration of the extractant above 2 mol/L decreases the degree of separation of individual rare earth metals and also increases the amount of impurities in the extract.

One way to improve extraction efficiency is to select the optimum solid carrier for the extractant and to improve it. Types of adsorbent materials include polymers, silica, membranes, microorganisms, hybrid and biological materials. The upgrading of carriers can improve the adsorption and selectivity of the extractant to the desired elements, as well as increase the contact surface area of the phases. The methods of chemical and physical modification of the carrier have different effects on the stability and the ability to extract. Typically, physical immobilisation methods such as impregnation, material doping and encapsulation create an extractant layer on a solid substrate. Chemical immobilization and modification methods increase the adsorption capacity of the material by manipulating the chemical bonding and ionic surface. Chemical modification is preferred because of the formation of a covalent bond between the solvent and carrier parts, which provides the ability to withstand cycles of adsorption and desorption. The modification affects the size and number of pores, the stability of the material, the composition of the aqueous phase after adsorption, the ability to re-adsorb and the recovery of REE after regeneration.

To increase the stability of impregnates and to prevent the carryover of extractants from them different methods are used: the choice of the most hydrophobic extractants or coating the pellet with an additional sorbent layer of polymer, which acts as a semi-permeable membrane (Ehrlich and Lisichkin 2017, p. 1233; Wang et al. 2017, p. 113).

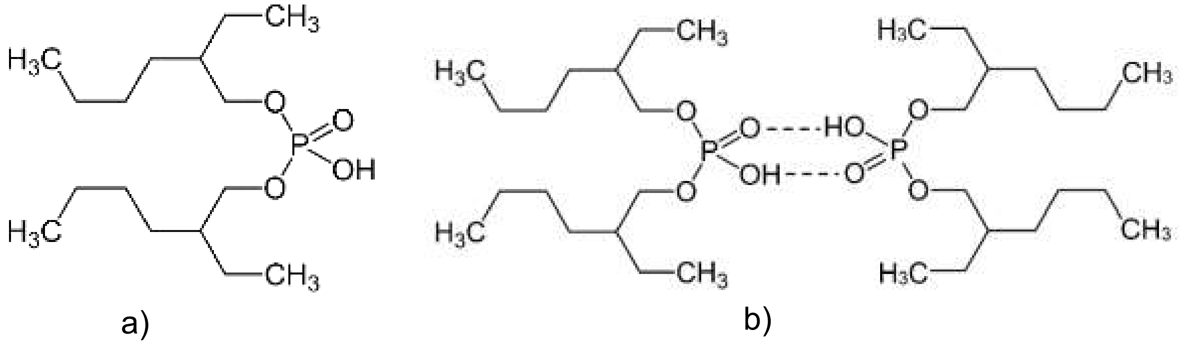
5.3 REE extraction using D2EHPA as an extractant

Di-2-ethylhexyl phosphoric acid is a phosphoric acid ester which is a clear oily liquid with a light yellow colour. Its main characteristics are shown in Table 2.

Formula	$C_{16}H_{35}PO_4$
Molar mass, g/mol	322.43
Density at 20 °C, g/mL	0.94–0.99
Melting point, °C	–50
Boiling point, °C	393
pH-value	3
Solubility, g/l	< 1

Table 2: General characteristics of the D2EHPA

D2EHPA can be found not only in monomeric form but also in dimerized form, which is due to the hydrogen bonds present between the proton and oxygen from the phosphoryl group P=O. The structural formulas of D2EHPA showing both hydrogen bonds are presented in Figure 6.



a) b)

Figure 6: Structural formulas of D2EHPA as a monomer (a) and dimer (b)

Extraction of di-2-ethylhexyl phosphoric acid can proceed by cation-exchange, solvate (donor-acceptor) or mixed mechanisms consisting in their combination. The authors (Radhika et al. 2010, p. 300) proposed a mixed mechanism of REE extraction from phosphoric acid solutions at pH of EPS process solutions:

$$Ln(H_2PO_4)^{2+} + \left(\frac{2+s}{2}\right)(HR)_2 = Ln(H_2PO_4)R_2 \cdot (HR)s + 2H^+, \qquad (2)$$

where *(HR)₂* is a dimer of di-2-ethylhexyl phosphoric acid; *Ln* is total REE; *S* is a solvate number.

Due to the practically identical physical and chemical properties of REMs, in order to realise their separation it is necessary to find and exploit the differences in the strength of the chemical bonds of their compounds. Lanthanide compression is the cause of polarisation effect and stronger electrostatic interaction of rare earth ions with extractant ligands, which enhances the covalent contribution to the solvate extraction mechanism. Consequently, an element with a smaller radius forms a stronger organic complex, which, in turn, leads to an increase in the degree of its extraction and allows for concentration in the extractant phase. The value of the solvation number, i.e. the number of acid molecules solvating, depends on the effective charge of the metal and increases from cerium to lutetium.

6 Materials and Methods

6.1 The Object of the Study

The master's thesis developed a method for extracting rare earth elements from technological solutions of phosphoric acid. The work used solutions obtained at PJSC PhosAgro (Balakovo Branch of Apatit, Saratov Region, Balakovo District, Russia) during the sulfuric acid processing of apatite concentrate of the Khibiny group by the dihydrate method.

The composition of the resulting solutions of phosphoric acid is given in Table 3.

REE	P_2O_5	SO_3	F	Al_2O_3	CaO	Fe_2O_3	SiO_2
0.07–0.10	26–28	1.2–1.8	1.4–1.5	0.1–0.4	0.3–0.8	0.3–0.4	0.8–1.1

Table 3: Composition of phosphoric acid solutions

The relative concentrations of rare earth element oxides in the EFC are shown in Figure 7.

