
Master Thesis

Rare Earth Metals Recovery from Apatite Processing Products Using Liquid-Liquid Extraction Method

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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.”

Preface, Dedication, Acknowledgement

I would like to express my special thanks of gratitude to my scientific supervisor Prof. Olga Cheremisina who gave me the golden opportunity to do this research

Abstract

The master's thesis considers the method of increasing the depth of apatite processing with the associated extraction of rare earth elements (REE) by liquid extraction with di-2-ethylhexylphosphoric acid (D2EHPA).

The purpose of the paper is to develop a technological solution for obtaining REE from wet process phosphoric acid using liquid-liquid extraction method with D2EHPA.

In the theoretical part of the work, the relevance of the topic of rare earth elements extraction, their properties, application and world reserves is substantiated. A literature review presents domestic and foreign methods of extraction of rare earth metals from phosphoric acid solutions.

In the experimental part, the dependences of the REE re-extraction degree and impurity metals (titanium and iron) from the organic extract by sulfuric and oxalic, respectively, are shown. Based on the data, effective parameters were determined and a scheme for obtaining individual compounds Dy, Y, Yb was compiled.

Zusammenfassung

Die Masterarbeit befasst sich mit der Methode zur Erhöhung der Aufbereitungstiefe von Apatit und der damit verbundenen Extraktion von Seltenen Erden (REE) durch Flüssigextraktion mit Di-2-ethylhexylphosphorsäure (D2EHPA).

Ziel der Arbeit ist es, eine technologische Lösung für die Gewinnung von Seltenen Erden aus Nassprozess-Phosphorsäure durch Flüssig-Flüssig-Extraktion mit D2EHPA zu entwickeln.

Im theoretischen Teil der Arbeit wird die Relevanz des Themas der Extraktion von Seltenen Erden, deren Eigenschaften, Anwendung und Weltreserven begründet. In einer Literaturübersicht werden in- und ausländische Methoden zur Extraktion von Seltenerdmetallen aus phosphorsauren Lösungen vorgestellt.

Im experimentellen Teil werden die Abhängigkeiten des REE-Rückextraktionsgrades und der Verunreinigungsmetalle (Titan und Eisen) aus dem organischen Extrakt durch Schwefelsäure bzw. Oxalsäure gezeigt. Anhand der Daten wurden effektive Parameter bestimmt und ein Schema zur Gewinnung der einzelnen Verbindungen Dy, Y, Yb erstellt.

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1 Introduction

The Rare Earth Elements (REE) are a group of 17 metals, including the lanthanides, yttrium and scandium. They are divided into three groups: light (^{57}La to ^{60}Nd), medium (^{62}Sm to ^{64}Gd) heavy (^{65}Tb to ^{71}Lu , including Y), also called HREE. These categories of rare earth elements occur in the same and mineral sources, with the exception of Sc. The most valuable group of rare earth elements is the heavy group, because, on the one hand, heavy rare earth elements are most in demand in industry, but on the other hand, they are found in lesser quantities in the earth's crust and are more difficult to separate (Abreu and Morais, 2014, p. 83; Liu u. a., 2019, p. 74; Swain and Mishra, 2019, p. 890).

Rare earth industries are directly linked to the development of technology and knowledge-intensive industries. They are widely used in three critical industries: green energy, smart technology and defence. Without them, the production of wind power generators, hybrid and electric vehicles, batteries, mobile phones, liquid crystal displays, high-precision optics and much more is unthinkable. With the high growth rate of advanced technology production in developed market economies, REEs are critically needed elements (Larochelle U. A., 2021, p. 5). In 2021, the amount of rare earth mined in terms of oxides reached 255,000 tonnes, an increase of 73% compared to 2016 (Reichl & Schatz, 2021, p. 267). The only way to meet the increasing demand is to increase the number of REE sources being developed.

Russia has the world's fourth-largest reserves of rare earth elements, but a global share of 1.1% (Reichl & Schatz, 2021, p. 268), which does not meet the domestic demand for these materials, with the share of imports equal to 90%. The development of methods for producing individual REE compounds in the Russian Federation is one of the highest priority tasks facing domestic scientists.

Russia's rare earth reserves are concentrated in complex ores that have no analogues in the world (Ioparite, perovskite, eudialite, apatite and others). Most of them are contained in the apatite-nepheline ores of the Kola Peninsula, which are not extracted during processing. However, apatite is processed at plants producing phosphate-containing fertilisers and feed additives. Up to 10 million tonnes of apatite is used annually in Russia. The REEs contained in apatite raw material are distributed between products and production wastes.

Extraction of metals from apatite processing products will allow not only to get a valuable by-product by itself, but also to mitigate negative effect of metal impact on crops when fertilizers are applied to the soil.

On the one hand, the introduction of the REE extraction stage into the existing technology is associated with a number of difficulties, such as the need to strictly monitor the consistency of the produced phosphorus-containing product, the complexity and multi-component nature of the mixture and the low concentrations of lanthanides in the system. On the other hand, it has a number of advantages, such as: no need for the construction of mining and processing plants, non-radioactivity and relative high content of the most valuable heavy group of REE.

Among the existing methods of REE extraction, the method of liquid extraction with organic solvents is the simplest and most versatile, which makes it possible to introduce it in production. Moreover, only extraction methods allow to extract and separate elements similar in chemical properties without changing the composition of technological product containing REE. The mechanism of lanthanide extraction is the formation of a strong chelate complex between the organophosphorus extractant and the metal. Using scientific approach based on Pearson's theoretical concepts of "hard" and "soft" acids and bases: REM cations, being "hard" acids, form strong anionic complexes with oxygen-containing inorganic ligands as "hard" bases, including ligands of di-2-ethylhexyl phosphoric acid. The formation of lanthanide complexes with inorganic oxygen-containing anions is facilitated by the formation of high-energy Ln-O bonds. Different electronic structures of REE cations make it possible to form organic complexes with different degrees of stability determining the order and extraction degree of lanthanides from complex phosphoric acid technological system with low pH value.

The aim of the study is to obtain prototypes of individual solutions of REE from saturated organic extract of metals of high purity.

To achieve this goal it is proposed to solve the following tasks:

1. To study the current information about the market of rare earth elements: applications of REE and distribution of their world reserves, including phosphate-bearing ores and products of their processing;

2. To review existing methods of rare earth elements extraction from apatite concentrate processing products;

3. To identify the problems in the considered technology of extraction method of lanthanides extraction;

To determine the effective parameters of purification of the extract from impurity metals and their selective re-extraction;

5. To develop a extraction scheme of heavy group metals, with obtaining individual compounds of high purity;

2 Applications of rare earth elements

Rare earth elements are used extensively in a variety of industries, particularly in green energy and defence (Table 1). Various forms of elements are used: pure metals, alloys, oxides and chlorides. The production of permanent magnets using Pr, Nd, Gd, Dy and Tb and catalysts where La and Ce are used as stabilizers are the main applications of REE.

Gadolinium and erbium compounds are used as additives in uranium fuel for high-power channel-type reactors and water-moderated vessel-type nuclear reactors. Application of Er and Gd increases enrichment degree of uranium due to which lifetime of reactors is prolonged. In the work (Kosynkin and Glebov, 2010, p. 14) the authors note that 0.4 - 0.6 % erbium oxide increases the degree of uranium enrichment by 0.4 - 0.6 %.

Dysprosium is used as a component of control system absorber rods and high-energy permanent neodymium magnets. Nd-Fe-B magnets are used to produce speeds high enough to separate uranium isotopes in centrifuges (Kosynkin and Glebov, 2010, p. 18). Rare earth elements in catalysts for refining processes (Wang u. a., 2010, p. 1041): hydrotreating (40% of the global catalyst market), catalytic cracking (30%), hydrocracking (7%) and reforming (5%). As of 2020, the global catalyst market was worth 880,000 tonnes and was valued at USD 33.8 billion. More than two-thirds of global catalyst production is in the US and Europe, and just under 30% is in China (Sinopec). Production capacity of Russian catalyst plants is relatively low, at around 2% of the world total. According to current forecasts, demand for catalysts in Russia will increase by 80%, to 24.4 million tons, in the period until

2027. However, the structure of demand will not change significantly (Informacionno - analiticheskij portal Gazpromneft'). Production of domestic catalysts is one of the priority tasks in the development of the country's industry, because dependence on imports (the share of imported catalysts for 2019 is 83%) in the current world situation can have a devastating effect on the entire sphere of oil refining and petrochemistry, as well as pharmaceuticals.

Industry of production	Scope of industrial applications
Electronics	TV displays, PCs, smartphones, silicon chips, monitors, batteries, camera lenses, LEDs, compact fluorescent lamps (CFLs), luggage scanners, marine propulsion systems
Industry	High-strength magnets, metal alloys, voltage sensors, ceramic pigments, dyes in glassware, chemical oxidants, polishing powders, creation of plastics, as additives for hardening other metals, automotive catalytic converters
Medicine	Portable X-ray machines, X-ray tubes, contrast agents for magnetic resonance imaging (MRI), imaging in nuclear medicine, applications for cancer treatment as well as for genetic screening tests, medical and dental lasers
High precision manufacturing	Lasers, optical glass, fibre optics, masers, radar detection devices, nuclear fuel rods, mercury vapour lamps, highly reflective glass, computer memory, nuclear batteries, high temperature superconductors.
Renewable energy	Hybrid cars, wind turbines, next generation batteries, biofuel catalysts.
Other	Europium is used as a way to identify legitimate notes for delivery in euros and to prevent counterfeiting. Approximately 1kg of REE can be found inside a typical hybrid car. Holmium has the highest magnetic strength of any element and is used to create extremely powerful magnets. This application can reduce the weight of many engines.

Table 1: Industrial applications of rare earth elements (Balaram, 2019)

REE and its oxides are widely used in the glass industry. Thus, addition from 5 to 40% of La_2O_3 to blend in manufacture of optical glass improves its thermal stability and acid resistance. Such product finds wide application in production of photographic lenses, cameras, laboratory glass and parts of telescopes (Informacionno - analiticheskij portal Gazpromneft').

Cerium compound glass is also used in the nuclear industry, as it does not darken or change colour when exposed to gamma rays (Savickij u. a., 1991, p. 34).

Glasses containing Pr_2O_3 have a green tint and do not transmit light rays of the ultraviolet spectrum. Personal protective equipment for the eyes of smelters and welders is manufactured using glass with praseodymium oxide impurities. Praseodymium is also used to generate infrared radiation in lasers and in polishing mixtures (Savickij u. a., 1991, p. 35).

Mishmetal is a mixture of cerium, lanthanum and neodymium. It is used as an additive when alloying magnesium to improve its strength and creep resistance (Savickij u. a., 1991, p. 38). In work (Cegel'nik, 2006, p. 19) The strength and abrasion resistance of cast iron is increased by a factor of two and three through the addition of 0.4% ferrocerium. Moreover, the cost of casting such an alloy is reduced by 25% thanks to the property of cerium to remove harmful sulphur and gas inclusions from the mixture. Titanium, aluminium and chrome-nickel steels are also alloyed with rare-earth oxides.

Only metallic lanthanides are used in the manufacture of industrial magnets. Neodymium and dysprosium are added to the mixture to obtain magnets which show large dimensional variations during the magnetisation and demagnetisation cycle. High-power magnets can be produced by incorporating cobalt and terbium into their composition, and terbium-iron alloys with a high magnetostrictive effect are widely used for the manufacture of audio equipment and ultrasonic wave emitters .

Ultra-pure holmium or Ho-Er alloy is applied to the pole tips of magnets to provide a more uniform distribution of magnetic flux density in the air. The components of magnetic recording devices include thulium. High-power magnets with lutetium in the alloy are only used in the space and defence industry because of their high cost (Cylikov and Rebrovskaya, 2013, p. 20).

Permanent rare-earth magnets in Russia are produced at Elemash OJSC, Electrostal, FGUP UEMZ, Ekaterinburg, POZ-Progress LLC, Verkhnyaya Pyshma, SPA Magneton, Vladimir, SPA Spetsmagnet and SPA Magnetic Systems, Moscow, Erga LLC, Kaluga. Rare-earth nanocrystalline magnetic powders are manufactured in OJSC "VNIINM" (Otchet issledovatel'skoj gruppy OOO «INFOMAJN». Obzor rynka redkozemel'nyh magnitov v Rossii, 2021, p. 43).

The use of rare-earth elements in the manufacture of magnets has given them strength, lightness and compactness, making them suitable for a wide range of applications: sound systems, video technology, smart home appliances, computers, laptops and tablets, electric cars, communication devices and military equipment (Otchet issledovatel'skoj gruppy OOO «INFOMAJN». Obzor rynka redkozemel'nyh magnitov v Rossii, 2021, p. 45).

With the development of REE applications, the demand for REE is increasing and production has steadily increased, averaging 10% per year over the past 4 years (Table 2).

	2015	2016	2017	2018	2019
Australia	10 916	13 872	17 264	18 556	17 613
Brazil	1 040	2 900	1 700	1 100	600
Burundi			31	631	68
China	105 000	105 000	105 000	120 000	132 000
India	956	2 265	2 274	4 215	4 200
Malaysia	565	1 876	302	86	114
Myanmar (Burma)	230	2 730	5 000	20 400	17 100
The Russian Federation	2 312	3 063	2 500	2 596	2 620
The USA	3 678	0	0	14 000	28 000
Total	124 697	131 706	134 521	181 584	202 315

Table 2: World production of rare earth element oxides (REEO), tonnes (Reichl and Schatz, 2021, p. 124)

3 Distribution of Global Reserves of Rare Earth Elements

Industrial production of REE oxides began only at the end of the 19th century in North Carolina (USA) and reached its peak only in the 1980s. Such a long interval between the discovery of the first rare earth element, the beginning of their industrial production and their name is not accidental, although not as obvious as it may seem at first glance.

The Rare Earths were named historically at the time of their discovery, i.e. in the 18th - 19th centuries, because only two minerals containing "yttrium and cerium earths" were known: gadolinite and samarskite. Nevertheless, REE occur in the Earth's crust quite often, for example, cerium content in the Earth's crust is 63 ppm, which is higher than the copper content (47 ppm) and slightly less than the chromium content (83 ppm). However, there are no deposits of high enough REE concentrations to be economically justified; therefore they are usually received as by-products of production. For example, the largest mine in Russia, Lovozersky GOK, produces REEs as by-products of tantalum and niobium production; and the largest mine in the world, Bayan-Obo in China, produces iron.

