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Extraction of rare earth elements from phosphogypsum and uranium in situ leaching solutions

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Abstract: The paper investigates the extraction of rare earth elements (REE) from technogenic sources – phosphogypsum and uranium *in situ* leaching (ISL) solutions. We found that mechanical activation significantly increases the degree of REE leaching from phosphogypsum. We also obtained data on sorption leaching of REEs from phosphogypsum. It has been shown that, depending on the ion exchanger used and its form, chemical activation can double the leaching degree of the target components. The paper presents the findings of the study on the sorption recovery of scandium from uranium *in situ* leaching solutions. We determined that Sc sorption from uranium ISL solutions on the Purolite S-957 cation exchanger is much more effective than on Lewatit TP-260, Purolite S-950, Tulsion CH-93 CH-93, and ECO-10 amphotites. However, it should be pointed out that none of the listed sorbents is highly selective towards scandium ions. The paper presents comparative data on Sc extraction from uranium ISL solutions using Lewatit VP OC-1026 and Axion 22 commercial solid extractants synthesized according to the method described in the paper. We determined the mechanism of scandium extraction from uranium ISL solutions using Axion-22 and proved that it shows high selectivity towards scandium ions. Studies on the desorption of scandium from the saturated solid extractant showed that the most effective desorption agent is an aqueous solution of hydrofluoric acid. Additionally, the paper investigates the sorption extraction of REEs from uranium ISL solutions on cation exchangers KU-2, KM-2P, and KF-11. We found that the best eluents for the desorption of REEs from the saturated cation exchanger are solutions of calcium chloride and ammonium nitrate. It has been shown that the concentration of REEs in the solution and the removal of major impurities (Fe and Al) are quite effective when REEs precipitate from the desorption solution by fractional hydrolysis. The paper describes the separation of La, Nd, and Sm by elution from the saturated impregnate containing phosphorylododecyl and Di(2-ethylhexyl) phosphoric acid in its structure. It should also be noted that ionic liquids can be useful for the extraction of REEs from the solutions of various electrolytes. We presented one of the technological schemes illustrating REE extraction from phosphogypsum.

Keywords: technogenic deposits, rare-earth elements (REE), scandium, ion exchange, solid extractant, extraction, uranium in situ leaching (ISL) solutions.

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Извлечение редкоземельных металлов из фосфогипса и растворов подземного выщелачивания урана

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Аннотация: Проведены исследования по извлечению редкоземельных элементов (РЗЭ) из техногенных источников – фосфогипса и растворов подземного выщелачивания урана (ПВУ). Установлено, что механоактивация в значительной мере увеличивает степень выщелачивания РЗЭ из фосфогипса. Также получены данные по сорбционному выщелачиванию РЗЭ из фосфогипса. Показано, что химическая активация в зависимости от используемого ионита и его формы может в 2 раза увеличить степень вы-

щелачивания по целевым компонентам. Представлены результаты исследования по сорбционному извлечению скандия из растворов подземного выщелачивания урана. Установлено, что сорбция Sc из растворов ПВУ на катионите Purolite S-957 происходит значительно лучше, чем на амфолитах Lewatit TP-260, Purolite S-950, Tulsion CH-93 и ЭКО-10. Однако необходимо отметить и тот факт, что все рассмотренные сорбенты не отличаются высокой селективностью по отношению к ионам Sc. Приведены сравнительные данные по извлечению Sc из растворов ПВУ коммерческим сорбентом ТВЭКС Lewatit VP ОС-1026 и ТВЭКС Axion-22, синтезированными по приведенной в работе методике. Определен механизм экстракции скандия из растворов ПВУ с использованием Axion-22 и установлено, что он имеет довольно высокую селективность по отношению к ионам Sc. Представлены результаты исследования по десорбции скандия из насыщенного ТВЭКС. Показано, что наиболее эффективным десорбирующим агентом является водный раствор фтористо-водородной кислоты. Также в работе рассмотрено сорбционное извлечение РЗЭ из растворов ПВУ на катионитах КУ-2, КМ-2П, КФ-11. Выявлено, что лучшими элюентами для десорбции РЗЭ из насыщенного катионита являются растворы хлорида кальция и нитрата аммония. Показано, что значительное концентрирование суммы РЗЭ и очистку от основных примесей (Fe и Al) достаточно эффективно можно осуществить на стадии осаждения РЗЭ из раствора десорбции посредством дробного гидролиза. Представлены данные по разделению La, Nd и Sm путем элюирования из насыщенного импрегната, содержащего в своей структуре фосфорилподанд и Д2ЭГФК. Также отмечено, что для экстракции РЗЭ из растворов различных электролитов значительный интерес представляют ионные жидкости. В качестве примера извлечения РЗЭ из фосфогипса представлена одна из разработанных технологических схем.

Ключевые слова: техногенные месторождения, редкоземельные элементы (РЗЭ), скандий, ионный обмен, твердый экстрагент, экстракция, растворы подземного выщелачивания урана (ПВУ).

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Introduction

The past few decades saw an unprecedented breakthrough in the development of artificial intelligence, digital economy, green energy, etc., which would have been impossible without rare and scattered metals [1]. Solid and liquid production wastes can be valuable sources of rare earth elements (REE). Such wastes are often referred to as technogenic mineral formations (TMF). Some of them can now be safely reclassified into technogenic deposits (TD).

Depending on the stage of the technological process that generated the given TD, all anthropogenic wastes can be classified as follows:

- mineral processing tailings from mining operations;
- waste from metallurgical and chemical processing of raw materials;
- waste generated from the combustion of fossil fuels;
- radioactive waste of industrial, scientific and military enterprises.

As a rule, in initial ore materials, rare earth metals (REM) are included in the structure of other mineral formations. Thus, the research conducted at Ural Federal University revealed the following scandium concentrates:

- in titanomagnetite ores — diopside $\text{Ca}(\text{Mg}, \text{Al})(\text{Si}, \text{Al})_2\text{O}_6$, hornblende $\text{Ca}_2(\text{Mg}, \text{Fe}, \text{Al})_5(\text{Al}, \text{Si})_8\text{O}_{22}(\text{OH})_2$,
- in ilmenite ores — ilmenite FeTiO_3 , pyroxene $(\text{Me}_x\text{Me}_y\text{Me}_z)\text{Si}_2\text{O}_6$,

- in bauxites — boehmite $\gamma\text{-AlO}(\text{OH})$, gibbsite $\alpha\text{-Al}(\text{OH})_3$,

- in uranium sandstones — metatuyamunite $\text{Ca}(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}$, and the following REM concentrates:

- in apatite ores — apatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH}, \text{F}, \text{Cl})_2$,
- in uranium sandstones — brunnerite $(\text{U}, \text{Ca}, \text{Th}, \text{Y})(\text{Ti}, \text{Fe})_2\text{O}_6$.

As the main component is separated, rare earth metals retain their original mineral forms (diopside in the tailings of wet magnetic separation (WMS) during the beneficiation of titanomagnetite ores), pass into uranium in-situ leaching (ISL) solutions, solutions of hydrolyzed sulfuric acid — waste of titanium dioxide pigment production from ilmenite ores) or are transformed into new mineral forms in the course of temperature and chemical treatments (phosphogypsum forms when apatite concentrates are processed into phosphate fertilizers and red mud is a by-product of bauxite processing into alumina) [2].

Solid products of feedstock processing pose the greatest difficulty for REE recovery during the target component extraction. Numerous researches [3–7] explored the issues of scandium extraction from wet magnetic separation wastes, and they are not addressed in this paper.

The aim of this work is to investigate the main techniques of enhancing the efficiency of REE extraction from solid technogenic waste on the example of their extraction from phosphogypsum.