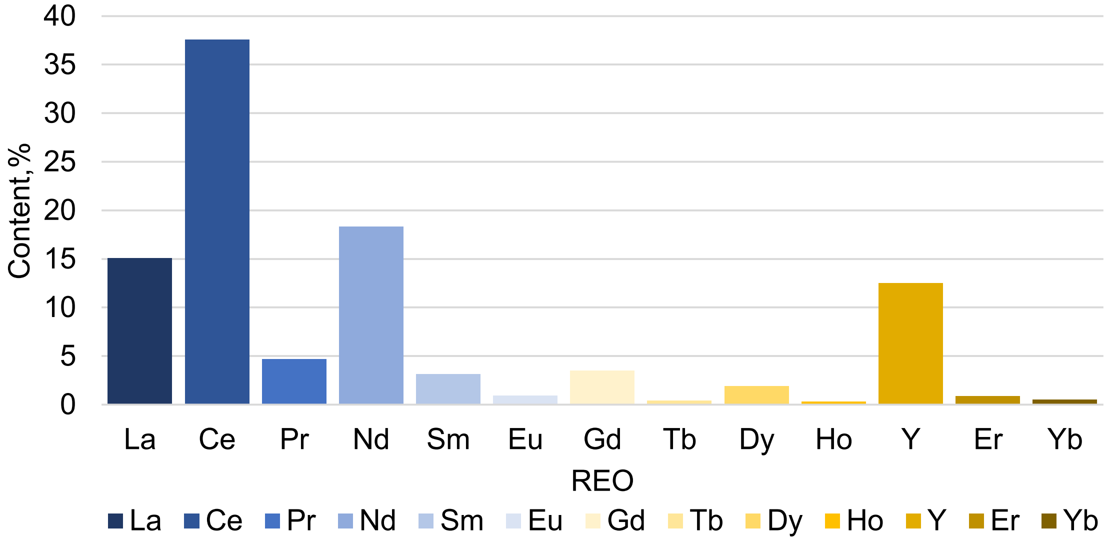


Figure 7: Relative content of rare earth oxides U.S. Geological Survey, Mineral commodity summaries 2022: U.S. Geological Survey 2022, p. 139)

6.2 Materials

The studies were carried out with phosphoric acid solutions simulating the composition of industrial phosphoric acid solutions. Thus, the solutions contained 4.5 mol/L phosphoric acid, 0.19 mol/L sulfuric acid and 0.07–0.10% of the sum of rare earth elements. Solutions were prepared from orthophosphoric acid with a concentration of 87% and a density of 1.71 g/cm^3, sulfuric acid with a concentration of 94% and a density of 1.83 g/cm^3, REE nitrates.

The extraction of REE from phosphoric acid solutions was carried out using two types of sorbents. The first is a polymer resin (a porous inert material based on polystyrene) impregnated with D2EHPA by prolonged wetting to saturation (solvent-impregnated resin, or SIR), and has the form of spherical opaque granules of white color with physicochemical characteristics according to the certificate:

- Mass fraction: at least 97%;
- working fraction granule size: 0.63–2.5 mm;
- Mechanical strength: at least 96%;
- mass fraction of phosphorus: not less than 5.3%.

Another sorbent produced by Smoly Group of Enterprises LLC, Moscow was obtained by copolymerization of D2EHPA in a mixture with styrene and divinylbenzene (extractant-extraction resin, or EER). It has a macroporous structure and is spherical opaque granules of white color with the following physicochemical characteristics ("ТВЭКС-D2EHPA (Ди-2-этилгексилфосфат) / D2EHPA (Di-2-ethylhexyl phosphate"):

- ionic form: H+;
- grain size in the swollen state: 0.63–1.60 mm;
- volume fraction of the working fraction: at least 90%;
- mass fraction of moisture in the swollen state: no more than 30%;
- mass fraction of moisture in the air-dry state: no more than 10%;
- Operating temperature: no more than 80 °C;
- Mechanical strength: at least 90%;
- Bulk density: (± 5%) 0.6 g/cm^3;

- Operating pH range: no more than 1-4;
- the degree of impregnation of the polymer D2EHPA: at least 36%.

Impregnation of polymer materials D2EHPA for impregnates was carried out at the Frumkin Institute of Physical Chemistry and Electrochemistry of the Russian Academy of Sciences, immobilization of sorbents with D2EHPA was carried out by the "Resin Group of Enterprises".

6.3 Methods

The sorption value under static conditions was determined at a temperature of 298 K by the method of variable concentrations with a ratio of solid and liquid phases of 1:10 (2 g of sorbent and 20 mL of solution) in a thermostatically controlled cabinet Shaking Incubator 3032 manufactured by GFL with constant stirring of 75 rpm and phase contact time of at least 3 hours, exceeding the time of reaching equilibrium.

The REE concentration varied from 0.14 to 63.0 mmol/L for cations $Pr(H_2PO_4)^{2+}$, $Eu(H_2PO_4)^{2+}$, $Dy(H_2PO_4)^{2+}$, $Ho(H_2PO_4)^{2+}$, $Er(H_2PO_4)^{2+}$, $Yb(H_2PO_4)^{2+}$, representing elements of all lanthanide groups. The aqueous phase and the sorbent were mixed in conical flasks and after extraction separated using a sieve for sorption processes.

Quantitative analysis of the data obtained, namely, concentrations of rare earth elements in the aqueous and organic phases before and after extraction, was performed by two methods:

- X-ray fluorescence spectroscopy using the X-ray fluorescence energy dispersive spectrometer PANalytical Epsilon 3, designed for the analysis of elements from Na to Am in the concentration range from 10^{-4} to 100%;
- Mass spectrometry using a Shimadzu ICPE 9000 inductively coupled plasma mass spectrometer.

To ensure the reliability and convergence of the results obtained during the research, all samples were measured several times, and experiments were carried out in a series.

To identify the possibility of regeneration of the organic layer of the sorbent and its repeated use for the extraction of REE, the sorption process was carried out under dynamic conditions. Concentration of $Yb(H_2PO_4)^{2+}$ in the initial solution was 0.01 mol/L.

A polymer material weighing 3 g, located in sorption columns (the height of the sorbent layer was 36 mm), was passed through a solution containing ytterbium cations at a speed of 0.3 rpm. The ion content of ytterbium dihydrophosphate $Yb(H_2PO_4)^{2+}$ was analyzed at the outlet of the column.

To regenerate the stationary phase of the extractant, a solution of H_2SO_4 with a concentration of 2 mol/L was used. The acid solution was passed through a sorbent saturated with ytterbium at a speed of 0.5 rpm, and portions of the solution were taken at the outlet of the column to determine the REE concentration. The regenerated material was used for repeated extraction of lanthanides from phosphoric acid solutions.

7 Solid-Phase Extraction from Phosphoric Acid Solutions

7.1 Extraction in Static Condition

According to the experimental data obtained, isotherms of extraction of dihydrophosphates of rare earth elements $Pr(H_2PO_4)^{2+}$, $Eu(H_2PO_4)^{2+}$, $Dy(H_2PO_4)^{2+}$, $Ho(H_2PO_4)^{2+}$, $Er(H_2PO_4)^{2+}$, $Yb(H_2PO_4)^{2+}$ on a styrene-divinylbenzene matrix impregnated with D2EHPA from phosphoric acid solutions modeling the composition of technological phosphoric acid (Figure 8).