The main minerals containing rare-earth elements are given in Table 3. Among them, only bastnaesite, monazite, xenotime and fluocerite are raw materials for the production of lanthanides on an industrial scale.

Mineral	Formula	REE, %	Average density, g/cm ³	Colour
Bastnaesite	Re[(CO ₃)F]	74,8	4,97	Yellow, reddish brown
Monazite	(Re, Th)PO ₄	65,1	5.15	Brown, colourless, greenish grey, white, yellow
Xenotime	Y(PO ₄)	62,0	4,75	Yellowish brown, greenish brown, grey, reddish brown, brown
Fluocerite	(Ce, La)F ₃	83,4	6,13	Pale yellow, yellowish brown, reddish brown
Parisite	Re ₂ Ca(CO ₃) ₃ F ₂	60,3	4,36	Brown, greyish-yellow, yellow
Fergusonite	YNbO ₄	39,9	5,05	Black, brownish brown, grey, yellow
Gadolinite	Y ₂ FeBe ₂ Si ₂ O ₁₀	48,3	4,25	Brown, greenish black, light green, black
Eschinite	(Y, Ca, Fe) (Ti, Nb) ₂ (O, OH) ₆	24,6	4,99	Black, brownish black, brownish black, brownish yellow, yellow
Euxenite	(Y, Ca, Ce) (Nb, Ta, Ti) ₂ O ₆	24,3	4,84	Brownish black, brownish brown, yellow, olive green
Synchisite	Ca (Y, Ce) (CO ₃) ₂ F	49,6	5.27	White, reddish brown
Samaritans	(Y, Fe, U) (Nb, Ta) ₅ O ₄	24,3	5,69	Black, brownish yellow, brown
Polyclases	(Y, Ca, Ce, U, Th) (Ti, Nb, Ta) ₂ O ₆	19,5	5,00	Black, brown
Loparite	(Ce, Na, Ca) ₂ (Ti, Nb) ₂ O ₆	29,8	4,77	Black

Table 3: The main rare earth minerals (Swain u.a., 2019, p. 885)

Although REE is found in numerous minerals including silicates, carbonates, oxides and phosphates, it is not embedded in most mineral structures and can only be found in certain geological environments. The main economic sources of REE minerals are bastnaesite, monazite and loparite, as well as lateritic ion-adsorption clays. There are more than 250 minerals that contain REE as important constituents in their chemical formula and crystal structure (Dostal, 2017, p. 1). As a rule, the light subgroup is concentrated in carbonates and phosphates, and the heavy subgroup in oxides and partially phosphates.

The largest percentage of the world's REE resources is found in bastnaesite deposits located in China and the USA. Bastnaesite does not contain uranium or thorium and is considered to be the main source of light REEs (Voncken, 2016, p. 5). It is often found in geological media such as vein-bearing sediments, contact metamorphic zones and pegmatites, as well as in carbonate-silicate rocks with alkaline intrusive and quartz veins, fluorite-bearing veins and breccia aggregates in the Permian sandstone (Dushyantha u. a., 2020, p. 3).

Monazite is the second most frequently mined REE mineral, with deposits in Australia, Brazil, China, India, Malaysia, South Africa, Sri Lanka, Thailand and the USA. Monazite is a widespread refractory mineral, and is commonly found in beach sands. As accessory mineral it is found in granite, gneiss, and other igneous and

metamorphic rocks. It is also found in complex ores, together with iron oxides, aluminosilicates and apatite. Monazite is usually associated with heavy minerals, such as ilmenite, magnetite, rutile and zircon, due to its high specific weight and resistance against chemical weathering. The mineral typically contains 10-40 % La_2O_3 , 4-12 % ThO_2 , 20-30 % Ce_2O_3 and large quantities of Nd, Pr and Sm. It is considered to be the main source of cerium and minor REE. The content of rare-earth oxides in monazite is approximately 70 %, which is commensurate with that in bastnaesite). However, unlike bastnaesite, monazite contains thorium and uranium, which are more often found in monazite from placer deposits than in carbonate deposits. The estimated volume of the domestic deposits of monazite placer deposits in 2005 amounted to 10.21 million tons, where China, the US and India hold 36, 13 and 3%, respectively (Dushyantha u. a., 2020, p. 4).

The deposits of halloysite, illite, kaolinite and montmorillonite have a unique geological nature. These deposits consist of clay on the surface of which, using the method of ionic adsorption, REM ions have been accumulating for millennia. Their content amounts to 0,05-0,30%, of which up to 60% are represented by the heavy rare-earth metals.

The remaining resources are xenotime, allanite, euxenite, apatite, eudialyte, loparite, phosphorites, rare-earth ion-sorption clays, secondary monazite and solutions of spent uranium. Xenotime is an yttrium phosphate mineral containing 67% REE in terms of oxides, most of which are of the heavy group. Allanite is commonly found as an accessory mineral in igneous rocks, such as granites, syenites, diorites and associated pegmatites. However, it is sometimes enriched to concentrations high enough to yield rare earth ores. Euxenite is a common oxide mineral commonly found in granitic pegmatites associated with quartz, feldspars, ferrocolumbite, ferrotantalite and monazite (Dushyantha u. a., 2020, p. 4).

Although REE content in the earth's crust is relatively high, unlike most other metals it is rarely concentrated in economically and technologically viable ore deposits. Potential REE deposits can be divided into primary and secondary deposits. Primary deposits are formed by magmatic, hydro-thermal and/or metamorphic processes. These deposits are most often associated with alkaline igneous rocks and carbonatites, located in spatial conditions. Secondary deposits are formed by erosion and weathering and may include dewclays, laterites and bauxites. Within these

two groups the REE deposits can be further subdivided depending on the genetic type of the deposit, the mineralogy and the form of occurrence. Since REE deposits occur in a wide variety of geological environments, it is difficult to classify them into different categories. The author of the paper („Rare Earth Element Deposits Geology for Investors“, 2013) The present study, however, has added four categories of economically important deposits, but due to the significant quantities of these elements in coal and marine sediments, the REE reserves categories have been expanded to include the following:

- alkaline igneous rocks (pegmatites and carbonatites)
- residual sediments;
- placers of heavy minerals;
- coals;
- sediments of the continental shelf and ocean floor;
- extraterrestrial sources.

To date, efforts to sustainably develop REE resources have focused on (Jyothi U. A., 2020, p. 10; Swain & Mishra, 2019, p. 15; Talan & Huang, 2022, p. 13):

1. REE recycling from industrial rare earth scrap/residues;
2. REE recovery from end-of-life products;
3. recovery of REE from industrial wastes mined from landfills or residues. At the moment, most of these studies have not found industrial scale application due to problems with material accumulation and sorting, difficulty in finding a technical solution and economic feasibility.

In addition, an enormous amount of research has focused on

4. the recovery of REE from ores with trace concentrations, such as uranium (U) ore, fluorite, marine sediments, and phosphate rocks, etc.. Among them, phosphate rock is considered to be one of the most promising potential new sources of REE in terms of the following advantages (Battsengel U. A., 2018, p. 5; Cheremisina U. A., 2019aa, p. 10; Hérès U. A., 2018, p. 9; Rey U. A., 2017, p. 4; Wu U. A., 2018aa, p. 7 2018bb, p. 11):

- i. Developed phosphoric acid and phosphate fertilizer industries consume about 250 million tonnes of phosphate rock per year. Typically, phosphate rock contains an average of 0.046 wt% REE, which translates into about 125,000 tonnes of potential annual production of REE of high value due to the high relative content of the heavy REE group.
- ii. There is no need to construct mining and processing facilities since the phosphate-bearing ore is already used in industry, and hence the cost of mining and processing is already covered by existing production.
- iii. Increasing demand for REE and increasing environmental restrictions require the removal of REE and other hazardous elements (e.g. uranium) from phosphoric acid, phosphogypsum and phosphoric acid sludge.

Russia has the world's fourth largest reserves of rare earth elements, most of which are contained in apatite-nepheline, a phosphate-bearing ore used to produce mineral fertilisers. Sustainable supply of rare earth products for the needs of the Russian economy is also determined by regulatory and legal documentation, in particular, the current "Strategy for the development of the mineral resource base of the Russian Federation until 2035", approved by the Government of the Russian Federation in 2018. The development and implementation of rare-earth element production technologies will reduce the impact on the environment, potentially increase the profitability of the enterprise and contribute to the innovative development of the metallurgical complex of Russia (Sizyakov u. a., 2016, p. 2).

The main phosphorus-bearing component of the apatite ore in the Khibiny group is fluorapatite, which has the formula $Ca_5(PO_4)_3F$. To obtain extraction phosphoric acid (EFA), apatite is leached, which, depending on the production technology, is carried out by nitric, hydrochloric or sulphuric acids; both in Russia and in the world, sulphuric acid is mostly used together with recycled phosphoric acid, returned to the reactor for greater slurry mobility. Then, from the product phosphoric acid, fertilizers (triple superphosphate, mono- and diammonium phosphates, etc.) are produced, and REEs, in the absence of by-product extraction technologies, partially pass into fertilizers (EPC contains 0.1 % REEs, including the most valuable heavy group), partially (mainly light and medium groups) - into a large-tonnage production waste, phosphogypsum, which finally contains about 0.45 % REEs.

4 Apatite Ore Processing Technology

Phosphorus is a biologically important trace element that is essential for the normal functioning of living organisms. Phosphorus compounds are used in medicine, engineering and agriculture.

Triple superphosphate, monoammonium phosphate, diammonium phosphate, amophos and other fertilisers are produced on the basis of H_3PO_4 . With the trend of increasing consumption of phosphate fertilizers, the rate of phosphoric acid production is also increasing. Figure 1 shows the dynamics of demand for mineral fertilizers. The drop in global demand in 2018/19 was caused by drought and lower agricultural production in the two largest consuming regions, India and China.

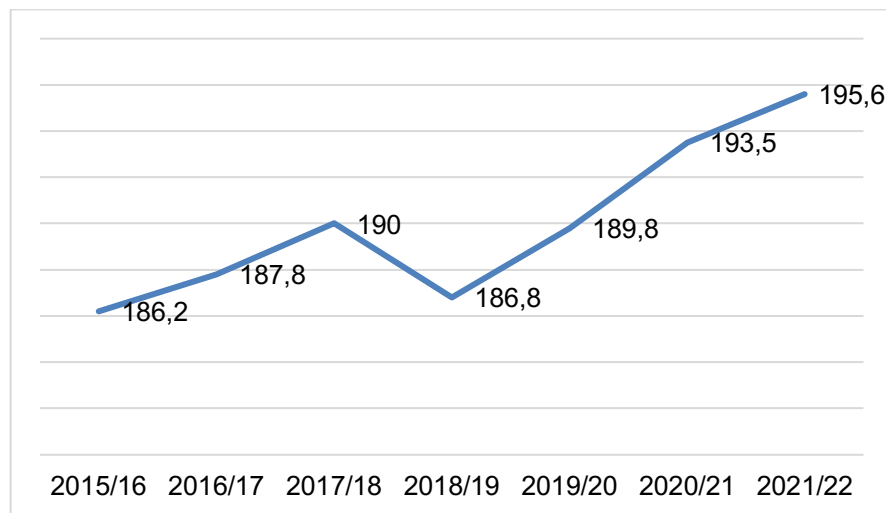
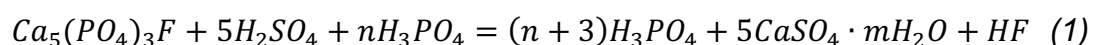


Figure 1: Global fertilizer consumption, mln tonnes of nutrient (Executive Summary Short-Term Fertilizer Outlook 2020–2021 Market Intelligence and Agriculture Services International Fertilizer Association (IFA), 2020)

Apatite has found wide application: for many decades it has been used in the inorganic industry as a source of phosphorus for mineral fertilizers and feed phosphates. The intermediate processing product of the mineral is wet process phosphoric acid (WPA), which is formed during the acidic leaching of the concentrate.

The chemistry of the decomposition process is described by the chemical equation 1:



Depending on the temperature of the decomposition process, the H_3PO_4 and impurities content in the liquid phase of the reaction slurry (Table 4), anhydrite ($m=0$),

half-hydrate ($m=0.5$) or dihydrate ($m=2$) calcium sulfate can precipitate. Anhydrite, half-hydrate and dihydrate processes are distinguished accordingly. The half-hydrate and dihydrate methods have advantages and disadvantages, as the dihydrate WPA contains less phosphorus and often needs to be digested for further use. On the other hand, the semi-hydrate acid is more concentrated and the filter surface utilisation rate is higher, but the high process temperature imposes additional requirements (and thus costs) on the corrosive properties of the apparatus. The anhydrite method, on the other hand, is not used industrially (Sokolovsky A.A., 2005, p. 22).

The decomposition conditions for fluorapatite are shown in the Table 4:

Process type	Temperature, °C	P ₂ O ₅ concentration in liquid phase, %	The heat of reaction, kJ/mol
Dihydrate	70-80	25-32	384.4
Semi-hydrate	95-100	38-48	371.0

Table 4: Fluorapatite decomposition conditions

Posphoric acid production consists of seven main stages:

- Preparatory, where apatite concentrate and acid stockpiles are received, prepared and stored;
- Feedstock is fed into an extractor, where the concentrate is degraded by a mixture of sulphuric acid and phosphoric acid, producing phosphogypsum sludge;
- The resulting slurry is separated in a vacuum filter, the sludge is washed and the washing water containing phosphoric acid is returned to the extractor;
- The dihydrate process requires an acidification step, i.e. an increase in the concentration of phosphoric acid by removal of water vapours;
- One of the most harmful impurities contained in apatite is fluorine (therefore the mineral is often even called fluorapatite). In the process of decomposition of apatite and evaporation of WPA, the vapours containing HF are captured by silicon oxide to form silicic fluorhydric acid;
- Storage of the resulting commercial product (WPA) and by-product (silicic hydrofluoric acid);
- Storage of phosphogypsum dumps at dedicated landfills.