Materials and methods

For our research, we used phosphogypsum generated as a waste product at the Balakovo mineral fertilizer plant of JSC Apatit (Russia). The raw material for its production is apatite concentrate from the Kola Peninsula processed according to the dihydrate scheme. For experiments on sorption extraction of REEs and Sc from uranium in-situ leaching solutions, we used the recovered solution (RS) of in-situ leaching of JSC Dalur (Russia).

Mechanical activation of phosphogypsum samples was carried out in a batch bead mill that includes a DISPERMAT LC75 laboratory dissolver equipped with an APS 500 grinding system (VMA-GETZMANN GMBH, Germany). We conducted wet activation of phosphogypsum in the 0.5 dm³ grinding chamber with the ZrO₂ inner coating. The beads used for milling were also of ZrO₂.

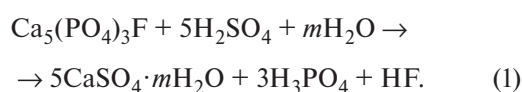
Sorption leaching was studied in 150 ml glass beakers. The mixture of acid and phosphogypsum prepared in advance in the required ratio was placed in a beaker and later ion exchange resin was added. During the sorption leaching, the solution was vigorously stirred by an overhead stirrer.

Tests on sorption extraction of REEs and Sc from uranium ISL solutions were carried out in 50-ml laboratory sorption columns filled with the investigated resin.

All water samples were analyzed on an ICP-MS NexION 350x mass spectrometer (Perkin Elmer, USA). Qualitative X-ray phase analysis of the samples was performed on a Xpert PRO MRD diffractometer (Malvern Panalytical B.V., the Netherlands) and their IR spectra were obtained on a Vertex-70 spectrometer (Bruker Corporation, USA).

Results and discussion

Phosphogypsum is formed when apatite concentrates are processed into phosphate fertilizers according to the following reaction:



Depending on the process conditions and impurities present in the phosphate raw material, calcium sulfate can be obtained in one of three forms: dihydrate CaSO₄·2H₂O (FDG), hemihydrate CaSO₄·0.5H₂O (FPG) or anhydrite CaSO₄ form [8]. In the dihydrate product, about 50 % of REEs from the solution crys-

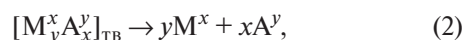
tallize in the solid phase. In the hemihydrate mode, the amount of co-crystallized REEs increases to 70–85 % [9; 10]. The average REE content of the resulting calcium sulfate generally ranges from 0.2 to 0.6 %.

Depending on reaction implementation method (1) REE can be present as an independent orthophosphate phase, enriching the celestine phase, or be a part of the crystalline phase of calcium sulfate, isomorphically replacing Ca [11; 12].

It is obviously difficult to extract REEs from phosphogypsum when they incorporate into the crystal structure of gypsum or celestine. To do so, the formed phosphogypsum phase should be fully dissolved or the minerals containing rare earth elements should be recrystallized. This process is very expensive and inefficient. The mechanical and chemical activation methods can help to significantly enhance the efficiency of REE extraction from such anthropogenic objects.

Mechanical activation increases the degree of REE extraction from minerals in which rare earth elements form part of the crystal lattice, which creates more defects and larger specific surface area. Therefore, this process underlies the technology for the extraction of scandium from wet magnetic separation (WMS) tailings [13] and REEs from red muds [14]. Figure 1 illustrates the impact of mechanical activation on the rates of REE recovery from phosphogypsum. It also significantly increases the degree of amorphization of phosphogypsum (Fig. 2), which is accompanied by the accumulation of residual stresses of III type: periodicity in the atoms arrangement in the crystal is disturbed. Meanwhile, gypsum retains its crystalline structure.

The scientific community shows great interest in sorption leaching as a type of chemical activation. In such a process, REE recovery increases due to the shift of the reaction equilibrium towards the products as the ion exchanger absorbs them according to the reactions



where M is a metal cation; A is an anion; x and y are valences of the cation and anion, respectively; R_yY^y is ion exchange resin.

For example, the use of cation exchanger in a hydrogen form triggers two processes:

1) equilibrium shift due to sorption:



where RH is the ion exchange resin in a hydrogen form;

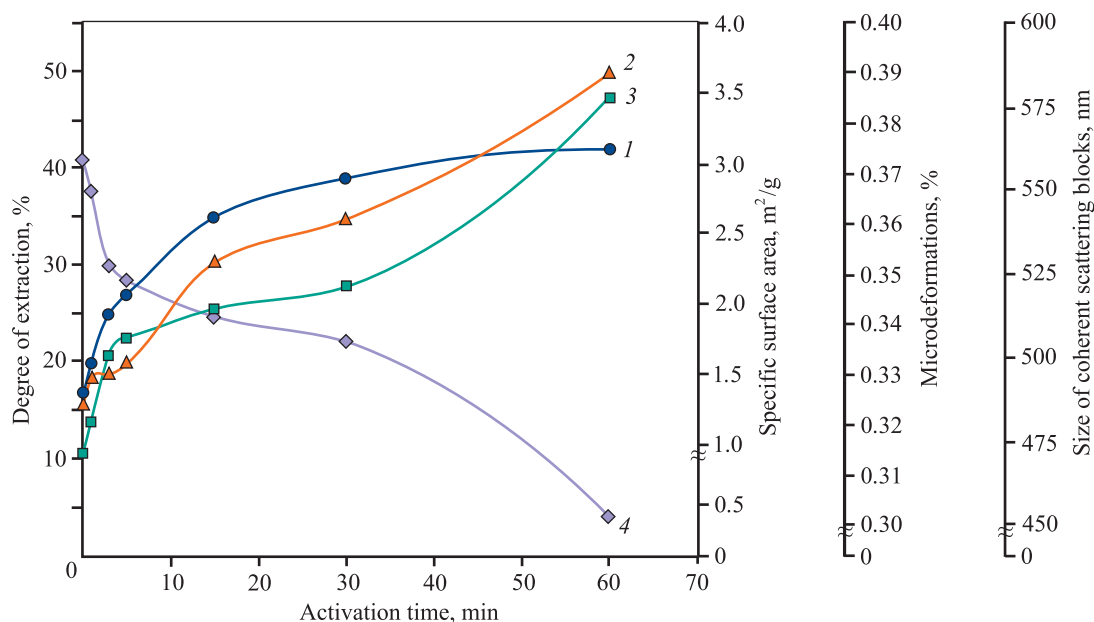


Fig. 1. Impact of mechanical activation on the degree of REE extraction from phosphogypsum with sul-furic acid with a concentration of 10 g/dm³ (1), as well as on the specific surface area (2), micro-deformations (3) and the size of coherent scattering blocks (4)

Рис. 1. Влияние механоактивации на степень извлечения РЗЭ из фосфогипса серной кислотой с концентрацией 10 г/дм³ (1), удельную поверхность (2), микродеформацию (3) и размер блоков когерентного рассеяния (4)

