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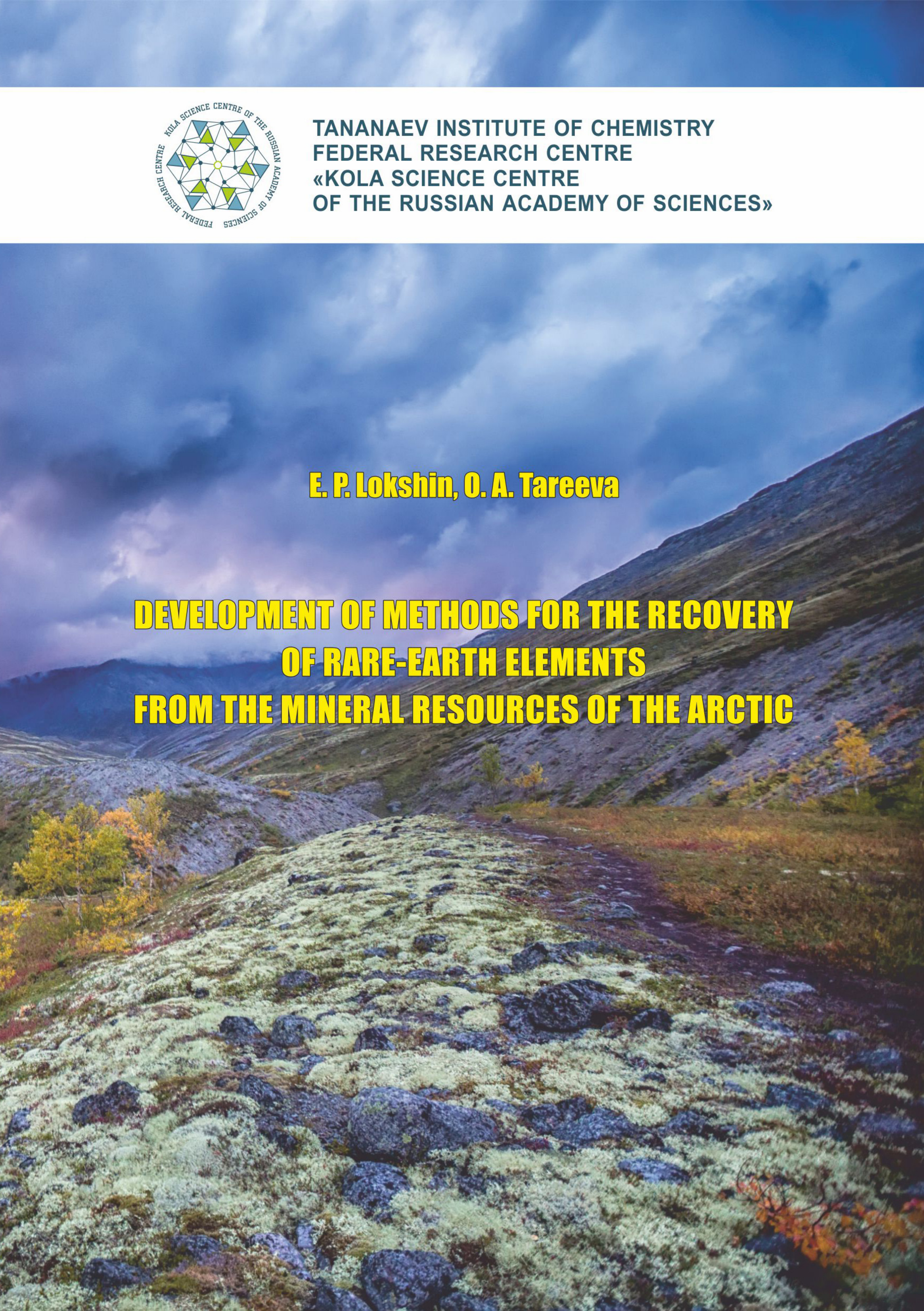

E. P. Lokshin, O. A. Tareeva

DEVELOPMENT OF METHODS FOR THE RECOVERY OF RARE-EARTH ELEMENTS FROM THE MINERAL RESOURCES OF THE ARCTIC

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This paper summarizes the findings of the research aimed at the development of a new method for the integrated processing of naturally occurring and anthropogenic rare-earth raw materials based on the decomposition of rare-earth element (REE) concentrates in the presence of sulfocationite. Sorption and desorption of REE cations on a strongly acidic ion exchanger, sorbent regeneration, and REE recovery from eluates are discussed. A virtually zero-waste integrated process for apatite concentrate is proposed.

The generalization of the research findings is aimed at demonstrating the prospects and universality of the proposed resource-saving and environmentally safe approach to the processing of various types of naturally occurring and anthropogenic rare-earth mineral feeds.

The new methodology made it possible to develop a number of new hydrochemical processes united by a single approach, providing a qualitative increase in the processing performance of various types of rare-earth mineral feeds.

The theoretical foundations of a unified approach to the processing of a wide range of minerals can significantly accelerate and cheapen the implementation of specific process circuits, significantly reduce reagent consumption and waste generation, simplify the separation of rare earth elements and impurities, and the separation of rare earth elements from naturally occurring radionuclides, fluorine, and phosphorus.

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TABLE OF CONTENTS

INTRODUCTION

Currently used methods of hydrochemical processing of naturally occurring and anthropogenic raw materials are usually resource- and energy-intensive and generate significant amounts of waste. Their efficiency can be significantly improved by applying the new approach presently under develop-ment — the sorption conversion method. The key distinctive features of the approach are presented in [1]. It is based on the decomposition of the mineral feed in a slightly acidic solution in the presence of sulfoxide cation exchanger.

The cations passing into the solution are absorbed by the cation exchanger as described by the reaction:

$$n(\text{-SO}_3\text{H}) + \text{Me}^{n+} \rightarrow (\text{-SO}_3)_n\text{Me} + n\text{H}^+, \quad (1)$$

while the anionic fraction of the feed accumulates in the solution.

When processing mineral feeds, which are salts of weak acids (phosphates, fluorides, carbonates, fluorocarbonates, etc.), acidic residues passing into the solution have little effect on the acidity of the reaction solution and therefore have no significant effect on the performance of cation sorption by sulfocationite. This allows the decomposition of the feed to continue until the sorbent is saturated with cations.

Although it is usually recommended to use concentrated solutions of strong mineral acids for desorption from sulfocationites, elements from a saturated sorbent can be effectively desorbed with solutions of ammonium [2] or sodium salts [3]. To recover desorbed cations from eluates, extraction recovery [4] and hydrolytic precipitation methods have been proposed. It is possible to develop equip-ment that eliminates the movement of the sorbent and, as a result, its mechanical abrasion.

Technology has been developed that prevents the movement of the sorbent and, as a result, its mechanical abrasion.

In hydrolytic precipitation, stepwise neutralization allows, at certain pH values, to sequentially precipitate first the impurity cake containing thorium, a major share of iron, and a significant share of aluminum, then non-radioactive REE concentrate and, finally, alkaline earth carbonates [5, 6]. The re-sulting solution after pH adjustments is repeatedly used for desorption.

Using ammonium and sodium salts for desorption results in low acidity eluates. This explains the low consumption of neutralizing reagents.

In this paper, more effective solutions for the processing of solutions of complex composition are proposed, which ensure the high performance of REE recovery by hydrolytic deposition. The theo-retical feasibility is shown of applying the developed approach for the removal of phosphorus impuri-ties from iron concentrates using low concentration phosphoric acid solutions, the disposal of which is much simpler compared to conventional processes.

This paper presents the key findings obtained by studying the applications of the method to the processing of certain types of naturally occurring and anthropogenic rare-earth raw materials in the Arctic, in particular, ancylite, bastnaesite, and monazite concentrates, as well as phosphate and fluoro-phosphate anthropogenic concentrates that can be obtained by processing apatite concentrate.

The presented findings support the good prospects of the sorption conversion method, which can be used as a foundation of resource-saving, minimum waste green chemical technology not only for rare-earth minerals, but also many other mineral feeds.

1. MATERIALS AND METHODS

Gel sulfo cation exchanger KU-2-8 (GOST 20298-74, Russia); macroporous sulfo cation ex-changer Purolite C-150 in H^+-form and reactive grade acids were used in this study. In a number of experiments, the sorbent was used in ammonium, sodium, or potassium form. The compositions of the concentrates used in the experiments are given in the corresponding sections of this paper.

The metal content of the process feeds and resulting products was analyzed by inductively coupled plasma mass spectrometry (ELAN 9000 DRC-e mass spectrometer by Perkin Elmer, USA). The concentration of phosphorus in the products was measured by spectrophotometry, of fluorine by potentiometry. Specific effective radioactivity was calculated by the equation:

$$A_{eff} = A_{Ra} + 1.3A_{Th} + 0.09A_{K},$$

where: A_{Ra} and A_{Th} are the specific radioactivity values of ^{226}Ra and ^{232}Th in radioactive equilibrium with other members of the series ^{238}U and ^{232}Th, respectively; A_K is the specific radioactivity of potas-sium — 40.

Figure 1. Lab-scale plant for scaled-up REE sorption conversion experiments.

An acid solution, a sample of the process feed, and a predetermined amount of sorbent were placed into a reaction vessel made of fluoroplastic. The reaction mixture was heated while stirring to a predetermined temperature and held for a predetermined time. The sorbent was separated from the pulp on a mesh filter. The pulp was separated by filtration into the undecomposed mineral fraction and the mother liquor. The content of components in the undecomposed mineral fraction and the mother liquor was measured. The amount of metals absorbed by the sorbent was calculated by the difference between the content thereof in the initial sample and the total content in the undecomposed mineral fraction and the mother liquor.

In the enlarged experiments the installation shown in fig. 1 was used. The plant consisted of a sorption column 1, reactor 2 with an overhead stirrer, intermediate vessel 3, metering pump 4, and thermostat 5.

The decomposition solution is poured into the intermediate vessel 3, the metering pump 4 is turned on, and the solution is pumped into the sorption column 1 and reactor 2. After filling the sorption column 1 and reactor 2, the concentrate to be decomposed is loaded into the latter, the reactor stirrer is switched on (and, if necessary, the thermostat), and the decomposition process is maintained for a predetermined time. The metering pump 4 maintains the set consumption of the acid solution, while the thermostat 5 maintains the set temperature of the solution.

The stirrer's speed is chosen so as to prevent strong agitation and entrainment of the decomposed product in the intermediate vessel 3. However, if the solid phase nevertheless is entrained in the solution exiting the reactor 2, it precipitates in the intermediate vessel 3 without getting the metering pump 4.

After complete decomposition of the concentrate, desorption is carried out and the sorbent is regenerated to its hydrogen form.

$K_{(s)}$ distribution coefficients during sorption were calculated using the equation:

$$K_{(s)} = \frac{m_{sorb} \cdot V_{sol}}{m_{sol} \cdot V_{sorb}}, \qquad (2)$$

where m_{sorb} and m_{sol} are weights of the components in the equilibrium sorbent and solution, V_{sol} is the volume of the solution, V_{sorb} is the volume of the sorbent.

The distribution coefficients during desorption were calculated according to the equation:

$$K_{(des).} = \frac{C \cdot V_{sorb}}{(100 - C) \cdot V_{sol}}, \qquad (3)$$

where C is the desorption of components (%).

Sorbent consumption (ß) was expressed as a percentage of the stoichiometric value necessary for the sorption of all metals in the concentrate sample in the form of Me^{n+} cations. Acid consumption (α) was expressed as a percentage of the stoichiometric value necessary for the formation by the metals contained in the concentrate sample of neutral salts.

2. STUDIES ON THE INTEGRATED PROCESSING OF APATITE CONCENTRATES BY SORPTION CONVERSION

Apatite is an important mineral resource containing rare earth elements (REE). Typically, the REE grade of apatite does not exceed 1 wt %, but in individual deposits it can be as high as ≥ 6 wt %. REE-containing apatite deposits are known in Russia, US, South Africa, Iran, Sweden, and other countries. In Russia alone, where about 3.8 million tons of apatite concentrate containing 1.05 wt % of REE oxides is processed, roughly 40,000 tons of REE oxides is recovered. Their content of yttrium, medium and heavy REEs is higher than in monazite or bastnaesite, which are considered the key mineral sources of REEs globally.

For the hydrochemical processing of apatite into mineral fertilizers, sulfuric acid and nitric acid processes are used. In the sulfuric acid process, the bulk of REEs passes into phosphogypsum, and a minor share into the extraction phosphoric acid. Upon evaporation of extraction phosphoric acid or ammonium phosphates synthesized on its basis, REEs precipitate as a calcium sulfate-based precipitate with various degrees of hydration.

Recovery of REE from phosphogypsum is discussed in [7]. This process is commercially viable if the purified gypsum product obtained after REE recovery is used. The experiments conducted show the possibility of simultaneous effective purification of the gypsum product obtained during the processing of the phosphogypsum of dihydrate and hemihydrate sulfuric acid processing of the Khibiny apatite concentrate. But the domestic demand for such minerals in Russia is still significantly lower than the amount of phosphogypsum produced in Russia.

REEs can be recovered from the extraction phosphoric acid of the dihydrate process by the sorption method [8–10] or precipitated as a fluorophosphate concentrate [11, 12]. The sorption method is poorly compatible with the existing mineral fertilizer technology. Fluorine-phosphate concentrate production process is significantly less intensive in terms of technology and time than the sorption method. Concentrates contain up to 7 wt % of the REE oxides sum ($\sum Tr_2O_3$). In these concentrates, compared to the initial apatite concentrate, $\sum Tr_2O_3$ is enriched in yttrium and lanthanides of medium and heavy groups. Such concentrates can be processed in a separate area, so this method is easier to combine with existing production. All this makes highly relevant the development of a process for the recovery of rare earth elements from such concentrates.

Known studies on the processing of the evaporation precipitates have not yet led to the development of a commercially viable process [13, 14].

Sulfuric acid process allows to obtain phosphoric acid and, as a result, a wide range of products based on it. But, despite its broad use, it has significant disadvantages. The decomposition of apatite in phosphate-sulfate solutions is carried out for a long time at elevated temperatures. This leads to high energy costs and complicates the purification of the resulting phosphoric acid from a number of impurities, such as titanium. In the sulfuric acid process, only phosphorus and partially fluorine in the apatite concentrate are currently used, since phosphogypsum together with REEs and strontium is almost completely dumped. This creates significant environmental challenges, and the sulfuric acid used to decompose the apatite concentrate is lost with phosphogypsum.

In nitric acid processing of apatite concentrate, REEs can in principle be concentrated by sorption from a nitric phosphate solution [15, 16]. However, this process, similarly to the recovery of REEs from extraction phosphoric acid, is poorly compatible with existing plants.

Therefore, although up to 40–45 % of REEs of medium and heavy groups is lost, REEs are recovered in the form of phosphate concentrate, which precipitates upon partial neutralization of the fluorine phosphate solution [17, 18]. The concentrate is dissolved in nitric acid. From the resulting solution, REEs are extracted with tributyl phosphate [19, 20]. Nitric phosphate solution containing thorium is recycled to a mineral fertilizer.

Nitric acid process allows apatite concentrate to be processed virtually waste-free into complex mineral fertilizers, phosphomel, REE, strontium, and fluorine compounds. However, it does not allow to produce phosphoric acid and some common products based on it, e.g. feed phosphates. The decomposition of apatite concentrate with nitric acid takes a long time at elevated temperature. The resulting hot nitric phosphate solutions for the precipitation of calcium nitrate are cooled to a negative temperature, and then reheated, which leads to an increased energy consumption. Although the recovery of cerium group REEs into the phosphate concentrate is quite high, the loss of medium and yttrium group REEs is significant.

Thus, the development of a more efficient processing method for apatite concentrate is of considerable practical relevance. It should provide for a high degree of use of all valuable components of the concentrate while reducing the consumption of energy resources and materials.

A number of studies are known on the hydrochemical processing of phosphate minerals based on the dissolution of phosphates in phosphoric acid with simultaneous sorption of calcium by cation exchanger.

It is proposed to recover phosphoric acid or its mixture with $Ca(H_2PO_4)_2$ from apatite ores through the interaction in an aqueous medium of the ore ground to a particle size of 1 mm with a sorbent in H^+-form. The interaction was carried out for 1 hour with stirring. At the recommended component ratio of the reaction mixture, acid with a concentration of 1.8 wt % was obtained. Using the obtained acid instead of water to decompose new apatite ore charges, the acid concentration was increased to 20 wt % after 26 cycles. To purify the acid from the calcium cation, it is proposed to additionally treat it with a H^+ or Na^+ sorbent in H^+- or Na^+- form. In the latter case, the product could be processed into sodium phosphates [21]. No methods for sorbent regeneration were reported. The behavior of REEs, radionuclides, and other impurities was not studied.

A similar solution was proposed in [22]. The main differences are the use of a phosphoric acid solution instead of water as early as in the first stage and interaction in countercurrent. The concentration of the resulting phosphoric acid was as high as 36 wt %. The sorbent was regenerated with a 4 M solution of HCl. The behavior of radionuclides and the disposal methods of the $CaCl_2$ solution formed during sorbent regeneration and HCl were not discussed.

It is proposed to produce phosphoric acid by dissolving the phosphate concentrate in phosphoric acid with a concentration of at least 50 wt % at a temperature above 95 °C to obtain a monocalcium phosphate solution, separate the undecomposed part of the concentrate, crystallize monocalcium phosphate by cooling the solution. Monocalcium phosphate isolated from the leaching liquid was dissolved in the presence of cation exchanger (H^+-form) in heated 40–50 wt % [23] or 10–14 wt % phosphoric acid [24]. The behavior of radionuclides and methods of sorbent regeneration were not discussed.

In the patents described above, the decomposition of phosphates was carried out without the use of mineral acids other than phosphoric, which in principle make possible the production of phosphoric acid that is not contaminated with sulfate, nitrate, or chloride ions. However, there is no information on the content of cationic impurities in the resulting phosphoric acid, the possibility of recovery of the REEs, strontium, and fluorine contained in the phosphate feedstock, the behavior of radionuclides and a number of other impurities that pass into solution upon the decomposition of the phosphate feedstock. Elevated temperatures were recommended for the process.

Sorbent regeneration is also rarely discussed. When using 4 M HCl [22] for regeneration, the disposal methods of the resulting hydrochloric acid solution with a high concentration of calcium were not considered.

A Khibiny apatite concentrate by Apatite-PhosAgro (to GOST 22275-90) (Table 1) and an experimental concentrate recovered by Lovozero GOK from loparite-apatite ore (Table 2) were used as phosphate mineral feedstocks. The choice of Lovozero apatite concentrate, whose potential production output is estimated at 10.000 tons annually, was based on its high REE and strontium grade. P_2O_5 content of the concentrates was 39.1 wt %, fluorine 3 wt %.

The concentrates differed not only in their REE and strontium grade, but also in the composition of accessory minerals and thorium grade.

Although a significant share of iron is present in the form of Fe^{2+} in the minerals contained in the concentrate, when estimating the gE value of the cations it was assumed that during processing iron will be oxidized to Fe^{3+}.

Table 1

Chemical composition of the Khibiny apatite concentrate

Content, wt %								
Na_2O	K_2O	MgO	CaO	SrO	Al_2O_3	TiO_2	Fe_2O_3	MnO
0.933	0.258	0.088	50.00	3.11	0.62	0.31	0.71	0.037
ThO_2	UO_2	Y_2O_3	La_2O_3	Ce_2O_3	Pr_2O_3	Nd_2O_3	Sm_2O_3	Eu_2O_3
0.003	0.00045	0.043	0.304	0.424	0.0458	0.158	0.0199	0.0058
Gd_2O_3	Tb_2O_3	Dy_2O_3	Ho_2O_3	Er_2O_3	Tm_2O_3	Yb_2O_3	Lu_2O_3	$\sum Tr_2O_3$
0.0227	0.0024	0.0097	0.001451	0.003	0.00031	0.00142	0.000165	1.042

Eq of cations in 1000 g of concentrate										
Na^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Al^{3+}	Ti^{4+}	Fe^{3+}	Mn^{2+}	$\sum Tr^{3+}$	Total
0.3	0.055	0.044	17.85	0.60	0.365	0.155	0.267	0.002	0.189	19.83

Table 2

Chemical composition of the Lovozero apatite concentrate

Content, wt %								
Na_2O	K_2O	MgO	CaO	SrO	Al_2O_3	TiO_2	Fe_2O_3	MnO
2.564	0.0384	0.0545	45.57	7.848	0.326	1.729	0.948	0.155
ThO_2	UO_2	Y_2O_3	La_2O_3	Ce_2O_3	Pr_2O_3	Nd_2O_3	Sm_2O_3	Eu_2O_3
0.025	0.00111	0.0862	1.396	3.657	0.345	1.268	0.148	0.0314
Gd_2O_3	Tb_2O_3	Dy_2O_3	Ho_2O_3	Er_2O_3	Tm_2O_3	Yb_2O_3	Lu_2O_3	$\sum Tr_2O_3$
0.137	0.0110	0.0394	0.00391	0.0086	0.00055	0.00340	0.000311	7.136

Eq of cations in 1000 g of concentrate										
Na^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Al^{3+}	Ti^{4+}	Fe^{3+}	Mn^{2+}	$\sum Tr^{3+}$	Total
0.83	0.08	0.27	16.28	1.52	0.19	0.86	0.36	0.04	1.40	21.83

The interaction was studied of apatite concentrate with phosphoric acid in the presence of sulfocationite, which usually follows the reaction:

$$Ca_5(PO_4)_3F + mH_3PO_4 \rightarrow 5Ca(H_2PO_4)_2 + (m-7)H_3PO_4 + HF. \tag{4}$$

Reaction (4) proceeds noticeably even at room temperature. The nepheline present in the concentrate also decomposes:

$$(Na,K)AlSiO4 + H_3PO_4 \rightarrow (Na,K)H_2PO_4 + Al(H_2PO_4)_3 + H_2SiO_3 + H_2O. \tag{5}$$

The resulting HF primarily interacts with silicic acid:

$$H_2SiO_3 + 6HF \rightarrow H_2SiF_6 + 3H_2O. \tag{6}$$

$$H_2SiF_6 + 2(Na,K)H_2PO_4 \rightarrow \downarrow(Na,K)_2SiF_6 + 2H_3PO_4. \quad (7)$$

The presence of isomorphic impurities and partial decomposition of other accessory minerals determine the entry of titanium, iron, manganese, a share of thorium and uranium into the solution.

We have studied the regularities of sorption conversion in phosphoric acid solutions using sulfocationites in H^+, NH_4^+, Na^+, and K^+- forms. It was taken into account that sorbents in NH_4^+, Na^+, and K^+- forms can be obtained when used in desorption processes of ammonium, sodium, and potassium salts.

2.1 Phosphoric acid decomposition of apatite concentrates using sulfocationite in H^+-form

An apatite concentrate charge and a predetermined amount of the gel sorbent KU-2-8 or macroporous sorbent Purolite 100 were placed in a H_3PO_4 solution (chemically pure grade, to GOST 6552-80) of a predetermined concentration $C_{H_3PO_4}$. The slurry was stirred for 4 hours at a set temperature. The sorbent consumption was 90–127 % of the theoretically necessary for the complete sorption of cations in the concentrate, under the assumption that Me^{n+} cations are sorbed. The ratio of the mass of the apatite concentrate to the volume of the phosphate solution in all experiments was 1:10.

After the reaction, the slurry was separated from the sorbent in a strainer, and the solid residue was removed from the slurry, if any. The experimental conditions are summarized in Table 3, and the results are shown in Tables 4–6.