The main product of technological production processes at present is phosphoric acid with P₂O₅ content of 42 %-53 %, at some plants producing acid by dihydrate method - depleted phosphoric acid with P₂O₅ content of 24 %-37 %.

The extraction phosphoric acid is used directly in the production of fertilizers, and phosphogypsum, which is a solid industrial waste, is sent to landfill and practically not used. In the process of decomposition of apatite concentrate, which contains up to 1 % of rare-earth metals, 15-20 % of the initial quantity in apatite ore is converted into solutions of WPA, including the most valuable group of heavy rare-earth metals. Thus, phosphoric acid contains up to 0.1 % of REE. The rest – mainly light and medium group - goes into phosphogypsum, which as a result contains about 0.45 % REE.

The recovery of REE from phosphogypsum is very promising, considering the increasing volumes of its tailings. However, there are also a number of cost challenges associated with such a solution: the need for pre-treatment of phosphogypsum and the need to ensure that phosphogypsum is sold after REE extraction, in particular in the building material industry. In the absence of practical realisation of the leach residue after lanthanide extraction, the processing of phosphogypsum appears to be economically viable (Jyothi u. a., 2020, p. 19).

5 Features of REE Extraction from Wet Process Phosphoric acid

In the 21st century, the technologies of obtaining and processing mineral raw materials strive to use them to the fullest extent possible and to minimise the volume of waste. The main challenges associated with the extraction of REE from phosphoric acid solutions are to maintain the initial composition of the commodity components and to obtain individual metal compounds with very similar physical and chemical properties.

The obvious advantage of using phosphoric acid is the absence of the need for its pretreatment. The choice of REE extraction technology is conditioned by the requirements to keep the composition of phosphoric acid unchanged for its further use in fertilizer production. Therefore, the use of such methods as precipitation or evaporation is not advisable due to the high content of impurities in the resulting sediment, which includes compounds of elements such as calcium, iron, titanium, etc.

Complex salt composition of apatite concentrate processing products and similar physicochemical properties of rare-earth metals create additional obstacles in the

process of their extraction and separation into individual components. Technological difficulties of REM extraction are also connected with their incommensurably low content of relatively impurity macroelements: Lanthanide amount concentration is 0.07 - 0.10 %, whereas the content of iron(III) ions competing during the extraction or sorption process in recalculation to oxide is 0.3-0.4 %.

The main methods of extraction of rare earth elements from their acidic solutions include extraction, sorption and precipitation. In modern literature preference is given to methods of obtaining individual lanthanides, as well as their separation from accompanying elements, including radioactive ones. The method of liquid extraction with organic solvents due to its simplicity, versatility and readiness for adaptation on an industrial scale meets these requirements to the greatest extent (Hidayah & Abidin, 2018, p. 5). Whereas the other methods mentioned above have significant disadvantages, e.g. the sorption method has low selectivity, lower throughput in multiple application cycles, complex extraction characteristics for different functional groups on the sorbent, low surface potential for its application in commercial/field operations and slow process speed (Hérès u. a., 2018, p. 9). The use of crystallisation and precipitation methods leads to a change in the composition of the phosphoric acid product, which is unacceptable if the recovery stage is introduced into existing production (Ponomareva u. a., 2021, p. 4).

The principle of liquid extraction is shown schematically in figure 2. It consists of a contact between two phases in which the target component is transferred from one phase to the other. In extraction, REE spontaneously passes from the aqueous phase to the organic extractant phase. This produces an extract, a phase saturated with the extracted component, and a raffinate, a solution that does not contain it. This is due to the fact that the REEs form much stronger compounds with the extractant compared to the inorganic ligands in the aqueous phase.

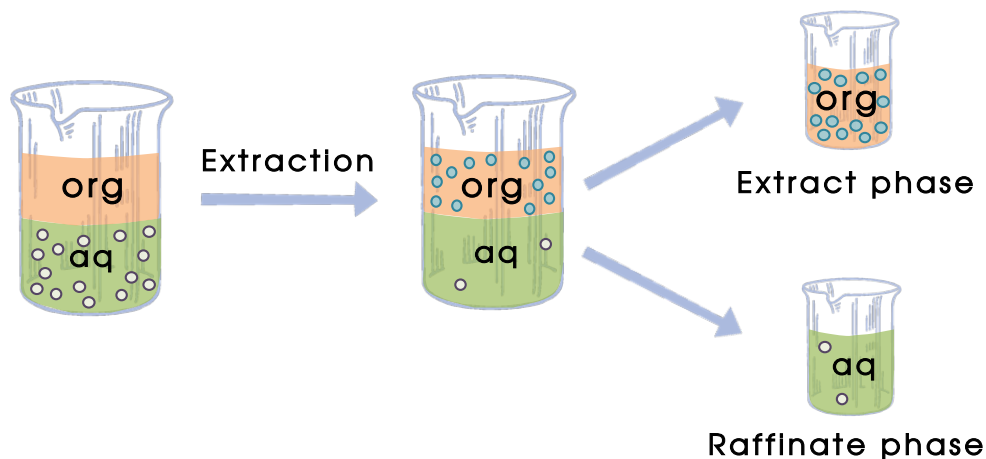


Figure 2: Liquid extraction scheme

The process of REE extraction using organophosphorus esters (tributyl phosphate, dialkyl methyl phosphonate) and organophosphorus acids (diisooctyl methyl phosphonate, di-2-ethylhexyl phosphoric acid (D2EHPA)) has been studied in sufficient detail as the most effective extractants (Hérès u. a., 2018, p. 4).

Authors of works investigated the selective separation of light and heavy REEs by liquid extraction from a solution obtained by leaching apatite ore with sulphuric acid with a concentration of 1 mol/l. Comparison of three organophosphorus extractants - di-2-ethylhexylphosphoric acid, mono-2-ethylhexyl ester of 2-ethylhexylphosphonic acid (PC88A) and tributyl phosphate showed the highest efficiency of D2EHPA for extraction of heavy REE and equal efficiency of compared extractants in relation to light REE. For extraction of light and heavy REEs the two-stage extraction is proposed. At the first stage of extraction more than 90 % (0.05 g/l) of heavy REE group is extracted from the leaching solution with 1.8 M D2EHPA in kerosene, then metals from the extractant are completely re-extracted with 4 M H₂SO₄. In the second stage of extraction, 1.1 g/l of light REEs present in the raffinate after extraction in the first stage are extracted using 1.8 M D2EHPA after adjusting the acidity of the raffinate to pH 1.6-1.7. As a result, 93 % (1.0 g/l) of the light REEs were extracted into the organic phase. Their re-extraction was carried out with 1 M H₂SO₄ and >90% (0.91 g/l). About 77,4 wt.% of light REE oxides as Ce_{0,56}La_{0,44}O_{1,78} and 65,2 wt.% of heavy REE oxides as Dy₉YO₁₅ can be obtained by the proposed method.

The efficiency of REE extraction by D2EHPA was also confirmed in the work (Arel-lano Ruiz V.C., u. a., 2020, p. 10) extractant showed a higher extraction capacity

compared to PC 88A, followed by Cyanex 272. The authors note an increase in the extraction rate with increasing temperature. The positive ΔH values obtained explain the shift of the equilibrium towards the formation of reaction products with increasing temperature.

The extraction of REE with di-2-ethylhexylphosphonic acid (Figure 3a) proceeds according to the cation-exchange mechanism in weakly acidic media. At the interface the extractant exchanges its hydrogen ion for a metal ion. The energy expended in the transition of the cation to the organic phase is compensated by the transition of an ion of the same sign from the organic phase to the aqueous phase.

In order to reduce the emulsification of the acid/extractant mixture during the extraction, solutions of D2EPHA in an inert diluent are used. In the solutions, the acid molecules are in dimerized form due to hydrogen bonds between the acid protons and the oxygen of the P=O group (Figure 3b).

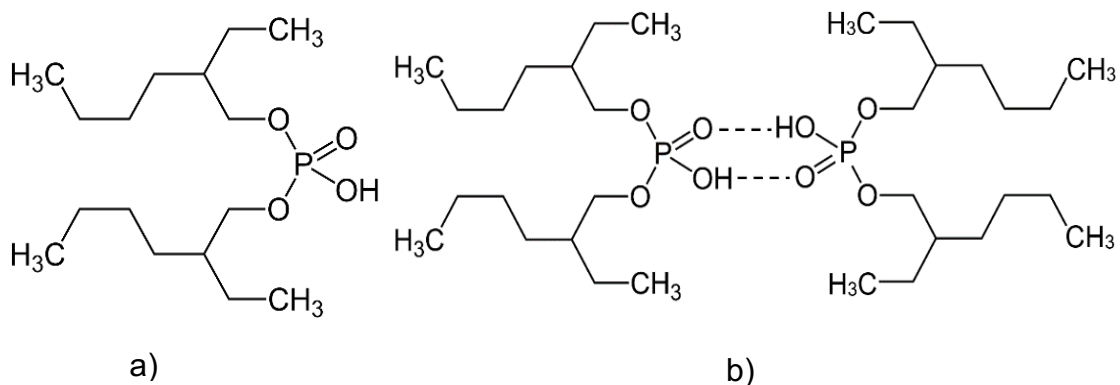
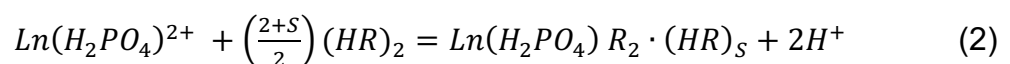


Figure 3: Structural formulae of the D2EHPA molecule (a) and its dimer (b)
 In strongly acidic media, in addition to the ion exchange reaction between the extractant and the REE cation, solvation also occurs, due to the presence of phosphoryl and carboxyl groups in the extractant and free electron orbitals in the metals. In summary, the reaction is as follows (Cheremisina u. a., 2019bb, p. 1):



where s is the number of acid solvating molecules,

$Ln(H_2PO_4)^{2+}$ — complex REE ions (III).

In view of the practically identical physico-chemical properties of the REEs 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 contraction 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, the element with a smaller radius forms a stronger organic complex, which, in turn, leads to an increase in its extraction rate and allows for concentration in the extractant phase (Lukyantseva & Sergeev, 2021, p. 5).

In liquid extraction, the diluent plays an important role by influencing the affinity of the metal in any phase (aqueous or organic). It is determined by the physical properties of the diluents, including specific gravity, viscosity, dielectric constant and solubility parameters. For example, the viscosity of the extractant often reduces the extraction efficiency, resulting in inhibition of the pure reagents (as such). Thus, suitable diluents must be selected to ensure consistency in the metal extraction process. Aliphatic and aromatic organic liquids are most often chosen as inert diluents which can significantly increase the density difference between the extractant and the aqueous phase and accelerate the stratification of the phases.

In the work (Batchu & Binnemans, 2018, p. 3) the effect on the extraction process of Nd and Dy from hydrochloric acid solutions using D2EHPA in 11 diluents (7 aliphatic: Shell solvents produced by GTL Gas-To-Liquid (GS190, GS215, GS250), Shell Fluid G70, ShellSol D70, ShellSol D80, n-dodecane; 2 aliphatic-aromatic: ShellSol 2325 and ShellSol 2046AR; 2 aromatic: ShellSol A150 and toluene). Analysis of the properties of different diluents showed that extractant mixtures with alkanes increase the degree of metal transfer into the extract, while mixtures with aromatic compounds prevent emulsification of the mixtures. Thus, the choice of an effective diluent can help to increase the efficiency of extraction extraction or separation of components.

In the work (Arellano Ruiz u. a., 2020, p. 2) investigated the effect on extraction for five different diluents such as Exxsol D80, n-heptane, cyclohexane, xylene and toluene at two different concentrations of extractant: 0.1 mol/L and 0.8 mol/L for rare earth element extraction using PC 88A, Cyanex 272 and D2EHPA. The most efficient extraction was obtained with aliphatic diluents than with aromatic diluents. At low dielectric constants (1.92 to 1.98) for aliphatic diluents such as n-heptane and Exxsol D 80, extraction efficiency was maximum compared to other diluents. There was an obvious trend towards higher REE recovery in the series: Exxsol D80 > n-

heptane > cyclohexane > xylene > toluene. Considering the higher extraction efficiency with Exxsol D80 as diluent, it was chosen as suitable for further extraction studies. However, the aforementioned diluent is also an economical reagent with the prospect of its use on a mass scale in continuous solvent extraction processes from REE.

As a diluent of di-2-ethylhexyl phosphoric acid in the extraction process, paraffin is most often used as the most available and inert with respect to the components of phosphoric acid solutions with low pH value, which is extremely important under the condition that the composition of technological phosphoric acid is kept constant.

The influence of impurity ions has been established (Fe^{3+} , Ca^{2+} , F^- , SO_4^{2-}) on extraction of REE from production solutions of EPC. Among impurity cations the greatest influence on REE extraction is exerted by iron (III), which interacts with the extractant, reducing its capacity for the target component. The negative effect of this impurity is reduced by reducing the phase contact time to 2-5 min., while the distribution coefficient decreases from 1.16 to 0.1. Also the use of an acidic re-extraction agent provides additional purification from the harmful impurity. The degree of recovery of REE is also reduced by the presence of fluoride ions, but in production solutions of phosphoric acid they are present mainly in bound form. Calcium and magnesium impurities in concentrations as in EFCs do not significantly affect the recovery of lanthanides (Cheremisina u. a., 2019aa, p. 6).

6 Working Methods and Methodology

This work considers the purification of REE extract obtained by the interaction of solutions simulating the composition of phosphoric acid extraction and directly production solutions.

Model solutions simulating the composition of wet-process phosphoric acid were prepared by dissolving six-water nitrates of the respective rare earth elements (Y, Yb, Dy), nine-water iron nitrate (3+) of grade "reagent-grade.", sulfuric acid with 94 % concentration and density of 1.83 g/cm^3 , orthophosphoric acid with 85 % concentration and density of 1.69 g/cm^3 .

The composition of WPA solutions obtained from the processing of apatite concentrate of the Khibiny group is given in Table 5, the relative content of individual rare-earth metal oxides is given in Table 6.