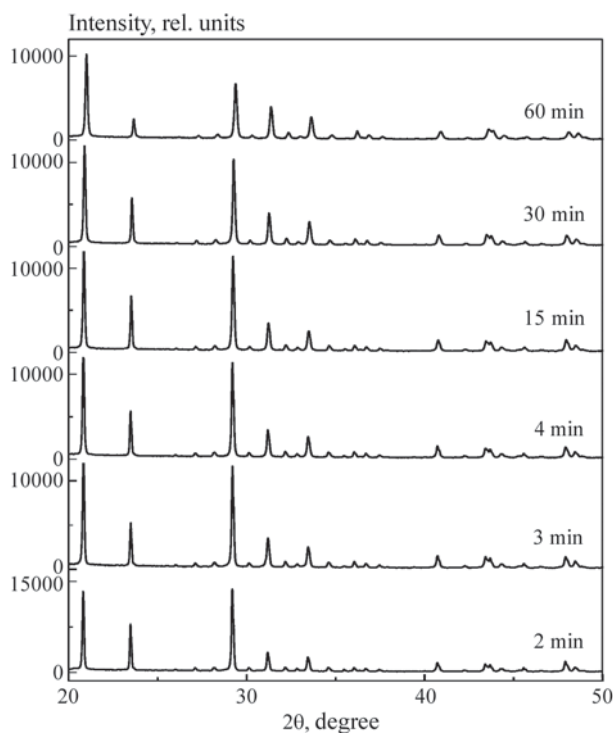


Fig. 2. Diffraction patterns of activated phosphogypsum at different times of mechanical activation

Рис. 2. Дифрактограммы активированного фосфогипса при различном времени механоактивации

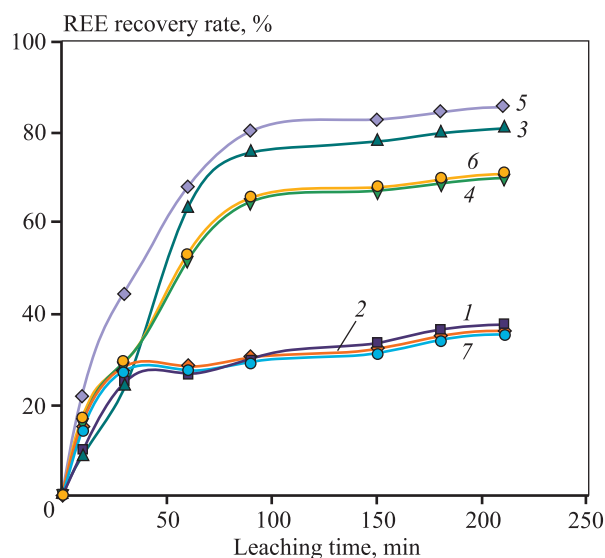


Fig. 3. Impact of chemical activation (sorption leaching) on the degree of REE extraction from phosphogypsum

1 – without an ion exchanger, 2 – S-150 Na⁺, 3 – SGC-650 Ca²⁺, 4 – SGC-650 H⁺, 5 – S-150 Ca²⁺, 6 – S-150 H⁺, 7 – SGC-650 Na⁺

Рис. 3. Влияние химической активации (сорбционное выщелачивание) на степень извлечения РЗЭ из фосфогипса

1 – без ионита, 2 – S-150 Na⁺, 3 – SGC-650 Ca²⁺, 4 – SGC-650 H⁺, 5 – S-150 Ca²⁺, 6 – S-150 H⁺, 7 – SGC-650 Na⁺

2) formation of an equivalent amount of acid involved in the leaching reaction:



The results confirming high efficiency of sorption leaching of REEs and Sc from red muds and phosphogypsum are presented in Fig. 3 and in research papers [14; 15]. Purolite C150 macroporous sulfocationite and Purolite SGC 650 gel sulfocationite were used in the studies. Figure 3 shows that the ion exchanger presence in the pulp, as well as its salt form, considerably affect the REE extraction from phosphogypsum.

Selective extraction of the target component and its subsequent concentration from solutions of complex composition is a challenging and important task to be considered when any technologies are developed. Solution of this task requires the use of ion-exchange materials of various compositions selective to any given element. As an example of such technology development, we present the data on sorption extraction of scandium from uranium in-situ leaching solutions of the following composition, mg/L:

Fe.....	1449	Mo	1.2
Na	1588	Y	5.3
Al	2218	Ti	2.3
Ca	444	Th	1.8
REM.....	33.4	U.....	0.5
Sc.....	0.81		

Fig. 4 features elution curves of scandium sorption from uranium ISL solutions on a number of commercial phosphorus-containing ion exchangers, the structure of which is presented in Table 1. The plotted dependences show that the sorption of scandium on S-957 cation exchanger is much more efficient than on the studied amphotolites.

When ions are sorbed from such complex objects as uranium *in situ* leaching solutions, it is important to understand the behavior of all the components, not only the main one (in our case, scandium). Figure 5 and Table 2 show the data on sorption and desorption of element ions present in uranium ISL solutions, on one of the sorbents used in the research — Tulsion CH-93.

Recently, solvent impregnated resins (SIR) that combine the extraction capacity of any given organic compound with the technique of applying sorption processes have been actively used for extracting elements from complex solutions. Solvent impregnated

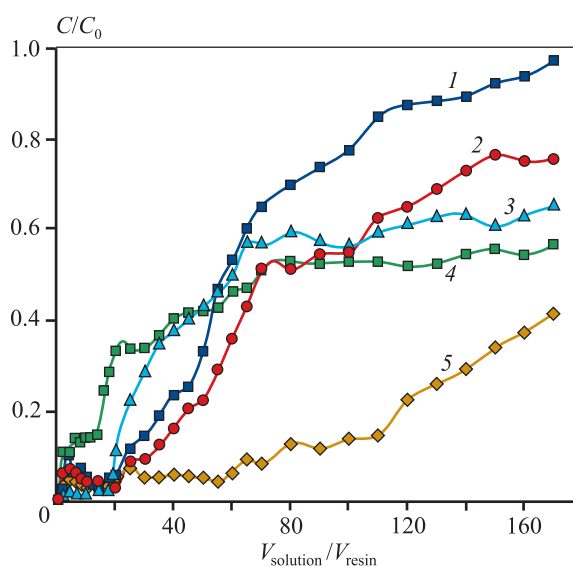


Fig. 4. Elution curves of scandium sorption from uranium ISL solutions on commercial ion exchangers

1 – TP-260, 2 – CH-93, 3 – S-950, 4 – ECO-10, 5 – S-957

C/C_0 – the ratio of the concentration at the column outlet to the initial concentration or sorbent saturation degree;

$V_{\text{solution}}/V_{\text{resin}}$ – the ratio of circulating solution volume to the sorbent volume or number of column specific volumes

Рис. 4. Выходные кривые сорбции скандия из раствора ПБУ на коммерческих ионитах

1 – TP-260, 2 – CH-93, 3 – S-950, 4 – ЭКО-10, 5 – S-957

C/C_0 – отношение концентрации на выходе из колонны к исходной, или степень насыщения сорбента;

$V_{\text{р-ра}}/V_{\text{смоли}}$ – отношение пропущенного объема раствора к объему сорбента, или количество удельных объемов колонны

resin — chelating sorbents — are most promising solvents for extracting scandium from solutions of various electrolytes [16].

Table 3 presents the sorption characteristics of some commercially available SIR obtained during the extraction of scandium from sulfuric uranium in-situ leaching solutions. According to the obtained data, Lewatit VP OC-1026, a solid extractant based on Di(2-ethylhexyl) phosphoric acid (DEHPA), has the highest capacity.