Table 3

Experimental conditions

Experiment	Concentrate	Sorbent	$C_{H_3PO_4}$, wt %	ß, %	Temperature, °C	Solid residue mass, rel %
1	Khibiny	KU-2-8	5	127	20	Not found
2	Lovozero	KU-2-8	5	100	20	2.0
3	Lovozero	Purolite 150	5	117	20	3.0
4	Khibiny	KU-2-8	10	127	20	Not found
5	Khibiny	KU-2-8	38	90	20	0.67
6	Khibiny	KU-2-8	38	90	80	Not found
7	Khibiny	KU-2-8	38	127	20	< 0.3
8	Lovozero	KU-2-8	38	100	20	3.0

Table 4

Recovery of cations into the sorbent

Experiment	Recovery, %											
	Na	K	Mg	Ca	Sr	Al	Ti	Mn	Fe	Th	U	$\sum Tr$
1	93.6	95.5	97.7	99.5	99.7	69.6	83.1	N. a.	82.1	81.9	46.6	99.9
2	85.7	76.9	76.6	97.8	98.3	71.7	71.9	84.9	71.6	87.6	60.5	98.2
3	72.1	56.0	54.2	91.2	91.6	62.5	65.4	66.2	61.3	78.6	53.5	96.4
4	94.0	96.1	96.1	99.2	99.6	73.9	81.7	N. a.	78.8	72.7	38.5	99.6
5	78.3	80.8	83.4	91.0	95.3	43.4	80.8	88.3	75.0	37.3	49.1	89.1
6	76.5	66.6	58.8	82.5	N. a.	6.4	5.4	N. a.	38.7	14.3	30.0	72.5
7	85.6	86.9	81.8	94.8	97.5	54.6	83.6	N. a.	68.4	7.0	32	95.1
8	65.1	57.0	60.9	91.0	92.8	34.9	54.1	63.6	57.5	66.5	48.1	88.1

Table 5

Content of the main cationic impurities in the mother liquors

Experiment	Concentration, $mg \cdot l^{-1}$											
	Na_2O	K_2O	MgO	CaO	SrO	Al_2O_3	TiO_2	MnO	Fe_2O_3	ThO_2	UO_2	$\sum Tr_2O_3$
1	60	11.6	2.0	269	8.7	189	52.4	N. a.	128	0.54	0.24	0.82
2	226	5.0	3.0	725	42.8	80	128.5	1.3	61	2.8	0.25	9.2
3	453	8.2	2.3	3868	539	97	48.1	10.6	43	1.7	0.26	101
4	56	10.2	3.4	383	11.3	162	56.9	N. a.	151	0.82	0.28	4.5
5	238	58.4	17.2	5312	171.5	414	70.2	N. a.	210	2.22	0.27	133
6	220	86.2	36.3	8750	N. a.	580	294	N. a.	437	2.56	0.32	286
7	135	33.8	16.0	2608	79.2	281	51.1	N. a.	225	2.94	0.46	51.4
8	509	4.6	1.2	3619	460	177	156	14.2	80	4.38	0.22	666

Table 6

Recovery of individual REEs into the sorbent

Experiment	Recovery into the sorbent, %							
	Y	La	Ce	Pr	Nd	Sm	Eu	Gd
1	99.8	99.9	99.9	99.9	99.9	99.8	99.8	99.8
2	99.1	97.5	98.1	98.0	98.4	98.6	98.8	98.5
3	97.0	95.0	96.2	96.0	96.7	96.9	96.8	96.8
4	99.4	99.7	99.6	99.5	99.6	99.5	99.6	99.5
5	64.1	90.2	92.4	64.4	77.7	78.8	59.3	68.6
6	42.2	81.2	74.3	72.1	67.3	57.1	57.6	59.6

End of table 6

7	87.5	97.1	95.7	95.1	93.8	89.5	88.7	90.4
8	78.5	87.3	88.2	85.1	85.6	84.1	84.4	85.5
	Tb	Dy	Ho	Er	Tm	Yb	Lu	Tr
1	99.8	99.8	99.7	99.8	99.6	99.6	98.6	99.9
2	98.8	99.1	99.1	98.9	98.9	99.0	98.9	98.2
3	97.2	98.2	97.4	97.9	94.6	97.2	96.6	96.4
4	99.5	99.4	99.3	95.9	97.5	94.7	94.9	99.6
5	63.2	73.9	68.5	73.1	60.2	62.6	56.9	87.2
6	54.4	46.5	42.1	33.5	30.6	14.1	27.3	72.5
7	89.2	88.3	90.8	91.7	94.2	94.7	93.6	95.1
8	84.9	86.0	84.8	84.5	82.0	79.7	79.2	88.1

As can be seen from the experimental data, the quantitative decomposition of the apatite concentrate took place already at a temperature of 20 °C. The calculation shows that the concentration of phosphorus in the solution after decomposition of the apatite concentrate increased by 2.6–3.1 wt %. Fluorine completely passed in the phosphate solution. The substitution degree of the functional groups of the sorbent under the assumption that Me^{n+} cations are sorbed was 66.7–79.5 %.

The decrease in the concentration of H_3PO_4 in the initial solution to 5–10 wt % and the increase in sorbent consumption improved the decomposition performance of the apatite concentrate (Table 4).

Table 7

Content of components in the decomposition residues
of the Lovozero apatite concentrate

Experiment	Concentration, wt%											
	Na_2O	K_2O	MgO	CaO	SrO	Al_2O_3	TiO_2	MnO	Fe_2O_3	ThO_2	UO_2	$\sum Tr_2O_3$
2	7.0	0.19	0.49	14.1	4.36	0.63	17.8	1.11	10.4	0.014	0.010	6.36
3	7.6	0.26	0.74	4.5	3.96	0.74	18.3	1.39	10.8	0.12	0.008	5.89
8	7.8	0.24	0.55	9.3	2.56	0.54	19.4	1.27	9.8	0.11	0.010	6.88

High completeness of dissolution of apatite concentrate was achieved even with a sorbent consumption equal to 90 % of the stoichiometrically necessary (experiments 5 and 6). With an increase in sorbent consumption, the share of cations absorbed by the sorbent increased, while their concentration in phosphoric acid solutions decreased (Table 5).

A noticeable undecomposed residue was only observed during the processing of the Lovozero concentrate. Its composition is shown in Table 7. The increased calcium content in the residue in experiment 2 indicates that there was some undecomposed apatite in the residue. Compared to the initial concentrate, the residues are enriched in sodium, titanium, manganese, iron, thorium due to the accumulation of aegirine and loparite. The presence of loparite also determines a rather high REE content.

Alkaline, alkaline-earth, and rare-earth elements were well absorbed by the sorbent, and thorium and uranium at a lower concentration of phosphoric acid. Titanium, aluminum and iron were more difficult to absorb (Table 4). The iron sorption performance was much higher than previously reported [25]. When using 38 wt % phosphoric acid, sorption of thorium decreased.

In the phosphoric acid solutions resulting from the decomposition of apatite concentrates and containing up to 3 g·l–1 of fluorine, aluminum, iron, titanium, thorium, and uranium are present in the form of hydrophosphate or hydrophosphate-fluoride complexes [26–30].

It is argued that in phosphoric acid solutions, titanium is present in both cationic and anionic forms [28]. The ratio of ionic forms depends on the concentration of H_3PO_4 and temperature. Therefore, the titanium absorption performance by the sorbent varied widely under different decomposition conditions of the apatite concentrate. This, as well as the possible effect of the fluorine present in the solution, explains the difficulties observed in the sorption of the fluoro-acceptor iron and aluminum.

The decrease in sorbent consumption from 127 to 90 % of the stoichiometrically necessary (Table 4, experiments 5 and 7) slightly reduced the recovery of the cationic components of the concentrate into the sorbent. The degree of absorption of most of them, especially thorium (titanium was an exception), naturally increased with a decrease in the concentration of phosphoric acid.

At the same sorbent consumption (Table 5, experiments 5 and 6), an increase in the process temperature led to an increase in the residual concentration in the solution of alkaline, alkaline earth, rare earth, and radioactive elements, and to an even greater extent of aluminum, titanium, and iron. A sharp decrease in the sorption of titanium at 80 °C (experiment 6) suggests that at elevated temperatures in the 38 wt % H_3PO_4 solution pyrophosphoric acid is formed:

$$2H_3PO_4 \rightarrow H_4P_2O_7 + H_2O, \qquad (8)$$

with which titanium forms a virtually non-dissociating pyrophosphate $TiOH_2P_2O_7$.

At a reduced sorbent consumption, REEs of the yttrium group were harder to sorb than REEs of the cerium group (Table 6, experiments 5, 6). With an increase in sorbent consumption, the difference in the sorption performance of individual REEs decreased.

Table 8 shows the distribution of REEs between the products obtained in experiment 8.

Table 8

Distribution of REEs between the products obtained in experiment 8

Product	Yield to the product, rel%							
	Y	La	Ce	Pr	Nd	Sm	Eu	Gd
Concentrate	100	100	100	100	100	100	100	100
Solution	21.0	8.4	8.6	11.9	12.2	14.4	14.5	13.3
Residue	0.5	4.3	3.0	3.0	2.2	1.5	1.2	1.1
Sorbent	78.5	87.3	88.2	85.1	85.6	84.1	84.3	85.6
	Tb	Dy	Ho	Er	Tm	Yb	Lu	∑Tr
Concentrate	100	100	100	100	100	100	100	100
Solution	13.6	13.5	14.5	15.0	17.4	17.9	20.1	9.1
Residue	1.5	0.5	0.7	0.6	0.5	2.4	0.8	2.9
Sorbent	84.9	86.0	84.8	84.4	82.1	79.7	79.1	88.0

From the data in Table 8, it can be seen that the bulk of the REE loss during the sorption conversion of the Lovozero apatite concentrate was due to entrainment in the phosphate solution. Loss can be reduced by increasing the consumption of the sorbent (experiment 7) or by conducting a scavenger sorption.

A smaller share of the REE loss is associated with non-decomposable loparite, the REEs in which are enriched in cerium group lanthanides.

Judging by the content of thorium and uranium (the contribution of potassium was ignored), A_{eff} of the resulting solutions did not exceed 0.016 and of the sorbent 0.061 $KBq \cdot kg^{-1}$.

As can be seen from the data in Table 9, the content of cationic impurities can be further reduced by treating the resulting phosphate solutions with a fresh sorbent. Thereby many impurities are efficiently removed, but the recovery of titanium and iron is noticeably lower, because their anionic or electrically neutral complexes are quite stable. Since only a small fraction of the sorption exchange capacity (SEC) is filled during sorption post-treatment, it can be used to decompose the phosphate concentrate.

Thus, at room temperature, the apatite concentrate in the presence of H^+ sulfocationite is quantitatively decomposed with a phosphoric acid solution, and a solution is obtained with an increased concentration of phosphorus and a decreased concentration of cationic impurities compared to the extraction phosphoric acid, which does not contain sulfate ion. The concentration of cationic impurities can be reduced by additional sorption with sulfocationite.

Table 9

Sorption treatment of the phosphoric acid solution obtained in experiment 7 (treatment conditions: H^+ sorbent consumption 1.4 dm^3 per 1 dm^3 of the solution, 20 °C, 2 hours)

Solution	Content in phosphoric acid solution, $mg \cdot l^{-1}$										
	Na_2O	K_2O	MgO	CaO	SrO	Al_2O_3	$\sum Tr_2O_3$	TiO_2	Fe_2O_3	ThO_2	UO_2
Initial	135	33.8	16.0	2608	79.2	281	51.4	51.1	225	2.94	0.46
Final	23.6	0.64	0.8	17.4	0.69	33.2	0.38	37.4	145	1.42	0.36

At room temperature, HF and SiF4 vapor pressure above their solutions in phosphoric acid is negligible, therefore, fluorine compounds are not sublimated. Defluorination methods of phosphoric acid solutions for subsequent processing into final products are well known [31–32].

Table 10 shows the values of K(s) calculated by equation (2).

Table 10

Values of K(s) of the key rare and impurity metals in the sorption conversion processes of apatite concentrates

Experiment	K(s)										
	Na	K	Mg	Ca	Sr	Al	∑Tr	Ti	Fe	Th	U
1	10.4	15.2	30.3	142	237	1.64	714	3.51	3.28	3.23	0.62
2	5.17	12.0	16.8	87.6	153	1.97	438	8.41	6.83	3.02	0.69
3	3.16	1.99	8.48	8.90	11.1	1.70	61.3	18.4	11.1	9.40	1.85
4	11.2	17.6	17.6	88.6	178	2.02	178	3.19	2.65	1.90	0.45
5	3.6	4.2	5.0	10.1	20.3	0.77	8.2	4.21	3.0	0.59	0.96
6	3.3	2.0	1.4	4.7	N. a.	0.07	2.64	0.06	0.63	0.17	0.43
7	4.2	4.7	3.2	13.0	27.9	0.86	13.9	3.64	1.55	0.054	0.34
8	2.2	2.1	7.4	9.1	10.8	0.48	8.1	4.55	4.96	2.83	1.60

From the data in Table 10 it can be seen that in the process of sorption conversion of the apatite concentrate at 20 °C, the distribution coefficients of alkaline, alkaline earth, rare earth elements, thorium, and uranium decrease markedly with increasing concentration of phosphoric acid, while the distribution coefficients of aluminum, titanium, iron vary only slightly. The effect of the concentration of phosphoric acid is governed by two factors: change in the composition of the complexes formed by cations and, to a lesser extent, equilibria in reactions (1). Therefore, it is likely that at 20 °C an increase in the concentration of phosphoric acid has little effect on the composition of the phosphate complexes formed by aluminum, titanium, iron, but complicates the dissociation of the phosphate complexes of alkaline, alkaline earth, rare earth elements, thorium, and uranium.

Distribution coefficients at 20 °C during sorption conversion of the Khibiny apatite concentrate in solutions $C_{H_3PO_4}$ = 5–10 wt % decrease in the sequence REE > Sr > Sa > Mg > K > Na > Ti > Fe > Al > U, and during sorption conversion of the Lovozero apatite concentrate form the sequence REEs > Sr > Sa > Mg > Fe > Na = Ti > K > Al ≈ U. The differences in the sorption sequences for the Khibiny and Lovozero apatite concentrates are determined by the difference in the composition of the solutions formed during their decomposition, caused by the differences in the composition of apatite and the amount and composition of some accessory minerals.

At 80 °C, in solutions $C_{H_3PO_4}$ = 38 wt %, the distribution coefficients decrease in the sequence Sr > Sa > REE > Na ≈ K > Mg > Fe > Ti > Th = U > Al.

When using the macroporous sulfocationite Purolite 150 (experiment 3) the distribution coefficients of alkaline, alkaline earth, and rare earth elements are lower, while those of iron, titanium, thorium, and uranium are higher compared to those obtained using the gel sorbent KU-2-8 (experiment 2).

It should be borne in mind that the fluorine contained in apatite concentrate, especially when there is a deficiency of hydrated silica in the solution, can bind fluoro-acceptor cations of aluminum, iron, and titanium to anion complexes that are not adsorbed by sulfocationite.

Thus, at 5–38 wt % H3PO4 when using sulfocationite in H+-form, high decomposition performance of apatite concentrates is achieved. The residual content of cationic impurities depends on the composition of the concentrate, sorbent consumption, temperature and can be reduced by additional sorption treatment. The radionuclide content is low, making it possible to use the resulting phosphoric acid to produce a wide range of phosphate products.

2.2 Sorption conversion using sulfocationite in NH_4^+, Na^+ or K^+-forms

From a sorbent saturated with cations, metals can be desorbed by concentrated solutions of ammonium salts [32]. By fractional neutralization of the eluate with ammonia, sequential separation is achieved of the cake of impurity metals (aluminum, titanium, iron, thorium, etc.), REE carbonate concentrate, and finally, alkaline earth metal carbonates [33]. However, the use of ammonia, especially on sites remote from ammonia suppliers, creates significant logistics challenges. In addition, ammonia is classified as a flammable and explosive substances, therefore, the equipment used to process gaseous and liquefied anhydrous ammonia must be explosion-proof.

To eliminate the problems associated with the use of ammonia, alternative methods for processing the sorbent based on the desorption of metals by concentrated solutions of sodium salts, which produce sodium sorbents, were studied (see Section

2.3.1 below). Although the regeneration of H^+ sorbents is possible, it was of interest to examine the possibility of directly using sorbents in NH_4^+, Na^+ or K^+-forms for sorption conversion of apatite concentrate. Judging by the sorption performance from sulfuric and phosphate solutions [34, 35], cations of alkaline earth and rare earth metals form stronger bonds with the functional groups of the sorbent than cations of ammonium, sodium, or potassium. Therefore, although ammonium, sodium, or potassium cations in the sorbent make it difficult for the sorbent to absorb cations of alkaline earth and rare earth metals, it was expected that such sorbents can improve the decomposition performance of apatite.

In the latter two cases, the intent was also to evaluate the possibility of precipitation of fluorine from a phosphoric acid solution directly in the process of decomposition of apatite concentrate in the form of sodium or potassium fluorosilicates. At the same time, it was taken into account that the solubility of potassium fluorosilicate in solutions of many mineral acids is noticeably lower than that of sodium fluorosilicate [36], and it was assumed that this pattern would hold for phosphoric acid solutions.

It was also assumed that, if necessary, alkali metals can be removed from the phosphate solution by electrodialysis.

For experiments, Na^+ or K^+ sulfocationites were prepared by treating H^+ sulfocationionite with a solution of sodium or potassium phosphate. The substitution performance of proton with an alkali metal cation was controlled by the change in the concentration of alkali metal in the mother liquor.

Experimental conditions and results are shown in Tables 11–15.

Table 11

Experimental conditions when processing the apatite concentrate using sulfocationite in NH_4^+, Na^+ or K^+-forms

Experiment	$C_{H_3PO_4}$, wt %	L:S*	ß, %	Form of sorbent	Temperature, °C	Solid residue mass, rel %
1	38	10	100	NH_4^+	20	0.6
2	38	10	127	NH_4^+	80	Not found
3	32	5.5	115	Na^+	20	24.1 + 7.8
4	32	12	115	Na^+	20	9.2
5	32	12	170	Na^+	20	3.0
6	32	12	115	Na^+	50	2.0
7	32	17	115	Na^+	50	1.0
8	32	12	115	K^+	20	19.4
9	32	12	165	K^+	20	4.8

** – here and further: the ratio of the volume of the solution to the mass of the solid*

Table 12

Recovery of metals into the sorbent when processing the apatite concentrate using sulfocationite in NH_4^+, Na^+ or K^+-forms

Experiment	Recovery, %										
	Na	K	Mg	Ca	Sr	Al	Ti	Fe	Th	U	∑Tr
1	84.8	82.5	86.0	88.7	92.1	46.4	83.6	68.4	8.2	8.9	83.6
2	98.9	85.6	88.8	95.9	97.8	47.7	63.0	51.9	25	29	94.3
3	–	82.1	55.1	67.0	68.0	28.8	47.6	45.2	22.4	30.2	59.8
4	–	74.2	69.2	73.4	82.9	35.5	74.0	56.9	0.66	11.1	64.8
5	–	70.0	48.2	83.0	79.6	31.6	63.8	54.8	6.6	24.7	70.1
6	–	23.6	31.3	78.3	83.8	9.1	69.2	57.8	22.1	24.8	52.0
7	–	59.7	40.8	80.2	83.7	7.5	66.9	59.4	16.3	23.1	55.3
8	12.6	–	46.8	72.8	72.9	26.2	67.4	57.4	22.8	29.4	59.6
9	77.7	–	78.0	90.3	93.4	42.7	77.4	67.1	32.1	27.1	84.4

Table 13

Concentrations of the main cations and fluorine in the phosphate solutions obtained when processing the apatite concentrate using NH_4^+, Na^+, and K^+ sulfocationite

Experiment	Concentration, $mg \cdot l^{-1}$										
	Na_2O	K_2O	CaO	SrO	Al_2O_3	TiO_2	Fe_2O_3	ThO_2	UO_2	$\sum Tr_2O_3$	F
1	141	45.1	5640	197	332	47.7	229	2.76	0.41	171	2640
2	9.9	37.2	2012	67.3	324	115	343	2.25	0.32	59.5	2440
3	51960	40.8	5572	180	599	74.8	312	2.37	0.32	248	N. a.
4	19260	42.4	6561	168	286	31.0	197	2.11	0.28	217	430
5	20310	21.4	2761	80	267	20.9	138	1.60	0.20	105	420
6	28272	162	8327	376	466	70.5	231	1.90	0.28	403	520
7	20426	58.1	5684	291	333	50.5	151	1.40	0.20	265	520
8	609	32626	3311	207	353	21.0	138	1.39	0.20	212	150
9	122	30550	2339	77	230	17.7	121	1.50	0.20	106	190

Table 14

Recovery of REEs into the sorbent when processing the apatite concentrate using sulfocationite in NH_4^+, Na^+ or K^+-forms

Experiment	Recovery into the sorbent, %							
	Y	La	Ce	Pr	Nd	Sm	Eu	Gd
1	67.4	89.3	84.8	83.0	79.6	70.4	68.5	73.0
2	86.4	93.8	95.8	95.3	94.5	91.8	91.5	92.5
3	53.1	64.9	58.3	61.7	59.8	51.1	50.2	50.2
4	43.0	76.2	65.3	61.6	56.4	46.6	40.7	50.9
5	58.9	75.2	69.8	70.6	69.2	57.8	58.8	61.6
6	25.7	64.9	49.2	51.3	50.3	32.4	35.9	34.6
7	33.4	68.4	51.4	55.0	54.4	37.0	39.7	39.7
8	43.7	69.0	57.3	59.3	59.5	42.0	46.0	39.8
9	71.8	89.0	85.3	83.9	81.8	72.1	71.4	76.5
	Tb	Dy	Ho	Er	Tm	Yb	Lu	∑Tr
1	70.1	68.0	66.5	64.9	62.8	55.6	53.9	83.6
2	91.7	89.1	86.9	84.4	80.3	73.9	69.7	94.3
3	51.9	48.5	49.2	40.1	52.9	42.6	44.6	59.8
4	44.0	43.2	43.8	39.3	35.6	30.7	28.8	64.8
5	60.7	52.9	57.2	52.6	51.4	49.5	53.0	70.1
6	33.9	33.8	28.7	21.3	21.2	6.6	9.3	52.0
7	38.9	35.9	34.2	24.2	22.1	22.8	25.5	55.3
8	44.2	45.0	42.9	33.0	33.8	29.0	30.0	59.6
9	74.7	71.6	70.2	59.1	67.9	58.6	56.8	84.4

Table 15

Composition of the residue produced when processing the apatite concentrate using sulfocationite in NH_4^+, Na^+ or K^+-forms

Experiment		Content, wt%						
		Na_2O	K_2O	MgO	CaO	SrO	Al_2O_3	$\sum Tr_2O_3$
Initial		0.93	0.258	0.088	50.0	3.11	0.62	1.04
3	3–1	0.23	0.06	0.04	46.3	3.11	0.03	0.99
	3–2	6.67	0.0045	0.25	25.6	1.77	0.55	0.53
4		0.53	0.08	0.10	51.1	3.08	0.06	0.95
5		0.28	0.03	0.05	39.5	3.34	0.04	1.13

End of table 15

6		1.52	0.15	0.26	42.2	2.55	0.19	0.82
7		3.67	0.52	0.69	21.6	1.32	0.72	1.43
8		0.44	1.72	0.13	49.5	3.06	0.18	0.86
9		0.30	7.22	0.21	36.9	2.09	0.35	0.69
		TiO_2	Fe_2O_3	ThO_2	UO_2	SiO_2	P_2O_5	F
Initial		0.31	0.71	0.003	0.00045	1.70	39.06	3.03
3	3–1	0.11	0.30	0.0026	0.00029	0.63	44.61	0.43
	3–2	1.10	1.38	0.00192	0.00031	12.78	32.51	9.61
4		0.41	0.56	0.0025	0.0004	N. a.*	43.54	0.23
5		0.16	0.36	0.0035	0.00038	N. a.	55.74	0.14
6		0.55	1.17	0.0031	0.00037	N. a.	35.59	0.76
7		1.68	3.33	0.0118	0.00078	N. a.	19.34	N. a.
8		0.39	0.71	0.0034	0.0004	N. a.	40.96	1.14
9		0.82	1.31	0.0023	0.0003	N. a.	23.91	10.87

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* *N. a. — here and further: not analyzed*

As can be seen from the data in Tables 11–15, when using the sorbent in NH_4+ form, almost complete decomposition of the apatite concentrate is achieved, and fluorine remains in the phosphoric acid solution. Increasing the temperature and sorbent consumption reduces the concentration of calcium, strontium, REEs in the resulting phosphoric acid solution, but practically does not affect or even cause an increase in the concentrations of aluminum, titanium, iron, thorium, and uranium. The deterioration of sorption of the latter is associated with an increase in the fraction of these elements in anionic form or in the form of undissociated molecules with increasing temperature, and not with an increase in the acidity of the solution. Indeed, when the temperature rises from 20 to 80 °C, based on the data in [37], the first dissociation constant of H_3PO_4 decreases by 33 %.