Compounds	Ln	P ₂ O ₅	SO ₃	F	Al ₂ O ₃	CaO	Fe ₂ O ₃	SiO ₂	TiO ₂
Content, %	0.1	28	1.8	1.5	0.4	0.8	0.4	1.1	0.04

Table 5: Composition of WPA solutions (LUKYANTSEVA & SERGEEV, 2021)

REO	Content, rel.%	REO	Content, rel.%	REO	Content, rel.%
La ₂ O ₃	15.07	Sm ₂ O ₃	3.18	Dy ₂ O ₃	1.92
Ce ₂ O ₃	37.54	Eu ₂ O ₃	0.96	Yb ₂ O ₃	0.51
Pr ₂ O ₃	4.67	Gd ₂ O ₃	3.51	Y ₂ O ₃	12.51
Nd ₂ O ₃	18.34	Tb ₂ O ₃	0.43	Er ₂ O ₃	0.88

Table 6: Relative content of REO in WPA (LUKYANTSEVA & SERGEEV, 2021)

Di-2-ethylhexylphosphoric acid produced by ZAO "Akrus" in Moscow with a D2EHPA content not less than 95% and inert solvent- paraffin containing not less than 95 wt.% of saturated hydrocarbons.

The composition of the extract obtained is shown in Table 7:

Component	Yb	Y	Er	Fe	Ti	Ca	Si
C, mmol/l	0.71	3.62	0.45	8.06	1.61	<0.01	<0.01

Table 7: Composition of rare earth element extract

To purify the D2EHPA-based rare earth element extract from iron and titanium, «reagent-grade» ethanedic acid solutions with H₂C₂O₄·2H₂O concentration not less than 99.5 %.

The reagent for the rare earth elements is "reagent-grade" sulphuric acid with H₂SO₄ concentration not less than 94 %.

Phase contact in the study of extraction equilibria was carried out using automated units: Parallel Auto-MATE Reactor System equipped with a magnetic stirrer, electric heater and thermocouple for work with mixtures of a total volume up to 200 ml and AutoLAB Chemical Reactor with an immersion stirrer, electric heater, temperature jacket and thermocouple for work with mixtures of a total volume of 1 l manufactured by H.E.L. (UK). Process parameters such as temperature needed to reach equilibrium state, phase contact time (t) and stirring speed were set and kept constant with the help of SCADA, an automated control system for the reactor plant.

Metal ion concentrations were determined by X-ray fluorescence analysis using PANalytical Epsilon 3 designed for the analysis of elements from Na to U in the concentration range from 10⁻⁴ to 100%.

The separation efficiency of the components was assessed by means of partition coefficients, representing the ratio of metal concentrations in the aqueous and organic phases and calculated according to equation 3:

$$\beta = \frac{D_1}{D_2}, \quad (3)$$

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

The extraction degree was defined as the degree of extraction, which was found according to equation 4:

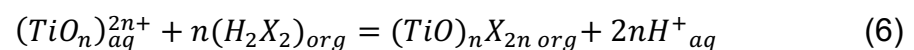
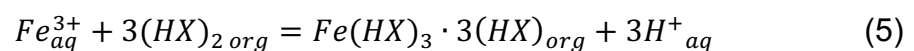
$$E = \frac{C_{org}V_{org}}{C_{org}V_{org} + C_{aq}V_{aq}} \cdot 100\%, \quad (4)$$

where C_{aq} — concentration of the element in the initial aqueous phase, M; C_{org} — concentration of the element in the organic phase after extraction, M; V_{aq} — aqueous volume, l; V_{org} — organic volume, л.

7 Purification of the Organic Extract from Impurity Metals

Besides rare-earth elements in the crystal lattice of apatite there are also titanium and iron, whose content is 4-5 times higher than the total content of REE. D2EHPA, interacting with phosphoric acid solutions, interacts not only with the target component, but also with the impurity iron, reducing the capacity of the extractant. Therefore, the first stage of investigation of REE re-extraction from its complexes with D2EHPA was the search for an efficient method of purification of organic extract from impurity metals.

Extraction of iron and titanium ions proceeds according to equations 5 and 6 (Cheremisina u. a., 2020, p. 5; Ponomareva u. a., 2020, p. 11):



There are several methods for the extraction of iron (III) from di-(2-ethylhexyl) phosphoric acid solutions. All of them are based on the use of concentrated solutions of inorganic acids or mixtures of these acids with aqueous solutions of salts as a reextractant (Fred J. Hurst u. a.; Wayne C Hazen and Angus V Henrickson; Yang

Liu u. a., 2014). The most selective iron extraction is achieved using oxalic acid (Maryam Akhlaghi, 2010). It forms strong oxalate complexes that are stable over a wide range of pH ($\lg K_{\text{stab}}(\text{Ti})=5,7$, $\lg K_{\text{stab}}(\text{Fe})=10,7$) (МАЛУКА, 2005), than REE complexes with D2EHPA $\lg K_{\text{stab}}(\text{Y})=3,47$ (Cheremisina O.V., 2015).

7.1 Determining the required concentration of re-extractant

To determine the optimum concentration parameters for reextraction we calculated the dependences of iron, REE (Fig. 4) and titanium extraction (Fig. 5) on oxalic acid concentration and on the ratio of aqueous phase to organic phase (Fig. 6 and 7).

The data obtained show that the process is most efficient under the following conditions: ethanedioic acid concentration 0.75 M, Aq:Org phase ratio = 2.

Increase of oxalic acid concentration to more than 0.25 mol/l up to 1 mol/l increases the titanium reextraction degree insignificantly: from 21 % up to 26 %. Further increase of its content is not reasonable as it leads to supersaturation of aqueous solution and considerable increase of its viscosity. The highest distribution coefficient ($D=0.31$) is observed when using Aq:Org = 0.5. Stirring speed higher than 400 rpm is technologically inadvisable due to the formation of persistent emulsion, significantly complicating the process of phase separation.

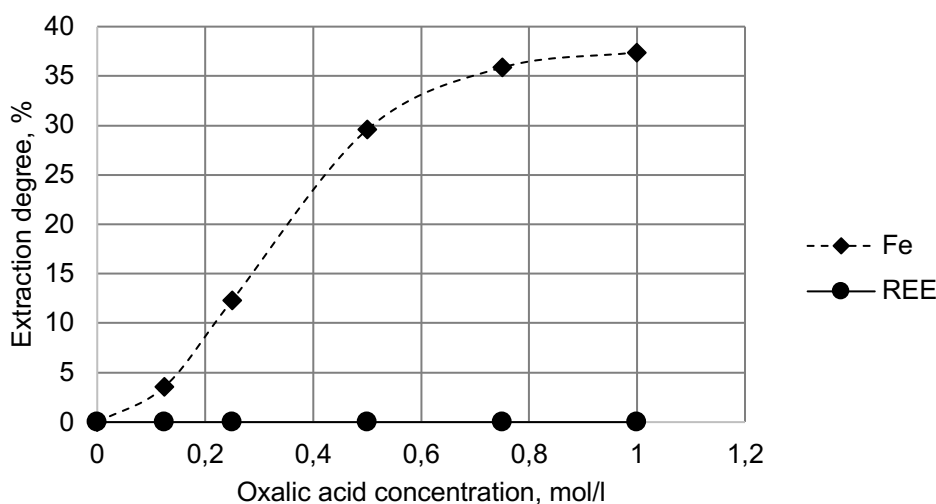


Figure 4: Dependence of Fe and REE extraction on ethanedioic acid concentration, 450 rpm, 15 min, volume ratio Aq:Org= 1:1

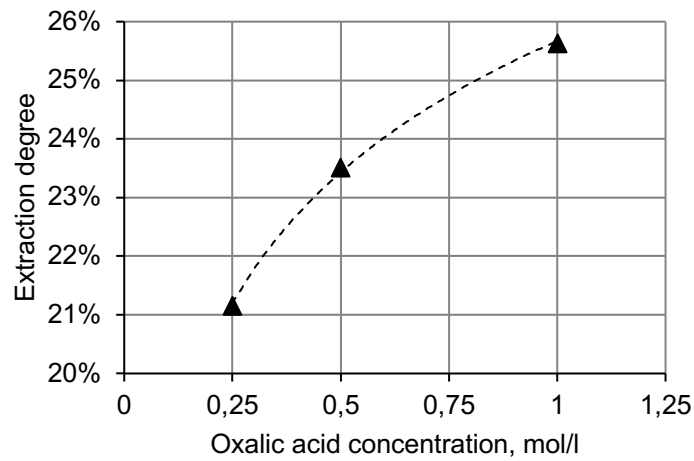


Figure 5: Dependence of Ti extraction on ethanedioic acid concentration, 400 rpm, 20 min, volume ratio Aq:Org= 1:1

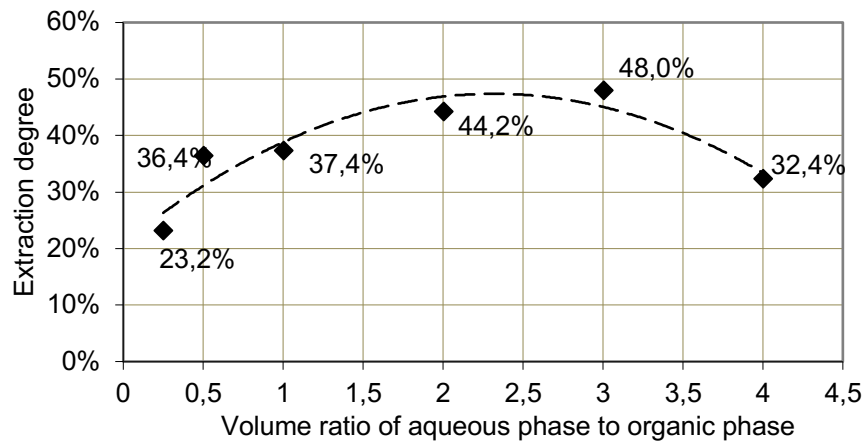


Figure 6: Dependence of iron (III) cations extraction on the aq-org phase ratio

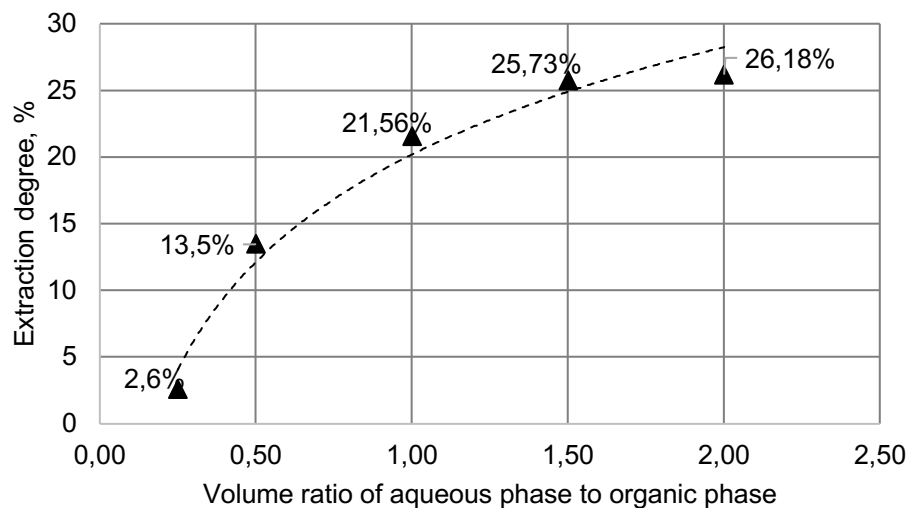


Figure 7: Dependence of Titanium (IV) extraction on the aq-org phase ratio

7.2 Determination of phase contact time and stirring speed

The next step of the study was to determine the required mixing time and speed. Using graphical relationship between degree of iron recovery from organic phase and stirring time (Fig. 8 and 9) and stirring speed (Fig. 10) it was possible to determine effective values. Thus, the limiting value of stirring speed is 400 rpm with a phase contact time of 15 min. Although at higher values there is some increase of target parameters, such technical solution is not practicable due to increase of specific process cost.