The sorption value of the element was calculated by the formula:

$$q = \frac{(C^0 - C^\infty) \cdot V}{m} \qquad (3)$$

where C^0 and C^∞ are the initial and the equilibrium concentration of REE in solution, mol/L; V is the volume of the solution, l; m is the mass of the sorbent, kg.

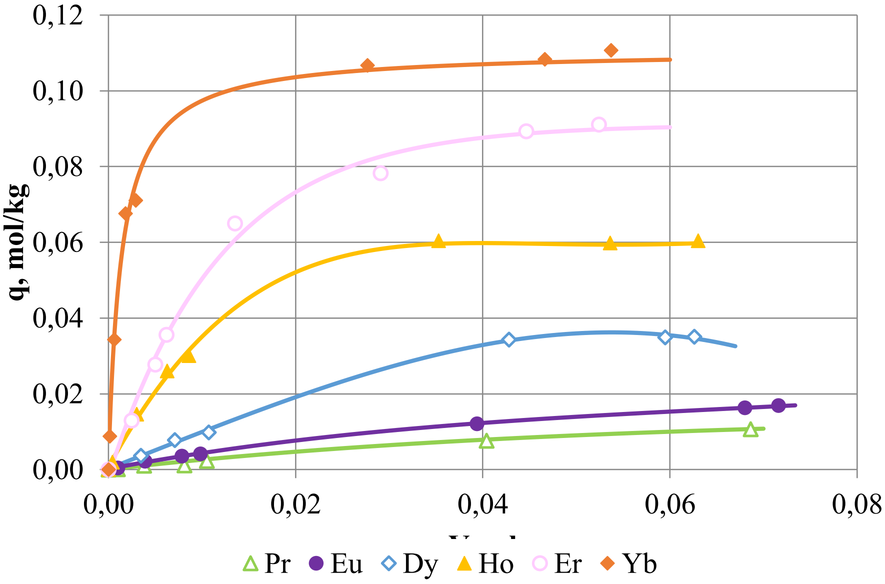


Figure 8: **Isotherms of the extraction of REE cations on D2EHPA impregnated (SIR) sorbent from phosphate solutions**

Despite the high determination coefficients ($R^2 = 0.99$) of the rectilinear dependences of the inverse sorption value on the inverse equilibrium concentration of REE obtained by mathematically describing the sorption isotherms by the Langmuir model, the use of concentration constants does not ensure the reliability of the calculated thermodynamic characteristics.

Therefore, the law of acting masses adapted to extraction processes was used to describe thermodynamic equilibria. D2EHPA extracts REE by the mechanism of ion exchange. However, due to the fact that oxygen of the polar phosphoryl group P=O is an electron donor, additional solvation of extractant molecules can occur up to the maximum coordination number of rare earth elements equal to 6.

In the series of lanthanides, with an increase in the effective charge of the atom, the values of solvate numbers increase from 2 for neodymium to 5 for ytterbium, calculated on the basis of experimental data in (Cheremisina et al. 2019, p. 4):

$$Nd(H_2PO_4)^{2+} + (HR)_2 = Nd(H_2PO_4)R_2 + 2H^+; \qquad (4)$$

$$Yb(H_2PO_4)^{2+} + 2.5(HR)_2 = Yb(H_2PO_4)R_2(HR)_3 + 2H^+, \qquad (5)$$

where *(HR)*2 is D2EHPA.

Taking into account the forms of finding lanthanides in the form of dihydrophosphate ions in concentrated solutions of phosphoric acid and extractant in a dimerized form (Wang et al. 2010, p. 45), the extraction process was expressed by the following equation, taking into account the solvation:

$$Ln(H_2PO_4)^{2+} + \overline{\left(\frac{2+S}{2}\right)(HR)_2} \rightarrow \overline{Ln(H_2PO_4)_2R_2(HR)_S} + 2H^+, \qquad (6)$$

where *S* is the number of solvating organic acid molecules.

The extraction equilibrium constant was expressed through the activity of the lanthanide dihydrophosphate ions in the phosphoric acid solution:

$$K = \frac{a_{H^+}^2 \cdot q_{Ln(H_2PO_4)R_2(HR)_S}}{a_{Ln(HPO_4)^{2+}} \cdot q_{HR}^{\left(\frac{2+S}{2}\right)}}, \qquad (7)$$

where $a_{H^+}, a_{Ln(HPO_4)^{2+}}$ are activities of hydrogen ions and REE dihydrophosphate ions in aqueous solution, mol/kg; $q_{Ln(H_2PO_4)R_2(HR)_S}$, $q_{(HR)_2}$ are equilibrium concentrations of REE and D2EHPA in the solid phase of the polymer matrix, mol/kg.

The activity coefficients were calculated according to the experimental equation (Lebedev 1978, p. 3221), which takes into account the high ionic strength of concentrated phosphoric acid solutions.

Expressing the value of equilibrium concentration of D2EHPA through the limit sorption $q_\infty = q_{Ln(H_2PO_4)R_2(HR)_S} + q_{(HR)_2}$, ual to the sum of equilibrium concentrations of extractant and rare earth element solvate in solid phase of resin, obtained the equation:

$$K = \frac{a^2_{H^+} \cdot q_{Ln(H_2PO_4)R_2(HR)_S}}{[Ln(H_2PO_4)^{2+}] \cdot \gamma_{Ln(H_2PO_4)^{2+}} \cdot (q_\infty - q_{Ln(H_2PO_4)R_2(HR)_S})^{\left(\frac{2+S}{2}\right)}}, \tag{8}$$

where $\gamma_{Ln(H_2PO_4)^{2+}}$ is the activity coefficient of REE dihydrophosphate ions in aqueous solution.