A fairly high sorption of titanium at 80 °C should be noted, which is explained by a decrease at the chosen L:S ratio of the concentration of free phosphoric acid by about 40 % due to its partial neutralization by the ammonium group.

Although the recovery of the REEs of medium and yttrium groups is lower than the recovery of the REEs of cerium group, it is much higher than the recovery of these elements into the phosphate REE concentrate obtained by nitric acid processing of apatite.

Using sorbents in Na^+ and K^+-forms made the decomposition of apatite concentrate more difficult. In the search experiment (experiment 3), judging by the amount of calcium in the sorbent and solution, as well as by the amount of the precipitate 3–1, the degree of decomposition of the concentrate was 73.7 %. Separating the reaction products was difficult. It was possible to isolate the undecomposed residue in the form of two products that differed significantly in composition (residues 3–1 and 3–2 in Table 15). As shown by chemical analysis and confirmed by X-ray phase analysis, residue 3–1, whose mass was 24.1 % of the mass of the apatite concentrate, consisted mainly of apatite, while residue 3–2, whose mass was 7.8 % of the mass of the apatite concentrate, was enriched in sodium fluorosilicate.

Thus, the search experiment has shown the possibility of using Na^+ sulfocationite for the sorption conversion of apatite concentrate with the simultaneous recovery of a part of fluorine from the phosphate solution.

It was hypothesized that the low decomposition degree of the apatite concentrate is limited by the insufficient sorption performance of the apatite concentrate cations from the phosphate solution due to competition in the sorption of these cations with the sodium contained in the sorbent. As sorption occurs, sodium from the sorbent passes into solution, its concentration in the solution increases until an equilibrium is established, determined by the ratio of the distribution coefficients of the sorbed cations, mainly alkaline earth elements, and sodium. In the search experiment at the chosen L:S and sorbent consumption, the sodium concentration in the equilibrium solution in terms of Na_2O was to 52 $g \cdot l^{-1}$ (Table 13). Calcium and strontium cations accumulating in the solution prevent the dissolution of apatite.

We investigated the possibility of improving the decomposition performance of the apatite concentrate by increasing the sorbent consumption, L:S, and process temperature. As can be seen from the experimental data presented in the tables, increasing at 20 °C the consumption of Na^+ or K^+ sorbent by a factor of 1.5 reduced the calcium concentration in the obtained phosphoric acid solution and increased the absorbed amount of calcium, the main cationic component of the apatite concentrate (see experiments 4 and 5, 8 and 9). An increase in L:S (see experiments 6 and 7) by a factor of 1.4 had little effect on the sorption conversion performance.

In the residues, especially those obtained at an increased sorbent consumption, the content of calcium is lower and the content of phosphorus is higher than in the initial apatite concentrate. It follows that the residues, in addition to the undecomposed apatite and alkali metal fluorosilicate, contain calcium phosphate formed in the process, probably $Ca(H_2PO_4)_2 \cdot H_2O$.

Under comparable conditions, the sorbent in K^+-form provided a higher decomposition performance of the apatite concentrate, as well as a higher recovery of REEs into the sorbent (see experiments 5 and 9). An increased content of Mg, Al, Ti, Fe impurities in the sediment, and a reduced content of REEs, Ca, Sr, and phosphorus indicate that accessory minerals (egirin, feldspars) were concentrated in it. In addition, the residue has an increased concentration of potassium fluorosilicate, whose solubility, judging by the residual fluorine content in the mother phosphoric acid liquor, is lower than that of sodium fluorosilicate.

Increasing the process temperature to 50 °C increased the conversion performance, which manifests itself in a decrease in the solid residue mass and an increase in the absorption of calcium by the sorbent. At the same time, a noticeable decrease in the distribution coefficients (see Table 16) of a number of cations was observed. The exceptions were iron, thorium, and uranium, whose distribution coefficients changed little or increased. The increase in the sorption of thorium is associated with an increase in the proportion of thorium in the form of cationic complexes in the solution due to decomposition with increasing temperature of its anionic phosphate complexes or neutral molecules.

The fluorine content in phosphate solutions when using the sorbent in Na^+-form was 420-430 $mg \cdot l^{-1}$, when using the sorbent in K^+-form 190 $mg \cdot l^{-1}$, i.e. phosphoric acid solutions obtained during sorption conversion contain when using the Na^+ sorbent not more than 0.11 wt %, and when using the sorbent in K^+-form not more than 0.05 wt % fluorine in terms of 100 wt % H_3PO_4. Thus, for most process applications, for example, production of feed calcium phosphate to GOST 23999-80, there is no need for additional treatment of the resulting phosphoric acid to remove fluorine impurities.

Under the studied conditions, REEs, especially yttrium and lanthanides of the medium and yttrium groups, were sorbed worse than alkaline earth metals. Other things equal, their absorption by the K^+ sorbent was much higher than by the Na^+ sorbent.

Table 16

Values of $K_{(s)}$ during the sorption conversion of the apatite concentrate using sulfocationite in NH_4^+, Na^+ or K^+-forms

Experiment	Form	$K_{(s)}$										
		Na	K	Mg	Ca	Sr	Al	Ti	Fe	Th	U	ΣTr
1	NH_4^+	5.07	4.29	5.58	7.14	10.6	0.79	4.63	1.97	0.081	0.089	4.63
2	NH_4^+	64.2	4.25	5.66	16.7	31.8	0.65	1.22	0.77	0.24	0.29	118
4	Na^+	–	3.55	3.42	4.40	12.1	0.60	5.84	1.62	0.007	0.14	2.45
5	Na^+	–	4.44	3.01	7.91	16.3	0.38	4.99	1.49	0.065	0.29	3.67
6	Na^+	–	0.78	0.47	3.70	5.46	0.10	2.40	1.40	0.27	0.32	1.01
7	Na^+	–	2.09	1.06	5.56	7.04	0.11	3.24	2.21	0.28	0.40	1.64
8	K^+	0.16	–	1.74	8.67	8.63	0.36	7.84	2.34	0.56	0.80	2.21
9	K^+	2.45	–	4.90	9.56	18.4	0.51	5.12	1.83	0.33	0.25	4.46
*	H^+	4.22	4.74	3.20	13.0	27.8	0.86	3.63	1.54	0.068	0.43	13.7

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* *— data of experiment 7 from Table 4 for conversion at 38 wt % H_3PO_4.*

At a reduced sorbent consumption, the sorption of thorium, the main source of radioactivity in the Khibiny apatite concentrate, decreases, and due to this, its separation performance from cations of other metals increases. Although the bulk of thorium remains in the phosphoric acid solution, A_{eff} is very low.

The values of $K_{(s)}$ depend on the form and consumption of the sorbent, L:S ratio, and temperature (Table 16). The performance of the sorbent forms decreases following the sequence $N^+ \approx NH_4^+ > K^+ > Na^+$. The exception was thorium, whose sorption, on the contrary, apparently increased due to a decrease in the acidity of the solution upon the transition into solution of sodium or potassium, which led to an increase in the proportion of thorium in cationic form due to the hydrolytic decomposition of its phosphate anion complexes.

Thus, when using sulfocationite in NH_4^+, Na^+ or K^+-forms, high degree of decomposition of the apatite concentrate even at room temperature is achievable. The use of these sorbents can simplify the process by eliminating the need for sorbent regeneration to H^+ form and treatment of the resulting phosphoric acid to remove fluorine impurities. However, to use the resulting phosphate solutions in industrial processes, ammonium, sodium, or potassium cations need to be isolated from these.

2.3 Processing the sulfocationite of phosphoric acid decomposition of the Khibiny apatite concentrate

2.3.1 Cation desorption from sulfocationite using sodium salts

The desorption of cations from sulfocationite with concentrated solutions of mineral acids or ammonium salts is possible and is usually described by the equations:

$$(\text{-SO3})_n\text{Me} + \text{nH+} \leftrightarrow \text{n}(\text{-SO}_3\text{H}) + \text{Me}^{n+} \qquad (9)$$

$$(\text{-SO3})_n\text{Me} + \text{nNH}_4\text{+} \leftrightarrow \text{n}(\text{-SO}_3\text{NH}_4) + \text{Me}^{n+}. \qquad (10)$$

When used for the desorption of mineral acids, H^+ form of the sorbent is regenerated, which simplifies its use in the process, however, for efficient desorption of multicharged cations, concentrated solutions are necessary. It was shown that a high completeness of REE desorption from sulfocationite KU-2 was achieved using a 5M HCl solution and a volume ratio of V_{sol} solution and V_{sorb} sorbent equal to 50:1 [38]. However, using for desorption even concentrated acid solutions at an acceptable V_{sol}:V_{sorb} ratio does not guarantee its high performance [39].

Although, as a result of reaction (9), the proportion of free acid in the eluate decreases during desorption, it remains high. Therefore, for the precipitation of desorbed cations from such eluate by neutralization, high low rates of reagents are required. As a result, large quantities of saline solutions requiring disposal are formed.

During desorption by concentrated solutions of ammonium salts, the consumption of reagents for hydrolytic precipitation of desorbed cations from the eluate is significantly reduced. However, precipitating alkaline earth metal carbonates from such solutions is challenging and requires pH ≥ 9, because as the pH increases, the absorption of ammonia or its mixture with carbon dioxide by ammonium salt solutions becomes more difficult, and the use of ammonium carbonate makes the process more expensive. In addition, as already noted in Section 2.2, the use of ammonia at operations remote from its sources of supply is problematic due to logistics challenges and more stringent industrial safety requirements.

Therefore, it is of interest to develop alternative methods for processing cation-saturated sulfocationite.

It was reported that calcium and magnesium cations can be desorbed from sulfocationite with a sodium chloride solution with a concentration of 1 $mol \cdot l^{-1}$, where a mixture of calcium and magnesium carbonates is then precipitated by sequential introduction of sodium carbonate and hydroxide into the eluate until pH = 13 [40]. When processing sorbents obtained during the sorption conversion of the apatite concentrate, which, in addition to calcium, contain desorption-resistant strontium, REEs, aluminum, titanium, iron, and radionuclides, this approach is less effective. In addition, it is of practical interest to develop methods for the separation of sorbed cations from eluates, providing for separation thereof into group concentrates, especially the separation of radionuclides into a separate product.

Table 17

Metal content in the initial sorbents (in terms of oxides)

№	Content in sorbents, $mg \cdot l^{-1}$										
	Na_2O	K_2O	MgO	CaO	SrO	Al_2O_3	TiO_2	Fe_2O_3	ThO_2	UO_2	Tr_2O_3
1	570	160	52	33850	2164	242	186	348	0.15	0.10	707
2	626	177	61	35443	2214	327	181	401	0.52	0.15	740
3	675	207	73	46208	2938	262	218	510	0.90	0.15	909
4	1392	18	28	34550	6075	95	781	454	13.8	0.42	5651
Content, mEq %											
1	1.39	0.26	0.20	91.27	3.15	1.07	0.70	0.98	<10-4	<10-4	0.97
2	1.45	0.27	0.22	90.92	3.07	1.38	0.65	1.08	3·10-4	<10-4	0.97
3	1.21	0.24	0.20	91.74	3.15	0.86	0.61	1.06	4·10-4	<10-4	0.92
4	2.88	0.02	0.09	79.08	7.37	0.36	2.50	1.09	0.027	6·10-4	6.58

Desorption patterns from sulfocationite of alkaline earth and rare earth metals, aluminum, iron, titanium, thorium, and uranium with concentrated solutions of sodium nitrate or chloride were investigated.

In the experiments, batches of sulfocationite KU-2-8, saturated with cations during the sorption conversion of the Khibiny (sorbents 1–3) and Lovozero (sorbent 4) apatite concentrates, were used. The content of components in the initial sorbents are shown in Table 17. Fluctuations in metal concentrations were due to the differences in the treatment conditions of the concentrates (sorbent consumption, the concentration of the phosphoric acid used for the decomposition, process temperature).

The utilization of the sorption exchange capacity by metal cations under the assumption that Me^{n+} cations were sorbed, for sorbents 1–4 was 74.1, 77.3, 100, and 87 %, and the value of A_{eff} was 0.002, 0.004, 0.0055, and 0.061 $KBq \cdot kg^{-1}$, respectively. The desorption performance will be determined primarily by the completeness of the desorption of calcium and strontium.

For desorption experiments, solutions were used (numbers of the solutions subsequently used are given in parentheses) containing 5 M NaCl (1), 5 M $NaNO_3$ (2), 7 M $NaNO_3$ (3), 5 M NaCl + 1 $g \cdot l^{-1}$ HCl (4), and 5 M $NaNO^3$ + 1 $g \cdot l^{-1}$ HNO_3 (5).

It was assumed that desorption is described by the equation:

$$(\text{-SO3})_n\text{Me} + n\text{Na}^+ \leftrightarrow n(\text{-SO3Na}) + \text{Me}^{n+}. \quad (11)$$

In addition, if complete proton substitution by sorbed cations was not achieved during sorption, the following reaction is possible:

$$\text{-SO}_3\text{H} + \text{Na}^+ \leftrightarrow \text{-SO}_3\text{Na} + \text{H}^+. \quad (12)$$

Thus, during desorption, the acidity of the solution should increase both due to the substitution of sodium in solutions with desorbed metals of lower basicity by reaction (11) and the displacement by sodium of the hydrogen cation by reaction (12) from sorbents 1 and 2 insufficiently saturated with metal cations.

Table 18

Dependence of the desorption performance on the process conditions

Eperi-ment	Sor-bent	t, °C	Desor-bent	Desorption, rel %								
				K	Mg	Ca	Sr	Al	Ti	Fe	Th	U
1	3	20	1	90.2	84.0	94.3	87.2	78.2	3.7	68.7	10.6	8.6
2	1	80	1	58.8	55.5	66.9	65.7	72.5	1.5	3.9	76.6	12.2
3	3	20	2	91.4	84.5	93.0	81.9	77.2	3.3	50.7	8.9	4.2
4	1	80	2	90.0	45.7	69.3	72.9	68.8	1.4	15.1	76.7	7.3
5	1	80	3	86.5	29.6	58.8	67.2	49.0	1.5	8.4	72.4	59.6
6	2	80	4	61.1	40.9	96.0	62.4	70.7	1.2	10.6	9.1	10.0
7	2	80	5	59.6	23.9	97.0	78.4	47.2	0.3	12.1	6.3	11.0
8	4	20	2	61.3	83.4	95.5	64.5	84.6	1.0	25.8	2.2	6.5

Desorption was carried out in static conditions. The sorbent was placed in a desorption solution (the initial ratio of the volumes of the solution and sorbent $V_{sol}:V_{sorb}$ = 4:1), the mixture was stirred for 2 hours at a set temperature. In some experiments, samples of the liquid phase were collected every 0.5 hours for analysis. In the liquid phase, the concentrations of potassium, alkaline earth and rare earth elements, aluminum, titanium, iron, thorium, and uranium were measured. The degree of desorption was calculated as the fraction of the components that had passed into the liquid phase of their total content in the sorbent sample.

The bulk of the components was desorbed after 0.5 hours. However, equilibrium was not reached even after 1.5 hours, although after one hour, the concentrations of the components in the eluate did not change significantly. Moreover, over time, the concentration in the solution of individual components after their accumulation could slightly decrease. To calculate the desorption values, the concentration values obtained upon 2 hours were adopted. Tables 18 and 19 show the desorption performance of the main cationic components of the apatite concentrate.

Table 19

Dependence of the REE desorption performance on the process conditions

Eperiment	Desorption, %							
	Y	La	Ce	Pr	Nd	Sm	Eu	Gd
1	89.7	65.0	71.0	84.7	83.4	89.9	87.2	86.8
2	46.5	39.8	39.1	41.3	49.5	42.5	37.4	44.4
3	70.8	54.9	59.7	74.2	73.4	77.7	78.0	76.7
4	35.2	28.3	28.7	29.8	28.2	31.1	27.4	32.2
5	26.7	29.8	29.2	28.7	25.9	30.2	27.4	31.8
6	51.9	38.4	42.4	39.8	40.1	49.3	44.2	51.0
7	37.2	37.4	40.3	35.9	36.0	43.0	38.2	43.1
8	60.2	72.3	67.8	68.0	65.3	68.7	69.6	64.8
	Tb	Dy	Ho	Er	Tm	Yb	Lu	∑Tr
1	88.2	88.5	87.2	89.8	88.2	91.5	92.0	72.9
2	42.4	37.1	40.3	38.1	42.5	39.0	52.3	41.4
3	77.5	71.6	74.8	70.6	77.6	78.0	79.2	61.8
4	30.1	32.3	33.6	39.1	31.5	41.3	31.7	29.0
5	28.4	29.1	30.1	33.1	26.7	35.2	26.2	28.9
6	44.6	56.0	54.6	70.0	67.2	74.3	79.1	41.8
7	38.7	40.0	38.1	43.1	41.6	51.6	46.8	38.6
8	63.2	55.4	56.7	58.9	59.1	59.2	58.6	62.4

During desorption, the pH decreased when using non-acidified solutions from ≈ 6.7 to 0.1–0.6, when using acidified solutions from 1.6–1.8 to 0.04–0.28, therefore spontaneous precipitation of hydroxides of aluminum, iron, titanium, thorium, uranium did not occur.

As can be seen from Table 18, solutions of sodium chloride and sodium nitrate with a concentration of 5 mol·l^{-1} (experiments 1–4) are suitable for desorption of alkaline-earth and rare-earth elements and aluminum from sulfocationite saturated in phosphoric acid solutions, and under certain conditions of iron, thorium, uranium, but are ineffective in the desorption of titanium. The desorption performance of most components with solutions of sodium chloride and sodium with a concentration of 5 M at 20 °C did not differ (experiments 1 and 3), however, the desorption of iron, REE, and uranium with a solution of sodium chloride was somewhat more complete than with a solution of sodium nitrate.

Increasing the desorption temperature from 20 to 80 °C reduced the desorption performance of most cations, especially iron, with solutions of both sodium chloride and sodium nitrate (compare experiments 1 and 2, 3, and 4), but sharply improved the desorption of thorium.

Increasing the concentration of sodium nitrate in the desorbate up to 7 M (sodium chloride solutions of this concentration do not exist) reduced the desorption performance of alkaline earth elements, aluminum, and iron, but significantly improved the desorption of uranium (experiment 5). Aluminum was noticeably desorbed by all the examined solutions, but sodium nitrate solution is more effective than sodium chloride.

At 80 °C, slight additional acidification of the solutions sharply reduced the desorption of thorium (experiments 2 and 6, 4 and 7), significantly improved calcium desorption, and had little effect on strontium desorption. The acidification of the sodium nitrate solution noticeably, while that of the sodium chloride solution only slightly reduced the aluminum desorption performance.

As can be seen from Table 19, the desorption of medium and yttrium group REEs is, as a rule, somewhat higher than that of cerium group REEs. Acidification had little effect on the performance of REE desorption by sodium chloride solution, but increased desorption by sodium nitrate solution.

According to equation (2), the values of $K_{(des)}$ at a temperature of 20 °C when using solutions of sodium salts and ammonium nitrate were calculated (see table 19). For calculations, we used the data of Table 18 and the results of desorption with a solution of ammonium nitrate from sorbent 2.

The data in Table 20 shows that solutions of sodium chloride and nitrate, compared to ammonium nitrate solution, more effectively desorb potassium, alkaline earth and rare earth elements, aluminum, and iron, but much less effectively thorium and uranium, which can be satisfactorily desorbed no sooner than at 80 °C.

The increased desorption performance of sodium salt solutions (see Table 20) is determined by their higher concentration in the solutions used for desorption.

Table 20

Values of $K_{(des)}$ at 20 °C for various desorbents

Desor-bent	Concentration, M	$K_{(des)}$									
		K	Mg	Ca	Sr	Al	Ti	Fe	Th	U	ΣTr
NaCl	5	2.30	1.31	4.14	1.70	0.90	0.0096	0.55	0.030	0.024	0.65
$NaNO_3$	5	2.66	1.46	3.32	1.13	0.85	0.0085	0.26	0.024	0.011	0.40
NH_4NO_3	3.75	0.40	0.30	0.36	0.78	0.50	0.015	0.11	0.79	0.44	0.22

Thus, solutions of sodium nitrate and chloride can reliably desorb most of the cations absorbed by sulfocationite during the phosphoric acid decomposition of the apatite concentrate. An exception is titanium, but since the titanium content in the sorbent is low (not more than 0.5 % of the exchange sorption capacity), its accumulation will not have a noticeable effect on the sorption performance with repeated use of the sorbent. As it accumulates, titanium can be desorbed, for example, with a solution of ammonium sulfate [7].

Sorbent KU-2-8 swells by 42 %. The sorbent fills about 67 % of the bulk volume, therefore, the volume of the solution absorbed by the sorbent during swelling is $67\cdot0.42:1.42 \approx 20$ % of the volume occupied by the swollen sorbent. At $V_{sol}:V_{sorb} = 4:1$, the volume of the dispersion solution is 5 % of V_{sol}. Assuming that the phosphorus levels in the dispersion and mother liquors are equal and all the phosphorus of the dispersion solution at the $V_{sol}:V_{sorb}$ value used for desorption enters the eluate, the concentration of P_2O_5 in the eluate should be 20 times lower than in the mother liquor, i.e. 1.82 $g\cdot l^{-1}$ at $C_{H_3PO_4} = 5$ wt % and 17.3 $g\cdot l^{-1}$ at $C_{H_3PO_4} = 38$ wt%. The eluates obtained during desorption from the gel sorbent KU-2-8 contained only 0.024–0.13 $g\cdot l^{-1}$ P_2O_5 (0.033–0.179 $g\cdot l^{-1}$ H_3PO_4), i.e. the sorbed complexes did not contain phosphate ligands.

Thus, concentrated solutions of sodium chloride and nitrate more effectively desorb from sulfocationite cations of alkaline earth and rare earth metals, aluminum, and iron, compared to a solution of ammonium nitrate. There were no significant differences during desorption using sodium chloride and nitrate.

Desorption of alkaline earth, rare earth elements, aluminum, and iron with solutions of sodium chloride and nitrate significantly decreases when increasing the process temperature from 20 to 80 °C. Thorium desorption by sodium chloride and nitrate increases significantly when increasing the temperature to 80 °C and decreases when the desorbate is slightly acidified. Increasing the concentration of sodium nitrate from 5 to 7 M reduced the desorption performance of alkaline earth elements, aluminum, and iron.

2.3.2 Processing of sodium salt-based eluates

The patterns of hydrolytic metal deposition during the stepwise neutralization of eluates using 5 M $NaNO_3$ and NaCl solutions were investigated.

The hydrolytic deposition sequence of metals is determined by their concentration in the solution, the value of the solubility products (SP) of their hydroxides and, as a consequence, the starting (pH_s) and terminal (pH_t) pH values of deposition. Table 21 shows the SP values of some hydroxides and the resulting pH_s and pH_t values under the assumption that the starting and end points of the deposition process correspond to the concentration of metals in solution equal to 1 and 10^{-6} g-ion·l^{-1}, respectively [41]. It follows that Al, Fe, Th, and U can be efficiently separated upon neutralization of the solution to pH = 4.5–5.0 and REE precipitated from the remaining solution by neutralization to pH = 9.5, while alkaline earth elements (with the exception of magnesium, but its initial concentration is usually low) will quantitatively remain in solution.