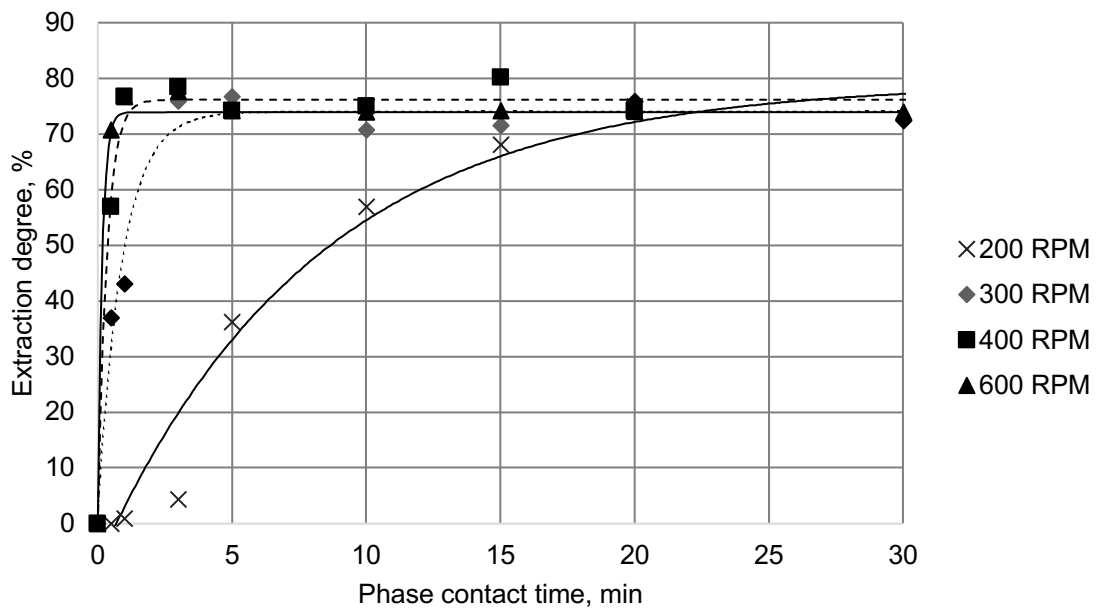


Figure 8: Dependence of degree of extraction on stirring time for iron reextraction, Aq:Org=2:1

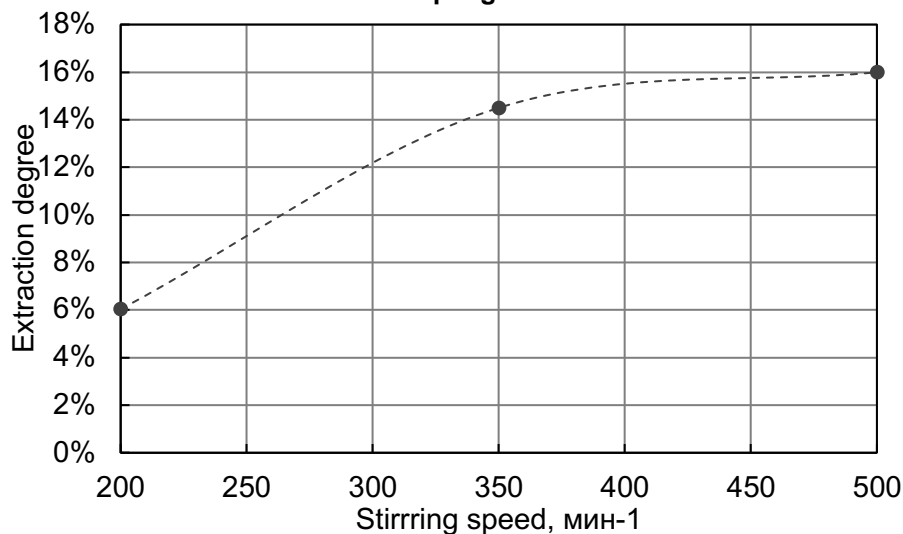


Figure 9: Dependence of the stirring speed on the degree of Fe recovery, 15 min, Aq:Org = 1:1

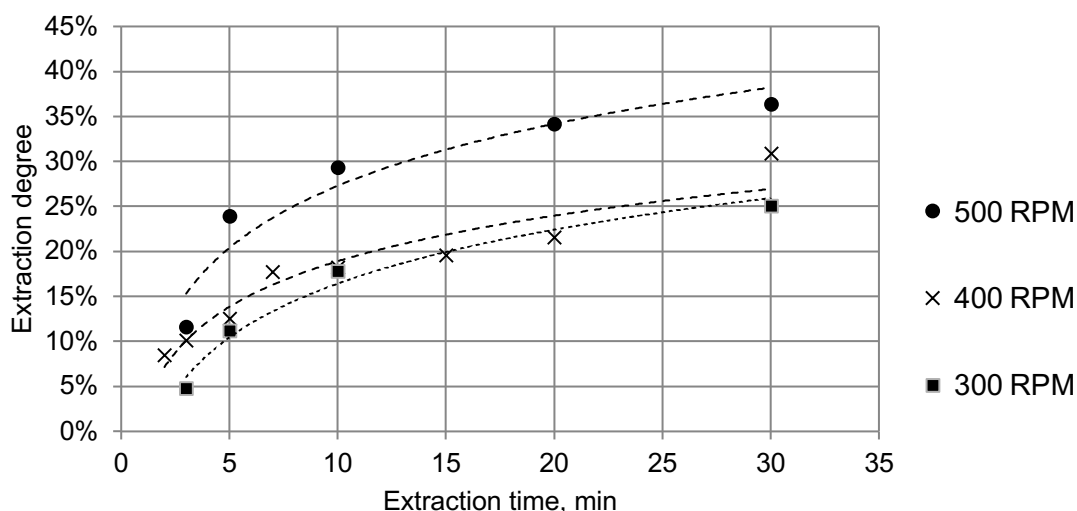


Figure 10: Time dependence of the titanium re-extraction degree at different stirring speeds, oxalic acid concentration 1 mol/l, volume ratio Aq:Org = 1:1

7.3 Increasing the REE capacity of the extractant with usage step-wise purification

In the course of the work it was hypothesised that the capacity of the extractant could be increased by using a staged iron purification, i.e. by introducing an additional iron re-extraction stage after each extraction cycle.

To investigate this hypothesis an experiment was carried out. As a comparison solution, a saturated extract of REE was prepared in a multi-step extraction (15 stages) from production solutions of extraction phosphoric acid. The control sample was not subjected to iron purification during all fifteen cycles.

The experiment was then repeated with the introduction of an iron reextraction step after each extraction step. Oxalic acid with a concentration of 0.5 mol/L was used as the reextractant. Both processes were carried out at 21 °C, at a stirring speed of 400 rpm, for 10 minutes. Extraction was carried out at a volume ratio of organic to aqueous phase of 1:10, iron re-extraction at 1:4. The results are shown in Table 8.

Stage	Clearing out the iron	Concentration, mmol/l			
		Fe/Org	Y/Org	Yb/Org	Er/Org
15	Not carried out	8.06	3.62	0.71	0.45
15	after every stage	6.65	6.57	1.27	1.14
18	after each stage, except for stage 18	9.63	7.43	1.57	1.14

Table 8: Concentrations of iron and REE in the extract after saturation without and with purification after each stage

As a result, due to the introduction of an additional stage of purification of the organic phase from iron after 15 pairs of extraction stages it was possible to increase the

capacity of the extractant for yttrium 1.81 times, for ytterbium 1.78 times and for erbium 2.53 times; after 18 pairs - for yttrium 2.05 times, for ytterbium 2.2 times and for erbium 2.53 times.

It was found that the degree of iron extraction increases with increasing number of stages of oxalic acid treatment of the extract (figure 11). When the extract was treated 8 times, the iron content in the extract decreased by 99%, while the content of the sum of REEs did not change (Table 9).

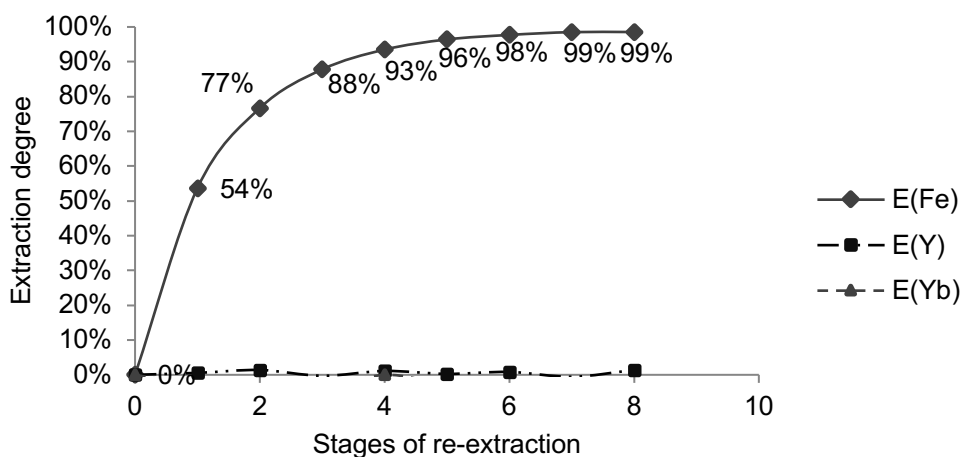


Figure 11: Time dependence of the titanium re-extraction degree at different stirring speeds, oxalic acid concentration 1 mol/l, volume ratio Aq:Org = 1:1

Stage	Iron cleaning	Concentration, mmol/l			
		Fe/Org	Y/Org	Yb/Org	Er/Org
Before cleaning	None	9.63	7.43	1.57	1.14
After 8 stages	After every stage	0.09	7.17	1.47	1.12

Table 9: Concentrations of iron and REE in the extract before and after purification

For titanium the degree of extraction also increases with the increase of extraction steps with oxalic acid, at the 14th step the titanium REE content was less than 0.9 %. After the 14th step of reextraction the TiO₂ content in the extract has decreased more than 10 times while REE content has not changed (Figure 12, Table 10). Thus, the method makes it possible to purify D2EHPA-based extract containing rare-earth metals from titanium impurities with at least 90% Extraction degree of the latter.

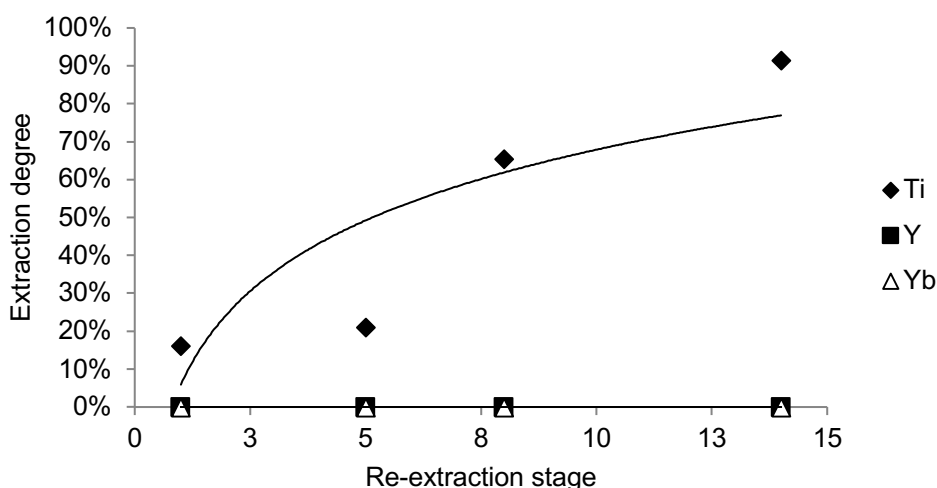


Figure 12: Dependence of Ti, Y and Yb recovery on the reextraction stage

Reextraction stage	Content in organic phase, 10 ⁻⁴ mol/l		
	Ti	Y	Yb
0	7.29	55.10	8.20
1	6.11	-	-
5	5.76	-	-
8	2.53	-	-
14	0.63	55.10	8.20

Table 10: Dependence of the concentration of the Ti extract components on the number of reextraction steps

Thus, the method makes it possible to purify the D2EHPA-based extract from iron (III) impurities without reducing the concentration of yttrium and ytterbium in the organic phase of the extractant.

The results obtained show that during iron (III) and titanium (IV) re-extraction with oxalic acid from D2EHPA-based re-extracts saturated with REE ions, the latter are preserved in the organic phase. This makes it possible to purify the extract from impurity metals during extraction as well as after it in order to increase the content of rare-earth metals in the extract due to the freed portion of the extractant capacity occupied by iron.

8 Study of Re-extraction Parameters

8.1 Effect of re-extractant concentration on the recovery of REE from organic complexes

The re-extraction process is the reverse of the extraction process, therefore a shift of equilibrium towards the formation of the starting substances is necessary for the destruction of D2EHPA complexes with REE. Metal cations form sufficiently strong complexes with the extractant by cation-exchange and donor-acceptor mechanisms (ЛЕБЕДЕВ И.А., 1978; МИХАЙЛИЧЕНКО А.И. & ПИМЕНОВА Р.М., 1969; ЧИРКСТ Д.Э. и. а., 2180). These complexes have different stability due to the different atomic structure of each metal (ЧЕРЕМИСИНА О.В., 2015). Therefore, in order to separate metals from the organic phase it is necessary to use acid. Sulphuric acid was chosen as a reextractant as it is available, cheap and already used in the technological scheme of WPA production at the stage of dissolution of apatite concentrate.

The study was carried out using D2EHPA solutions in kerosene (volume fraction of 0.3), taken after extraction of REE from model solutions of industrial phosphoric acid (4.5 M orthophosphoric acid and 0.19 M sulfuric acid). Aqueous sulphuric acid solutions prepared from concentrated sulphuric acid (94%) were used as the reextractant.

For each metal an individual solution of the organic phase was taken. The reextraction was carried out in automated reactors controlling constant parameters: temperature – 295 K, stirring speed, phase contact time - 5 min. The obtained data are shown in tables 11-13.

C(H ₂ SO ₄), M	V _{org} , ml	V _{aq} , ml	C _{org isx} (Y), mmol/l	E, %	Ca _{aq} , mmol/l	C _{org} , mmol/l	D	Aq:Org
6	40	20	10.58	98.11	20.76	0.3	36.80	0.5
4,5	40	20	10.58	88.09	18.64	1.26	14.79	0.5
3	40	20	10.58	56.81	12.02	4.57	2.63	0.5
2	40	20	9.55	30.05	5.74	6.68	0.86	0.5
1	40	20	9.55	2.62	0.5	9.3	0.05	0.5

Table 11: Yttrium ions re-extraction

C(H ₂ SO ₄), M	V _{org} , ml	V _{aq} , ml	C (Dy) org isx, mmol/l	E, %	Caq, mmol/l	C _{org} , mmol/l	D	Aq:Org
6	40	20	3.98	99.62	7.93	0.015	328.67	0.5
4.5	40	20	3.98	97.49	7.76	0.1	77.60	0.5
3	40	20	4.13	77.48	6.4	0.93	6.88	0.5
2	40	20	3.98	72.36	5.76	1.1	5.24	0.5
1	40	20	3.98	19.10	1.52	3.22	0.47	0.5

Table 12: Dysprosium ions re-extraction

C(H ₂ SO ₄), M	V _{org} , ml	V _{org} , ml	C (Yb) org isx, mmol/l	E, %	Caq, mmol/l	C _{org} , mmol/l	D	Aq:Org
6	40	20	12.75	62.04	15.82	4.84	3.27	0.5
4.5	40	20	12.75	33.10	8.44	8.53	0.99	0.5
3	40	20	12.75	10.67	2.72	11.39	0.24	0.5
2	40	20	11.49	4.26	0.98	11.0	0.09	0.5
1	40	20	11.49	0.87	0.2	11.39	0.02	0.5

Table 13: Yttrium ions re-extraction

The experimental results show that more concentrated reextractant solutions increase the extraction of metals from the organic phase.

At the same time the recovery of metal ions differs. A less strong complex of dysprosium ions allows to extract it several tens of times more effectively than ytterbium ions (Table 14). These regularities allow to separate adjacent cation pairs into individual components (Table 15).