The linear form of this equation, after a series of transformations, is as follows:

$$\frac{1}{q_{Ln(H_2PO_4)R_2(HR)_S}} = \frac{1}{K^{1/\left(\frac{2+S}{2}\right)} \cdot q_\infty} \cdot \frac{a_{H^+}^{2/\left(\frac{2+S}{2}\right)} \cdot q_{Ln(H_2PO_4)R_2(HR)_S}^{\left(\frac{2+S}{2}\right)}}{a_{Ln(H_2PO_4)^{2+}}^{1/\left(\frac{2+S}{2}\right)}} + \frac{1}{q_\infty}. \tag{9}$$

The concentration argument was taken as (c):

$$(c) = \frac{a_{H^+}^{2/\left(\frac{2+S}{2}\right)} \cdot q_{Ln(H_2PO_4)R_2(HR)_S}^{\left(\frac{2+S}{2}\right)}}{a_{Ln(H_2PO_4)^{2+}}^{1/\left(\frac{2+S}{2}\right)}} \tag{10}$$

The graphical solution of dependence of concentration argument on inverse value of concentration of rare earth element in extractant phase $\frac{1}{q_{Ln(H_2PO_4)R_2}}$, shown in Figure 9, are values of effective extraction equilibrium constant K and ultimate sorption *q*∞ by solid resin phase.

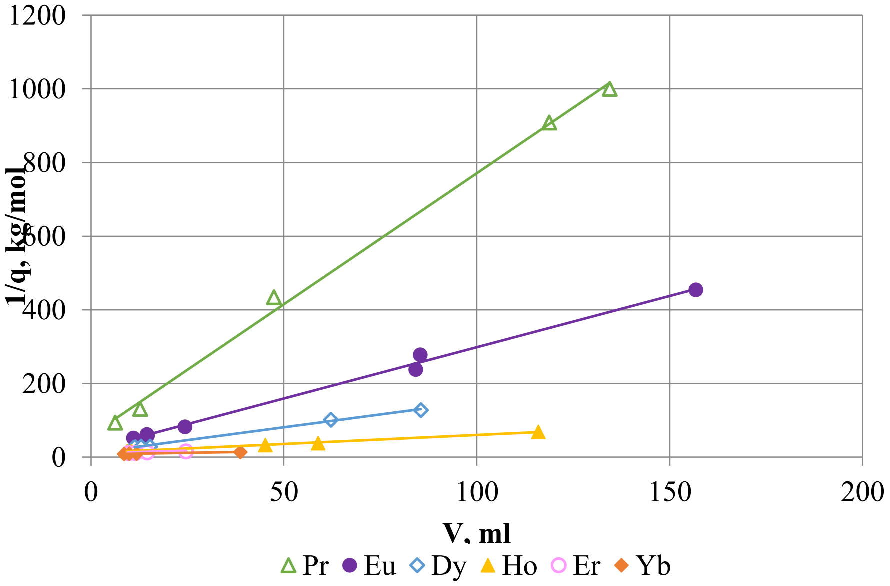


Figure 9: **Linear shapes of the REE extraction isotherm of the impregnated polymer**

The obtained values of effective extraction equilibrium constants, REE sorption limits and Gibbs energies of the extraction process are presented in Table 4. The Gibbs energies were calculated using the equation:

$$\Delta G_{298} = -RT \cdot lnK, \tag{11}$$

where R is a universal gas constant, 8.314 $\frac{J}{mol \cdot K}$; T is experiment temperature, 298 K.

According to the results obtained in full accordance with the regularity of the process of solvent extraction, the value of the extraction equilibrium constant increases with the increase of the effective charge on the REE atom and its solvation number, which is explained by the formation of strong chemical complexes of lanthanides with D2EHPA (Wang et al. 2010, p. 1244).

REE	Equation	R^2	q_∞, mmol/kg	K	$-\Delta \boldsymbol{G}_{298}$, kJ/mol
Pr	y = 7.12x + 58.74	0.997	10.66 ± 0.55	8.25 ± 0.41	5.23 ± 0.26
Eu	y = 2.79x + 19.62	0.995	19.09 ± 0.95	18.67 ± 0.93	7.25 ± 0.36
Dy	y = 1.40x + 10.75	0.996	38.04 ± 1.90	21.28 ± 1.06	7.58 ± 0.38
Ho	y = 0.49x + 10.89	0.998	60.40 ± 3.02	104.41 ± 5.07	11.52 ± 0.58
Er	y = 0.30x + 8.00	0.983	91.10 ± 4.56	691.65 ± 34.58	16.20 ± 0.81
Yb	y = 0.17x + 7.51	0.999	110.69 ± 5.53	1968.64 ± 98.43	18.79 ± 0.94

Table 4: Values for effective extraction equilibrium constants, REE sorption limits and Gibbs energies of the extraction process

Depending on the REE concentration in phosphoric acid solutions, the separation coefficients of the lanthanides β reach the following values: $\beta(Yb/Pr)$ = 131.1; $\beta(Yb/Eu)$ = 975.2; $\beta(Yb/Dy)$ = 53.3; $\beta(Yb/Ho)$ = 87.1; $\beta(Yb/Er)$ = 12.2. which characterises the technological efficiency of using solid-phase extraction.

The separation factor of the two elements was calculated according to the formula:

$$\beta = \frac{D_1}{D_2}, \tag{12}$$

where D_1 is a distribution coefficient of the first element; D_2 is a distribution coefficient of the second element.

The element distribution coefficient, in turn, was calculated using the formula:

$$D = \frac{C_{org}}{C_{aq}}, \qquad (13)$$

where C_{org} is an equilibrium concentration in the organic phase after extraction, M; C_{aq} — equilibrium concentration in the aqueous phase, M.

To compare the results of REE extraction by polymeric materials impregnated and immobilized by D2EHPA, extraction isotherms of ytterbium, holmium and europium on a polymeric sorbent with a rigidly fixed organophosphorus extractant during material synthesis were obtained (Figure 10).