Table 21

Solubility products, pH_s and pH_t of some hydroxides [41]

Indicator	Value							
	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	Al^{3+}	Fe^{3+}	Mn^{2+}	Sc^{3+}
SP	$1.6 \cdot 10^{-11}$	$7.9 \cdot 10^{-7}$	$3.2 \cdot 10^{-4}$	$1.6 \cdot 10^{-2}$	$1.9 \cdot 10^{-33}$	$1.0 \cdot 10^{-38}$	$3.9 \cdot 10^{-14}$	$2.0 \cdot 10^{-30}$
pH_s	8.50	10.85	12.15	13.00	2.99	1.43	7.20	4.00
pH_t	11.50	13.85	-	-	4.99	3.43	10.20	6.00
	La^{3+}	Ce^{3+}	Pr^{3+}	Nd^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}	Tb^{3+}
SP	$1.0 \cdot 10^{-19}$	$1.5 \cdot 10^{-20}$	$2.7 \cdot 10^{-20}$	$1.9 \cdot 10^{-21}$	$6.8 \cdot 10^{-22}$	$3.4 \cdot 10^{-22}$	$2.1 \cdot 10^{-22}$	$4.9 \cdot 10^{-27}$
pH_s	7.67	7.29	7.38	6.99	6.84	6.74	6.67	5.13
pH_t	9.67	9.29	9.38	8.99	8.84	8.74	8.67	7.13
	Dy^{3+}	Ho^{3+}	Er^{3+}	Yb^{3+}	Lu^{3+}	Y^{3+}	Th^{4+}	U^{4+}
SP	$1.3 \cdot 10^{-24}$	$2.8 \cdot 10^{-27}$	$1.3 \cdot 10^{-22}$	$2.9 \cdot 10^{-24}$	$2.5 \cdot 10^{-24}$	$8.1 \cdot 10^{-23}$	$1.0 \cdot 10^{-46}$	$2.5 \cdot 10^{-50}$
pH_s	5.27	5.05	6.27	6.05	6.03	6.54	2.50	1.70
pH_t	7.27	7.05	8.27	8.05	8.03	8.54	4.00	3.20

In preliminary experiments, neutralization was carried out with a 104 g·l^{-1} solution of Na_2CO_3 or a 96.1 g·l^{-1} NaOH solution while stirring. The onset of precipitation was monitored visually, and subtle turbidity was observed only at pH = 4.9–5.0.

The neutralizing reagents were added drop by drop while stirring vigorously. After reaching the desired pH value, the precipitate formed was filtered and the mother liquor was analyzed. The change in the concentration in the solution was used to evaluate the degree of precipitation of the components and the composition of the precipitate formed.

Table 22

Levels of rare-earth metals and impurities in the initial eluate

Content, $mg \cdot l^{-1}$							
Y_2O_3	La_2O_3	Ce_2O_3	Pr_2O_3	Nd_2O_3	Sm_2O_3	Eu_2O_3	Gd_2O_3
5.13	38.33	59.68	5.6	22.52	3.032	0.663	2.99
Tb_2O_3	Dy_2O_3	Ho_2O_3	Er_2O_3	Tm_2O_3	Yb_2O_3	Lu_2O_3	$\sum Tr_2O_3$
0.31	1.289	0.187	0.388	0.0388	0.156	0.0198	140.33

K_2O	MgO	CaO	SrO	Al_2O_3	TiO_2	Fe_2O_3	MnO	ThO_2	UO_2
47.28	15.46	10740	601.3	50.53	1.814	64.52	5.804	0.02	0.0017

The content of components in the eluate based on a 5 M $NaNO_3$ solution is given in Table 22. The initial pH of the solution was 0.55.

After reaching a pH of 4 and stopping the introduction of Na_2CO_3 solution, the pH of the solution spontaneously increased to 5, and after reaching a pH of 6.4 to 8.0. This is due to the fact that with the introduction of a sufficiently concentrated Na_2CO_3 solution, local supersaturation zones arise in which $Na_2CO_3CaCO_35N_2O$ forms [42]. When the neutralizing solution is no longer added, this compound slowly decomposes with the release of Na_2CO_3 into the solution, which causes a gradual increase in the pH of the solution.

The onset of turbidity was visually observed first at a pH of 5. Upon reaching the set pH value, the precipitate formed was filtered off, a filtrate sample was taken for analysis, and neutralization was continued. Table 23 shows the change in the level of the components in the mother liquors as these were neutralized.

The data in Table 23 made it possible to calculate the precipitation performance of the components depending on the completeness of neutralization (Table 24) and the composition of the resulting precipitates (Table 25).

Table 23

Effect of pH on the level of components in the mother liquors

pH	Content, $mg \cdot l^{-1}$									
	MgO	CaO	SrO	Al_2O_3	TiO_2	MnO	Fe_2O_3	ThO_2	UO_2	$\sum Tr_2O_3$
0.55	15.5	10740	601	50.5	1.81	5.80	64.5	0.02	0.002	140.3
5.0	1.98	8946	599.3	0.15	0.10	1.45	13.5	0.0015	0.0005	2.53
7.5	1.92	2255	567.6	0.02	0.08	0.80	10.7	0.0009	0.0002	0.35
8.0	1.88	1515	535.8	0	0.05	0	0	0.0004	0.0001	0.01
9.4	0.43	7.52	3.31	0	0.01	0	0	0.0003	0.0001	0

Table 24

Recovery of components into the precipitates formed as a result of neutralization with a sodium solution

pH range	Recovery, rel%									
	Mg	Ca	Sr	Al	Ti	Mn	Fe	Th	U	∑Tr
0.55-5.0	87.23	16.70	0.28	99.70	94.48	75.00	79.07	92.5	75.0	98.20
5.0-7.5	0.39	62.30	5.27	0.26	1.10	11.21	4.34	3.0	15.0	1.55
7.5-8.0	0.26	6.89	5.29	0.04	1.66	13.79	16.59	2.5	5.0	0.24
8.0-9.4	9.35	14.04	88.60	0	2.20	0	0	0.5	0	0
Total	97.22	99.93	99.45	100	99.44	100	100	98.5	95.0	100

Table 25

Composition of the precipitates obtained by stepwise neutralization with sodium solution

pH range	Content, wt %									
	MgO	CaO	SrO	Al_2O_3	TiO_2	MnO	Fe_2O_3	ThO_2	UO_2	$\sum Tr_2O_3$
0.55–5.0	0.66	87.30	0.10	2.45	0.08	0.21	2.48	$9\cdot10^{-4}$	$6\cdot10^{-5}$	6.71
5.0–7.5	$7\cdot10^{-4}$	99.45	0.47	$2\cdot10^{-3}$	$4\cdot10^{-4}$	0.01	0.04	$9\cdot10^{-6}$	$4\cdot10^{-6}$	0.03
7.5–8.0	0.01	94.41	4.06	$3\cdot10^{-3}$	$4\cdot10^{-3}$	0.10	1.37	$6\cdot10^{-5}$	$1\cdot10^{-5}$	0.04
8.0–9.4	0.07	73.85	26.08	–	$1\cdot10^{-3}$	0	0	$5\cdot10^{-6}$	0	$5\cdot10^{-4}$

Analysis of the data in Tables 23–25 shows that when neutralizing 5 M $NaNO_3$ eluates with a sodium solution, the behavior of the components differs significantly from that observed when neutralizing the 5 M NH_4NO_3 eluate with a mixture of ammonia and carbon dioxide [33]. Specifically, from the 5 M $NaNO_3$ eluate, not only titanium, iron, thorium precipitated at pH 5.0, but also the bulk of REEs and aluminum, a significant amount of manganese, calcium, uranium, and magnesium. Only strontium remained almost completely in solution.

As the pH increased to 7.5–8, calcium precipitated intensively, while the bulk of strontium remained in solution even at pH = 8, and its quantitative precipitation was achieved only at pH = 9.4.

Thus, when neutralized with a sodium solution to pH = 5, 98.2 % of REEa was released from the 5 M $NaNO_3$ eluate into the product with a content of $\sum Tr_2O_3$ relative to the sum of oxides of other elements of 6.7 wt %, while the main impurity was calcium carbonate. With an increase in pH to 8, another 69 % of calcium precipitated as a product in which the CaO content relative to the sum of oxides of other elements was 98.9 wt %. Finally, the last precipitate was a strontium-enriched product, in which the SrO content relative to the sum of oxides of other elements was 26.1 wt %. Strontium yield into this product was about

90 %, the main impurity was calcium. When optimizing the consumption of sodium solution with a yield of > 77 %, strontium concentrates were produced containing 68.5–74.5 wt % SrO relative to the sum of SrO and CaO.

Component precipitation when neutralized with a sodium chloride eluate proceeded in a similar manner.

The separation of REEs and alkaline earth elements, as well as calcium and strontium when using a sodium hydroxide solution for neutralization, had an even lower performance.

The high degree of REE and calcium precipitation cannot be associated with the presence of a phosphate ion in eluates, as observed in [43], because the concentration of phosphorus in solutions is low, and it remained quantitatively in solution. Neither is it determined by sorption on the hydroxides of more easily hydrolyzed elements, as proposed in [44], because in the precipitates, the sum of equivalent amounts of REEs and calcium significantly exceeded the equivalent amount of more easily hydrolyzed elements.

The precipitation of REE at pH = 5 and a significant share of calcium at pH ≤ 8 can be explained as follows. The low solubility of hydroxides of most metals, including REEs, is determined as shown in Fig. 2 by polymerization due to the formation of olic bonds [45]:

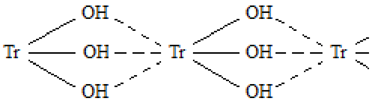

Figure 2. Scheme of polymerization of metal hydroxides

When a neutralizing reagent is introduced in the form of a solution or a solid, the composition is not averaged instantly. A layer is formed at the contact boundary, in which the pH changes sharply from weakly acidic to strongly alkaline (Fig. 3). There are zones with pH ≥ 10. In these zones, all the salts contained in the solution undergo hydrolysis, including the more resistant salts of REEs and alkaline earth element.

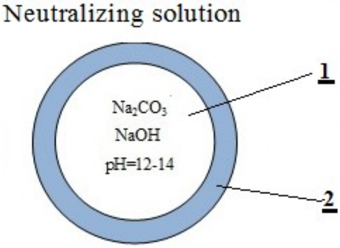

Figure 3. pH gradient on the contact interface between a drop of the neutralizing solution and the solution to be neutralized: 1 — neutralizing solution drop; 2 — intermediate layer with variable pH value

Therefore, during the neutralization of solutions containing various cations, not only those components precipitate that are hydrolyzed at an equilibrium pH value, but also those that are stable at a given average pH value of cations. Hydroxide complexes are formed, the composition of which depends on the elemental composition of the solution, the concentration ratio of the elements in the solution and local pH gradients, which are determined by the type, concentration, and method of introducing the neutralizing reagent. Multiple reports on the hydrolytic deposition of the precursors of double salts of alkaline earth and REEs — aluminates, titanates, niobates, etc. from solutions containing their salt mixtures suggest that during the deposition process not only olation reactions occur, but also oxolation reactions with the formation of hydroxide polymers containing various cations. When the solution composition is subsequently averaged, components more resistant to hydrolysis, as the experiment shows, do not leach from such complexes.

Thus, the separation performance of components during hydrolytic precipitation is influenced not only by the type, but also by the method of introducing a neutralizing reagent. Homogeneous precipitation with urea, which gradually decomposes with the release of ammonia [46], performs well. In industrial process conditions, this method is inconvenient, because urea breaks own requires a long exposure of the neutralized solution at a temperature of 90–100 °C. In addition, it is difficult to control the consumption of the product necessary to maintain the desired pH.

Another method is close to homogeneous, based on the use to neutralize the mixture of gaseous ammonia and air at a molar ratio of ammonia to air of 1:(2–4) [47].

From solutions based on 5 $mol \cdot l^{-1}$ ammonium nitrate or sulfate, thorium, uranium, titanium, iron, and a significant fraction of aluminum (thorium cake) were sequentially isolated by stepwise neutralization with gaseous ammonia was at pH = 4.8–5.05, REE carbonate concentrate at pH = 7.35–7.5, alkaline earth metal carbonate precipitate at pH > 8.5. The loss of REE with thorium cake was 0.1–0.5 %, and practically no calcium was entrained. With the rare earth concentrate, 1.2–1.7 % of the calcium contained in the solution precipitated [33]. However, when a NaOH solution was used to neutralize, 12.9 % REE was found in the precipitate that formed at pH = 5.0.

Precipitation of alkaline earth metals by neutralization with gaseous ammonia is challenging, because as the pH increases, the absorption of ammonia by solutions of ammonium salts becomes more difficult. The use of gaseous ammonia, especially on sites remote from ammonia suppliers, creates significant logistics challenges. In some cases, the entry of ammonium ion into solutions is unacceptable, making it difficult to dispose of or recover the mother liquors. In addition, ammonia is a flammable and explosive substance.

This explains the desire to use other reagents for hydrolytic precipitation, among which alkali and alkaline earth metal hydroxides and carbonates are considered suitable. However, in this case, the REE recovery performance is significantly reduced.

For instance, when neutralizing perovskite nitric acid decomposition solutions with a calcium hydroxide suspension with thorium cake, 17.1 % REE precipitated at drop by drop introduction, and 29.4–51.8 % REE at a higher consumption [48].

When neutralizing the solutions obtained during the processing of loparite concentrate to pH = 5.0–5.8 with a solution of sodium hydroxide with thorium cake, up to 10 % of the REEs in the solutions precipitated [49]. This led not only to a high REE loss, but also an increase in the quantity of the radioactive residue to be disposed of.

In a study of REE capture by the iron hydroxide precipitate obtained by the simultaneous introduction of solutions containing 0.2 mol^{-1} $Fe_2(SO_4)_3$ and 50 g^{-1} NaOH into a heated to 75 °C aqueous solution containing REE sulfates with a pH of 3.5, it was found that REE precipitation is controlled not by the formation of poorly soluble double sulfates with sodium, but by REE adsorption on the surface of iron hydroxide [44]. Moreover, from solutions containing < 1 g l^{-1} cerium group REEs, up to 70 % REEs precipitated, down to 15 % in more concentrated solutions. The coprecipitation of heavy REEs not forming double sulfates increased with an increase in their concentration in solution, reaching 5–8 wt % at a REE concentration of 10 g l^{-1}.

So, to achieve effective separation, a method is needed of introducing Na_2CO_3 or NaOH, which prevents the development of significant pH gradients in the neutralized solution. It was hypothesized that this can be achieved if neutralization is carried out with Na_2CO_3 or NaOH alloys with the salt used for desorption. When such alloys are dissolved, the neutralizing reagent will enter the solution gradually, which should lead to a decrease in the local concentration gradient.

An analysis of the melting diagrams of Na_2CO_3-$NaNO_3$ and NaOH-$NaNO_3$ systems [50] showed that in the Na_2CO_3-$NaNO_3$ system, pre-eutectic compositions not containing Na_2CO_3 crystals with a Na_2CO_3 concentration of $C_{Na_2CO_3} \le 3$ wt % are most promising. Alloys in the NaOH-$NaNO_3$ system are also of interest, where solid solutions based on NaOH · $NaNO_3$ and 2NaOH · $NaNO_3$ are formed and the NaOH phase is absent in a wide range of concentrations. It was possible that during fast cooling of Na_2CO_3-$NaNO_3$ alloys with $C_{Na_2CO_3} > 3$ wt % the released small crystals of Na_2CO_3 being in excess of $NaNO_3$ crystals would dissolve slowly, which would also reduce the local concentration gradients of the neutralizing reagent.

In further work, eluates obtained by desorption with a 5 mol^{-1} $NaNO_3$ solution from the cation exchanger KU-2-8, saturated during phosphoric acid decomposition of the Lovozero apatite concentrate. These had a pH of 0.41–0.68 and contained (mg·l^{-1}): 5157–5905 CaO, 703–1123 SrO, 3.85–10.8 MnO, 14.1–63.5 Al_2O_3, 18.8–31.0 Fe_2O_3, 559–881 $\sum Tr_2O_3$, 0.6–4.1 TiO_2, 0.08–0.19 ThO_2, 0.003–0.008 UO_2, 12–130 P_2O_5. This corresponded to (mEq·l^{-1}): 184–211 Ca, 13.6–21.7 Sr, 0.11–0.30 Mn, 0.83–3.74 Al, 0.70–1.16 Fe, 10.2–16.0 $\sum$Tr, 0.03–0.21 Ti, 0.001–0.003 Th, (4.4–12)·10^{-5} U, 0.51–5.5 PO_4^{3-}.

Compared with the solutions based on ammonium salts used in [33], the content of REE was approximately 20 times lower, and the content of calcium, iron, and aluminum relative to REE was much higher.

Part of the studies was performed using model nitrate solutions containing 5 mol·l^{-1} $NaNO_3$ and nitrates of a number of elements, whose concentration in oxide terms was (mg·l^{-1}): CaO 5780, SrO 1780, Al_2O_3 43, Fe_2O_3 84, Y_2O_3 206, La_2O_3 180, Ce_2O_3 990, Nd_2O_3 387. The solution was acidified with HNO_3 to pH 0.68.

The experiments were carried out at a temperature of 20 °C. For neutralization, specially prepared alloys with sodium nitrate were used. To prepare the alloys, sodium carbonate or sodium hydroxide at a predetermined ratio was mixed and the mixture was melted in corundum crucibles. The resulting melts were rapidly cooled by pouring onto a thick sheet of metal. The obtained alloy plates were ground to a particle size of –1 mm before use.

Using the Tyndall effect, it was found that the solid phase started forming already at pH = 1.6–1.8. Therefore, in order to reduce the consumption of alloys and the amount of $NaNO_3$ introduced into the solution neutralization to pH = 1.6–1.8, at which the solid phase nucleation was observed, was carried out with a concentrated NaOH solution. Results of the study of the effect of changes in Na_2CO_3 concentration $C_{Na_2CO_3}$ in its alloys with $NaNO_3$ on the precipitation degree of REEs and alkaline earth elements upon neutralization to pH = 5 are shown in Table 26.

Table 26

Effect of Na_2CO_3 concentration $C_{Na_2CO_3}$ in its alloys with $NaNO_3$ on the precipitation degree of elements upon neutralization to pH = 5

$C_{Na_2CO_3}$, wt %	Precipitation degree, rel %							
	Ca	Sr	Al	Ti	Fe	Th	U	Y
2.5	0.14	0	46.4	100	80.4	91.9	100	11.9
5.0	0.2	0	N. a.	N. a.	N. a.	N. a.	N. a.	13.3
7.5	0.2	0	N. a.	N. a.	N. a.	N. a.	N. a.	20.0
11	8.06	0	N. a.	N. a.	N. a.	N. a.	N. a.	29.4
15	9.63	0	N. a.	N. a.	N. a.	N. a.	N. a.	29.4
	La	Ce	Pr	Nd	Sm	Eu	Gd	∑Tr
2.5	0.21	0.20	1.02	2.95	9.73	9.28	1.58	1.16
5.0	5.3	13	N. a.	13.3	N. a.	N. a.	N. a.	11.6
7.5	10.5	14	N. a.	13.3	N. a.	N.a.	N. a.	14.1
11	12.8	40.8	27.9	41.1	21.4	N. a.	68.4	34.5
15	18.3	43.0	35.1	49.2	32.6	N. a.	68.4	38.8

From the data in Table 26, it can be seen that when neutralized to pH = 5 with an alloy containing 2.5 wt % Na_2CO_3, 1.16 % of the REE sum fell into thorium cake, and 0.14 % of calcium into the REE concentrate. Increasing Na_2CO_3 concentration in the alloy led to a rapid increase in the capture by the thorium cake of the REEs, and by the REE concentrate of calcium. The deposition degree of REEs with greater basicity — of the cerium (except for lanthanum) and medium group — could exceed that of the more easily hydrolyzed yttrium. This also confirms the discussed nature of the hydrolytic deposition of metals in solutions containing components with significantly different hydrolytic stability.

At neutralization to pH = 4.4–4.8 even when using alloys containing 15 wt % Na_2CO_3 or 15–30 wt % NaOH, capture by the thorium cake of REEs and alkaline earth elements greatly decreased (Table 27). High precipitation degree of Al and Fe was achieved already at pH ≥ 4.6 when using alloys with Na_2CO_3 and at pH ≥ 4.4 when using alloys with NaOH. REE precipitation with thorium cake depended on the type of neutralizing reagent: at pH = 4.6 and using an alloy containing NaOH, the REE precipitation in the cerium group was greater, that of yttrium was less than when using an alloy containing Na_2CO_3.

Table 27

Dependence of hydrolytic deposition efficiency on the concentration (C) of Na_2CO_3 or NaOH in sodium nitrate-based alloys

C, wt%	pH	Precipitation degree, %							
		Al	Fe	Y	La	Ce	Nd	Ca	Sr
Alloys $NaNO_3 + Na_2CO_3$									
15	4.6	88.4	96.4	5.00	1.23	0.90	3.95	1.38	0.79
	4.8	88.4	96.4	5.00	1.23	1.10	5.26	1.38	0.79
Alloys $NaNO_3$ + NaOH									
15	4.4	50.0	91.7	0.50	0.53	0.10	0.26	0.13	0.33
	4.6	88.4	94.0	3.40	2.79	1.01	5.94	0.69	0.79
30	4.4	82.6	94.0	2.73	2.06	2.04	1.68	1.46	1.16
	4.6	82.6	94.0	3.43	2.63	2.06	2.10	1.64	1.16

When analyzing the data in Table 27, it should be borne in mind that the size of Na_2CO_3 or $NaOH \cdot NaNO_3$ (exists at a $NaNO_3$ concentration ≥ 70 wt %) crystals in alloys may depend on the cooling conditions of the melt, affecting the local concentration gradients of the neutralizing reagent arising during the dissolution of alloy particles.

Table 28 shows the neutralization results of the eluate with alloys containing 30 wt % Na_2CO_3 or NaOH. Obviously, the quantitative precipitation of thorium, which determines the radioactivity of the REE concentrate, was achieved at pH = 4.4. Precipitation of aluminum, iron, titanium, manganese was relatively small, and REE losses are significant (6.7–7.5%). When neutralized to pH = 7.35, a high degree of REE precipitation was achieved with a low coprecipitation of alkaline earth elements, and upon neutralization with a NaOH allow, the entrainment of alkaline earth elements, especially strontium, in the REE concentrate slightly increased.

Table 28

Precipitation performance upon neutralization with $NaNO_3$ alloys containing 30 wt % of sodium carbonate or hydroxide

pH	Precipitation degree, %									
	Al	Ti	Fe	Mn	Th	U	∑Tr	Mg	Ca	Sr
Alloy 70 % $NaNO_3$ + 30 % Na_2CO_3										
0.4–4.4	25.6	38.8	30.6	12.2	92.6	46.3	6.7	12.8	0.08	0
4.4–7.35	71.2	3.4	4.8	0	4.3	0	93.1	4.0	0.39	0.03
7.35–10	0.6	0	48.8	86.7	2.0	17.1	0.2	83.1	99.43	99.87
0.4–10	97.4	42.2	84.2	98.9	98.9	63.4	100	99.9	99.9	99.9
Alloy 70 % $NaNO_3$ + 30 % NaOH										
0.5–4.4	50.8	34.1	53.9	32.6	98.9	61.0	7.5	15.4	0.47	0.27
4.4–7.35	42.7	8.8	8.0	10.6	0.8	3.6	92.4	7.6	0.12	0
7.35–10	2.6	3.9	33.4	56.7	0.2	34.2	0.1	76.9	99.31	99.63
0.5–10	96.1	46.8	95.3	97.9	99.9	98.8	100	99.9	99.9	99.9

So, in order to achieve effective separation of the components contained in the solution into group concentrates, it is advisable to first neutralize the solution with concentrated Na_2CO_3 or NaOH solutions to pH = 1.6–1.8, continue neutralization with a $NaNO_3$-Na_2CO_3 alloy with pre-eutectic Na_2CO_3, precipitating thorium cake at pH = 4.4, and then precipitate the REE concentrate at pH = 7.35, neutralizing the solution with $NaNO_3$-Na_2CO_3 or $NaNO_3$-NaOH alloys containing up to 30 wt % of the neutralizing reagent. Precipitation of alkaline earth metals at pH = 10 should be carried out with solid Na_2CO_3 or NaOH or their concentrated solutions.