C (H ₂ SO ₄), M	Distribution coefficient			
	Dy	Y	Er	Yb
6	328.67	36.80	28.65	3.27
4.5	77.60	14.79	11.93	0.99
3	6.88	2.63	1.52	0.24
2	5.24	0.86	0.48	0.09
1	0.47	0.05	0.02	0.02

Table 14: Distribution of REE in the organic phase

C (H ₂ SO ₄), M	Separation ratio					
	β (Dy/Y)	β (Y/Er)	β (Er/Yb)	β Dy/Yb	β Y/Yb	β Dy/Er
6	9.06	1.28	8.77	161.74	11.3	18.45
4.5	5.25	1.24	12.06	78.43	14.95	6.50
3	2.62	1.73	6.38	28.82	11.01	4.52
2	6.08	1.80	5.35	58.78	9.64	10.98
1	8.70	2.72	1.13	26.88	3.06	23.88

Table 15: Separation of adjacent REEs in the re-extraction stage at different concentrations of re-extractant

Consequently, the possibility of separating dysprosium and ytterbium from the group at the reextraction stage has been experimentally proven. Another pair of cations: erbium and yttrium have similar extraction rates, but their separation is also possible, with high purity yttrium concentrate obtained. Based on calculated partition coefficients, it is reasonable to use concentrated sulfuric acid solutions of 4.5 and 6 M for separation of heavy REEs and maximum concentration at the reextraction stage. At sulphuric acid concentrations above 6 M there is a risk of increased solubility of the extractant in the aqueous solution.

8.2 Influence of process parameters on REE re-extraction

Important parameters for re-extraction processes are process parameters such as mixing speed and mixing time.

The stirring speed allows the optimum hydrodynamic regime, which in turn provides the maximum phase contact surface and the intensity of mass transfer. In order to determine the optimum stirring speed, model solutions of D2EHPA organic phase in paraffin with 0.3 volume fraction saturated in Yb and Y and reextractant with 6M sulfuric acid were taken. Figure 13 shows the graphical relationship between the degree of metal reextraction and the number of revolutions per minute.

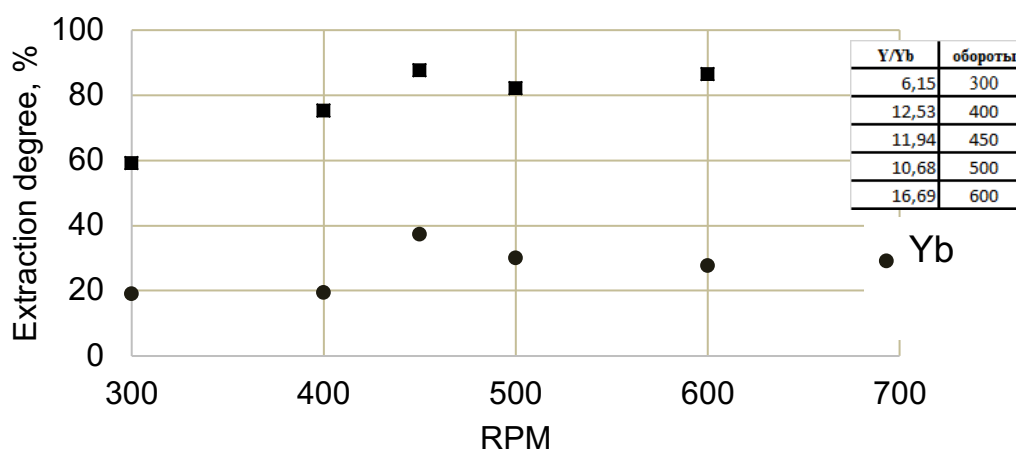


Figure 13: REE re-extraction depending on stirring speed (6M H₂SO₄, 295 K, Vorg/Vaq=10)

The diagram shows that the re-extraction values are relatively constant in the range of 400-600 rpm and agree with the concentration dependence of the sulphuric acid with reasonable accuracy. Thus an optimum mixing speed of 450 rpm is more favourable.

Also we studied the influence of other factors like increasing temperature, addition of inorganic salts and treatment with reagent possessing redox properties.

We found that pretreatment with organic hydrogen peroxide solution, addition of ammonium oxalate to the reagent and an increase of the temperature had little effect on the reextraction process. The results of the experiment are shown in Table 16.

Parameter	The presence of salt	Increase in temperature	With no salt
Initial concentration of Yb in org. ph., M	0.0110	0.0110	0.0110
Yb concentration after re-extraction, M	0.0041	0.0041	0.0047

Table 16: Influence of temperature and presence of inorganic salt on the re-extraction process

8.3 Influence of phase ratio on heavy REE group re-extraction parameters P3Э

The effect of the phase ratio was studied using a model solution of the organic phase D2EHPA in paraffin with a volume fraction of 0.3; Yb, Y, Er. The results are shown in table 17 and figure 14.

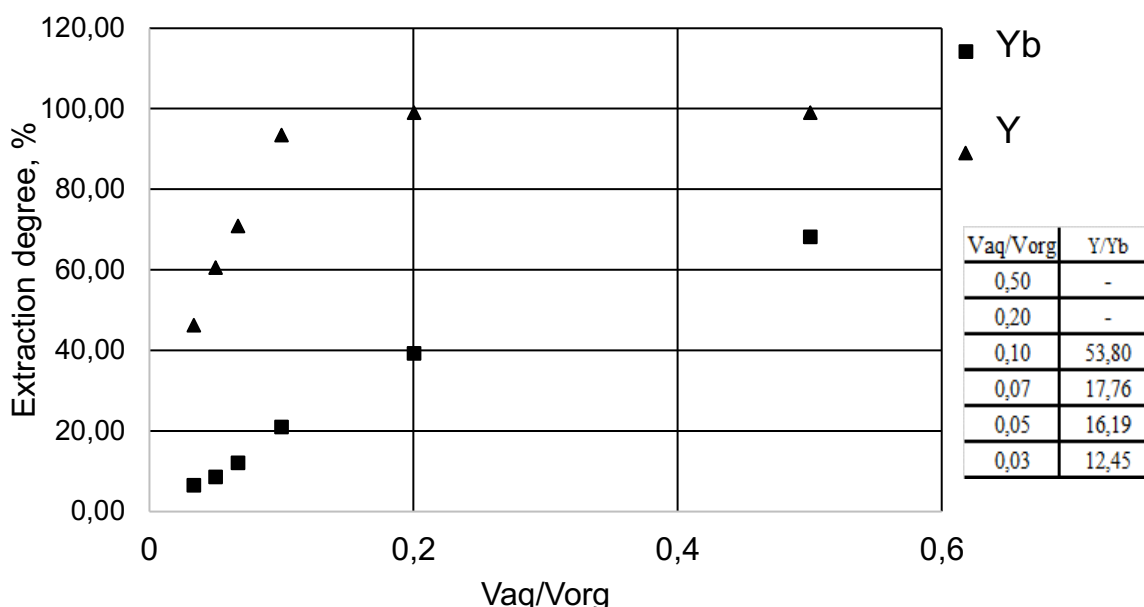


Figure 14: Re-extraction of REE from the organic phase depending on the phase ratio (6M H₂SO₄, 295 K, 450 об/мин)

C (H ₂ SO ₄), M	Vorg, ml	Vaq, ml	C (Yb) orgisx, M	E, %	Caq, M	Corg, M	D	RPM	Vaq/Vorg
6	20	10	0.00324	68.2	0.00442	0.00103	4.29	400	0.5
6	50	10	0.00324	39.2	0.00635	0.00197	3.22	400	0.2
6	100	10	0.00324	20.9	0.0068	0.00256	2.66	450	0.1
6	150	10	0.00324	12.0	0.00585	0.00285	2.05	450	0.066
6	200	10	0.00324	8.6	0.0056	0.00296	1.89	450	0.05
6	300	10	0.00324	6.4	0.0063	0.00303	2.08	450	0.033
C (H ₂ SO ₄), M	Vorg, ml	Vaq, ml	C (Y) orgisx, M	E, %	Caq, M	Corg, M	D	RPM	Vaq/Vorg
6	20	10	0.00367	99.0	-	0.0073	>100	400	0.5
6	50	10	0.00367	99.0	-	0.017	>100	400	0.2
6	100	10	0.00367	93.4	0.0343	0.034	>100	450	0.1
6	150	10	0.00367	70.8	0.039	0.00107	36.45	450	0.066
6	200	10	0.00367	60.4	0.0444	0.00145	30.62	450	0.05
6	300	10	0.00367	46.3	0.051	0.00197	25.89	450	0.033
C (H ₂ SO ₄), M	Vorg, ml	Vaq, ml	C (Dy) org isx, M	E, %	Caq, M	Corg, M	D	RPM	Vaq/Vorg
6	20	10	0.00122	99.0	-	0.00122-	>100	400	0.5
6	50	10	0.00122	99.0	-	0.0071-	>100	400	0.2
6	100	10	0.00122	99.0	-	0.011-	>100	450	0.1
6	150	10	0.00122	90.1	0.0165	0.00012	>100	450	0.066
6	200	10	0.00122	72.1	0.0176	0.00034	51.76	450	0.05
6	300	10	0.00122	58.2	0.0213	0.00051	41.76	450	0.034

Table 17: Re-extraction of REE at different phase ratios

It is established that at a B:O phase ratio greater than 0.07 the degree of reextraction of Yttrium and Erbium is greater than 90%. Also it is observed a decrease of partition coefficients into organic phase of REE with increase of organic phase volume.

Thus, it can be stated that the partition coefficient Y/Yb takes values in the range (11 - 18), depending on conditions of partitioning. The highest value of the re-extraction coefficient is achieved at a phase ratio of 1/10 and 1/20, stirring speed of 450 rpm and sulfuric acid concentration of 6 M.

9 Production of Individual HREE Compounds

9.1 Description of the technical solution for the production of individual HREE compounds from WPA

To obtain individual compounds of yttrium, ytterbium and dysprosium with purity not less than 90 % from extraction phosphoric acid with Extraction degree not less than 90 %, it is necessary to implement a stepwise multi-stage process of countercurrent extraction, purification and reextraction.

To achieve the most efficient extraction of each element the concentration parameters of reextractant - sulphuric acid and temperature are varied in the range from 1 M to 6 M from 20 to 50 - 60°C respectively and using an extractant with the volume fraction of D2EHPA in paraffin from 30 to 70 %. Received extracts of individual compounds of rare earth metals are sent for carbonate ion precipitation to produce individual REE carbonates. A general scheme of REE separation is shown in Figure 15.

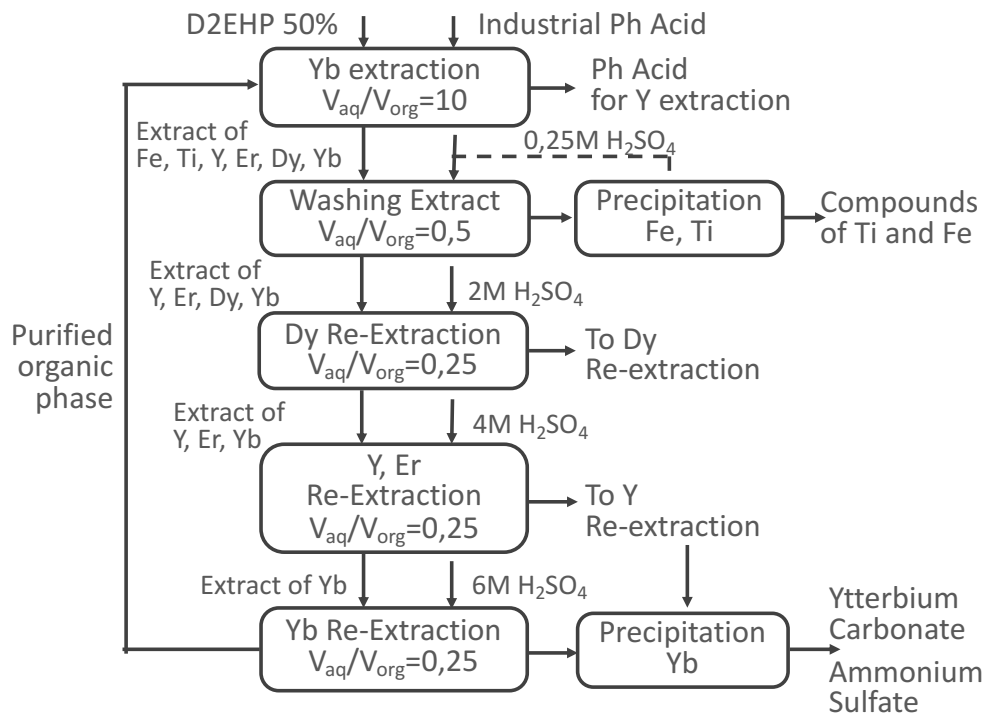


Figure 15: HREE from WPA allocation scheme

9.2 Obtaining an organic extract of REE

For approbation of the methodology of individual REE compounds production solutions of WPA obtained in conditions of "Balakovo Apatite" were used. Initial average mass content of heavy REE group in 1 l of phosphoric acid is presented in Table 18. The data and calculated material balance of the process of production of individual REE compounds are given for 1 l of WPA with solution density 1360 kg/m³.

Compound	Content, mg
Yb ₂ O ₃	6.8956
Y ₂ O ₃	170.136
Dy ₂ O ₃	26.112
WPA	1360000

Table 18: Mass content of HREE in 1 l of WPA

Extraction of metals was carried out by a solution of D2EGFK in paraffin from the production solution of phosphoric acid in an automated reactor, in which a given temperature and stirring speed were maintained. To achieve maximum saturation of the organic phase with the target component the process should be carried out in several stages, therefore after conducting the 10th stage of the saturation process the obtained extract is sent for iron re-extraction with oxalic acid. The composition of the resulting organic phase is shown in Table 19.

Compound in WPA	Content, mg	Average Extraction degree in 10 stages	Content in 14.3 ml of the organic phase, mg	Content in total organic phase, g/l	Relative content, %
Ytterbium	5.90	0.45	2.653	0.094	5.26
Yttrium	138.06	0.03	4.142	0.290	16.22
Dysprosium	22.20	0.01	0.222	0.016	0.89
Iron	3128.24	0.003	9.384	1.342	75.06
Other REE and impurities	43521.35	-	below the detection limit	0.01	0.56

Table 19: Extraction of REE from WPA into the organic phase of the extractant

The resulting total extract was treated with 0.25 M oxalic acid in a 1:1 ratio (V_{org}/V_{aq}), 8 steps for 99.9 % iron purification.