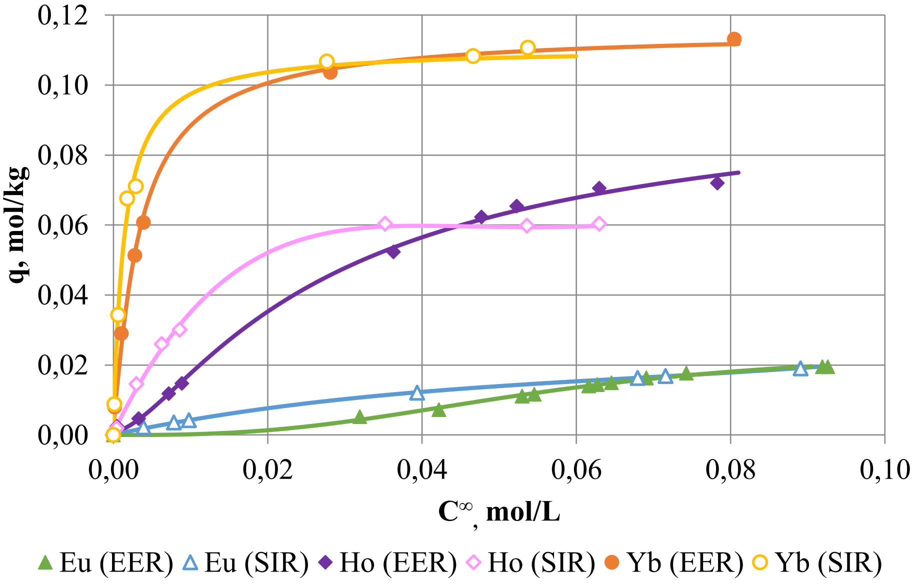


Figure 10: Extraction isotherms of REE D2EHPA

When cross-linking D2EHPA with styrene and divinylbenzene, the dimerized form of the organic acid is broken due to electronic effects. Therefore, the REE extraction process proceeds only by the cation-exchange mechanism and is described by the following equation:

$$Ln(H_2PO_4)^{2+} + \overline{2HR} \rightarrow \overline{Ln(H_2PO_4)R_2} + 2H^+, \qquad (14)$$

$$K = \frac{a_{H^+}^2 \cdot q_{Ln(H_2PO_4)R_2}}{a_{Ln(HPO_4)^{2+}} \cdot q_{HR}^2}. \qquad (15)$$

The linear form of the equation of action masses, modified for the extraction process, is as follows:

$$\frac{1}{q_{Ln(H_2PO_4)R_2}} = \frac{1}{K^{1/2} \cdot q_\infty} \cdot \frac{a_{H^+} \cdot q_{Ln(H_2PO_4)R_2}^{-1/2}}{a_{Ln(H_2PO_4)^{2+}}^{1/2}} + \frac{1}{q_\infty}. \quad (16)$$

Values of the effective thermodynamic equilibrium constants and Gibbs energies calculated from the graphical dependence of the concentration argument $\frac{a_{H^+} \cdot q_{Ln(H_2PO_4)R_2}^{-1/2}}{a_{Ln(H_2PO_4)^{2+}}^{1/2}}$ on the reverse sorption value $\frac{1}{q_{Ln(H_2PO_4)R_2}}$ (Figure 11), are given in Table 5.

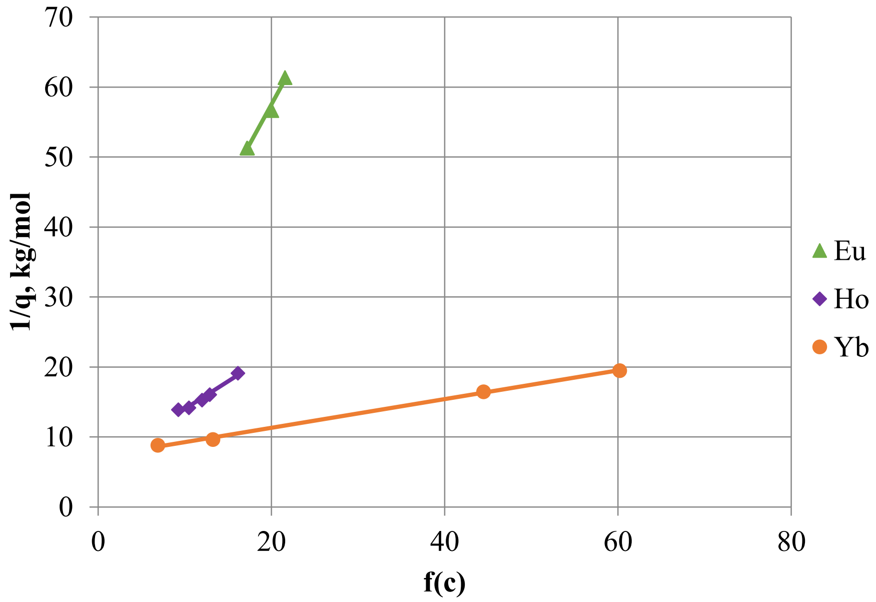


Figure 11: **Linear shapes of REE extraction isotherms of polymer immobilized by D2EHPA**

Linear shapes of REE extraction isotherms of polymer immobilized by D2EHPA

REE	Equation	R^2	q_∞, mmol/kg	K	$-\Delta G_{298}$, kJ/mol
Eu	$y = 2.27x + 12.18$	0.989	19.50 ± 0.98	28.86 ± 1.44	8.33 ± 0.42
Ho	$y = 0.79x + 6.14$	0.973	71.97 ± 3.60	60.93 ± 3.05	10.18 ± 0.51
Yb	$y = 0.21x + 7.07$	0.999	113.16 ± 5.66	1129.07 ± 56.45	17.42 ± 0.87

Table 5: **Thermodynamic characteristics of REE extraction by a polymer immobilized with D2EHPA**

Extraction of rare earth elements using D2EHPA immobilized at the stage of sorbent synthesis in comparison with impregnated extractant is characterized by some difference in values of effective constants and Gibbs energies, while a regular growth of thermodynamic parameters is observed with the increase of element order number.

The insignificant difference of thermodynamic constants is explained by peculiarities of chemical interactions in solid phase of polymer resin.

Dimerized D2EHPA in the surface layer of the solid phase forms strong solvates with metals due to the hydrogen ion substitution. In addition, donor-acceptor interactions between undivided electrons of the oxygen atom in the phosphoryl group and the free orbitals of the lanthanide ions take part in the reaction. In this case, D2EHPA molecules fixed by hydrocarbon radicals in the resin matrix are able to extract REE only by the cation-exchange extraction mechanism.

The spectral analysis of both samples before and after REE extraction is represented by infrared spectroscopy spectra in Figures 12-13. The measurement range of the spectra ranged from 4600 to 600 cm^{-1}, however, the regions with characteristic frequencies of 1300–950 cm^{-1} are informative ones.