Fig. 6 shows the data on the behavior of scandium and ions of other elements in the solution and below are the values of the total exchange capacity (TEC), mg/g:

Sc.....	3.94	Ti	2.3
Na	0.6	Fe.....	17.4
Al	0.7	Th	0.05
Ca	0.22	U.....	0.3

We see that scandium is effectively sorbed when this SIR, VP OC-1026 grade, is used, and as the solution

Table 1. Characteristics of ion exchangers used in the research

Таблица 1. Характеристика использованных в работе ионитов

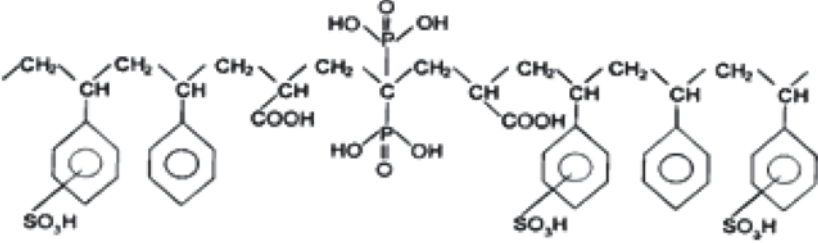
Ion exchanger grade	Functional group	Capacity, mg-eq/L
Purolite S-950	$\cdots - \text{CH} - \text{CH}_2 - \text{CH} - \text{CH}_2 - \cdots$	2.3
Lewatit TP-260		2
Tulsion CH-93	$\cdots - \text{CH} - \text{CH}_2 - \cdots$	1.9
ECO-10	$\text{NH} - \text{CH}_2 - \text{PO}(\text{OH})_2$	—
Purolite S-957		3.1

Table 2. Total dynamic exchange capacity (TDEC) of the Tulsion CH-93 ion exchanger by elements and the degree of their desorption by Na_2CO_3 solution (180 g/dm^3) in the dynamic mode

Таблица 2. Полная динамическая обменная емкость (ПДОО) ионита Tulsion CH-93 по элементам и степень их десорбции раствором Na_2CO_3 (180 г/дм^3) в динамическом режиме

Indicator	Sc	Al	Fe	Ti	Th	U
TDEC, mg/g of the ion exchanger	0.3	7.4	3.2	1.4	0.6	0.4
Desorption degree, %	94.15	21.25	28.1	18.7	98.85	64.1

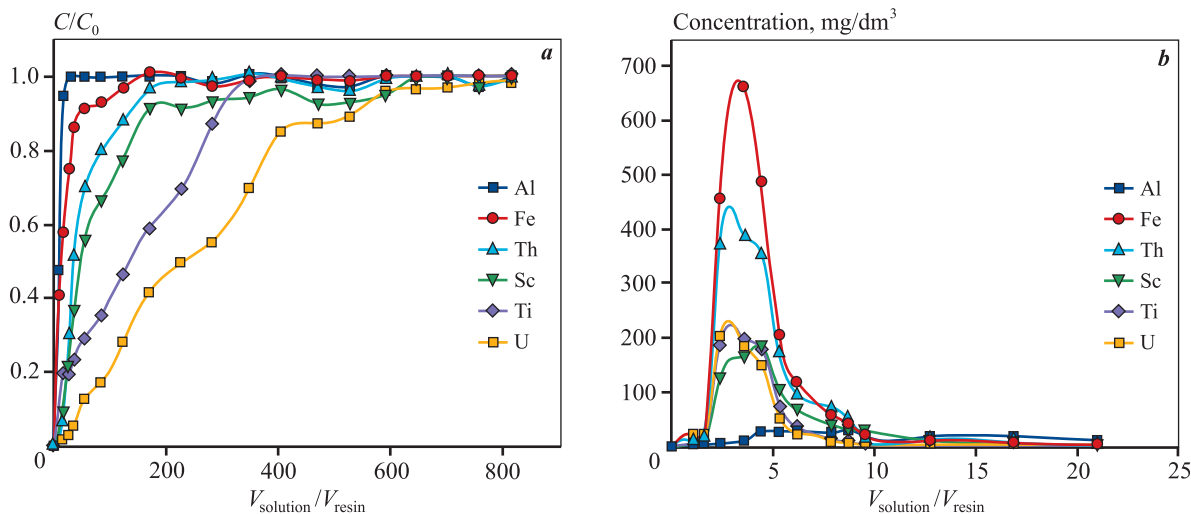


Fig. 5. Elution curves of sorption from uranium ISL solutions on Tulsion CH-93 ampholyte (a) and de-sorption of elements from the phase of the ion exchanger saturated with Na_2CO_3 solution with the concentration of 180 g/dm^3 (b)

Рис. 5. Выходные кривые сорбции из растворов ПВУ амфолитом Tulsion CH-93 (a) и десорбции элементов из фазы насыщенного ионита раствором Na_2CO_3 с концентрацией 180 г/дм^3 (b)

Table 3. Static exchange capacity of solid extractants for scandium during its sorption from the uranium ISL solution

Таблица 3. Статическая обменная емкость ТВЭКС по скандию при его сорбции из раствора ПВУ

SIR	Active ingredient (extractant)	Capacity, mg _{Sc} /g
TP-923	Mixture of trialkylphosphine oxides	2.94
VP OC-1026	DEHPA	4.05
TP-272	Bis(2,4,4-trimethylpentyl) phosphinic acid	2.44
TR-TBF	Tributyl phosphate	2.22

passes through the sorbent for a long time, thorium is displaced. In addition to scandium, iron is well sorbed, and so is titanium in appreciable amounts.

Despite all its good properties, VP OC-1026 sorbent has disadvantages as well. The main reasons are its small granule size and unsatisfactory scandium sorption kinetics. Therefore, a new SIR was synthesized for selective extraction of scandium from uranium ISL solutions. Its active functional component was composed of DEHPA, tributyl phosphate (TBP) and trioctylphosphine oxide (TOPO) [17]. Axion solid extractant was synthesized using reagents of the following composition, wt.%:

DEHPA.....	8.74—9.93
Tri-n-octylphosphinoxide	1.10—2.18
Tributyl phosphate.....	0.22—0.44
Benzoyl peroxide	0.22—0.25
Isododecane	4.41—5.46
0.7 % starch solution in water.....	72.48—73.26
Styrene.....	8.03—8.48
Divinylbenzene	2.12—2.68

Figure 7 shows the results of sorption of REE from the uranium ISL solution by Axion solid extractant and Fig. 8 presents the comparative data on scandium extraction the uranium ISL solutions by the commercial solid extractant, VP OC-1026 grade, and synthesized extractants following the given technique. The sorption rate and dynamic exchange capacity of these solid extractants increase, as they are affected by the conditions of the synthesis, during which open macropores are formed due to the use of isododecane or kerosene, which are characterized by delamination properties for the monomer-polymer mixture. The polymerization results in emergence of a certain intrapore space, and tri-n-octylphosphinoxide and tributyl phosphate serve as intermediates

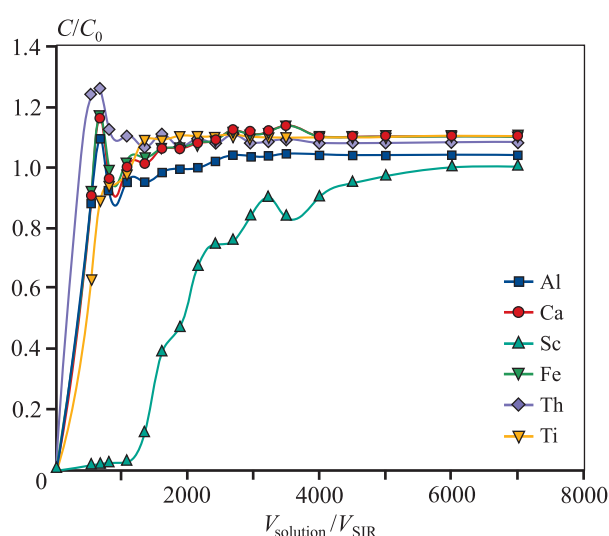


Fig. 6. Elution curves of sorption of element ions by the SIR, VP OC-1026 grade, from uranium ISL solutions

Рис. 6. Выходные кривые сорбции ионов элементов на ТВЭКС марки VP OC-1026 из растворов ПВУ

that increase the DEHPA and scandium interaction rate.