9.3 Extraction of dysprosium from the organic phase as carbonate

Dysprosium was first extracted from the organic phase using 1M sulphuric acid. After purification from iron, the extract was sent to the last step of the first series of

the dysprosium purification cascade. The extract was successively run through ten purification stages of the first series of stages, the re-extractant being taken from the preceding reactor and in turn saturated with dysprosium. From the first step of the first series the extract was fed to the last step of the next series and the operation was repeated until the complete 3 series of purification cascades were passed. The results are shown in Table 20.

The extract obtained after the final stage of each series was directed to the precipitation of dysprosium carbonates, and the purified extract was fed to yttrium and erbium purification. Dysprosium carbonate was obtained by precipitation with sodium carbonate, further dilution of the solution to dissolve sodium sulphide crystals, and subsequent filtration of insoluble dysprosium carbonate.

Element	Initial content in the organic phase, g	Extraction degree in 38 stages (sums)	Content in organic phase after re-extraction, g	Relative content, %
Ytterbium	0.094	~0	0.0940	22.59
Yttrium	0.290	0.02	0.2842	68.28
Dysprosium	0.016	0.90	0.0016	0.38
Iron	1.342	0.999	0.0013	0.31

Table 20: Purification of the organic phase from iron and recovery of dysprosium

9.4 Method for the production of yttrium carbonate

To extract yttrium and erbium from the organic phase, sulfuric acid with a concentration of 3 mol/L was added to the iron (3+) purified extract. The choice of sulphuric acid concentration was due to the creation of conditions preventing the re-extraction of ytterbium. In order to achieve the most complete recovery of ytterbium the treatment of the extract was carried out in 14 stages at a phase ratio of 1:1 (Vorg/Vaq). The result is shown in Table 21. The control of the organic phase for yttrium and erbium content was carried out continuously during all phases of the re-extraction.

Yttrium carbonate was obtained by precipitation with sodium carbonate, further dilution of the solution to dissolve sodium sulphide crystals and the subsequent filtration of insoluble yttrium carbonate.

Element	Initial content in the organic phase, g	Extraction degree in 14 stages (sums)	Content in organic phase after re-extraction, g	Relative content, %
Ytterbium	0.0940	0.3	0.0658	93.60
Yttrium	0.2842	0.99	0.0028	3.98
Dysprosium	0.0016	~1	~0	~0
Iron	0.0013	~0	0.0013	1.85

Table 21: Ytterbium concentrate in organic phase after yttrium extraction

9.5 Method for isolating ytterbium as carbonate

In order to provide a high degree of ytterbium extraction we used a sulfuric acid solution with a concentration of 6 mol/L and a volume 4 times less than the volume of the organic phase. The total number of re-extraction stages for iron (III) ions and REEs was 2. Technological parameters of the experiment, characteristics of re-extractants, initial and final concentrations of components in the organic phase, expressed in mmol/L, are presented in Table 22.

Number of re-extraction stages	Re-extractant, mol/l	Aq:Org	t, min	C ₀ (Fe)	C _∞ (Fe)	C ₀ (Y)	C _∞ (Y)	C ₀ (Er)	C _∞ (Er)	C ₀ (Yb)	C _∞ (Yb)
8	H ₂ C ₂ O ₄ 0.37	1	10	8.06	<0.01	3.62	3.58	0.45	0.43	0.71	0.70
14	H ₂ SO ₄ 1-3	1	5	<0.01	<0.01	3.58	0.03	0.43	<0.01	0.70	0.43
4	H ₂ SO ₄ 6	0.25	5	<0.01	<0.01	0.03	<0.01	<0.01	<0.01	0.43	<0.01

Table 22: Technological parameters of the experiment

Figure 16 shows the recovery of target components and iron (3+) as a function of the number of reextraction stages.

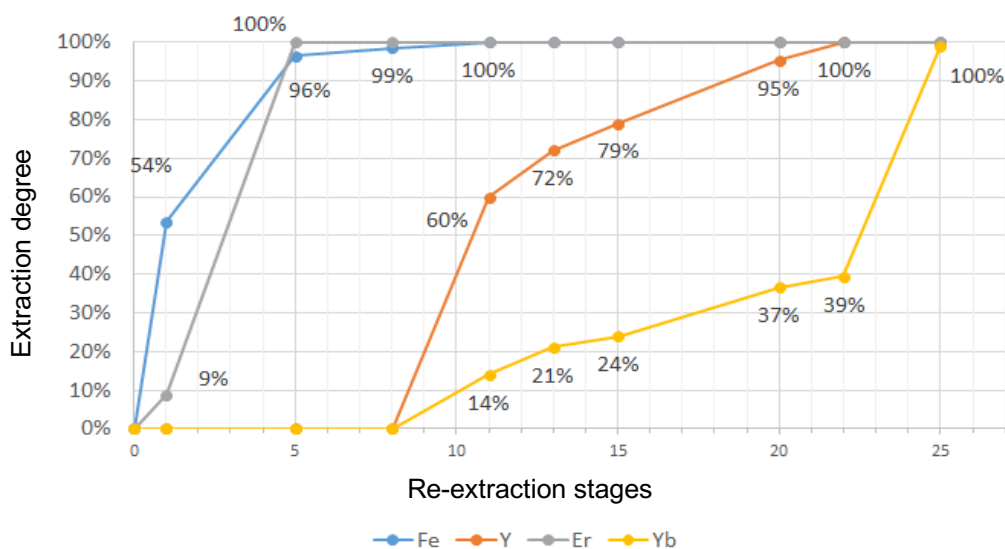


Figure 16: Dependence of REE and iron (3+) recovery on the number of reextraction stages

As the experiment shows, during five cycles of extraction with oxalic acid the recovery rate of iron reaches 96%, and the use of sulphuric acid with concentrations from 2.5 to 6 mol/l provides a complete extraction of yttrium, erbium and ytterbium. Re-extracts obtained in the process of ytterbium concentration were also used to produce yttrium and dysprosium compounds.

Ytterbium carbonate was obtained by precipitation with sodium carbonate, further dilution of solution for dissolution of sodium sulfide crystals and the subsequent filtration of insoluble ytterbium carbonate.

A summary of the material balance of the process steps is shown in Table 23.

Income, g			Outcome, g		
1	Wet Phosphoric Acid	1360	1	Wet Phosphoric Acid	1356,8
	including Y ₂ O ₃	170.1·10 ⁻³	2	Y ₂ O ₃	153.1·10 ⁻³
	Dy ₂ O ₃	26.1·10 ⁻³	3	Dy ₂ O ₃	23.5·10 ⁻³
	Yb ₂ O ₃	6.9·10 ⁻³	4	Yb ₂ O ₃	6.2·10 ⁻³
	Fe ₂ O ₃	5.44	5	Extractant *	51
				D2EHPA	17
2	Extractant	51		Kerosene	34
	D2EHPA	17	6	Ammonium sulphate (commercial)	467.5
	Kerosene	34	7	Ferrous sulphate concentrate (99%, titanium sulphate 1%)	7,52
3	Sulphuric acid (commercial, concentrated)	320	8	Carbon dioxide	155
4	Oxalic acid	43	9	Water vapor	33
5	Ammonium carbonate (Chemically clean)	340	10	Oxalic acid*	43
TOTAL		2114	TOTAL		2114

*– Regenerated reagent losses of <0.01%

Table 23: Material balance of the process (on a laboratory scale)

9.6 Results of spectral analyses of the compounds

The results of spectral analysis of the obtained concentrates after sodium carbonate precipitation according to the principle scheme of separation developed in this work are shown in Figures 17, 18 and 19.

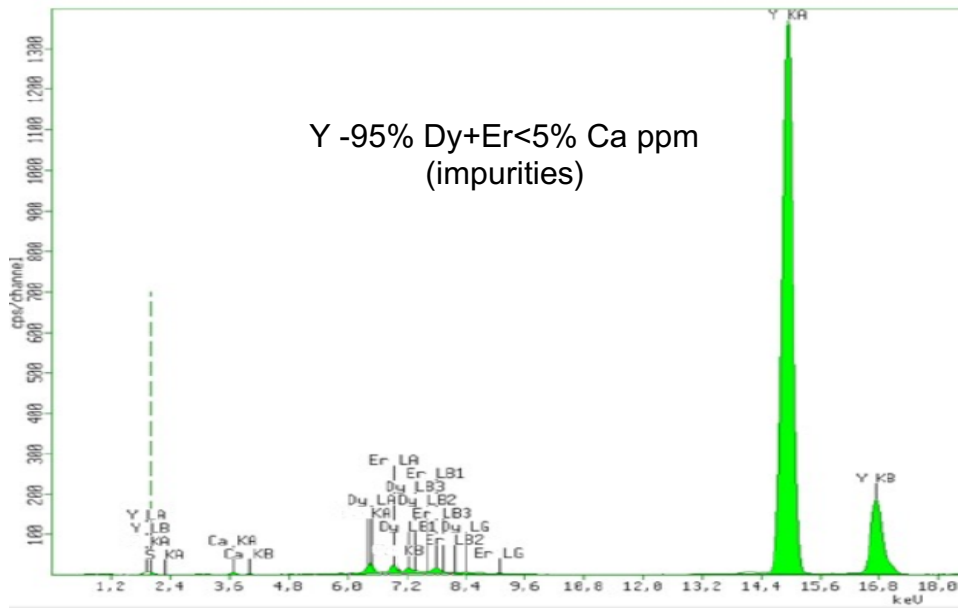


Figure 17: X-ray fluorescence spectrum of yttrium carbonate concentrate obtained from EPC, data presented in terms of pure metals

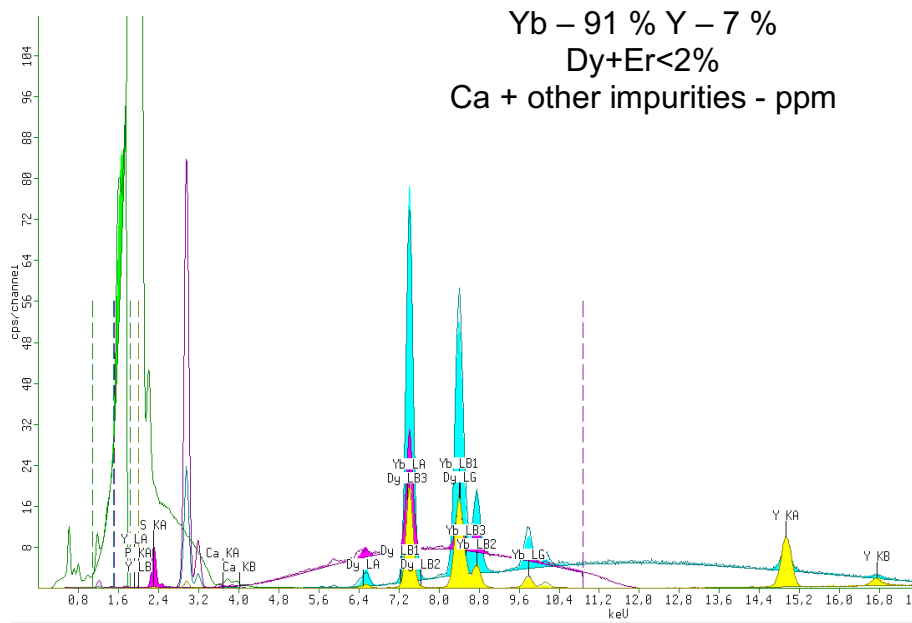


Figure 18: X-ray fluorescence spectrum of ytterbium carbonate concentrate obtained from EFC, data presented in terms of pure metals

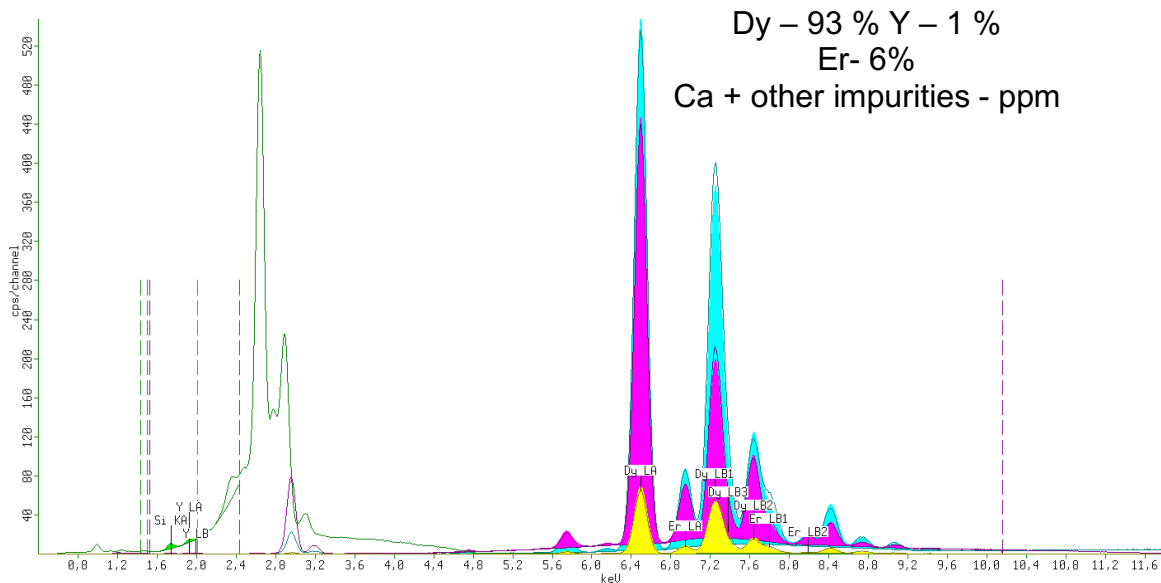


Figure 19: X-ray fluorescence spectrum of dysprosium carbonate concentrate obtained from EPC, data presented in terms of pure metals

According to X-ray fluorescence spectra (Figure 17), yttrium carbonate concentrate contains up to 95 % yttrium proper and about 5 % dysprosium and erbium. Calcium is diagnosed as an impurity with a content of not a few ppm.