The characteristic oscillations of the IR spectrum region 1100–950 $см^{-1}$ determine the presence of an inorganic ion $(H_2PO_4)^{2-}$ as part of the solvate complexes of REE in the solid phase of polymer resins. Strong oscillation bands in the region of 1320–1140 $см^{-1}$ nly for a sample impregnated with D2EHPA after holmium extraction, unlike resin with a rigidly fixed extractant, characterize the stretching of the P=O bond (in the absence of polarization of the bond ν = 1250–1210 $см^{-1}$ for P=O in the composition of $(RO)_2(HO)P{=}O)$. In this frequency range, asymmetric and symmetrical oscillations appear, and the position of the asymmetric oscillations will vary depending on the properties of the REM ion that is part of the extractant.

The shift of the electron density is caused by the participation of the electron pair of the oxygen atom in the donor-acceptor bond with the REE ion (Ravikumar et al. 2012, p. 1662). Thus, the change in the dipole moment is explained by the formation of a donor-acceptor bond with the REE ion.

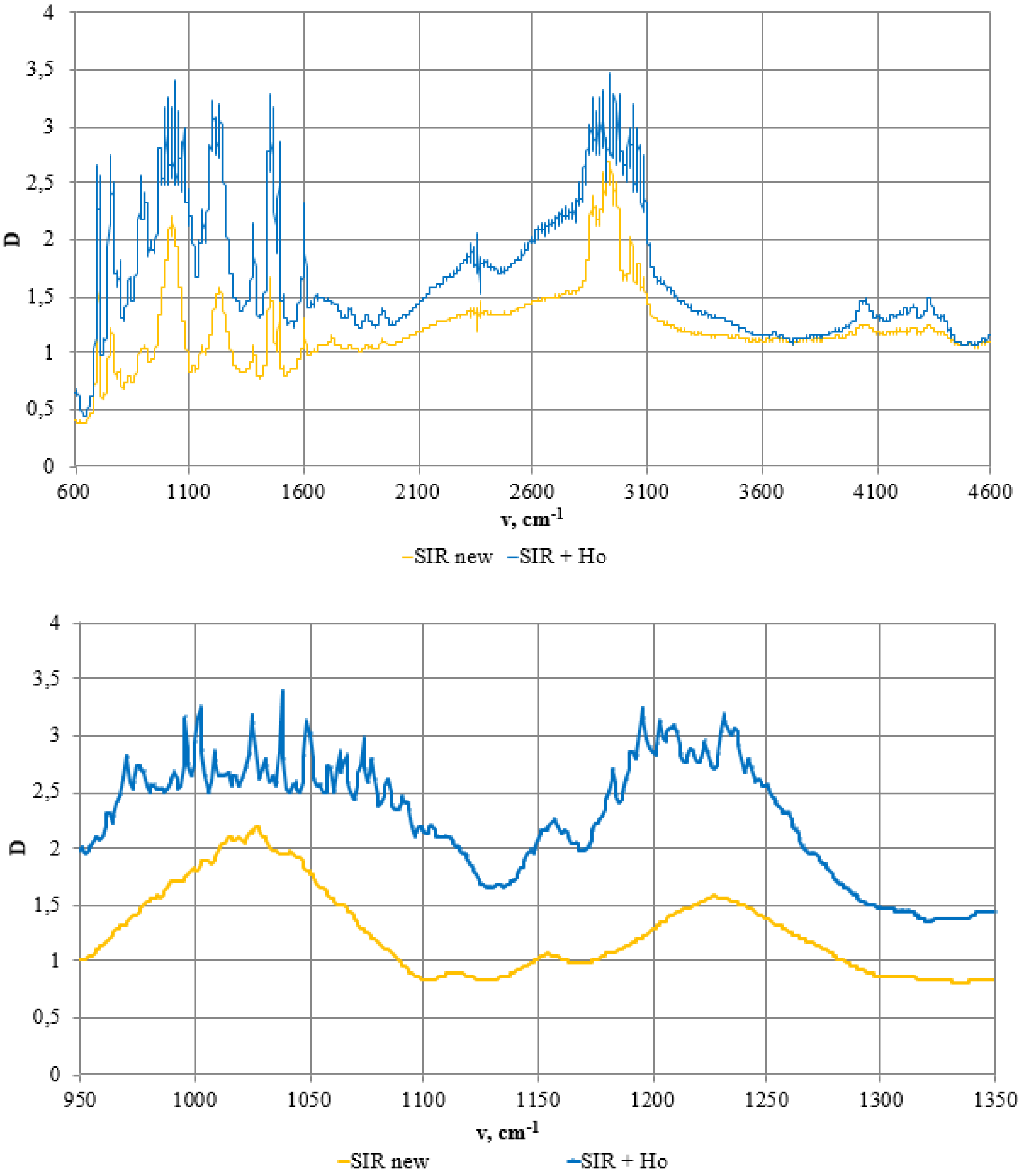


Figure 12: IR spectra of samples impregnated with D2EHPA before and after holmium extraction