A calculation based on the above experimental data shows that the recovery of REE into the carbonate or hydroxide concentrate is not less than 98.6 % at a $\sum Tr_2O_3$ content relative to the sum of oxides of controlled cations ∑Tr ≈ 96.5 % and a specific effective radioactivity of the calcined sum of oxides of less than 400 $Bq \cdot kg^{-1}$.

Thus, the study of hydrolytic precipitation at room temperature from eluates based on 5 M solutions of sodium salts showed that neutralization with solutions of sodium or sodium hydroxide does not provide efficient separation of REEs from the alkaline earth metals, aluminum, titanium, manganese, iron, thorium, uranium contained in the eluates.

For effective hydrolytic precipitation of group concentrates, including REE concentrate, it is proposed to use Na_2CO_3- or NaOH-containing salt alloys for neutralization. The use of such alloys made it possible to significantly improve the separation performance of components into group concentrates, supporting a reduction in REE losses during the precipitation of thorium cake from 98.2–99.6 % to 1.16 % and high performance of REE separation from alkaline earth metals.

2.4 Regeneration of sorbent in Na^+-form into sorbent in H^+-form

We studied the conversion of the sulfocationite KU-2-8 in Na^+ form to H^+ form. Sorbent in Na^+ form was placed in a column 600 mm high and 15 mm in diameter. The voids in the sorbent layer were filled with water, then a solution of nitric acid of a given concentration was passed at a consumption of 1 column volume per hour, which corresponded to a linear flow velocity of the acid solution relative to the sorbent of ≈ 1.8 $m \cdot h^{-1}$. The eluate was collected in batches and sodium concentrations were determined by flame photometry and free acid titration. The results are shown in Table 29.

The data in Table 29 allowed to calculate the recovery of sodium in the eluate (Fig. 4).

Table 29

Dependence of the composition of the resulting eluates on the concentration of nitric acid and the consumption of the eluting solution

V_{sol}:V_{sor}	Concentrations $NaNO_3$ and HNO_3 in eluates (g l^{-1}) at the initial C_{HNO_3} (wt %)							
	5		7.5		10		15	
	C_{NaNO_3}	C_{HNO_3}	C_{NaNO_3}	C_{HNO_3}	C_{NaNO_3}	C_{HNO_3}	C_{NaNO_3}	C_{HNO_3}
0–0.35	23.22	35.60	22.40	56.57	22.40	68.92	8.72	8.84
0.35–0.85	–	–	–	–	–	–	167.53	31.16
0.85–1.35	46.23	14.11	76.17	21.42	98.35	30.87	111.93	83.75
1.35–1.85	–	–	–	–	–	–	11.24	150.9
1.85–2.35	51.16	14.11	52.89	39.06	43.24	72.58	1.73	161.4
2.35–3.35	25.72	33.52	7.68	72.45	0.68	105.4	–	–
3.35–3.55	12.20	40.63	–	–	0.08	105.4	–	–

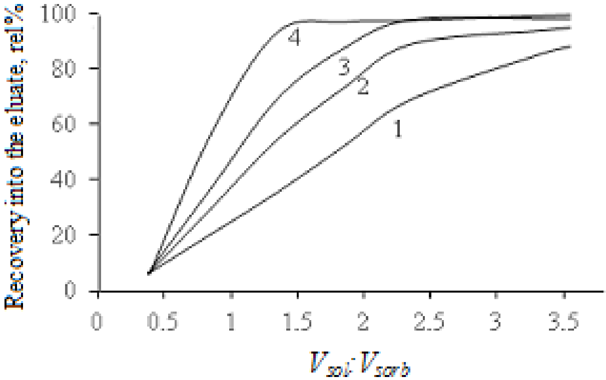

Figure 4. Dependence of sodium recovery into the eluate on the consumption and the concentration of acid used for elution. Acid concentration (wt %): 1 — 5, 2 — 7.5; 3 — 10, 4 — 15

The results show that 10–15 wt % HNO_3 solutions is achieved by effective conversion (> 97 %) with a high utilization of the acid (≈ 62 %) and obtaining sufficiently concentrated solutions of $NaNO_3$. At C_{HNO_3} = 15 wt %, the consumption of the eluting solution was only 1.85 times higher than the volume of the sorbent, and the resulting eluate contained 80.2 $g \cdot l^{-1}$ $NaNO_3$ and 73.5 $g \cdot l^{-1}$ HNO_3.

Conducting the process in countercurrent will ensure the production of eluates containing at least 167 $g \cdot l^{-1}$ $NaNO_3$ and no more than 31.2 $g \cdot l^{-1}$ HNO_3 by increasing the utilization of HNO_3 up to ≈ 80 %.

Regeneration of NaOH and HNO_3 by electrodialysis is possible [51]. In this case, the process can be carried out either in a three-chamber electrodialyzer or in a two-chamber one. In the latter case, it is not necessary to achieve complete extraction of the sodium cation from the nitric acid solution, since nitric acid is used (see section 2.5) in those circuits where residual sodium does not interfere with the use of nitric acid solution.

2.5 Schematic process flow diagram for apatite concentrate

The research results made it possible to propose a schematic process flow for the integrated processing of apatite concentrate to produce phosphoric acid, rare earth concentrate, fluorine compounds, calcium carbonate, and strontium concentrate (Fig. 5).

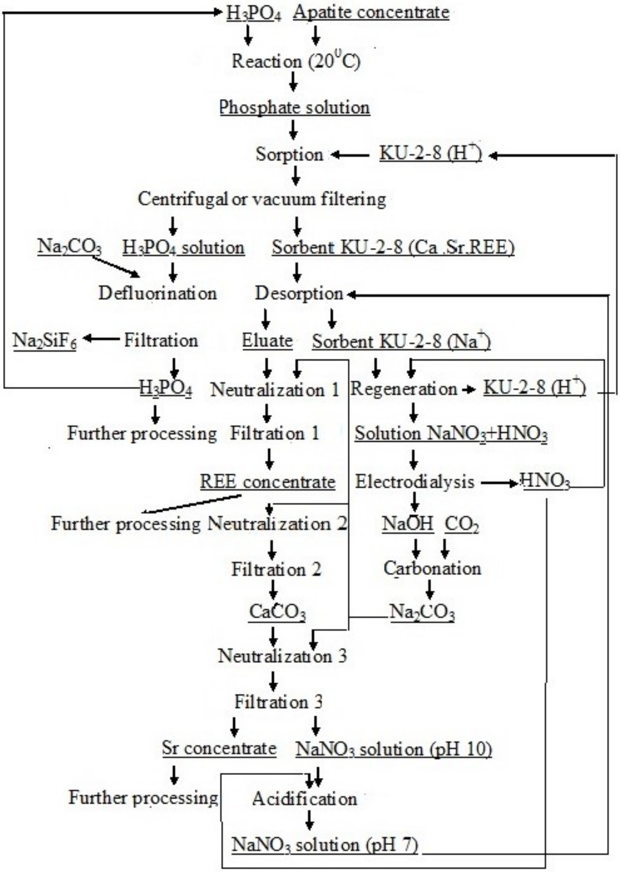

Figure 5. Schematic flow diagram for the processing of apatite concentrate

The diagram in Figure 5 does not show evaporation of the excess part of the sodium nitrate solution used for elution and preparation of sodium nitrate alloys with sodium carbonate. When developing the process flow, published literature on phosphoric acid defluorination was used [52].

The low content of impurities in phosphoric acid allows it to be used not only for the production of phosphate fertilizers, but also other saleable products, for example, feed calcium phosphates or sodium tripolyphosphate, whose production from the phosphoric acid produced in Russia requires its additional treatment.

Only to produce high grade tricalcium phosphate (to GOST 23999-80), in which the arsenic content should not exceed 0.0001 wt %, is additional treatment of phosphoric acid to remove arsenic impurities necessary, which can be carried out with sodium sulfide [53] or hydrogen sulfide [54].

From the experimental data and data on the composition of the apatite concentrates, it follows that decomposition of 1 ton of the Khibiny apatite concentrate requires no more than 13.8 m^3 of the sorbent KU-2-8 and 15.2 m^3 to decompose the Lovozero concentrate.

In the experiments, complete decomposition of the concentrate was carried out by mixing the concentrate and sorbent placed in the phosphoric acid solution. To prevent mechanical breakage of the sorbent, the lab-scale plant shown in Figure 1 was developed and successfully tested, in which concentrate dissolution and sorption from the phosphoric acid solution took place in different vessels: for the phosphate decomposition of the apatite concentrate, an agitated reactor was used, while for sorption, a column was used, into which the phosphoric acid solution saturated with the concentrate components was pumped from the reactor.

After saturation of the sorbent, the feed of the phosphoric acid solution to the column stopped, and the sorbent was sent to centrifugal or vacuum filtration, which ensured the removal of the phosphoric acid solution from the intergranular space of the sorbent. Judging by the amount of calcium, strontium, REE entering the solution during washing of the sorbent with water (alkali metal impurities begin to desorb when washed with water), the phosphate solution remaining in the sorbent contains 0.003–0.05% of the content of these metals in the apatite concentrate.

The recovery of REEs from eluates into non-radioactive rare earth carbonate concentrate reached 98.6 %. After calcination, it contained more than 78 wt % $\sum Tr_2O_3$ (the main impurities were oxides of alkaline earth elements) at $A_{eff.} \approx 0.035$ KBq·kg^{-1}.

Thus, the theoretical foundations of a new apatite concentrate process have been developed, whose advantages are as follows:

– high degree of complexity of using raw materials to produce phosphoric acid or products based on it, fluorine compounds, REE concentrate, calcium carbonate and strontium concentrate,

- — the resulting phosphoric acid has a much higher purity grade than commercial extraction process-based phosphoric acid,
- — high recovery of REEs, including yttrium and lanthanides of the medium and heavy groups,
- — low reagent consumption,
- — energy efficiency, as the majority of process operations (decomposition of the apatite concentrate, processing of sorbent and eluate) take place at room temperature,
- — zero harmful gaseous emissions, including fluorine and ammonia compounds,

— low generation of waste in the form of non-decomposable accessory minerals of the apatite concentrate (aegirine, feldspars),

— the possibility of specifying cheaper materials for the process equipment, whose corrosion rate is reduced due to the low process temperature.

2.6 Removal of phosphorus impurities from iron ore concentrates

Iron ore concentrates from a number of deposits may have an elevated phosphorus level due to the presence of apatite in the run-of-mine ores. Such concentrates are produced by Kovdor GOK (Russia), in Kiruna (Sweden), China, South Africa, and other countries. The most common phosphorus treatment are acid-based methods where the apatite is dissolved with nitric or sulfuric acid [55, 56]. In the process of dephosphorization, sulfuric or nitric acid is consumed and phosphate-containing sulfate or nitric acid solutions are obtained, whose disposal is problematic.

Disposal of solutions can be greatly simplified by using low concentrated phosphoric acid solutions to dissolve apatite. Table 30 shows the data on the equilibrium concentrations of calcium and some REEs achieved during the interaction at 20 °C of the Khibiny apatite concentrate containing 1.05 wt % $\sum Tr_2O_3$ in solution containing 0.94–5.03 wt. % H_3PO_4.

Table 30

Effect of the concentration of phosphoric acid on the decomposition of apatite at 20 °C

Experiment	$C_{H_3PO_4}$, wt %	Equilibrium concentration in solution, mg·l^{-1}		
		CaO	La_2O_3	Ce_2O_3
1	0.94	798	≤0.005	≤0.005
2	3.15	2674	14.1	16.4
3	5.03	4816	18.8	19.9

It can be seen that with increasing concentration of H_3PO_4 the equilibrium concentration of calcium in the solution increased rapidly. Unlike calcium, REE dissolution is problematic due to the low solubility of their phosphates in phosphoric acid solutions. However, at least at $C_{H_3PO_4} \geq 3.15$ wt % REE concentration is sufficient for effective absorption by sorbent. Moreover, in the process, phosphoric acid is not consumed, and its amount and concentration will increase.

Thus, the use of the sorption conversion method based on phosphoric acid solutions seems promising for the treatment of iron ore concentrates to remove phosphorus impurities.

3. IMPROVING THE SORPTION EXTRACTION OF REE FROM NATURALLY OCCURRING AND ANTHROPOGENIC RARE EARTH MINERAL FEEDS

3.1 Processing of ancylite products

Deposits of ancylite carbonatites are known in the US (Bear Lodge rare earth deposit, Wyoming), Russia (Vuorijarvi, Murmansk Region). Ancylite is not yet used in industry. Although ancylite predominantly contains REE of the cerium group, a rather high content in ore (up to 20 wt % of the sum of REE oxides), relatively low radioactivity and the possibility of ore concentration to produce concentrates rich in REE [57] explain the interest in developing a process for producing rare-earth products from this type of mineral feed. The possibility of using the sorption conversion method to extract REE from ancylite-containing carbonatite mineral feeds was investigated.

Ancylite concentrate was produced using a proprietary process at the Mining Institute of the Federal Research Center at the Kola Research Center of the Russian Academy of Sciences from an ore sample collected from the Vuoriyarvi deposit (Russia). The compositions of the ore and concentrate are shown in Table 31. Compared to the initial ore, the ancylite concentrate contained almost 4 times more REE and 2 times more strontium, but much less magnesium, calcium, barium, alkali metals. The ratio of strontium and REE in the ore and concentrate shows that a significant share of strontium in ancylite is apparently substituted by calcium.

Concentrate mass loss on ignition (1000 °C) was 28.7 %. A_{eff} of the ore sample was 0.68 $KBq\cdot kg^{-1}$, of the ancylite concentrate 0.60 $KBq\cdot kg^{-1}$.

It was taken into account that due to the high content of alkaline earth metal carbonates, especially strontium and barium, using of sulfuric acid could prove to be problematic. In the case of nitric acid, a much more thorough washing of the solid waste to be disposed of may be required since according to the standards adopted in the Russian Federation, the permissible content of nitrate ion in surface waters is much lower than that of chloride ion. Sorption conversion was studied in dilute hydrochloric acid. It was assumed that the decomposition of ancylite took place according to the reaction:

$$SrCe(CO_3)_2(OH)\cdot H_2O+5HCl \rightarrow SrCl_2 + CeCl_3 + 2CO_2\uparrow+3H_2O. \qquad (17)$$

Similarly, other carbonates contained in the ore interact with the formation of carbon dioxide. The ease of interaction of alkaline earth and rare earth metal carbonates with hydrochloric acid, the high solubility of the formed salts in aqueous media suggested that the decomposition of ancylite with a low concentrated acid solution (C_{HCl} = 1–2 wt %) can be achieved at room temperature.

Table 31

Content of oxides of the main metal components and phosphorus
in the ancylite ore (product 1) and its concentrate (product 2)

Product	Content, %							
	Y_2O_3	La_2O_3	Ce_2O_3	Pr_2O_3	Nd_2O_3	Sm_2O_3	Eu_2O_3	Gd_2O_3
1	0.0069	2.85	3.53	0.255	0.606	0.041	0.0077	0.102
2	0.0099	10.2	14.0	1.16	2.83	0.171	0.0286	0.331
	Tb_2O_3	Dy_2O_3	Ho_2O_3	Er_2O_3	Tm_2O_3	Yb_2O_3	Lu_2O_3	$\sum Tr_2O_3$
1	0.0029	0.0024	0.00027	0.0036	0.00052	0.00080	0.000025	7.41
2	0.0152	0.0077	0.00079	0.0010	0.0063	0.00055	0.000083	28.76
	Na_2O	K_2O	MgO	CaO	SrO	BaO	Al_2O_3	
1	0.26	0.49	12.6	27.1	3.74	3.42	0.17	
2	0.10	0.12	2.86	9.8	7.21	1.28	0.052	
	TiO_2	Fe_2O_3	MnO	ThO_2	UO_2	P_2O_5	SiO_2	
1	0.10	2.64	0.80	0.0022	0.0063	0.46	2.44	
2	0.17	3.08	0.23	0.018	0.00039	0.1	1.43	

The use of such solutions supported the sorption of the dissolved cations and ensured the rate of decomposition of the concentrate, which excluded the foaming of the slurry by the released carbon dioxide. This made it possible to avoid preliminary calcination, which is usually used in the acid decomposition of rare-earth carbonate raw materials [58].

Data on the effect of the process conditions on the decomposition performance of ancylite products by sorption conversion is shown in Table 32. The distribution of cationic ore components between the products obtained in experiment 2 is shown in Table 33. The numbering of the experiments in Table 32 is kept in Tables 34, 36 and 37 below.

From the data in Tables 32 and 33, it can be seen that the decomposition of ore at room temperature 1 wt % HCl, added at 41 % of the stoichiometrically necessary amount, allowed to recover 93.18% REE into the sorbent. There was a high degree of absorption by the sorbent of most cationic ore components, including thorium and uranium.

Our calculation using the data in Table 33 showed that the sorbed metals filled no more than 64% of the sorption exchange capacity of the sorbent. Since it is possible to achieve a higher utilization degree of the SEC with the acid concentration used, it was concluded that sorption did not limit the completeness of the process.

Table 32

Conditions during the ancylite ore and concentrate processing experiments

Experiment	Product	C_{HCl}, Wt %	L:S	t, °C	α, %	ß, %	Time, h	Solid residue mass, rel %
1	Ore	1	20	20	27.4	144	4	13
2	Ore	1	30	20	41.0	144	2	6.7
3	Concentrate	2	20	20	84.3	152	4	14.1
4	Concentrate	2	20	20	84.3	208	4	14.0
5	Concentrate	1	20	50	42.1	152	4	8.5

Table 33

Distribution of cationic ore components between the products obtained in experiment 2: 1 — sorbent, 2 — solution, 3 — residue of undecomposed minerals

Product	Entered the product, rel%							
	Y	La	Ce	Pr	Nd	Sm	Eu	Gd
1	84.51	93.41	93.24	93.62	91.70	88.79	87.94	95.06
2	2.78	0.56	0.63	0.75	1.00	1.31	1.40	0.53
3	12.71	6.03	6.13	5.63	7.30	9.90	10.66	4.41
	Tb	Dy	Ho	Er	Tm	Yb	Lu	∑Tr
1	89.55	79.67	85.19	89.85	<80.77	85.00	78.06	93.18
2	1.04	3.81	3.70	0.84	-	2.50	0.90	0.64
3	9.41	16.52	11.11	10.06	19.23	12.50	20.4	6.18

	Na	K	Mg	Ca	Sr	Ba
1	66.87	95.83	89.84	94.20	97.47	82.90
2	25.38	0.76	5.41	3.20	1.76	0.18
3	7.75	3.41	4.75	2.60	0.77	16.92
	Al	Fe	Mn	Ti	Th	U
1	79.43	77.08	90.98	87.98	90.74	93.54
2	18.88	3.99	4.76	5.16	4.63	0.24
3	1.69	18.93	4.26	6.86	4.63	6.22

In the undecomposed residue (wt %): 6.85 $\sum Tr_2O_3$, 0.30 Na_2O, 0.25 K_2O, 8.92 MgO, 10.51 CaO, 0.43 SrO, 8.65 BaO, 0.043 Al_2O_3, 0.10 TiO_2, 7.47 Fe_2O_3, 0.51 MnO. Thus, the REE content in the residue was quite high. The residue is enriched in barium, iron and manganese, depleted in other alkaline earth elements.

The ratio of individual REEs in the sorbent and the residue of undecomposed minerals was different: losses with the remainder of the REEs of the medium and yttrium groups (10.06–20.4 rel %) were several times greater than of the REEs of the cerium group (5.63–7.3 rel %). This suggests that some of the REEs in the ore are associated not with ancylite, but with other, more difficult to unlock minerals.

Ancylite concentrate was somewhat more difficult to decompose than ancylite ore. A comparable degree of decomposition was achieved by increasing either the HCl concentration to 2 wt % or the temperature to 50 °C (see experiments 3–5 in Table 32). The degree of decomposition of the concentrate at a temperature of 20 °C did not exceed 86 % even with an increase in the consumption and concentration of HCl, as well as the consumption of the sorbent (experiments 3 and 4). The increase in sorbent consumption, all other things being equal, did not increase the degree of decomposition of the concentrate (experiments 3 and 4 in Table 32), therefore, the process was limited not by sorption, but by the performance of the chemical interaction of the concentrate with the acid solution.

At a temperature of 50 °C, despite the decrease in the consumption and concentration of acid, as well as the consumption of sorbent, the mass of the undecomposed residue is almost 2 times less than at a temperature of 20 °C (experiment 5 in Table 32).

Table 34

Metal content in the mother liquor obtained by sorption conversion of ancylite ore and concentrate

Experiment	Concentration, mg·l^{-1}							
	Y_2O_3	La_2O_3	Ce_2O_3	Pr_2O_3	Nd_2O_3	Sm_2O_3	Eu_2O_3	Gd_2O_3
1	0.12	2.57	4.85	0.32	1.26	0.074	0.010	0.062
2	0.064	5.31	7.39	0.64	2.03	0.18	0.036	0.180
5	0.039	3.57	5.53	0.47	1.30	0.10	0.019	0.114
	Tb_2O_3	Dy_2O_3	Ho_2O_3	Er_2O_3	Tm_2O_3	Yb_2O_3	Lu_2O_3	$\sum Tr_2O_3$
1	0.0038	0.0066	0.0009	0.0025	0.0002	0.0012	0.0001	9.3
2	0.010	0.031	0.002	0.007	0.0005	0.006	0.001	15.9
5	0.007	0.012	0.001	0.002	0.0003	0.0022	0.0003	11.2
	Na_2O	K_2O	MgO	CaO	SrO	BaO	Al_2O_3	TiO_2
1	19.9	2.03	249	268	28.5	1.7	3.1	3.57
2	22.0	1.25	226	289	22.0	2.05	10.7	1.72
5	17.8	9.31	49.1	120.7	59.7	2.68	1.73	0.89
	Fe_2O_3	ZrO_2	HfO_2	Nb_2O_5	Ta_2O_5	MnO	ThO_2	UO_2
1	50.6	0.27	0.005	0.05	0.004	14.5	0.019	0.003
2	35.1	0.20	0.01	0.31	0.001	12.7	0.019	0.005
5	40.5	0.34	H.a.	0.056	0.0013	3.02	0.022	0.0061

The cations contained in the mother liquors (Table 34) neutralize no more than 10 % of the acid contained. Therefore, firstly, the incomplete leaching of rare earth elements is not controlled by the lack of acid, and secondly, such solutions can be used for the decomposition of ancylite ore and concentrate.

The distribution of cationic ore components between the products obtained in experiment 5 is shown in Table 35.