The ytterbium carbonate concentrate (Fig. 18), obtained from EPC, contains up to 91 % ytterbium, 7 % yttrium and sum of dysprosium with erbium in amount of about 2 %, calcium content does not exceed some ppm.

Dysprosium carbonate concentrate (Fig. 19), obtained from ESPK, contains up to 93 % dysprosium, 1 % yttrium and 6 % erbium, the calcium content does not exceed some ppm.

10 Bibliography

Abreu, Renata D. ; Morais, Carlos A.: Study on separation of heavy rare earth elements by solvent extraction with organophosphorus acids and amine reagents. In: Minerals Engineering Bd. 61 (2014), S. 82–87

Arellano Ruiz, Verónica Cristina ; Kuchi, Rambabu ; Parhi, Pankaj Kumar ; Lee, Jin-Young ; Jyothi, Rajesh Kumar: Environmentally friendly comprehensive hydrometallurgical method development for neodymium recovery from mixed rare earth aqueous solutions using organo-phosphorus derivatives. In: Scientific Reports Bd. 10 (2020), Nr. 1, S. 16911

Balaram, V.: Rare earth elements: A review of applications, occurrence, exploration, analysis, recycling, and environmental impact. In: Geoscience Frontiers Bd. 10 (2019), Nr. 4, S. 1285–1303

Batchu, Nagaphani Kumar ; Binnemans, Koen: Effect of the diluent on the solvent extraction of neodymium(III) by bis(2-ethylhexyl)phosphoric acid (D2EHPA). In: Hydrometallurgy Bd. 177 (2018), S. 146–151

Battsengel, Ariuntuya ; Batnasan, Altansukh ; Narankhuu, Ariunbolor ; Haga, Kazutoshi ; Watanabe, Yasushi ; Shibayama, Atsushi: Recovery of light and heavy rare earth elements from apatite ore using sulphuric acid leaching, solvent extraction and precipitation. In: Hydrometallurgy Bd. 179 (2018), S. 100–109

Cheremisina, O. V. ; Sergeev, V. V. ; Fedorov, A. T. ; Il'ina, A. P.: Rare Earth Metal Extraction from Apatite Ores. In: Metallurgist Bd. 63 (2019a), Nr. 3–4, S. 300–307

Cheremisina, O. V. ; Sergeev, V. V. ; Fedorov, A. T. ; Lukyantseva, E. S.: Associated recovery of heavy rare-earth metals in the processing of phosphate raw materials. In: Obogashchenie Rud (2019b), S. 29–35

Cheremisina, Olga ; Sergeev, Vasilij ; Ponomareva, Maria ; Ilina, Alexandra ; Fedorov, Alexander: Kinetics Study of Solvent and Solid-Phase Extraction of Rare Earth Metals with Di-2-Ethylhexylphosphoric Acid. In: Metals Bd. 10 (2020), Nr. 5, S. 687

Dostal, J: Rare earth element deposits of alkaline igneous rocks. In: Resources Bd. 6 (2017), Nr. 34, S. 1–2

Dushyantha, Nimila ; Batapola, Nadeera ; Ilankoon, I.M.S.K. ; Rohitha, Sudath ; Premasiri, Ranjith ; Abeysinghe, Bandara ; Ratnayake, Nalin ; Dissanayake, Kithsiri: The story of rare earth elements (REEs): Occurrences, global distribution, genesis, geology, mineralogy and global production. In: Ore Geology Reviews Bd. 122 (2020), S. 103521

Fred J. Hurst ; Gilbert M. Brown ; Franz A. Posey: Removing oxygen from a solvent extractant in an uranium recovery process., 2021

Hérès, Xavier ; Blet, Vincent ; Di Natale, Patricia ; Ouaattou, Abla ; Mazouz, Hamid ; Dhiba, Driss ; Cuer, Frederic: Selective Extraction of Rare Earth Elements from Phosphoric Acid by Ion Exchange Resins. In: Metals Bd. 8 (2018), Nr. 9, S. 682

Hidayah, Nur Nadiatul ; Abidin, Sumaiya Zainal: The evolution of mineral processing in extraction of rare earth elements using liquid-liquid extraction: A review. In: Minerals Engineering Bd. 121 (2018), S. 146–157

Jyothi, Rajesh Kumar ; Thenepalli, Thriveni ; Ahn, Ji Whan ; Parhi, Pankaj Kumar ; Chung, Kyeong Woo ; Lee, Jin-Young: Review of rare earth elements recovery from secondary resources for clean energy technologies: Grand opportunities to create wealth from waste. In: Journal of Cleaner Production Bd. 267 (2020), S. 122048

Larochelle, Tommee ; Noble, Aaron ; Ziemkiewicz, Paul ; Hoffman, David ; Constant, James: A Fundamental Economic Assessment of Recovering Rare Earth Elements and Critical Minerals from Acid Mine Drainage Using a Network Sourcing Strategy. In: Minerals Bd. 11 (2021), Nr. 11, S. 1298

Liu, Tianchi ; Chen, Ji ; Li, Hailian ; Li, Kai ; Li, Deqian: Further improvement for separation of heavy rare earths by mixtures of acidic organophosphorus extractants. In: Hydrometallurgy Bd. 188 (2019), S. 73–80

Lukyantseva, E.S. ; Sergeev, V.V.: Increasing the depth of apatite processing by extracting rare-earth elements. In: LITVINENKO, V. S. (Hrsg.) E3S Web of Conferences Bd. 266 (2021), S. 02002

Maryam Akhlaghi: Stripping of Fe (III) from D2EHPA using different reagents Bd. Volume 1 (2010), S. 255–262

Ponomareva, Maria ; Cheremisina, Olga ; Mashukova, Yulia ; Lukyantseva, Elena: Increasing the efficiency of rare earth metal recovery from technological solutions during processing of apatite raw materials. In: Journal of Mining Institute Bd. 252 (2021), S. 1–10

Reichl, C. ; Schatz, M.: World Mining Data 2021 (Nr. 36). Vienna : Federal Ministry of Agriculture, Regions and Tourism, 2021

Rey, J. ; Atak, S. ; Dourdain, S. ; Arrachart, G. ; Berthon, L. ; Pellet-Rostaing, S.: Synergistic Extraction of Rare Earth Elements from Phosphoric Acid Medium using a Mixture of Surfactant AOT and DEHCNPB. In: Solvent Extraction and Ion Exchange Bd. 35 (2017), Nr. 5, S. 321–331

Sizyakov, V. M. ; Vlasov, A. A. ; Bazhin, V. Yu.: Strategy tasks of the russian metallurgical complex. In: Tsvetnye Metally (2016), S. 32–37

Cheremisina, O. V. ; Sergeev, V. V. ; Fedorov, A. T. ; Alferova, D. A. : Separation of rare-earth metals and titanium in complex apatite concentrate processing. In: Obogashchenie Rud (2020), S. 30–34

Swain, Nilam ; Mishra, Sujata: A review on the recovery and separation of rare earths and transition metals from secondary resources. In: Journal of Cleaner Production Bd. 220 (2019), S. 884–898

Talan, Deniz ; Huang, Qingqing: A review of environmental aspect of rare earth element extraction processes and solution purification techniques. In: Minerals Engineering Bd. 179 (2022), S. 107430

Voncken, j. H. L.: The Rare Earth Elements: An Introduction, SpringerBriefs in Earth Sciences. 1st ed. 2016. Cham : Springer International Publishing : Imprint: Springer, 2016 — ISBN 978-3-319-26809-5

Wang, Meiyuan ; Zhang, Xia ; Hao, Zhendong ; Ren, Xinguang ; Luo, Yonguang ; Wang, Xiaojun ; Zhang, Jiahua: Enhanced phosphorescence in N contained Ba₂SiO₄:Eu²⁺ for X-ray and cath-ode ray tubes Bd. 32 (2010), Nr. 9, S. 1042–1045

Wayne C Hazen ; Angus V Henrickson: Recovery of metal values from aqueous solution by solvent extraction with an organo phosphorus extractant, 1962

Wu, Shengxi ; Wang, Liangshi ; Zhang, Patrick ; El-Shall, Hassan ; Moudgil, Brij ; Huang, Xiaowei ; Zhao, Longsheng ; Zhang, Lifeng ; U. A.: Simultaneous recovery of rare earths and uranium from wet process phosphoric acid using solvent extraction with D2EHPA. In: Hydrometallurgy Bd. 175 (2018a), S. 109–116

Wu, Shengxi ; Wang, Liangshi ; Zhao, Longsheng ; Zhang, Patrick ; El-Shall, Hassan ; Moudgil, Brij ; Huang, Xiaowei ; Zhang, Lifeng: Recovery of rare earth elements from phosphate rock by hydrometallurgical processes – A critical review. In: Chemical Engineering Journal Bd. 335 (2018b), S. 774–800

Yang Liu ; Sang-Ho Nam ; Manseung Lee: Stripping of Fe(III) from the Loaded Mixture of D2EHPA and TBP with Sulfuric Acid Containing Reducing Agents Bd. Vol. 35 (2014), Nr. No. 7

Косынкин, В.Д. ; Глебов, В.А.: Возрождение российского производства Редкоземельных металлов – важнейшая задача Отечественной экономики. In: . Суздаль, 2010 (Kosynkin, V.D. ; Glebov, V.A.: The revival of Russian production of rare-earth metals is the most important task of the domestic economy. In: . Suzdal, 2010)

Лебедев И.А.: Термодинамические константы устойчивости фосфатных комплексов Bd. 23 (1978), Nr. 12, S. 3215–3227 (Thermodynamic stability constants of phosphate complexes.A.: Thermodynamic stability constants of phosphate complexes Bd. 23 (1978), No. 12, S. 3215-3227)

Малука, Л. М.: Кинетика, термодинамика и механизм окислительно-восстановительных процессов с участием комплексов титана и других координационных соединений. Кубан. гос. технол. ун-т. - Краснодар, автореферат дис. доктора хим. наук: 02.00.04, 2005 (Maluka, L. M.: Kinetics, thermodynamics and mechanism of redox processes involving titanium complexes and other coordination

compounds. Kuban. state technol. un-T. - - Krasnodar, abstract of the dissertation of the Doctor of Chemical Sciences: 02.00.04, 2005)

Михайличенко А.И. ; Пименова Р.М.: Некоторые вопросы экстракции нитратов редкоземельных элементов НФОС Bd. 14 (2009), Nr. 6, S. 1611–1617 (Mikhailichenko A.I., Pimenova R.M.: Some issues of the extraction of nitrates of rare earth elements NSF Bd. 14 (2009), No. 6, S. 1611-1617)

Савицкий, Е.М. ; Терехова, В.Ф. ; Буров, И.В. ; Маркова, И.А. ; Наумкин, О.П.: Сплавы редкоземельных металлов. М. : издательство академии наук СССР, 1991 (Savitsky, E.M. ; Terekhova, V.F. ; Burov, I.V. ; Markova, I.A. ; Naumkin, O.P.: Alloys of rare earth metals. Moscow : Publishing House of the USSR Academy of Sciences, 1991)

Соколовский А.А., Унанянц Т.П.: Краткий справочник по минеральным удобрениям. Москва : Химия, 2005 (Sokolovsky A.A., Unanyants T.P.: A short guide to mineral fertilizers. Moscow : Chemistry, 2005)

Цегельник, Э.: Элемент с неба. Церий Bd. 21 (2006), Nr. 3, S. 19–21 (Tsegelnik, E.: An element from the sky. Cerium Bd. 21 (2006), Nr. 3, S. 19-21)

Цыликов, О.В. ; Ребровская, Д.А.: Магнитные материалы на основе редкоземельных металлов. Ульяновск : УлГТУ, 2013 (Tsegelnik, E.: An element from the sky. Cerium Bd. 21 (2006), Nr. 3, S. 19-21)

Черемисина О.В.: Экстракция редкоземельных металлов ди-2-этилгексилфосфорной кислотой из фосфорнокислых растворов (2015), Nr. 214, S. 39–50 (Cheremisina O.V.: Extraction of rare earth metals with di-2-ethylhexylphosphoric acid from phosphoric acid solutions (2015), Nr. 214, S. 39-50)

Чиркст Д.Э. ; Дибров И.А. ; Черемисина О.В.: Растворимость фосфата церия (III) в фосфорной кислоте Bd. 65 (2180), Nr. 8 (Chirkst D.E. ; Dibrov I.A. ; Cheremisina O.V.: Solubility of cerium (III) phosphate in phosphoric acid Bd. 65 (2180), Nr. 8)

Rare Earth Element Deposits | Geology for Investors. URL <https://www.geologyforinvestors.com/rare-earth-element-deposits/>. - abgerufen am 2021-11-23

Executive Summary Short-Term Fertilizer Outlook 2020–2021 Market Intelligence and Agriculture Services International Fertilizer Association (IFA), 2020

Отчет исследовательской группы ООО «ИНФОМАЙН». Обзор рынка редкоземельных магнитов в России. Москва, 2021 (Report of the research group of LLC "INFOMINE". Overview of the rare earth magnets market in Russia. Moscow, 2021)

Информационно - аналитический портал / [Электронный ресурс] // Газпром-нефть — Режим доступа: <http://www.gazprom-neft.ru/press-center/sibneft-online/archive/2016-april/1113024/> (2021) (Information and analytical portal / [Electronic resource] // Gazpromneft — Access mode: <http://www.gazprom-neft.ru/press-center/sibneft-online/archive/2016-april/1113024/> (2021))

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13 List of Abbreviations

Aq	Aqueous phase
C	Molar concentration
C ₀	Initial molar concentration of the component
C _{org}	Equilibrium molar concentration of the component in the organic phase
D	Distribution coefficient
D2EHPA	Di-2-ethylhexyl phosphoric acid
E	Extraction degree
HREE	Heavy Rare Earth Elements
Ln	Lanthanoids
M	mol/l
Org	Organic phase
REE	Rare Earth Elements
REO	Rare Earth Oxides
WPA	Wet Phosphoric Acid