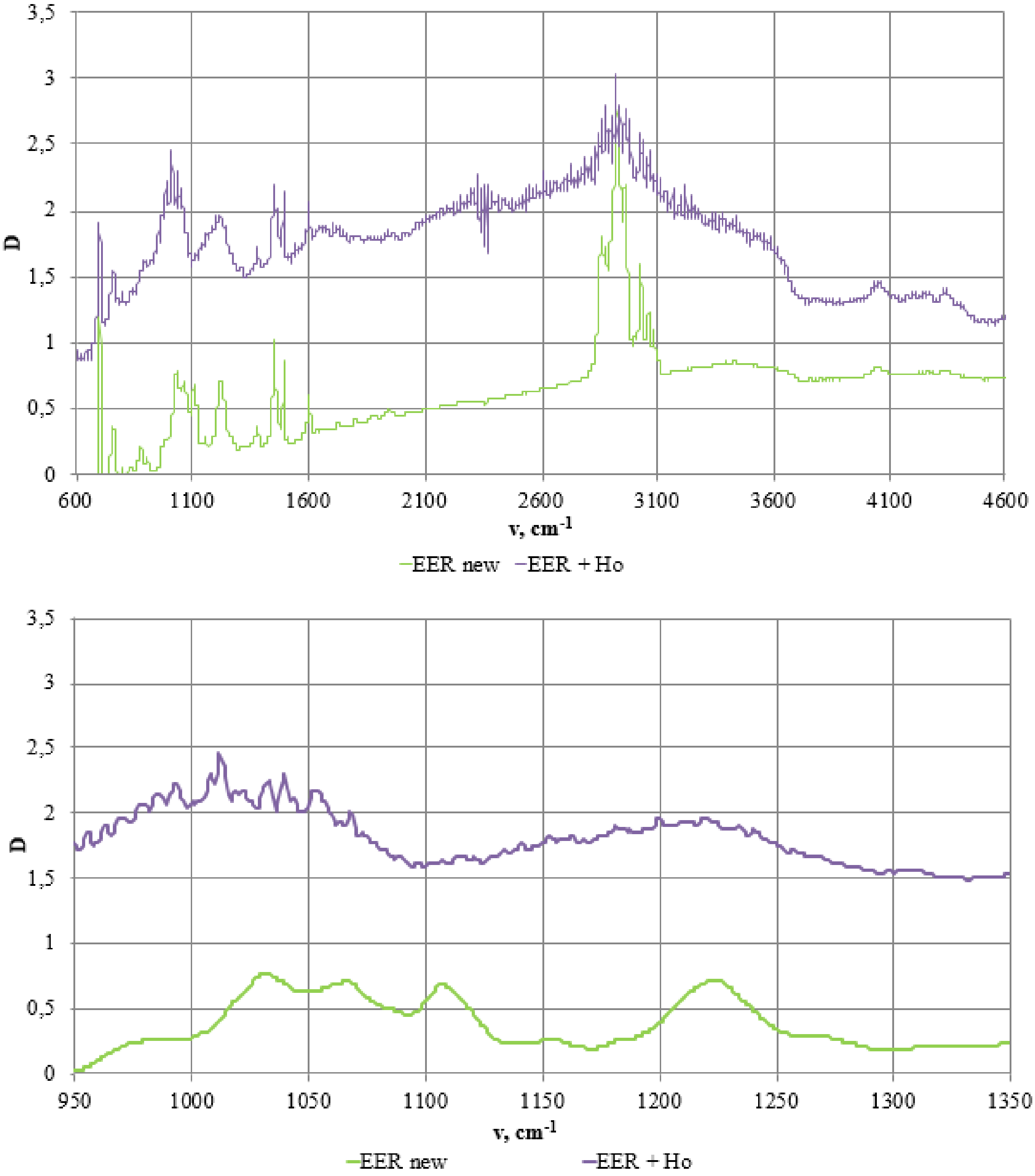


Figure 13: IR spectra of samples immobilized with D2EHPA before and after holmium extraction

To determine the amount of extractant in the polymer matrix, resin samples were treated with toluene at 70 °C for 5 hours and then with different solvents - paraffin and n-heptane - at room temperature for 24 hours. The extractant content irrespective of the solvent was 58.8-60.5% in the impregnated sorbent and 35.7-36.3% in the immobilized D2EHPA sorbent.

Despite the different amount of D2EHPA in the solid phase of the resin, both extractants are characterized by almost the same values of extraction capacity with respect to REE due to the ion-exchange mechanism of extraction.

7.2 Extraction in Dynamic Conditions

Extraction under dynamic conditions was studied using two types of sorbents for the extraction of $Yb(H_2PO_4)^{2+}$ from phosphoric acid solutions. The value of the extraction capacity under dynamic conditions was calculated by the formula:

$$q = \frac{1}{m}\sum_{C_n = 0}^{C_n = C_0}(V_{n+1} - V_n) \cdot (C_0 - C_n), \tag{17}$$

where m is sorbent mass, g; C_0 and C_n are Initial and current ytterbium concentrations at the column outlet, mg/mL; $V_{n+1.}$ V_n are the volumes of the solution corresponding to the concentration of the element at the column outlet C_{n+1} and C_n, mL.

After saturation of the resin with ytterbium ions regeneration was carried out with sulfuric acid solution of 2 mol/L. Dependences of ytterbium concentration at the column outlet on the volume of the passed solution are shown in figure 14 for impregnated and in figure 15 for immobilized D2EHPA polymer before and after regeneration with solution H_2SO_4 2 M.

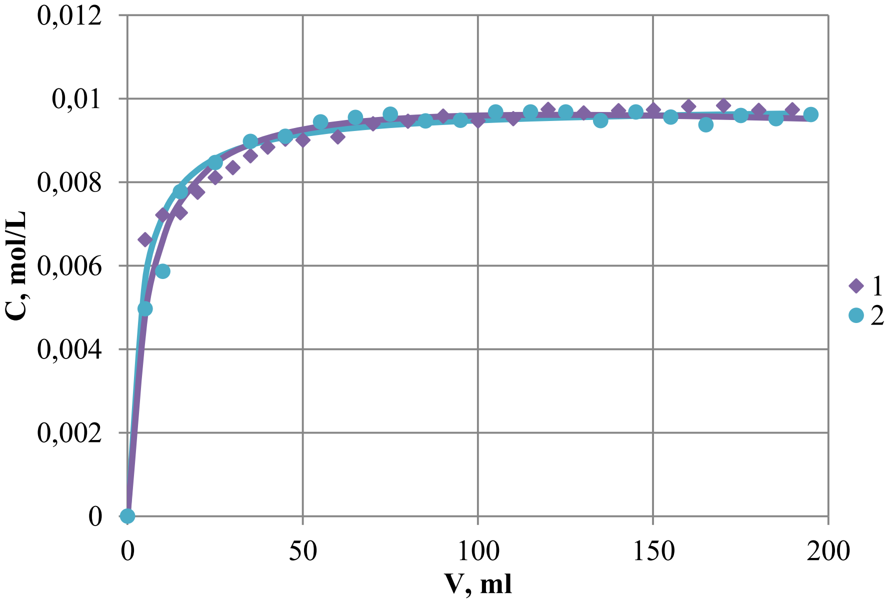


Figure 14: Saturation curves of impregnated polymer with cations of $Yb(H_2PO_4)^{2+}$ from phosphoric acid solutions, where 1 is a new polymer; 2 is a polymer after solution regeneration H_2SO_4 2 M