Scandium extraction using Axion solid extractants proceeds by the following reaction:

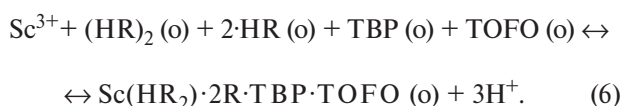


Figure 9 shows that in the IR spectrum of Axion-22 solid extractants in the Sc^{3+} form, the band in the region $\nu = 1232 \text{ cm}^{-1}$, responsible for valence and strain vibrations of P=O groups, is narrowed, and absorption bands, about $\nu = 1200 \text{ cm}^{-1}$ [18], related to stretching vibrations of the P=O $\rightarrow$ Sc group, emerge. Such changes in the spectra suggest the formation of strong coordination bonds between scandium ions and functional groups of the SIR. In the region $\nu = 1150 \text{ cm}^{-1}$, the intensity of P—O—(H) valence vibrations subsides,

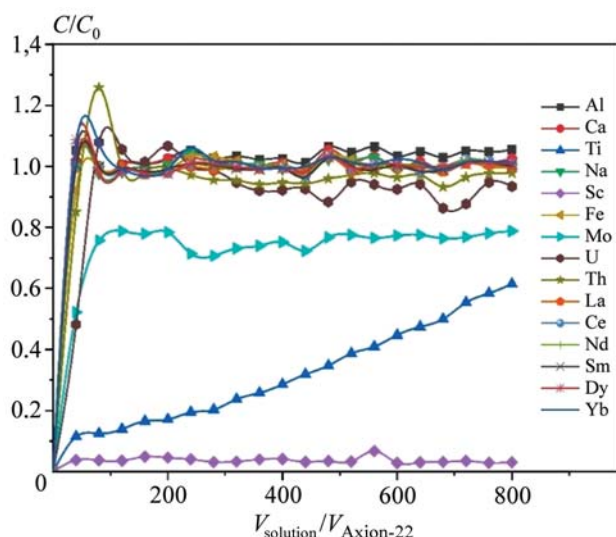


Fig. 7. Elution curves of Sc and related elements sorption from the uranium ISL solutions by Axion-22 solid extractants

Рис. 7. Выходные кривые сорбции Sc и сопутствующих элементов из растворов ПВУ на ТВЭКС Axion-22

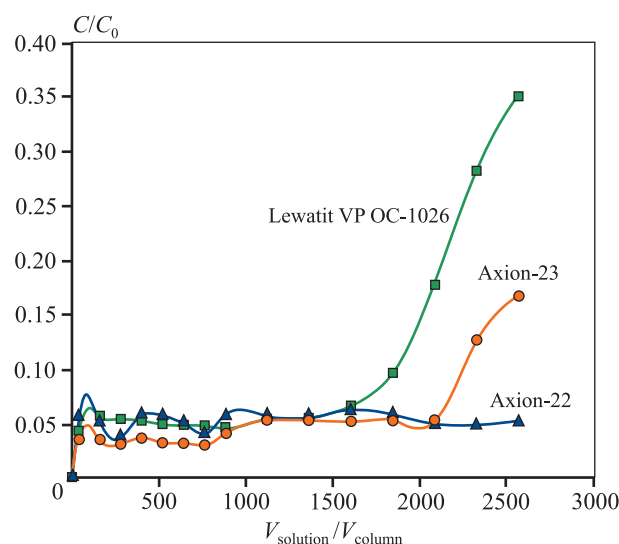


Fig. 8. Elution curves of scandium sorption from the uranium ISL solutions by Lewatit VP OC-1026, Axion-22 and Axion-23 SIR

Рис. 8. Выходные кривые сорбции скандия из растворов ПВУ на ТВЭКС Lewatit VP OC-1026, Axion-22 и Axion-23

indicating that cation-exchange groupings are involved in the sorption reaction. [19].

To determine the number of DEHPA molecules involved in the exchange reaction, the graph was plotted in logarithmic coordinates showing the experimental dependence of the scandium distribution coefficient on the DEHPA concentration (Fig. 10). The value of the slope angle of this linear dependence indicates the

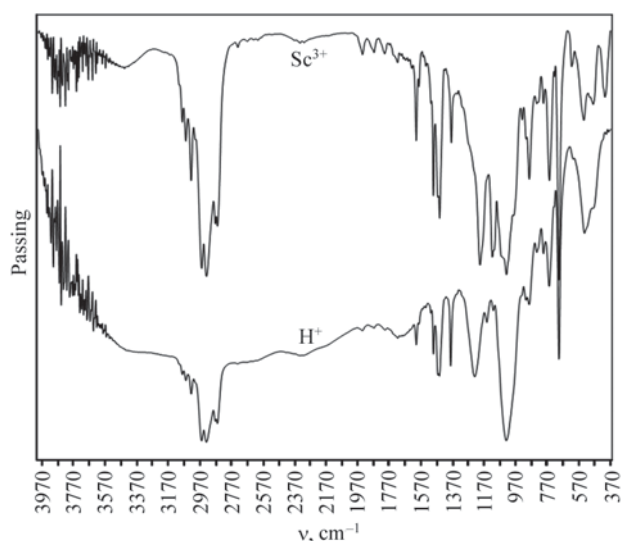


Fig. 9. IR-spectra of Axion-22 in H⁺ and Sc³⁺ form

Рис. 9. ИК-спектры ТВЭКС Axion-22 в H⁺-форме и Sc³⁺-форме

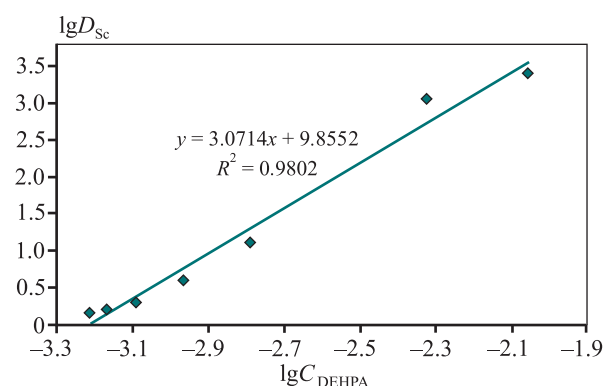


Fig. 10. Dependence of $\lg D_{\text{Sc}}$ on DEHPA concentration during scandium sorption with the use of Axion-22 solid extractants

Рис. 10. Зависимость $\lg D_{\text{Sc}}$ от концентрации ДЭГФК при сорбции скандия с использованием ТВЭКС Axion-22

number of DEHPA molecules. The activity coefficients for the compounds involved in the extraction were assumed to be constant [20]. The evidence presented suggests that when scandium is extracted from sulfuric acid aqueous solutions by Axion-22 SIR, the slope angle is equal to 3.

The analysis of the IR spectrum and the dependence $\lg D_{\text{Sc}} = f(\lg C_{\text{DEHPA}})$ (see Fig. 9 and 10) gives grounds to conclude that the selectivity of scandium extraction is achieved through donor-acceptor bonds with the complex compound being formed in the solid extractant phase (Fig. 11).