Table 35

Distribution between products during sorption conversion of ancylite concentrate: product 1 — sorbent, product 2 — liquid phase; product 3 — undecomposed mineral residue

Product	Entered the product, rel %							
	Y	La	Ce	Pr	Nd	Sm	Eu	Gd
1	78.79	94.33	93.93	93.44	92.51	90.53	92.87	93.59
2	1.01	0.07	0.08	0.09	0.11	0.11	0.14	0.07
3	20.20	5.60	5.99	6.47	7.38	9.36	6.99	6.34
	Tb	Dy	Ho	Er	Tm	Yb	Lu	∑Tr
1	94.27	86.29	88.36	91.00	83.10	73.82	75.18	93.83
2	0.07	0.26	0.25	0.35	1.00	0.73	0.72	0.08
3	5.66	13.45	11.39	8.65	15.90	25.45	24.10	6.05
	Na	K	Mg	Ca	Sr	Ba	Al	Fe
1	45.90	72.94	96.15	95.37	97.46	74.01	69.18	51.67
2	33.90	15.63	3.43	2.47	1.66	0.42	6.59	2.63
3	20.19	11.43	0.42	2.16	0.88	25.57	24.23	45.70
	Mn	Ti	Zr	Nb	Ta	Th	U	∑Tr
1	77.03	51.28	51.87	49.33	53.00	94.31	58.41	93.87
2	2.59	1.03	41.88	0.35	1.44	0.22	3.13	0.08
3	20.39	47.69	6.25	50.32	55.56	5.47	38.46	6.05

The main patterns of sorption conversion of ancylite ore and concentrate are the same. The undecomposed residue contained (wt %): 20.5 $\sum Tr_2O_3$, 0.25 Na_2O, 0.16 K_2O, 0.14 MgO, 2.49 CaO, 0.75 SrO, 3.86 BaO, 0.15 Al_2O_3, 0.97 TiO_2, 16.6 Fe_2O_3, 0.56 MnO. The residue is enriched in barium, iron, titanium and manganese and depleted in strontium and REEs, apparently due to the accumulation of non-decomposable accessory minerals in the process. $SrO:Tr_2O_3$ molar ratio ∑in the ore, concentrate, and the resulting undecomposed mineral residue was, respectively, 0.62, 1.25, 0.2 and 0.012. Thus, selective leaching of strontium from ancylite occurs during the acid treatment. This is confirmed by the XRD results of the undecomposed mineral residue in experiment 3 (Fig. 6), in which no ancylite was found, but REE carbonate was found.

Our calculation using the data in Table 5 showed that the sorbed metals filled no more than 54% of the sorption exchange capacity of the sorbent.

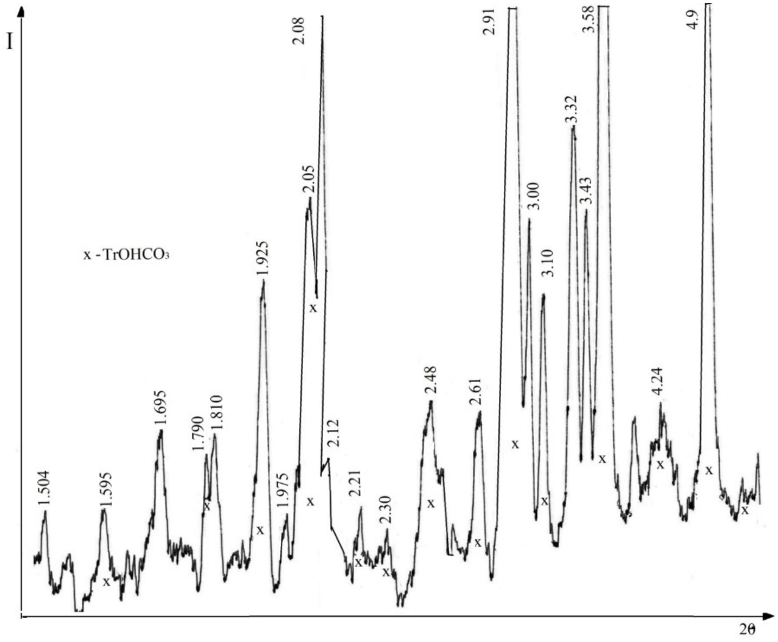

Figure 6. X-ray diagram of the undecomposed mineral residue

The mother liquor (composition as given in Table 34) is neutralized by the cations contained in it by only 2.6 %. The lower degree of neutralization than in experiments 1 and 2 was determined by lower concentrations of magnesium and calcium. The possibility of using this solution is beyond doubt.

Table 36 shows the values of the distribution coefficients $K_{(s)}$.

Table 36 shows that REEs, barium, and uranium had the highest sorption performance. Sorption of alkali metals deteriorates with increasing temperature from 20 to 50 °C and HCl concentrations from 1 to 2 wt %. Sorption of magnesium, calcium, REEs, manganese, thorium with increasing temperature increases, but decreases with increasing acidity of the solution. Multiple decrease in a more acidic solution of $K_{(s)}$ in aluminum, manganese, and uranium is probably due to the partial formation under these conditions of anionic chloride complexes.

Table 36

Component distribution coefficients during sorption conversion in low concentrated hydrochloric acid solutions

Experiment	C_{HCl}, wt %	V_{sol}: V_{sorb}	t, °C	$K_{(s)}$							
				Na	K	Mg	Ca	Sr	Ba	Al	Fe
1	1	1.25	20	5.4	142	27.3	59.5	79	836	25.9	24.5
2	1	1.875	20	5.0	237	31.2	55.2	104	864	8.0	36.2
5	1	1.67	50	2.3	7.8	46.7	64.4	97.8	294	17.5	32.7
3	2	1.82	20	0.93	2.7	4.2	9.0	14.2	73.9	0.28	32.4
				∑Tr	Ti	Zr	Nb	Ta	Mn	Th	U
1	1	1.25	20	429	13.7	12.2	20.1	N.a.	30.3	65.2	1174
2	1	1.875	20	273	32.0	19.4	2.9	N.a.	35.8	36.7	731
5	1	1.67	50	1956	83.0	2.0	235	61.3	208	714	31.1
3	2	1.82	20	198	26.0	4.5	19.7	0.56	3.9	37.4	0.40

The metal content in terms of oxides in the resulting sorbents is shown in Table 37.

Sorbent processing can be carried out according to a method similar to that developed for processing apatite concentrates. Although the desorption of thorium with a 5 M NaCl solution is problematic, its content in the sorbents, as can be seen from the data in Table 37, is low: max 0.014 and 0.2 % of the sorption exchange capacity of the sorbent during ore and concentrate processing, respectively, is bound per cycle. It is advisable to carry out desorption of thorium as it is accumulated woth a solution heated to 80 °C.

Table 37

Metal content in sorbents

Experiment	Content, $g \cdot l^{-1}$						
	Tr_2O_3	Na_2O	K_2O	MgO	CaO	SrO	BaO
2	4.316	0.109	0.294	7.047	15.943	2.278	1.772
5	22.496	0.029	0.072	2.292	7.764	5.856	0.790
	Al_2O_3	TiO_2	Fe_2O_3	MnO	ThO_2	UO_2	Total
2	0.084	0.005	1.272	0.455	0.0012	0.0037	33.58
5	0.030	0.074	1.326	0.147	0.014	0.0002	40.90

It was found that after dissolving the sum of alkaline earth metal carbonates in nitric acid from the resulting solution by introducing stoichiometric amounts of

Na_2SO_4 first on $BaSO_4$ and then on $SrSO_4$ formations, barium and strontium concentrates can be sequentially isolated.

In terms of the specific effective radioactivity of the ore, concentrate, intermediate and resulting products belong to class I materials containing natural radionuclides, which can be used in an industrial context without restrictions [59]. The radioactivity of thorium-containing cake may be elevated.

Thus, a method has been proposed for processing ancylite ore and ancylite concentrate, characterized by a low consumption of reagents and zero liquid waste. The expediency of directly processing ancylite ore or concentrating it first can be assessed after optimization and verification of the process including an economic analysis of both options. When the concentrate is processed, the required scope of equipment and the cost of chemical processing are reduced, however, the concentration of ancylite ore is challenging, while REE losses reach 50 rel % [57].

3.2 Processing of bastnaesite concentrate

Bastnaesite concentrates are some of the key sources of REE used by the global industry. They are characterized by a high REE content, mainly of the cerium group. Bastnaesite is a fluorocarbonate (Ce, La, Y) CO_3F. Its processing primarily requires defluorination in order to exclude the formation of poorly soluble REE fluorides during the subsequent acid dissolution.

Information on the processing methods of bastnaesite concentrates is summarized in [58]. For decomposition, sintering with concentrated H_2SO_4 at 480 °C has been proposed, and in some cases, has industrial applications, chlorination at 1000–1200 °C, calcination for CO_2 removal and Ce^{3+} oxidation to Ce^{4+} at a temperature of 620 °C or 800–900 °C followed by leaching, respectively, with hydrochloric or nitric acid.

Sulfuric acid bastnaesite concentrate decomposition process is used in China. Its disadvantages are increased consumption of reagents (sulfuric acid, hydroxide or sodium carbonate), the formation of a large amount of a solution requiring disposal and containing impurity sulfates and part of thorium, increased energy consumption due to the high temperature of the sulfuric acid treatment process, the need to capture of fluorine compounds from the gas phase.

The transition of fluorine to the gas phase can be eliminated by using hydrometallurgical decomposition methods. In the process implemented by Molykorp, US, pre-calcined at 620 °C concentrate is leached with 20 wt % HCl for 4 hours at 95 °C. The consumption of 100 % HCl was 0.5 kg per 1 kg $\sum Tr_2O_3$, while part of the REEs passed into the solution, and part in the form of fluorides remained in the residue. REE fluorides were converted to hydroxides by treatment with a NaOH solution at 0.73 kg NaOH per 1 kg $\sum Tr_2O_3$. The reaction equations are given below [60]:

$$TrCO_3F + 9HCl \rightarrow \downarrow TrF_3 + 2TrCl_3 + 3HCl + 3H_2O + 3CO_2\uparrow; \qquad (13)$$

$$TrF_3 + 3NaOH \rightarrow \downarrow Tr(OH)_3 + 3NaF; \qquad (14)$$

$$Tr(OH)_3 + 3HCl \rightarrow TrCl_3 + 3H_2O. \qquad (15)$$

REE recovery was about 94%. The disadvantages of the process include the significant consumption of hydrochloric acid and sodium hydroxide and, as a consequence, the formation of a large quantity of fluorine-containing hydrochloric acid and alkali solutions requiring disposal.

In our sorption conversion studies, we used bastnaesite concentrate by Mountain Pass, US, the chemical composition of which is given in Table 38, sulfocationite KU-2-8chS, and acids: H_2SO_4, HNO_3, HCl.

Table 38

Chemical composition of the bastnaesite concentrate

Content, wt %							
Y_2O_3	La_2O_3	Ce_2O_3	Pr_2O_3	Nd_2O_3	Sm_2O_3	Eu_2O_3	Gd_2O_3
0.0563	24.02	33.16	2.619	7.797	0.475	0.0701	0.778
Tb_2O_3	Dy_2O_3	Ho_2O_3	Er_2O_3	Tm_2O_3	Yb_2O_3	Lu_2O_3	ΣTr_2O_3
0.0398	0.0233	0.00299	0.00577	0.00024	0.00338	0.00024	69.05
Li_2O	Na_2O	K_2O	MgO	CaO	SrO	BaO	ZnO
0.0073	1.01	0.89	0.30	3.76	4.33	2.51	0.0045
Al_2O_3	TiO_2	ZrO_2	PbO	Nb_2O_5	Sb_2O_5	WO_3	MnO
0.074	0.0018	0.00087	0.11	0.0033	0.0036	0.0018	0.043
Fe_2O_3	NiO	ThO_2	UO_2	CO_3^{2-}	P_2O_5	F	SO_4^{2-}
0.47	0.0016	0.116	0.0134	26.5	1.02	3.05	1.47

gE of cations in 1000 g of concentrate									
Na_2O	K_2O	MgO	CaO	SrO	BaO	Fe_2O_3	ΣTr_2O_3	ThO_2	Σ
0.33	0.19	0.15	1.34	0.83	0.33	0.18	12.55	0.02	15.92

In bastnaesite concentrate $A_{eff} \approx 5$ KBq kg^{-1}. According to the standards adopted in the Russian Federation, this concentrate is classified in class IV as a material with a high content of natural radionuclides [59].

The main ore minerals in the Mountain Pass deposit are: calcite (40 %), barite-celestine (25 %), strontianite (10 %), bastnaesite (12 %), quartz (5 %) [9]. According to X-ray phase and crystal-optical analysis, bastnaesite $(Ce,La)(CO_3)F$, strontianite $SrCO_3$ and probably datsinshanite $(Ce)(Sr,Ca,\ Ba)_3(Ce,La)(PO_4)(CO_3)_{3-x}(OH,F)_x$ were found in the bastnaesite concentrate. Judging by the fluorine content, the bulk of the concentrate is hydroxyl bastnaesite. It was assumed that bastnaesite and most accessory minerals (with the exception of quartz) will interact with low concentrated solutions of mineral acids, which will allow the use of the sorption conversion method for processing the concentrate.

Judging by the particle size distribution composition of the concentrate (2.5 % +0.1 mm, 27.9 % +0.07 mm, 15.8 % +0.04 mm, 53.8 % -0.04 mm), it was assumed that no regrinding was required.

Experimental conditions: medium — 1 — 2 wt % H_2SO_4, 2.0 — 2.5 wt % HNO_3; KU-2-8chS sorbent consumption in H^+ form ß = 125 — 450 %; volume ratio of the acid solution to the concentrate mass L:S = 50. H_2SO_4 quantity amounted to 96–128 % of the stoichiometrically necessary for the sulfatization of rare earth and alkaline earth elements, HNO_3 100–125 %. As expected, the increase in acid consumption did not affect the decomposition performance of the bastnaesite concentrate.

Preliminary experiments showed that, although at 20 °C the processing of bastnaesite concentrate is theoretically possible, increasing the temperature to 80 °C increases the degree of its decomposition with a 2 wt % H_2SO_4 solution by a factor of 1.4–1.45, with a 2.5 wt % HNO_3 solution by a factor of 2.2. Therefore, the process was carried out at a temperature of 80 °C. The treatment time of 4 hours was insufficient and was increased to 6 hours.

The evolution of carbon dioxide did not cause foaming, as decomposition of the concentrate with low concentrated acid solutions took place gradually, therefore there was no need for preliminary calcination.

Table 39

Recovery of cations into the sorbent during decomposition of the bastnaesite concentrate with an acid solution: 1 — 1.5 wt % H_2SO_4; 2 — 2 wt % H_2SO_4; 3 — 2.5 wt % HNO_3; 4 — 2.5 wt % HNO_3+15 $g{\cdot}l^{-1}$ F+7.5 $g{\cdot}L^{-1}$ H_3PO_4

Experiment	Recovery, %					
	Na	K	Mg	Ca	Sr	Ba
1	91.8	98.0	93.8	97.3	97.3	99.2
2	82.1	98.8	80.2	98.7	99.3	N.f.
3	85.8	97.2	92.9	96.4	96.6	99.4
4	89.1	83.3	88.4	88.9	90.0	98.3
	Al	ΣTr	Mn	Fe	Th	U
1	62.2	89.6	98.7	97.6	89.8	96.2
2	43.3	75.6	83.7	79.5	99.0	76.9
3	59.7	98.9	98.1	97.4	98.1	95.2
4	52.7	80.5	96.0	91.2	85.2	90.5

The degree of REE transition into the sorbent somewhat exceeded the mass loss during decomposition of the concentrate. This was determined by the fact that in the bastnaesite concentrate there are small amounts of difficult to decompose impurity minerals not containing REEs. Therefore, a rough estimate of the decomposition performance of the concentrate can be given based on the magnitude of the mass loss.

The recovery of cations into the sorbent under individual sulfuric and nitric acid treatments is presented in Table 39, the composition of the mother liquors in Table 40.

Table 40

Concentration in the mother liquor of metals, phosphorus and fluorine

Experiment	Concentration, $mg \cdot l^{-1}$						
	Na_2O	K_2O	MgO	CaO	SrO	BaO	Al_2O_3
1	11.7	2.9	2.5	14.5	15.6	1.3	3.8
2	16.4	2.2	2.6	11.4	N. f.	N. f.	7.0
3	15.1	4.4	0.1	21.7	23.7	2.4	5.6
4	11.3	27	5.3	58.1	60.3	6.6	8.4
	Tr_2O_3	MnO	Fe_2O_3	ThO_2	UO_2	P_2O_5	F
1	1.8	0.08	0.7	0.05	0.05	136.6	500
2	3.2	0.12	1.7	0.25	0.16	N. a.	N. a.
3	7.3	0.14	1.0	0.10	0.06	180.4	590
4	7.4	0.28	6.4	0.09	0.19	N. a.	N. a.

In the sulfuric acid process, a solution containing 1.5 wt % H_2SO_4 turned out to be the most effective: the degree of decomposition of the bastnaesite concentrate was 86 % with a REE recovery into the sorbent of 89.6 %. The degree of decomposition of the concentrate with a 2.0 wt % H_2SO_4 solution amounted to 82 %, 1.0 wt % H_2SO_4 75 % The difference in recovery between individual REEs was within the analysis method's error margin. When decomposed with a solution of 2 wt. % H_2SO_4, a decrease of ß from 300 to 125 % reduced the degree of decomposition from 82 to 75 %. However, reducing the sorbent consumption to 125–160 % made it possible to increase the REE concentration per 1 liter of the sorbent from 19.4 — 22.2 to 40.4 — 47.1 g, which greatly facilitates the subsequent processing of the sorbent.

The content in the sorbent of ThO_2 did not exceed 0.005, UO_2 0.0006 wt %. In terms of A_{eff} not exceeding 0.450 $KBq \cdot kg^{-1}$, saturated REE sorbents belong to class I materials with a high content of natural radionuclides, which can be handled in an industrial setting without restrictions [59].

When using a nitric acid solution with a concentration of 2.5 wt %, the decomposition degree of the concentrate was 98 % at ß = 450 % and 89 % at ß = 160 %.

Undecomposed residues are depleted in comparison with the initial bastnaesite concentrate in a number of components, especially calcium, strontium and thorium, and are slightly enriched in phosphorus (P_2O_5 in residues 1.32–1.45 wt %). X-ray phase analysis showed the presence of monazite in the residues, which was not unlocked by low concentrated sulfuric and nitric acid solutions. Judging by the amount of REE and phosphorus, the residue in experiment 3 practically did not contain bastnaesite. The amount of fluorine in the residues of sulfuric acid decomposition is proportional to the amount of REE, indicating the presence of undecomposed bastnaesite in these. The residue in experiment 3, containing only 34.4 wt % $\sum Tr_2O_3$, is slightly enriched in uranium and fluorine, which may indicate the presence in the bastnaesite concentrate of a small amount of a refractory accessory mineral containing uranium and fluorine.

The sorption of REE and most impurity cations had very high performance, explaining their low residual concentration in the mother liquors. A high degree of absorption by the sorbent of barium and strontium, the sulfates of which are poorly soluble in water, should be noted here. A_{eff} of the mother liquors does not exceed 0.003 KBq·kg^{-1}. The low metal content in the mother liquor (Table 40) shows that sorption does not limit the performance of the process. Therefore, a significant increase in the consumption of the sorbent had little effect on the degree of decomposition of the bastnaesite concentrate.

Using experimental data according to equation (2), the values of the distribution coefficients $K_{(s)}$ were calculated for the sorption conversion of the concentrate in sulfate and nitric acid conditions (Table 41).

Table 41

Values of $K_{(s)}$ during sorption conversion of bastnaesite concentrate in sulfate and nitric acid conditions

Experiment	$K_{(s)}$										
	Na	K	Mg	Ca	Sr	Ba	Al	Fe	Th	U	∑Tr
1	29.9	114	42.2	95	102	735	4.5	260	824	103	12900
2	19.1	147	32.9	123	–	–	1.7	89	191	18.3	6190
3	14.4	49	21.6	42	44	262	2.0	113	284	53	2350
4	19.8	6.9	12.5	14	16	94	3.7	17	309	17	1880

From the data of Table 41 it can be seen that sorption performance from those sulfate and nitric acid solutions that do not contain elevated concentrations of fluorine and phosphorus, is usually described by the following sequence: Tr>>Th≈Ba>Fe>Sr≈U≈Ca≈K>Mg>Na>Al. Minimal $K_{(s)}$ value of aluminum, which is a strong fluorine acceptor, indicates partial formation by it of fluorine-containing anion complexes.

Reducing $C_{H_2SO_4}$ from 2 to 1.5 wt % contributed to the increase of $K_{(s)}$ of REE and, as a consequence, an increase in the degree of decomposition of bastnaesite (experiments 1 and 2). Simultaneously, *K(s)* increased of many metals other than calcium and strontium.

In a 2.5 wt % HNO_3 solution, $K_{(s)}$ values of alkali, alkaline earth and rare earth metals are lower than in a 2 wt % H_2SO_4 solution. Decrease in $K_{(s)}$ is explained by increased concentration of hydrogen ion. Accumulation in the nitric acid solution of H_3PO_4 and fluoride ion (experiment 4) reduced $K_{(s)}$ of many elements, especially iron and uranium, due to the partial formation by these elements of difficult-to-sorb fluoride (fluorophosphate) complexes.

It was found that under similar conditions, the decomposition performance of the bastnaesite concentrate with nitric and hydrochloric acids was the same.

From the data in Table 40 it follows that the cations present in the solution neutralized only 0.3 rel % of H_2SO_4 and 0.6 rel % of HNO_3 in the solution. Thus, the metal content in the mother liquor is low and practically does not lead to a decrease in the concentration of acids used for decomposition. However, fluorine and phosphorus in the bastnaesite concentrate pass into the solutions: at a S: L ratio of 1:50, after 1 cycle the concentration in the mother liquor can reach a maximum of ($g \cdot l^{-1}$) 0.204 of P_2O_5 and 0.610 of fluorine. Accumulating in the mother liquor, fluorine and phosphorus should prevent the decomposition of bastnaesite, limiting the possibility of using acidic solutions in industrial processes.

In order to clarify the possibility of reuse of acidic solutions, the effect of accumulation of fluorine and phosphorus in acidic solutions on the decomposition performance of the bastnaesite concentrate was examined. When introducing into solutions 7.5 $g \cdot l^{-1}$ of H_3PO_4 and 15 $g \cdot l^{-1}$ of fluorine, the decomposition degree of the bastnaesite concentrate was 83 % for a 2.5 wt % HNO_3 solution and 75 % for a 2.0 wt % HNO_3 solution. Decomposition degree of the bastnaesite concentrate with a solution containing 2 wt % H_2SO_4, 15 $g \cdot l^{-1}$ fluorine and 7.5 $g \cdot l^{-1}$ H_3PO_4 at 80 °C was only 30 %, and at 95 °C 50 %. The difficulty in decomposing the bastnaesite concentrate during the accumulation of fluorine in the sulfuric acid solution is probably associated with a decrease in the acidity of the solution due to the formation of fluorosulfonic acid with the accumulation of fluorine [61]:

$$H_2SO_4 + HF \rightarrow HSO_3F + H_2O. \tag{16}$$

When processing the resulting residue with a 2 wt % H_2SO_4 solution containing 10 $g \cdot l^{-1}$ HF, the mass loss was 56 %, i.e. was slightly less than that observed under the same conditions when processing the initial bastnaesite concentrate (61 %). A slight decrease in the degree of decomposition during the processing of residues compared with the initial bastnesite concentrate is associated with an increase in the content of the refractory accessory minerals in them.

When processing a bastnaesite concentrate of the investigated composition and at the used ratio of the acid solution volume to the mass of the concentrate, a fluorine content of 15 $g \cdot l^{-1}$ achieved after ≈ 25 cycles, while the phosphorus content does not exceed 5 $g \cdot l^{-1}$. Therefore, repeated use of the acid solution allows to reduce the consumption of acids to ≤ 5 % of the stoichiometrically necessary.

Thus, the possibility was shown of decomposition of bastnaesite concentrate with low concentrated solutions of mineral acids: sulfuric (≤ 2 wt %), nitric (≤ 2.5 wt %) in the presence of sulfocationite in hydrogen form with absorption of REEs and a number of impurity cations by sulfocationite and the transition of fluorine into the acid solution.

Increasing the process temperature from 20 to 80 °C increases the rate of decomposition. Sulfuric and nitric acid decomposition at 80°C of the bastnaesite concentrate is achieved at a sorbent consumption of 125–160 % of the stoichiometrically necessary (11–14 m^3 per ton of concentrate), while the concentration of the sum of REE oxides in the sorbent exceeds 40 $g \cdot l^{-1}$.

The radioactivity of the obtained sorbent and solution is classified in class 1 of materials containing natural radionuclides, which allows handling in an industrial environment without restrictions.