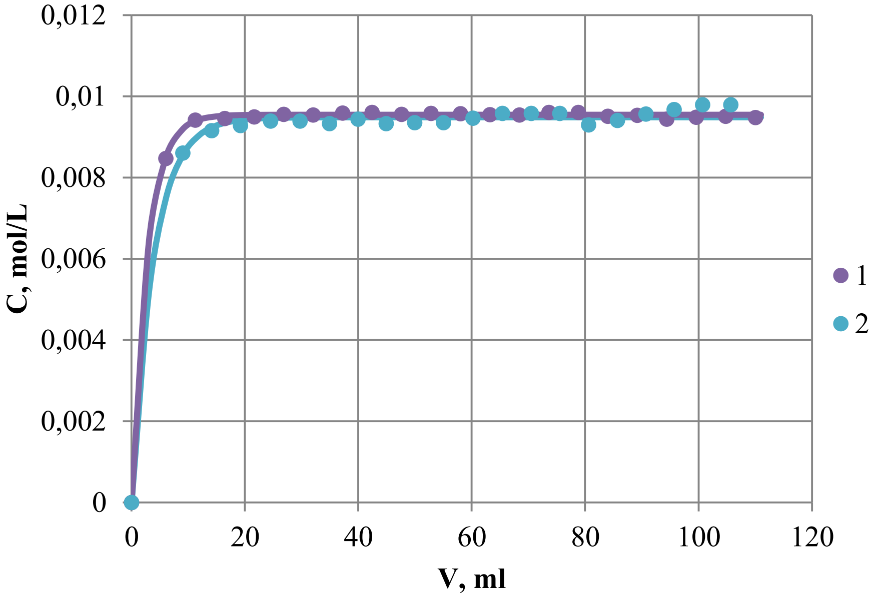


Figure 15: Saturation curves of the immobilized polymer with cations of $Yb(H_2PO_4)^{2+}$ from phosphoric acid solutions, where 1 is a new polymer; 2 is a polymer after solution regeneration H_2SO_4 2 M

The value of the total capacity at saturation of the new impregnated sorbent was 132.0 ± 6.6 mmol/kg and 95.0 ± 4.8 mol/kg after regeneration. The decrease in the capacity of the extractant is only due to the partial loss of D2EHPA during treatment with sulphuric acid solution. Amount of component absorbed $(1.32 \pm 0.07) \cdot 10^{-4}$ mol ytterbium within a satisfactory error coincided with the value of the extracted component in the aqueous phase $(1.24 \pm 0.06) \cdot 10^{-4}$ mol.

For the polymer immobilized with D2EHPA, the dynamic capacity was an order of magnitude lower than that of the polymer impregnated with the extractant, but not different from that of the regenerated material, 41.9 ± 2.2 mol/kg. The loss of D2EHPA during extraction was not more than 3.2%.

Lower value of dynamic capacity compared to static capacity is explained by kinetic peculiarities consisting in limitation of ytterbium mass transfer in extractant layer rigidly fixed at the stage of polymer synthesis.

Efficient extraction of REE from the organic phase is possible through the use of compounds that form strong complexes with lanthanides in aqueous medium. Thus, solutions of sulfuric acid were used as a re-extractant. By increasing the concentration of citrate ions to 1 M the degree of ytterbium re-extraction from the organic phase was more than 95% without loss of the extractant layer.

In addition to sulphuric acid, it is possible to extract REEs from the organic phase efficiently by using compounds that form strong complexes with lanthanides in aqueous medium. Thus, solutions of sodium citrate with concentration from 0.1 to 1 mol/l were also used as a reextractant. By increasing the concentration of citrate ions to 1 M the degree of ytterbium reextraction from the organic phase was more than 95% without loss of the extractant layer.

8 Ending

Rare earth elements are an extremely important mineral resource in modern reality, without which it is impossible to imagine most high-tech technologies, starting with the production of ceramics and ending with aerospace equipment. Consumption of products produced with their use is steadily increasing, and prices for REE, according to forecasts, will also remain at a high level. In this regard, for Russia, which has huge reserves of rare earth metals in the form of apatite, it is necessary to develop domestic technologies for the production of rare earth elements.

One of the main technological obstacles to the widespread extraction of rare-earth elements is their extremely low concentrations in ores for economically justified extraction. Also, unlike other metals, which are often found in ores as an individual component, REE are always present in them together, which makes it difficult to obtain individual metals.

For economically profitable production of REE, it is advisable to introduce the stage of their extraction in the form of by-products into already functioning production facilities. Thus, a promising way to extract rare earth elements from domestic raw materials may be the associated production of REE from phosphoric acid, which forms during the processing of apatite into phosphoric fertilizers and contains about 0.1% of the amount of REE.

The choice of the REE extraction method is limited by the need to maintain the composition and properties of phosphoric acid returned to the fertilizer production cycle unchanged, as well as its high acidity. Among the known methods for obtaining REE, extraction is the most effective. Extraction makes it possible to extract and concentrate REE without changing the properties of the initial aqueous solution. Solid-phase extraction, in comparison with solvent extraction, has a number of advantages, such as an increased contact surface area of the phases, the absence of an emulsion formed by mixing two liquid phases, and the exclusion of the participation of flammable toxic diluents. Using the solid-phase extraction method, it is possible to concentrate and separate REE, as well as separate them from impurities with further isolation of individual components.

The most effective and selective extractant for extraction from strongly acidic solutions and separation of REE into individual lanthanides, which include technological phosphoric acid solutions, is di-2-ethylhexylphosphoric acid. According to Pearson's theory, REE, which are "hard" acids, form strong dative bonds with "hard" bases - organophosphate ligands.

The master thesis presents an analysis of the current state of the industry of rare earth products and the main scientific achievements in the world, the main problems associated with the process of extracting rare earth elements are formulated, as well as potential ways to solve them are proposed. A method of solid-phase extraction of rare-earth elements from phosphoric acid solutions obtained during apatite processing was developed. The extraction was conducted using two types of extractant: impregnated and immobilized with di-2-ethyl-hexylphosphoric acid.

In the course of the study, thermodynamic characteristics of the extraction of praseodymium, europium, dysprosium, holmium, erbium and ytterbium were obtained, namely, the values of Gibbs constants and energies. It was revealed that with an increase in the strength of the solvate complex of rare earth elements, an increase in the values of the extraction equilibrium constants is observed, regardless of the mechanism of fixing D2EHPA in the matrix of the polymer material. The obtained values of the static capacity of the sorbent immobilized by the extractant, due to diffusion limitations, exceed the dynamic capacity. The use of complexing agents ensures a high degree of extraction of REE into the aqueous phase while maintaining the integrity of the organic extractant layer. It is possible to regenerate the material immobilized by D2EHPA using sulfuric acid.

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12 List of Abbreviations

REE	Rare earth elements
REO	Oxides of rare eath elements
Ln	Sum of rare earth elements
D2EHPA	Di-2-ethylhexylphosphoric acid
SIR	Solvent-impregnated resin
EER	Extraction-extractant resin
IR spectra	Infrared spectra