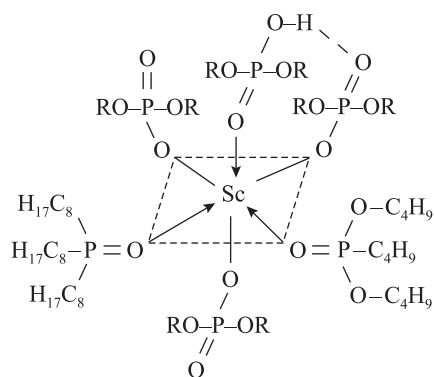


Fig. 11. Coordination scheme for the sorption of scandium ions by Axion-22 solid extractant

Рис. 11. Координационная схема сорбции ионов скандия на ТВЭКС Axion-22

Along with scandium, uranium ISL solutions contain a significant amount of rare earth elements, the total content of which is comparable to the concentration of the main element to be extracted — uranium. The composition of the uranium ISL solutions used in the cited studies was as follows, mg/dm³:

La.....	3.6	Tm	0.06
Ce	8.1	Yb	0.55
Pr.....	1.61	Lu	0.07
Nd.....	7.0	Y	5.65
Sm.....	1.55	Sc.....	0.75
Eu	0.38	Th	15.5
Gd.....	1.15	Fe.....	1150
Tb	0.29	Al.....	1453
Dy.....	1.08	Ca	425
Ho.....	0.31	Mg	370
Er.....	0.55	U.....	0.04

It should be noted that the content of the REE heavy group in the solution is abnormally high.

Ion exchangers of various classes and structures were used for the extraction and concentration of REE from the uranium ISL solutions: cation exchangers, aminocarboxylic and aminophosphoric acid ampholytes [21; 22]. This research analyzes the REE sorption from the uranium ISL solutions by cation exchangers. Fig. 12 shows the impact of solution acidity on the sorption of lanthanum (REE representative). Universal sulfocationite KU-2, carboxylic KM-2P, phosphoric acid KF-11 were used as cation exchangers (Table 4).

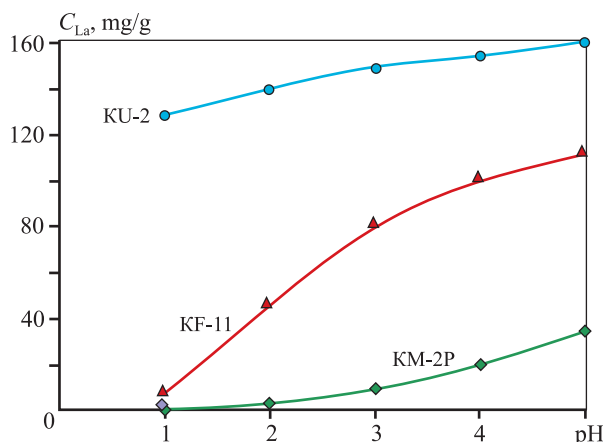


Fig. 12. Impact of the sulfate solution pH on the sorption of lanthanum (III) ions by cation exchangers

Рис. 12. Влияние величины pH сульфатного раствора на сорбируемость ионов лантана (III) катионитами

We selected cation exchanger KU-2 for further use although it is universal and is not characterized by high selectivity towards rare earth elements. We made this decision because uranium ISL solutions are acidic (pH = 1.0÷.5) and the REE sorption from them will be higher compared to other sorbents. Figure 13 shows the elution curves of element ions sorption from uranium ISL solutions after uranium is extracted from them. This information enables to draw the following conclusions:

- macroporous cation exchangers are characterized by a sufficiently high degree of selectivity towards rare earth metals;
- they are most selective towards light REEs;
- in the process of ion sorption in the dynamic mode, some cations, in particular calcium, are displaced from the cation exchanger by rare-earth metals.

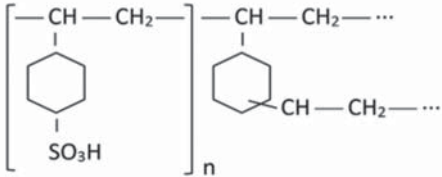
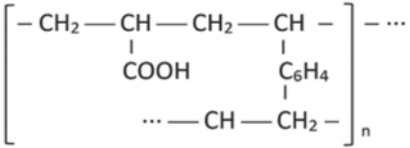
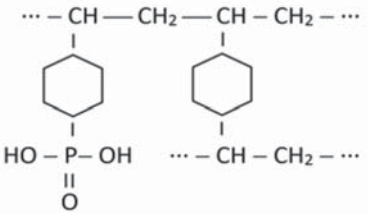
It should be noted that the selectivity of macroporous cation exchangers is correlated with the radii of hydrated ions, the average values of which are given below, Å:

Sc ³⁺	8.4	Al ³⁺	7.6
K ⁺	2.7	Fe ³⁺	9.1
Na ⁺	3.2	Y ³⁺	4.8
Ca ²⁺	3.8	La ³⁺	4.6
Mg ²⁺	4.2		

consequently, it correlates with the dehydration energy of these ions as well. It can be argued that the ion selectivity is significantly affected by the sieve effect.

Table 4. Comparative characteristics of used cation exchangers

Таблица 4. Сравнительная характеристика использованных катионитов

Cation exchanger	Functional group	SEC, mg-eq/cm ³
KU-2		2.0
KM-2P		3.5
KF-11		3.6

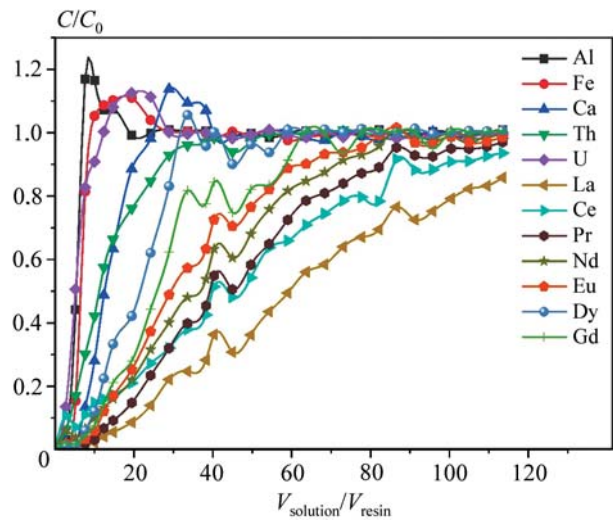


Fig. 13. Elution curves of ion sorption from uranium ISL solutions by macroporous cation exchanger Purolite C-100

Рис. 13. Выходные кривые сорбции ионов из растворов ПВУ макропористым катионитом Purolite C-100

REE concentration and decontamination can be implemented at the desorption stage. The hydrochloric and nitric acid solutions of alkali and alkaline earth metals are often used for desorption of rare earth metals from strongly acidic cation exchangers. Figure 14 shows dependences of REE desorption from sulfo-

cationite on the concentration of ammonium, calcium and sodium salts. It can be observed that calcium chloride and ammonium nitrate solutions are the best eluents for REEs.

When SIR are used for extracting scandium from uranium ISL solutions, the process selectivity is attributed to the formation of high-strength coordination compounds. It complicates the desorption of scandium from these sorbents by many mineral acids and their salts. The complex compound can be destroyed by forming stronger ones. Alkali metal carbonates or hydrofluoric acid can be chosen as such eluents. The use of carbonate solutions leads to the extractant stripping from the resin phase, which ultimately causes a significant decrease in the amount of scandium that can be extracted. Therefore, the results of scandium desorption from Axion SIR by hydrofluoric acid solutions are presented below. Figure 15 shows that HF solutions are effective eluents for scandium during its desorption from the SIR.

At the stage of REE precipitation from solutions, they can be separated from a number of impurities, not only transferred from the solution to the precipitate with subsequent concentration. This can be clearly seen in Fig. 16, which features the curves showing hydrolysis of REEs and impurities in the solution. Table 5 presents the composition of the objects obtained during fractional hydrolysis.