The possibility of regeneration of mother liquors by partial neutralization of calcium carbonate is shown, which allows to further reduce the consumption of mineral acids and the amount of waste requiring disposal. At the same time, the performance of fluorine separation from nitric acid solutions is much higher than from sulfate solutions.

3.3 Processing of monazite concentrate

Monazite concentrate is an important source of REEs. This will determine the relevance of developing more efficient methods for its processing.

For the hydrochemical unlocking of monazite concentrate, the sulfuric acid method was the first to be applied. In various process variants, either REEs of the cerium group were recovered with separation from the bulk of thorium, or all REE and thorium. In this process, the disposal of the sulfate phosphate solution is problematic [58].

The alkaline method is more efficient, in which the monazite concentrate is treated with a heated to 120-140 °C NaOH solution with a concentration of 60–70 wt % [62, 63]. Optimal conditions for alkaline decomposition: 1 hour at 175 °C or 2.5 hours at 150 °C, NaOH solution concentration 500 $g \cdot l^{-1}$, NaOH consumption 150 % of stoichiometrically necessary. Na_3PO_4 and excess NaOH are leached from the high-temperature alkaline product with hot water to obtain hydroxide cake. A number of solutions have been proposed for the recovery of REE from the hydroxide cake with the separation of uranium and thorium into separate products. Acid methods include HCl, HNO_3 or H_2SO_4 cake leaching. From sulfate solutions, precipitation of double sodium sulfates and REEs is possible. When neutralizing hydrochloric and nitric acid solutions with sodium carbonate, precipitation of REE carbonates is possible with the retention of thorium and uranium in solution in the form of their double carbonates with sodium. Thorium and uranium peroxide complexes can be precipitated by introducing H_2O_2, where REEs remain in solution. By the introduction of oxalic acid, precipitation of REEs and thorium oxalates is possible, while uranium remains in solution in the form of $UO_2(C_2O_4)$ and can be isolated as $(NH_4)_2U_2O_7$. From the REE and thorium oxalate precipitate, the latter can be leached with a mixed solution of Na_2CO_3 and $NaHCO_3$ [62].

The disadvantages of the method are the high consumption of the quite expensive NaOH, the conversion of phosphorus to the moderately saleable Na_3PO_4, elevated temperatures of alkaline treatment and water leaching. In addition, if the monazite concentrate contains an admixture of manganese, cerium recovery is significantly reduced [58, 64].

It was proposed to sinter monazite concentrate with chloride and calcium carbonate in a reducing atmosphere (SO_2) at a temperature of 1250–1460K. REE leaching is carried out with a 3 wt % HCl solution. The leach residue contains chlorapatite and thorium oxide. The recovery of REE in solution reaches 89 %; thorium mainly remains in the leach residue in the form of ThO_2, but part of it enters the leach solution. Due to the reducing environment, the presence of manganese did not affect the REE recovery. The method is characterized by insufficiently high REE recovery, phosphorus loss, high sintering temperature, the need to provide and maintain a reducing atmosphere [65].

Recently, it has been proposed to dephosphorize monazite by sintering with soda [66], combining alkaline and mechanochemical treatment [62], and decomposing alkali metal nitrates in the melt [67]. Decomposition in the melt of nitrates is carried out at a temperature of 400–900 °C, phosphorus removal is carried out by separating the clarified phase of the melt and/or leaching of alkali metal phosphate (Na or K) in an aqueous solution.

Thus, the known processes are carried out at high temperatures, which determines the complexity of the process equipment involved. Such processes consume a significant amount of fairly expensive reagents (acids, carbonate, hydroxide or sodium nitrate). A consequence of this is the formation of a large amount of liquid waste requiring disposal. When using sintering processes, it is necessary to use pressurized equipment and treat the exhaust gases for thoron. Therefore, the development of a more efficient method for processing monazite concentrate is of interest.

The studied method of processing monazite concentrate by sorption conversion is based on the fact that REE phosphates are limitedly soluble in a phosphoric acid solution, probably forming acid phosphates in the solution:

$$TrPO_4 + 2H_3PO_4 \rightarrow Tr(H_2PO_4)_3, \quad (17)$$

partially dissociating with the formation of REE-containing cations by the reaction:

$$Tr(H_2PO_4)_3 \rightarrow Tr(H_2PO_4)_2^+ + H_2PO_4^-. \quad (18)$$

In section 2.1, it was shown that at temperatures of 20–80 °C REEs can be efficiently sorbed from a 38 wt % H_3PO_4 solution by sulfocationite:

$$3(\text{-SO}_3\text{H}) + \text{Tr}(\text{H}_2\text{PO}_4)_2^{+} + \text{H}_2\text{PO}_4^{-} \rightarrow (\text{-SO}_3\text{H})_3\text{Tr} + 3\text{H}_3\text{PO}_4. \qquad (19)$$

Thus, in the process, the concentration of H_3PO_4 slightly increases, but the concentration of hydrogen ions varies little, because the first dissociation constant of H_3PO_4 is low ($7.52 \cdot 10^{-3}$) Consequently, increasing the concentration of H_3PO_4 will only slightly affect REE sorption performance.

From equation (2) it follows that the amount of cation absorbed by the sorbent is determined by the equation:

$$m_{sorb} = K_{(s)} \cdot C_{sol} \cdot V_{sorb} \qquad (20)$$

From equation (20) it follows that the most important factor determining the possibility and depth of the sorption conversion process is the value of C_{sol}, determined by the solubility of the mineral in the acid solution. In addition, the kinetics of dissolution, depending on the hydrodynamic conditions, the free surface of the solute, and the viscosity of the solution, are of importance.

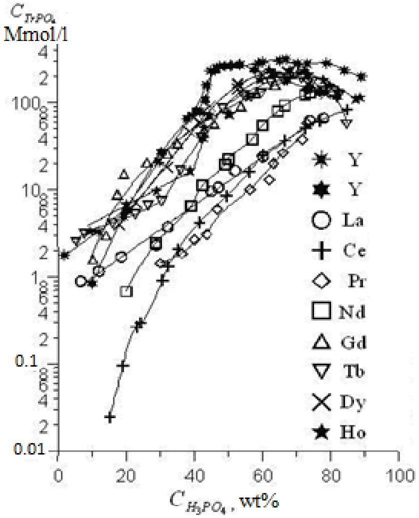

Figure 7. Dependence of the REE solubility in phosphoric acid on its concentration at 25 °C (for Ce — 20°C) [see review in 7]

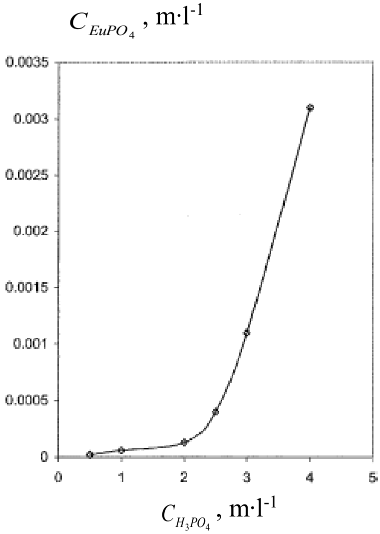

Figure 8. Dependence of europium phosphate solubility (m·l^{-1}) on the concentration of H_3PO_4 (at 101–104 °C) [73]

The solubility of REE phosphates in phosphoric acid solutions was studied by a team of scientists led by Tananaev [see review in 7]. The equilibrium solubility of REE phosphates increases with increasing $C_{H_3PO_4}$ (see Fig. 7 and 8) and decreases with increasing temperature. Thus, when the temperature rises from 25 to 80 °C, the solubility of $LaPO_4$ in 38 wt % phosphoric acid decreases by an order of magnitude [68–70], of $CePO_4$ by a factor of 20 [71–72].

When choosing the experimental conditions, it was taken into account that, although an increase in temperature decreases the equilibrium solubility of REE phosphates in a phosphoric acid solution, it can accelerate the dissolution of monazite. Increasing $C_{H_3PO_4}$ has a multidirectional effect, on the one hand, increasing the solubility of REE phosphates, and on the other, reducing the performance of REE sorption.

We are unaware of any standards governing the grade of monazite concentrate. In this study, we used monazite concentrate, whose chemical composition is given in Table 42.

Table 42

Composition of monazite concentrate

Content, wt %							
Y_2O_3	La_2O_3	Ce_2O_3	Pr_2O_3	Nd_2O_3	Sm_2O_3	Eu_2O_3	Gd_2O_3
1.962	11.14	23.73	2.683	9.88	1.676	0.0614	1.454
Tb_2O_3	Dy_2O_3	Ho_2O_3	Er_2O_3	Tm_2O_3	Yb_2O_3	Lu_2O_3	$\sum Tr_2O_3$
0.132	0.572	0.0671	0.138	0.0124	0.0779	0.0096	53.60
Na_2O	K_2O	MgO	CaO	SrO	Al_2O_3	TiO_2	Fe_2O_3
0.7	0.08	0.22	3.31	0.02	1.39	4.16	6.68
ZrO_2	Nb_2O_5	Ta_2O_5	MnO	ThO_2	UO_2	P_2O_5	SiO_2
3.03	0.11	0.07	0.084	3.92	0.31	22.5	10.7

Content in 1 g, mgEq						
Na^+	K^+	Mg^{2+}	Ca^{2+}	Al^{3+}	Ti^{4+}	Fe^{3+}
0.61	0.04	0.11	1.18	0.82	2.08	2.5
Zr^{4+}	Nb^{+5}	MnO	Th^{4+}	U^{4+}	Tr^{3+}	$\sum$
0.98	0.04	0.02	0.59	0.046	9.74	18.76

The content of REEs, thorium, phosphorus, and zirconium in the studied sample matched the content of these elements in the monazite concentrate stored in the Krasnoufimsk area [74], but the content of calcium, titanium, iron, and silicon is much higher, indicating an increased content of accessory ilmenite and calcium aluminosilicates. Particle size distribution of the monazite concentrate: 14.8 % +0.1 mm, 39.4 % +0.07 mm, 40.7 % +0.05 mm, 5.1 % -0.05 mm. For a number of experiments, the concentrate was further ground in an Activator 2 SL planetary mill to a particle size of 100 % -0.05 mm.

In our preliminary experiments, the monazite concentrate was treated with a solution of 40 wt % H_3PO_4 with a liquid phase to concentrate mass ratio L:S of 40:1. The high L:S ratio was determined by the need for guaranteed immersion of the sorbent in the liquid phase and to ensure mixing of the slurry. Experimental conditions and results are shown in Table 43.

Table 43

Conditions and results of the preliminary experiments on the decomposition of monazite concentrate with a particle size of -0.07 mm

Experiment	ß, %	Temperature, °C	Reaction time, h	Residual mass, rel %
1	200	20	4	80
2	200	40 then 60	8+5	50
3	300	60	16	62

From Table 43, it follows that the sorption conversion of monazite concentrate begins already at 20 °C. Increasing the process temperature from 20 to 80 °C, sorbent consumption, and processing time did not lead to complete decomposition of the concentrate. Moreover, increasing sorbent consumption, reaction time and temperature had little effect on the degree of decomposition. X-ray phase analysis found only monazite in the residue.

Table 44

Distribution of components between the products

Product	Recovery into the products, %						
	Na	K	Mg	Ca	Sr	Al	∑Tr
Solution	8.3	12.0	4.1	4.5	34.0	7.0	0.02
Residue	39.3	62.5	67.9	38.5	25.0	80.5	33.71
Sorbent	52.4	25.5	28.0	57.0	41.0	12.5	66.27
	Fe	Si	Ti	Zr	Nb	Th	U
Solution	12.5	44.7	2.7	0.9	7.4	1.5	2.9
Residue	61.4	55.3	90.6	61.9	70.1	53.6	64.1
Sorbent	26.1	0	6.7	37.2	22.5	44.9	33.0

Table 44 shows data on the distribution of the experiment 2 cationic components between the solution, the residue and the sorbent, and Table 45 shows the content of the components in the mother liquor and precipitate.

Table 45

Content of impurities in the mother liquor and residue

Product	Content in terms of oxides						
	Na_2O	K_2O	MgO	CaO	SrO	Al_2O_3	$\sum Tr_2O_3$
Solution, $mg \cdot l^{-1}$	29.1	4.78	4.50	73.8	3.38	48.8	6.25
Residue, wt %	0.55	0.1	0.3	2.55	0.01	2.23	36.14
	Fe_2O_3	SiO_2	TiO_2	ZrO_2	Nb_2O_5	ThO_2	UO_2
Solution, $mg \cdot l^{-1}$	418	N.a.	55.8	13.6	3.95	30.0	4.42
Residue, wt %	8.2	11.8	7.55	3.75	0.15	4.2	0.4

Within the error margin of the analysis, the ratio of REEs in the solution and, especially, the residue matched the ratio in the initial concentrate. The content of $\sum Tr_2O_3$ in the sorbent amounted to 17.76 $g \cdot l^{-1}$. The content of REEs in solution is very low (6.25 $mg \cdot l^{-1}$ $\sum Tr_2O_3$), and it is much lower than the equilibrium solubility of REE phosphates. Therefore, the limiting stage is not the sorption of REE from the phosphate solution, but the dissolution of monazite.

Changing the concentration of phosphoric acid in the solution from 30 to 40 %, processing time up to 15 hours and, most importantly, grinding in the planetary mill had little effect on the decomposition performance of the concentrate.

It was suggested that an insufficient degree of decomposition of the concentrate can be explained by:

- — lack of sorbent,
- — problems with REE diffusion deep into the sorbent grains due to the formation of a barrier composed of sorbed thorium cations on the surface of these grains due to their low diffusion rate [75],
- — possible transition of cerium during the processing into tetravalent state,
- — diffusion problems caused by the accumulation in solution of stable non-absorbable forms (undissociated molecules, anionic complexes) of phosphates of impurity metals that impeded the dissolution of monazite,
- — diffusion problems caused by the formation of films on the surface of monazite grains that are chemically stable in a phosphoric acid solution that impeded the contact between the monazite grains and the phosphoric acid solution.

When the residues were retreated in the presence of fresh phosphoric acid and sorbent, their mass remained practically unchanged. This meant that the first reason was not decisive.

The absence of an increase in the concentration of cerium relative to other REEs in the residue indicated that cerium was not converted to tetravalent state during the treatment.

With an increase in L:S to 650, only 73.2 % and 0.53 % Tr_2O_3 passed into the sorbent and the solution, respectively ∑. Thus, the insufficient decomposition performance of monazite is not caused by the accumulation in the solution of stable non-absorbable forms that impede the dissolution of monazite.

As can be seen from the data in Tables 42 and 45, in the process of treatment the level $\sum Tr_2O_3$ in the residue decreased from 53.6 to 36.14 wt %. The calculation based on the obtained experimental data showed that the amount of cations absorbed by the sorbent should lead to a loss of 72.9 % of the mass of the initial concentrate. Consequently, the mass of the residue should be 27.1 % of the mass of the initial concentrate, but it turned out to be significantly higher (50 %). This means that a part of the components of the monazite concentrate that dissolve in phosphoric acid forms secondary phases that do not contain REEs and are deposited on monazite grains, which increase the mass of the residue and, as a result, determine the decrease in the REE content in the residue.

Thus, the problems in the decomposition of monazite concentrate were associated with the formation of coatings blocking dissolution during decomposition. In a 38 wt% phosphoric acid solution, the solubility of calcium, aluminum, and iron phosphates is quite high (in the extraction phosphoric acid of the dihydrate process, the content of these metals is several grams per liter each, significantly exceeding the content in the mother liquor of monazite concentrate decomposition — see Table 45). A slight increase in the concentration of aluminum in the precipitate was apparently determined by the presence of accessory minerals containing aluminum that are poorly soluble in phosphoric acid and not detectable by X-ray diffraction analysis due to their low content in the monazite concentrate.

Components of the concentrate causing the formation of coatings blocking the dissolution of monazite can be soluble phosphates of titanium, zirconium, thorium, and hydrated silica. The accumulation of zirconium and thorium in the residue was not observed or was low. Particularly noticeable is the accumulation of titanium in the precipitate, which in the phosphoric acid solution forms poorly soluble phosphate compounds [28].

Ultrasonic treatment of the residues, which could lead to the breakage of the resulting film, was not successful.

The possibility of preventing the formation of titanium dihydrogen phosphate films by introducing hydrogen peroxide into a phosphate solution was investigated. When H_2O_2 was added to phosphoric acid solution in an amount many times greater than stoichiometrically necessary to form a titanium peroxide complex, the fraction of titanium absorbed by the sorbent increased from 6.7 to 56.8 rel %, the mass of the residue decreased from 50 to 37.9 rel %, and the level of TiO_2 in the residue from 7.55 to 4.49 %, which is within the analysis error margin from the level in the initial concentrate. The concentration of titanium in solution decreased to 39 $mg \cdot l^{-1}$. However, the absorption of REEs by the sorbent increased only to 68.8 %. Thus, the hypothesis about the formation of films on the surface of monazite crystals based on hydrated titanyl phosphate was not confirmed.

It was hypothesized that the films consist of hydrated silica and can be destroyed by introducing a fluorine ion into the phosphate solution. Introduction into the solution of a fluorine ion in the form of HF or NaF in the amount of 90 % of the stoichiometrically necessary for the formation of SiF_6^{2-} ions by the silicon present in the concentrate did not improve the performance of the process. With the introduction of fluorine in an amount of 100 % of the stoichiometrically necessary for the formation of MeF_6^{3-} (Me = Al, Fe) and MeF_6^{2-} (Me = Si, Ti, Zr, Th) ions by the impurities present in the concentrate, the sorbent absorbed 94.1 % of the REEs (Table 46). At the same time, the concentration of Al, Ti and Fe in the solution increased significantly, which indicates the formation of fluoride or fluorophosphate anion complexes by them, and their recovery into the solution increased to 71.9–77.6 % (Table 46).

Table 46

Distribution of the main components between the products obtained by sorption conversion with the addition of HF

Product	Distribution between products, rel%							
	Na	K	Mg	Ca	Sr	Al	∑Tr	Ti
Solution	21.03	31.25	39.91	37.69	16.5	74.03	0.48	71.88
Residue	7.74	20.75	8.96	3.61	10.0	8.64	5.41	12.24
Sorbent	71.23	48.0	51.13	58.70	73.50	17.33	94.11	15.88
	Fe	Zr	Hf	Nb	Ta	Mn	Th	U
Solution	77.57	1.12	19.5	62.52	48.51	12.50	13.76	13.49
Residue	5.32	1.45	9.0	9.53	7.14	5.24	6.60	6.09
Sorbent	17.11	93.43	71.50	27.95	44.35	82.26	79.64	80.42
	Y	La	Ce	Pr	Nd	Sm	Eu	Gd
Solution	0.84	0.99	0.26	0.31	0.32	0.56	0.64	0.54
Residue	5.45	5.85	4.87	5.65	5.62	5.94	8.06	7.58
Sorbent	93.61	93.16	94.87	94.04	94.06	93.50	91.30	91.98
	Tb	Dy	Ho	Er	Tm	Yb	Lu	∑Tr
Solution	1.06	0.70	0.88	0.87	1.67	1.79	2.00	0.48
Residue	9.09	6.15	7.06	5.51	5.00	5.38	4.00	5.41
Sorbent	89.85	93.16	92.06	93.62	93.33	92.84	94.00	94.11

Table 47

Content of impurities in the mother liquor and residue

Product	Content						
	Na_2O	K_2O	MgO	CaO	MnO	Al_2O_3	Fe_2O_3
Solution, mg·l^{-1}	14.7	2.5	8.8	125	1.05	103	518
Residue, wt%	0.51	0.16	0.19	1.13	0.04	1.13	3.35
	ΣTr_2O_3	SiO_2	TiO_2	ZrO_2	ThO_2	UO_2	P_2O_5
Solution, mg·l^{-1}	25.5	3880	299	15.8	53.9	4.21	N.a.
Residue, wt%	27.4	N.a.	4.81	0.02	2.44	0.18	17.6

Thus, in phosphate solutions, as well as in sulfate ones [76], Al, Ti, and Fe complexes containing fluoride ligands are more stable than the SiF_6^{2-} complex, and the latter is more stable than REE complexes containing fluoride ligands. At the same time, in a phosphoric acid solution, zirconium does not form a stable anionic complex with fluorine, which determined its high absorption by the sorbent from phosphoric acid solutions, both not containing and containing significant concentrations of fluorine ion.

Table 48

Values of $K_{(s)}$ during the sorption conversion of monazite concentrate
in solutions: 1 — 38 wt % H_3PO_4; 2 — 30 wt % H_3PO_4 + 9.7 wt % H_2O_2;
3 – 30 wt % H_3PO_4 + 0.3 wt % HF

Solution	t, °C	$K_{(s)}$										
		Na	K	Mg	Ca	Sr	Al	Ti	Fe	Th	U	ΣTr
1	60	6.3	2.1	6.8	12.7	1.2	1.8	2.5	2.1	29.9	11.4	3313
2	60	6.3	0.2	5.4	13.8	3.6	7.8	28.2	7.6	29.7	19.0	2292
3	80	3.0	13.9	1.7	0.26	N.a.	1.8	3.8	6.0	11.1	9.8	276

As can be seen from Table 48, which shows data on the values of $K_{(s)}$ during sorption conversion of monazite concentrate in phosphoric acid solutions of various compositions, an increase in temperature from 60 to 80 °C and the introduction of fluorine ion significantly reduced the efficiency of sorption of magnesium, calcium, REEs and thorium, and the introduction of H_2O_2 into the solution improved the sorption of titanium and to a lesser extent iron.

The highest value of A_{eff} in mother phosphate liquors did not exceed 0.2 KBq·kg^{-1}, which allows using these without any restrictions based on radiation concerns. Mother liquors produced using 38 wt % H_3PO_4 contained (mg·l^{-1}) up to 30.7 ThO_2, 3 UO_2, 16 $\sum Tr_2O_3$, 18 Na_2O, 3 MgO, 7 CaO, 16 Al_2O_3, 30 TiO_2, 73.5 SiO_2, 220 Fe_2O_3. The metal content in these is low, which allows the use of such solutions for the treatment of the following batches of monazite concentrate and for the production of certain types of phosphate products.

When fluoride ion was introduced into the phosphate solution, the level of many impurities increased (Table 47). The possibility of using such solutions in a circuit without removal of fluoride complexes of aluminum, iron, silicon and titanium requires verification.

Since usually monazite concentrates contain not more than 4 wt % SiO_2, during their processing, the amount of formed silica gel will not be enough for the formation of such films and the introduction of fluorine compounds into the phosphate solution is not necessary.

The content in the sorbent reached ($g \cdot l^{-1}$) 11 $\sum Tr_2O_3$, 0.69 ThO_2, 0.054 UO_2, 0.42 CaO, 2.48 Fe_2O_3, 0.62 $ZrO_2$0.14 TiO_2, 0.05 Al_2O_3. With optimal process conditions, the level of $\sum Tr_2O_3$ in the sorbent will be $\geq 17.5\ g \cdot l^{-1}$. Its A_{eff} is 3.5 $KBq \cdot kg^{-1}$, i.e. the resulting sorbent is classified as a class 3 material with a high level of natural radionuclides [59]. The thorium content in the monazite concentrate can significantly exceed its content in the examined batch, which will lead to an even higher radionuclide content in the sorbent.

Processing of the sorbent to produce thorium concentrate and non-radioactive carbonate concentrate of REEs is possible using for desorption concentrated solutions of ammonium salts [5] or 5 M solutions of chloride or sodium nitrate [3]. In the latter case, REEs are desorbed at room temperature, while the desorption of thorium is problematic. But thorium is effectively desorbed by such solutions at a temperature of 80 °C [3]. From eluates based on sodium salts, thorium is quantitatively precipitated by neutralization to $pH \approx 4.4$, REEs by neutralization to $pH = 7.35–7.5$.

Thus, a new resource-saving processing method for monazite concentrate has been proposed, based on its decomposition with a phosphoric acid solution in the presence of sulfocationite. The final products are REE carbonate or hydroxide concentrate, phosphoric acid and thorium concentrate.