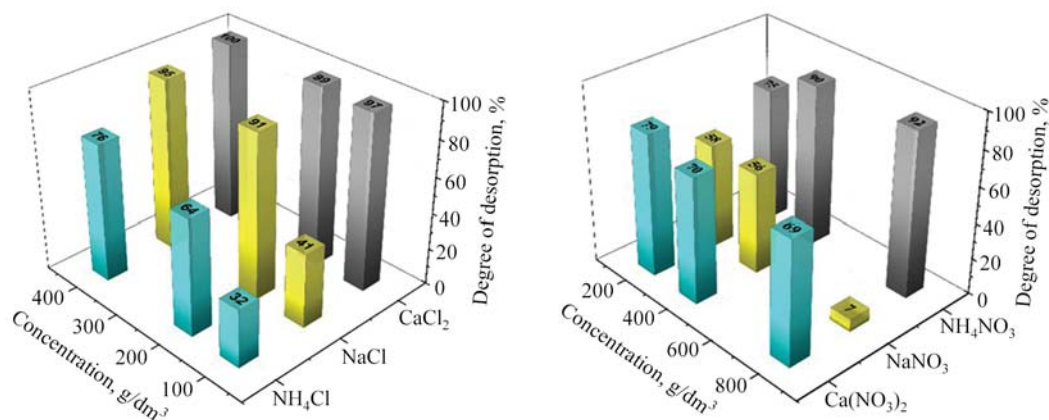


Fig. 14. Dependence of the degree of REE desorption from the cation exchanger phase by solutions of different desorbates

Рис. 14. Зависимость степени десорбции РЗЭ из фазы катионита растворами различных десорбатов

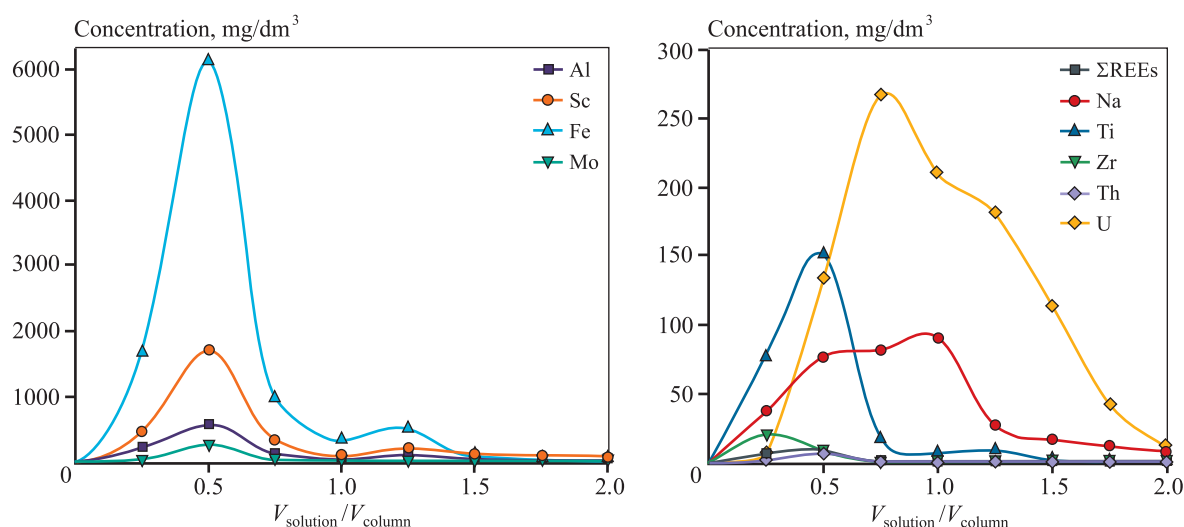


Fig. 15. Elution curves of desorption from saturated Axion-22 SIR by the HF solution with the concentration of 150 g/dm³

Рис. 15. Выходные кривые десорбции из насыщенного ТВЭКС Axion-22 раствором HF с концентрацией 150 г/дм³

The final stage of the REE extraction from anthropogenic wastes is secondary cleaning from impurities to obtain a high-purity product. As a rule, liquid extraction is used for this purpose.

At JSC Dalur JSC (Kurgan Region, Russia), the research team of the Ural Federal University developed and implemented the technique for producing scandium oxide of a purity exceeding 99.9 %. It includes the following operations:

- scandium extraction by SIR from recovered solutions of uranium in-situ leaching solutions;
- solid-phase re-extraction using fluoride-containing solutions;
- conversion of scandium fluoride to hydroxide;

- dissolution of the obtained scandium hydroxide in nitric acid;
- scandium oxalate precipitation;
- calcination to obtain scandium oxide.

Currently, the use of impregnates for the separation of collective REE concentrate into individual compounds seems to be a promising option [23]. The modern technologies usually use liquid extraction for this purpose. Figure 17 gives an example of some rare earth elements separation from the saturated impregnate at the elution stage. Control points, including peaks of the separated elements, were analyzed by mass spectrometry. The impregnates used contained phosphorylpodand XXa and DEHPA as active organic matter.

Table 5. Composition of concentrates and semi-products of REE concentrate secondary cleaning

Таблица 5. Состав концентратов и полупродуктов перечистки концентрата РЗЭ

Element	Precipitation mother solution, mg/dm ³		Concentrate, %	
	Fe–Al	REEs	Fe–Al	REEs
Al	34	7.8	31.1	0.13
Ca	545.7	520.1	6.2	0.7
Fe	3.41	2.8	1.6	0.03
Th	0.02	0.003	0.09	0.002
U	0.05	0.002	0.04	0.003
Σ REEs	695	3.1	2.3	51.9

Figure 17 shows quantitative separation of lanthanum, neodymium and samarium by the impregnate containing 33 % phosphorylpodand. However, the impregnate containing DEHPA only proved ineffective for REE separation.

The use of ionic liquids as extractants for REE extraction is a scientific challenge of great importance [24; 25]. Thus, when bis[(trifluoromethyl)sulfonyl]imide 1-butyl-3-methylimidazolium (C₄mimTf₂N) ionic liquid is added to 2-phosphoryl-phenoacetic acid amide (compound I), the REE recovery rate surges dramatically (Fig. 18).

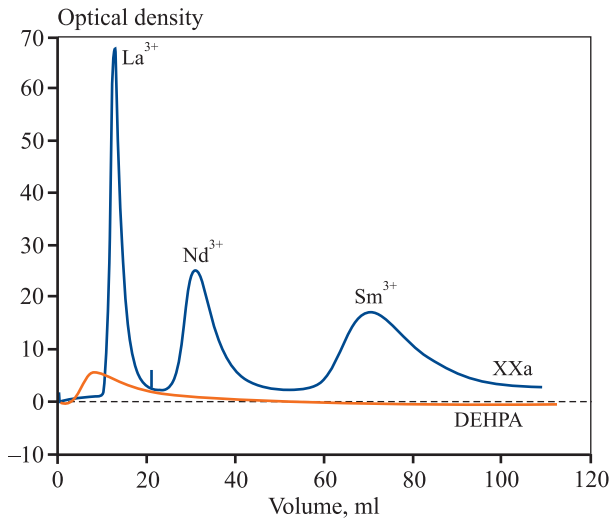


Fig. 17. Separation of La³⁺, Nd³⁺ and Sm³⁺ at elution with 0.08 M HNO₃ by impregnates containing 33 % DEHPA and 33 % phosphorylpodand (XXa)

Sorbent carrier is LPS-500

Рис. 17. Разделение La³⁺, Nd³⁺ и Sm³⁺ при элюировании 0,08 М ННО₃ на импрегнатах, содержащих 33 % ДЭГФК и 33 % фосфорилподанда (XXa)

Сорбент носитель – LPS-500

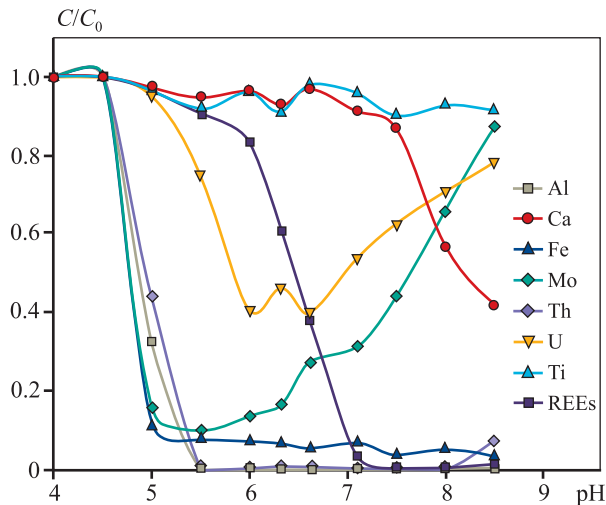
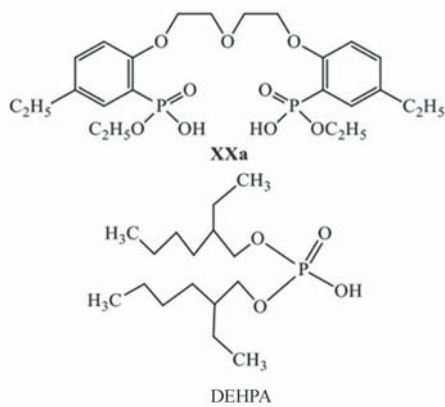


Fig. 16. Co-hydrolysis of ions of REE eluate elements

Рис. 16. Совместный гидролиз ионов элементов элюата РЗЭ

Figure 19 gives an example of one of the developed technological schemes for REE extraction from phosphogypsum. The obtained concentrate has the following composition, %:

Σ LREE.....	49	Sr	0.03
Σ HREE.....	2.5	Na	0.15
Ca	0.9	K.....	0.16
Fe.....	0.8	Th	0.004
Al.....	0.1		



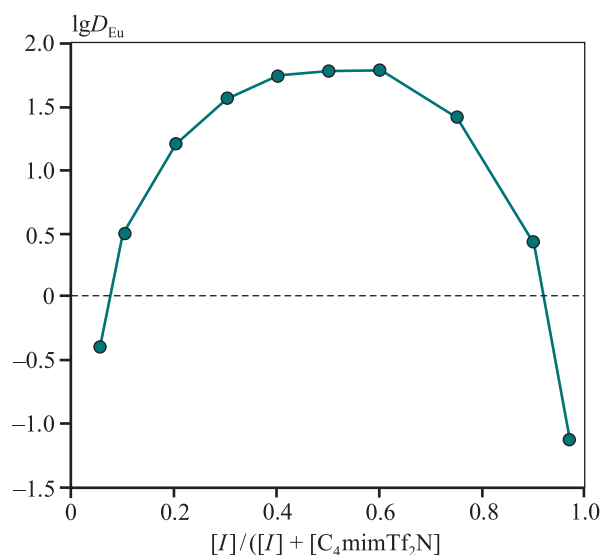


Fig. 18. Extraction of Eu^{3+} from 0.1 M HNO_3 solutions with isomolar mixtures of compound *I* and C_4mimTf_2N in dichloroethane depending on their initial molar ratio in the organic phase

$[I] + [C_4mimTf_2N] = 0.1$ M

Рис. 18. Экстракция Eu^{3+} из 0,1 М растворов HNO_3 изомольными смесями соединения *I* и C_4mimTf_2N в дихлорэтано в зависимости от их исходного мольного соотношения в органической фазе

$[I] + [C_4mimTf_2N] = 0,1$ М

The presented data conclusively prove that in addition to obtaining REE-rich concentrate, the developed method enables to solve the issues related to complex processing of phosphogypsum.

Conclusion

The experimental and estimated data on the extraction of rare-earth metals from phosphogypsum and uranium in-situ leaching solutions, both of which are production wastes (technogenic deposits), presented in this paper prove that these objects can serve as potential sources of REEs.

The technologies for extracting rare earth elements using modern sorption extraction materials and ionic liquids developed and tested at the enterprises demonstrate that the prospects of their practical application are quite encouraging.

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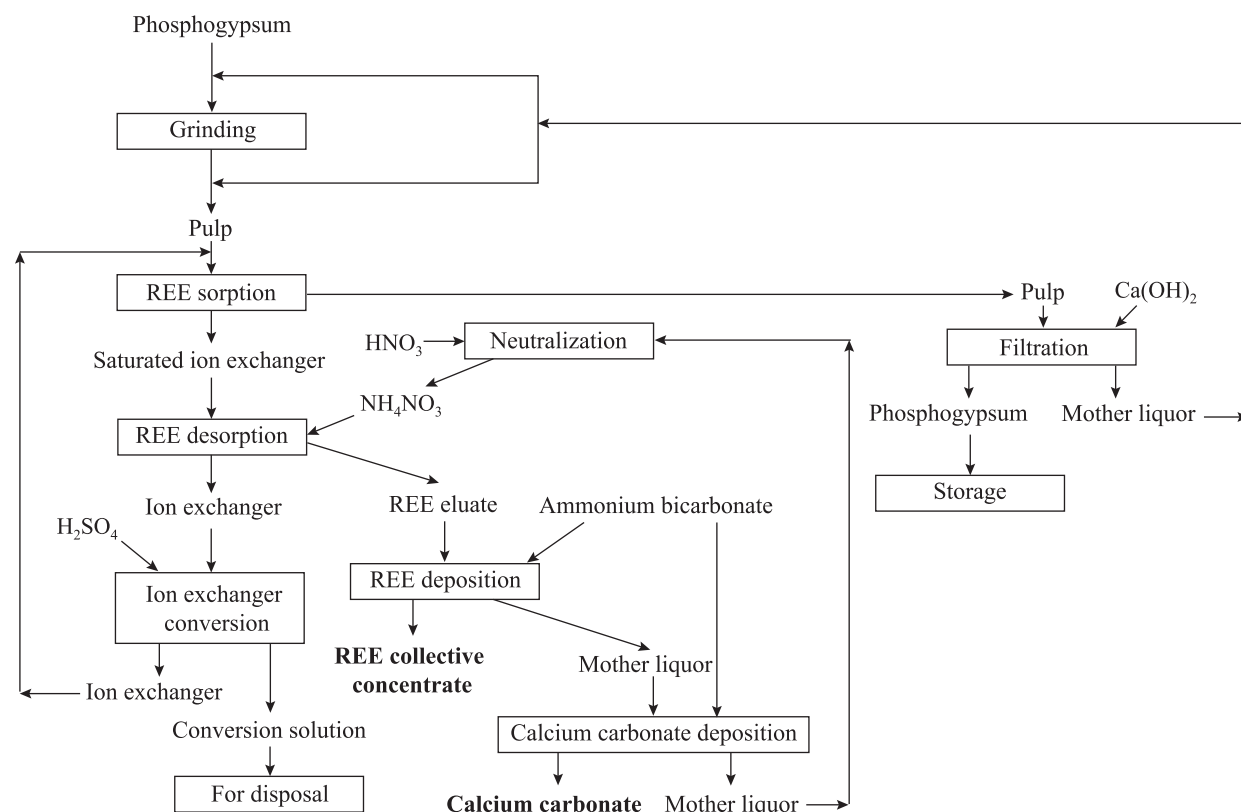


Fig. 19. Technological scheme for extracting rare earth elements from phosphogypsum

Рис. 19. Технологическая схема извлечения РЗЭ из фосфогипса

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