In this process, practically no reagents are consumed. The metal content in the mother phosphate liquor is low, which allows its use for the treatment of the following batches of monazite concentrate.

3.4 Recovery of REE from the phosphate concentrate of nitric acid decomposition of apatite concentrate

When neutralizing a nitric phosphate solution, an intermediate product of nitric acid processing of the Khibiny apatite concentrate, REEs can be isolated in the form of a phosphate concentrate [17]. A significant share of the radionuclides contained in apatite, mainly thorium, enters the rare earth concentrate. Recently, a more efficient method for producing this concentrate has been developed, which can significantly increase the yield and REE grade of the concentrate [18]. In this method, the formation of the concentrate takes place at an elevated temperature of 85–95 °C.

Processing of the concentrate should include separation of REEs from phosphorus and radionuclides. A number of approaches have been proposed for separating phosphorus from REE phosphates. These include the conversion of REE phosphates to oxalates [77], carbon-thermal distillation of phosphorus [78].

The most studied method is based on the dissolution of the concentrate in 56–58 wt % HNO_3 containing H_2O_2, followed by extraction of REE from the resulting nitric phosphate solution [19, 20].

We investigated the possibility of processing such concentrates by sorption conversion. At the same time, it was taken into account that hydrated REE phosphates, which should dissolve in mineral acids much lighter than monazite, enter the concentrate.

3.4.1. Decomposition using nitric acid solutions

The performance of dissolution in mineral acids of hydrated REE phosphates, which make up a significant share of the concentrate, depends on their hydration degree, which is affected by the synthesis temperature. Hydrated REE phosphates obtained at elevated temperatures may have a reduced degree of hydration (less than 1 water molecule per phosphate molecule). This reduces their solubility in solutions of sulfuric [79] and nitric [80] acids.

Therefore, it was possible that the use of elevated temperature in the preparation of the concentrate according to the method in [18] can cause a decrease in the hydration degree of REE phosphates and, as a result, greatly complicate sorption conversion.

The composition of the phosphate concentrates used in the study is given in Table 49. The calculation of the molar ratio of the sum of cations and phosphorus confirms that some of the cations are present in concentrates in the form of acid phosphates. The presence of a small amount of fluorine in concentrates is determined by the ingress of alkali metal fluorosilicates Na_2SiF_6 and/or K_2SiF_6 and fluorophosphate complexes of aluminum and other cations with fluorine-acceptor properties (Ti^{4+}, Fe^{3+}). The total content of chemically bound water was about 26.2 — 37.4 wt %, decreasing with increasing REE concentration in the concentrate. Table 50 shows the content of individual REE oxides in the concentrate. Comparison of the ratio of REE oxides in phosphate concentrates and the initial apatite concentrate shows that when precipitating a phosphate concentrate, the recovery of yttrium group REEs does not exceed 40 %, of medium group REEs 60 %.

Table 49

Composition of the resulting concentrates

Concentrate	Content, wt%					
	Na_2O	K_2O	MgO	CaO	Al_2O_3	TiO_2
1	0.85	0.14	0.30	6.50	0.94	0.59
2	0.59	0.20	0.08	3.05	0.59	1.28
3*	0.21	0.23	0.03	12.2	3.21	0.53
Concentrate	Content, wt %					
	Fe_2O_3	ThO_2	UO_2	P_2O_5	F	$\sum Tr_2O_3$
1	0.19	0.077	0.002	28.7	0.81	23.50
2	1.16	0.121	0.0013	28.8	0.28	33.70
3*	2.24	0.078	0.0003	47.4	1.77	23.53

** — the concentrate was heat treated in an aqueous environment at a temperature of 95 °C.*

Table 50

Content of individual REEs in the concentrates

Concentrate	Content, wt %							
	Y_2O_3	La_2O_3	Ce_2O_3	Pr_2O_3	Nd_2O_3	Sm_2O_3	Eu_2O_3	Gd_2O_3
1	0.484	5.818	11.33	1.034	3.476	0.469	0.12	0.486
2	0.870	8.04	17.08	1.483	4.532	0.601	0.163	0.607
3	0.59	6.04	11.27	0.99	3.30	0.48	0.123	0.441
Concentrate	Content, wt %							
	Tb_2O_3	Dy_2O_3	Ho_2O_3	Er_2O_3	Tm_2O_3	Yb_2O_3	Lu_2O_3	$\sum Tr_2O_3$
1	0.043	0.17	0.0195	0.0431	0.003	0.012	0.0011	23.5
2	0.057	0.205	0.024	0.051	0.004	0.023	0.002	33.7
3	0.049	0.166	0.023	0.046	0.005	0.014	0.002	23.53

REE phosphate concentrate samples were placed in a nitric acid solution (L:S = 10) of a given concentration. The resulting mixture was stirred for 2 hours at a given temperature. If the conversion was not complete, the sorbent was separated from the mother liquor of the nitric acid slurry containing a suspension of insoluble components of the phosphate concentrate, the treatment of the mother liquor of the nitric acid pulp was repeated, adding a new batch of the sorbent.

Sorption conversion of the concentrate 1 was carried out at a temperature of 20 °C, of concentrates 2 and 3 at a temperature of 80 °C. Data on the sorption conversion performance is presented in Table 51.

Table 51

Sorption conversion performance of the phosphate concentrate at a temperature of 20 °C (for concentrates 1 and 2, ß = 225 %, for concentrate 3, ß = 150 %)

Concentrate	C_{HNO_3} ,wt %	Stage	Recovery into the sorbent, rel %							
			Y_2O_3	La_2O_3	Ce_2O_3	Pr_2O_3	Nd_2O_3	Sm_2O_3	Eu_2O_3	Gd_2O_3
1	3	1	88.3	82.6	66.3	81.4	83.0	82.0	82.3	77.3
		1+2	99.1	98.7	97.7	98.7	98.9	98.7	98.7	98.3
1	6	1	88.1	83.6	62.2	81.7	81.2	81.0	82.3	76.8
		1+2	98.2	98.6	96.3	98.4	98.6	98.3	98.4	97.8
2	2	–	98.3	97.4	94.6	96.6	96.6	96.4	96.6	96.3
3	2	–	98.3	98.2	96.6	97.6	97.6	97.7	97.8	97.3

Concentrate	C_{HNO_3} ,wt %	Stage	Recovery into the sorbent, rel %							
			Tb_2O_3	Dy_2O_3	Ho_2O_3	Er_2O_3	Tm_2O_3	Yb_2O_3	Lu_2O_3	$\sum Tr_2O_3$
1	3	1	82.1	83.2	83.6	84.0	83.3	85.0	81.8	74.8
		1+2	98.7	98.7	98.7	98.8	99.0	98.8	99.1	98.3
1	6	1	82.1	81.9	84.1	83.1	83.3	83.3	81.8	72.7
		1+2	98.4	98.4	98.4	98.5	98.3	98.9	98.2	97.4
2	2	–	96.3	96.6	96.5	97.0	95.8	96.4	95.8	95.8
3	2	–	97.9	97.6	98.1	97.8	98.4	97.3	98.2	97.3

Concentrate	C_{HNO_3} ,wt %	Stage	Recovery into the sorbent, rel %							
			Na_2O	MgO	CaO	Al_2O_3	TiO_2	Fe_2O_3	ThO_2	UO_2
1	3	1	99.9	99.6	98.9	99.8	86.7	86.8	86.8	93.8
		1+2	100	100	99.4	100	91.7	99.2	99.8	99.0
1	6	1	90.8	93.5	80.0	65.6	28.9	98.5	36.8	95.0
		1+2	96.2	97.6	98.1	93.9	67.6	99.8	87.0	98.5
2	2	–	78.1	97.3	95.1	91.7	75.4	87.9	85.2	98.1
3	2	–	74.2	90.9	97.4	71.7	9.7	84.2	75.4	87.7

The data presented in Table 51 shows that the sorption conversion of the REE phosphate concentrate in the nitric acid medium performs well, while there is a high degree of absorption of almost all cations by the sorbent. At room temperature, to achieve a high degree of conversion, it had to be carried out in 2 stages, while at a temperature of 80 °C at the same ratio of reagents, a single stage was sufficient for complete conversion. Increasing C_{HNO_3} from 3 to 6 wt % hindered sorption conversion. The completeness of the transition to the sorbent of all REEs, as a rule, was the same. When using a 6 wt % solution and at a limited sorbent consumption (stage 1), the transition of thorium to the sorbent was lower, which indicates the fundamental possibility of partial separation of thorium during the sorption conversion of phosphate concentrate, but the degree of REE sorption was also reduced. In general, separating thorium from REEs directly in the process of sorption conversion in nitric acid media is not considered a viable option.

Titanium had the lowest absorption by the sorbent, which is probably due to its presence in the concentrate in the form of poorly soluble pyrophosphate.

The degree of saturation of the sorbent calculated from experimental data (it was assumed that cations are adsorbed rather than positively charged complexes not containing anionic ligands) was 74.1, 36.7, and 34 rel % at C_{HNO_3} of, respectively, 2, 3 and 6 wt %. Thus, decreasing the concentration of nitric acid from 6 to 3 wt % had little effect on the actual sorption capacity of sulfocationite. The significant increase in the actual sorption capacity of sulfocationite at $C_{HNO_3} = 2$ wt % can be explained by a decrease in the concentration of hydrogen cations.

Thus, during sorption conversion, REEs pass into sulfocationite by 95.8 — 98.3 % almost equally, and the conversion level is only slightly reduced for cerium. The bulk of cationic impurities, including thorium and uranium, pass into sulfocationite, but to a somewhat lesser extent compared to REEs. No significant difference in the degree of absorption of REEs and radionuclides by the sorbent was found.

1 m^3 of the sorbent in the process of sorption conversion of the phosphate concentrate of the studied composition may contain more than 32 кg $\sum Tr_2O_3$. Increasing the REE content of the phosphate concentrate will contribute to an increase in the REE content in the sorbent. Consumption of 56 wt % HNO_3 amounted to about 1 kg per 1 kg of REE oxides in the phosphate concentrate, i.e. 4 times lower than in the known method [20].

The sorption conversion performance of phosphate concentrate at 95 °C and of the phosphate concentrate obtained using the conventional precipitation conditions at 80 °C [17], did not differ much.

In the mother phosphate liquor, the concentration of P_2O_5 reached 25 $g \cdot l^{-1}$, of fluorine 1.6 $g \cdot l^{-1}$. Their composition and relatively small volume determine the possibility of their use in full-scale processes.

3.4.2 Decomposition using fluorinated nitric acid solutions

As can be seen from the data in Table 51, during the nitric acid decomposition of the REE phosphate concentrate, thorium, aluminum, titanium, and iron are effectively absorbed by the sorbent. Subsequent processing of the sorbent as one of the products results in an impurity cake enriched in thorium. Having increased radioactivity, it requires special treatment methods, which complicates the implementation of this process. In addition, thorium is poorly desorbed with solutions of ammonium nitrate and, when these are used, will accumulate in the sorbent. Thorium can be desorbed by solutions of ammonium sulfate, but their disposal on sites processing apatite concentrate with the nitric acid method is challenging. Therefore, it was of interest to find methods that allow to separate REEs and thorium directly during the sorption conversion of the REE phosphate concentrate with the prevention of radioactive waste generation.

We investigated the possibility of separating thorium from REE directly in the process of dephosphorization of the concentrate by sorption conversion. We hypothesized that the introduction of fluoride ions into the nitric acid solution would solve the problem, because:

- thorium would form with fluorine ions poorly soluble in low concentrated nitric acid solutions of thorium fluoride, which would reduce the absorption of thorium by the sorbent,
- although REE also form poorly soluble fluorides (in 2 wt % HNO_3 solubility of Yf_3 is 0.1 g^{-1} [81], solubility of LaF_3 is almost 3 times lower [82]), their solubility is much higher than the solubility of thorium fluoride, which opens up the possibility of finding the process conditions that will ensure efficient separation of REEs and thorium.

The treatment was carried out for 2 hours at a temperature of 80 °C in solutions containing 1–2.5 wt % HNO_3 in which fluorine-ion-containing compounds were first introduced: NaF (GOST 4463-76), NH_4F (GOST 4518-75), NH_4HF_2 (GOST 9546-75) or HF. The ratio of the mass of the concentrate to the volumes of the acid solution and the sorbent was 1:10:6, ß = 85 %. Depending on the concentration of HNO_3 its consumption was 21.6–54 % of the consumption theoretically necessary for the formation of nitrates by the metal cations contained in the concentrate.

It was assumed that the lack of a sorbent would not reduce the absorption of REEs more readily adsorbed by sulfocationite, but will lead to a decrease in the absorption of certain impurities.

The composition of the initial concentrate is given in Table 52. It also contained (wt %): 3.76 NH_4^+ and 1.03 SiO_2. The main cationic impurities were ammonium, calcium, aluminum, iron (III) and titanium.

From the ratio of equivalents of cations and anion PO_4^{3-} it follows that in the concentrate cations are present mainly in the form of medium phosphates.

Table 52

Composition of the initial concentrate

Content, wt %											
$\sum Tr_2O_3$	Me_2O	MgO	CaO	SrO	Al_2O_3	TiO_2	Fe_2O_3	ThO_2	UO_2	PO_4^{3-}	F
12.21	0.15	0.041	5.704	0.591	2.093	0.854	3.517	0.0294	$1\cdot10^{-4}$	31.84	1.55
gEq in 1000 g											
2.22	0.044	0.020	2.04	0.114	1.23	0.43	1.32	$1.1\cdot10^{-3}$	$3.7\cdot10^{-6}$	10.05	0.82

Compared to previously studied [83], the concentrate was higher in calcium, aluminum, iron and lower in REEs and natural radionuclides - thorium and uranium.

According to the thorium content relative to the content of $\sum Tr_2O_3$ we estimated the value of A_{eff}. of the rare earth products that could be obtained from concentrate. Moreover, the content of $\sum Tr_2O_3$ was assumed equal to 100 %. The uranium content was neglected because due to its low concentration, its contribution to the total activity is less than 1 rel %. In the initial concentrate, $A_{eff} = 7.56$ KBq·kg^{-1}.

The experimental conditions and results are shown in Tables 53–55. Fluorine ion consumption is given in grams per 1 kg of the concentrate.

Table 53

Effect of the sorption conversion conditions on the recovery of REEs into the sorbent, the proportion of substituted cation exchange centers in the sorbent α (rel %), the content of $\sum Tr_2O_3$ in 1 liter of sorbent m (g) and A_{eff} (KBq kg^{-1})

Experiment	Solution					Sorbent				
	Added F^-, g	Compound	C_{HNO_3}, wt%	$C_{NH_4^+}$, mol·l^{-1}	C_{Na^+}, mol·l^{-1}	t, °C	ε_{Tr}	α	m	A_{eff}
1	0	–	2	0.21	–	80	92.9	54.2	18.9	4.70
2	25	NaF	2	0.21	0.13	80	97.7	64.5	19.9	3.59
3	50	NaF	2	0.21	0.26	80	95.5	72.1	19.4	3.32
4	75	NaF	2	0.21	0.39	80	93.1	75.1	18.4	1.61
5	100	NaF	2	0.21	0.53	80	82.9	75.1	16.9	1.21
6	125	NaF	2	0.21	0.66	80	67.6	85.9	13.8	0.31
7	125	NaF	2.5	0.21	0.66	80	75.1	89.0	15.3	2.38
8	50	NH_4F	1	0.47	–	80	70.2	49.3	14.4	2.3
9	75	NH_4F	1	0.60	–	80	70.8	51.5	14.3	2.4
10	75	NH_4F	2	0.60	–	20	64.3	37.7	13.1	3.24
11	75	NH_4F	2.5	0.60	–	20	66.2	41.4	13.5	3.57
12	75	NH_4F	2	0.60	–	80	82.8	47.1	16.8	2.46
13	100	NH_4F	2.5	0.74	–	80	81.6	47.8	16.6	2.32
14	125	NH_4F	2.5	0.87	–	80	68.0	48.9	13.8	1.27
15	100	NH_4HF_2	1	0.47	–	80	92.7	54.0	18.9	0.39
16	125	NH_4HF_2	1	0.54	–	80	88.1	52.0	17.9	0.11
17	100	HF	1	0.21	–	80	95.7	53.3	19.5	0.21
18	125	HF	1	0.21	–	80	91.8	52.5	18.7	0.12

Table 54

Recovery of the main impurity cations of the concentrate into the sorbent

Experiment	Recovery into the sorbent, rel%								
	Na	K	Mg	Ca	Al	Ti	Fe	Th	U
1	44.5	40.4	42.8	90.0	58.1	45.1	74.0	65.2	72.3
2	67.9	22.6	75.6	94.1	56.8	39.3	73.6	53.7	N.a.
3	72.3	22.6	71.7	93.9	52.3	37.6	70.7	45.9	N.a.
4	67.3	22.3	31.2	90.4	50.5	26.1	59.4	22.4	N.a.
5	56.4	22.3	27.2	91.4	47.8	30.0	65.3	15.0	N.a.
6	67.2	61.3	14.6	88.2	43.4	28.1	55.4	3.1	N.a.
7	69.8	3.2	58.5	86.7	38.3	36.1	59.4	26.8	70.0
8	8.3	22.6	0.7	88.5	60.2	13.8	81.3	24.5	65.0
9	37.4	30.0	4.9	91.9	63.8	35.0	84.3	25.5	65.0
10	6.0	6.8	53.7	81.1	32.1	20.5	41.2	31.2	60.0
11	14.4	6.5	54.8	81.1	36.6	30.3	51.9	35.4	60.0
12	13.4	23.2	54.6	88.6	45.0	31.6	72.7	30.6	71.0
13	13.1	1.0	48.0	88.8	40.2	32.1	69.3	28.6	68.0
14	12.7	15.2	34.9	85.9	36.4	22.5	65.9	12.9	65.0
15	6.0	3.2	51.2	92.8	42.6	66.0	73.6	5.4	N.a.
16	6.0	3.2	51.2	90.9	37.8	63.7	73.6	1.4	N.a.
17	6.0	3.2	56.1	92.8	47.4	23.9	72.2	3.0	N.a.
18	6.0	3.2	51.2	93.9	42.6	23.9	74.7	1.7	N.a.

Table 55

Recovery of individual REEs into the sorbent

Experiment	Recovery, rel %							
	Y_2O_3	La_2O_3	Ce_2O_3	Pr_2O_3	Nd_2O_3	Sm_2O_3	Eu_2O_3	Gd_2O_3
15	96.7	91.6	94.3	92.0	88.2	93.5	93.5	96.7
16	88.8	86.6	90.0	86.1	84.6	89.6	90.2	90.9
17	98.3	95.3	97.0	96.0	92.3	96.5	96.7	97.5
18	96.7	90.3	93.0	93.0	N.a.	92.2	91.8	96.3

End of table 55

Experiment	Recovery into the sorbent, rel %							
	Tb_2O_3	Dy_2O_3	Ho_2O_3	Er_2O_3	Tm_2O_3	Yb_2O_3	Lu_2O_3	ΣTr_2O_3
15	N. a.	86.8	90.5	N. a.	N. a.	87.7	N. a.	≥92.7
16	N. a.	85.6	81.0	N. a.	N. a.	87.7	N. a.	≥88.1
17	N. a.	83.2	84.8	N. a.	N. a.	87.7	N. a.	≥95.8
18	N. a.	81.9	90.5	N. a.	N. a.	87.7	N. a.	≥91.8

** — REE content was analyzed by induction plasma atomic emission spectrometry (ICP-ES Plasma 400), which did not support reliable measurement of Tb, Er, Tm, and Lu due to low concentrations.*

We took into account that:

- in the process of sorption conversion, phosphoric acid will be formed in the solution by reaction (19): for a given ratio of reagents and complete decomposition of the concentrate, its concentration can reach ≈ 3.3 wt %,
- the introduction of fluorine-ion-containing compounds leads to an increase in the concentration of ammonium or sodium cations in the solution, which upon sorption compete with the metal cations passing into the solution from the concentrate.

The study as an additive of NaF (experiments 1–7) was due to its lower cost and the possibility of production at operations producing apatite concentrate by nitric acid method. However, the acidity of the solution was significantly reduced in the solution, as NaF is a salt of a strong base and a weak acid.

The high recovery of REEs in the sorbent was achieved only a NaF consumption (consumption of additives is hereinafter given in terms of fluorine) of not more than 75 g per 1 kg of the initial concentrate. A rather high filling degree of cation exchange centers and REE concentration in the sorbent were achieved. Increasing the concentration of fluorine ions in the solution, as expected, hindered the absorption of thorium to a much greater extent than REEs, however, with a high recovery of REEs into the sorbent, thorium was not sufficiently separated, and with a high degree of thorium separation, the recovery of REEs decreased. Simultaneous with fluorine, an increase in the sodium concentration naturally increased the utilization degree of the sorbent, but reduced the REE content in the sorbent.

Adding NaF to the solution practically did not change the recovery of calcium into the sorbent, but led to a decrease in the recovery of aluminum, titanium, and iron. At a constant value of C_{HNO_3} the recovery of aluminum, titanium, and iron decreased with an increase in the concentration of added NaF, which is apparently explained by their transition to anionic forms upon interaction with fluorine ions.

With a slight increase in acidity (compare experiments 6 and 7), the separation performance of REE and thorium decreased sharply.

Thus, at the optimum acidity of the solution, the introduction of fluoride ions in the form of NaF during sorption conversion into the nitric acid solution allows to separate thorium from REEs (see experiment 6), but the recovery of REEs into the sorbent is insufficient.

When using NH_4F (experiments 8–14), the ammonium concentration in the slurry increased from 0.21 to 0.47–0.87 $mol \cdot l^{-1}$. Due to the competition with additionally introduced NH_4^+ cations, the absorption by the sorbent of sodium and potassium, the fraction of the cation-exchange centers of the sorbent substituted by metal cations (when estimated, the sorption of NH_4^+ cations not taken into account) and the concentration of REEs in it decreased. No noticeable effect on the absorption by the sorbent of alkaline earth metals, aluminum, iron, and titanium was observed (Table 54).

With an increase in fluoride ion consumption up to 125 g, the transition of thorium to the sorbent decreased by 2.5 times, while that of REEs by only about 14%. This contributed to a decrease in the relative thorium content, but did not provide the necessary separation performance of REEs and thorium. Same as in the absence of fluoride-containing additives, reducing the temperature from 80 to 20 °C complicated the sorption conversion process and reduced the separation performance of REEs and thorium.

With the introduction of NaF or NH_4F, REEs of the cerium group had a slighlt lower sorption than REEs of the medium and yttrium groups.

High performance of thorium separation while maintaining an acceptable degree of conversion was achieved by reducing C_{HNO_3} to 1 wt % and using NH_4HF_2 (experiment 15) and, especially, HF (experiment 17). In the latter case, neither NH_4^+ nor Na+ cation was added.

The absorption of cerium group REE cations by the sorbent slightly exceeded the absorption of yttrium group cations (Table 55). When using HF, the transition of titanium to the sorbent also decreased.

In contrast to the conversion of concentrates in sulfuric acid solutions, the sorbent absorbed noticeable amounts of uranium, despite its much lower concentration in the initial product. This indicates that uranium does not form fluorine-containing anionic complexes in the presence of a fluorine ion in nitric acid environments.

REE desorption at 19.5 g $\sum Tr_2O_3$ in 1 liter of sorbent is not expected to cause problems. The mother slurry obtained under optimal conditions contained 40 $g \cdot l^{-1}$ H_3PO_4 and 0.003 wt % Th. It is not radioactive and can be disposed of at mineral fertilizer plants.

Although REE desorption will result in NH_4^+ sorbent, when processing apatite concentrate with nitric acid, its regeneration back into the N^+ form is not expected to cause problems.

It was hypothesized that thorium, fluoroceptor elements (aluminum, iron, titanium) and REEs compete for the fluorine ion introduced into the nitric acid solution, while the fluoroaluminate complex is the most durable. Then, similarly to sulfate solutions [84], ThF_4 is formed only after aluminum and, possibly, iron are "saturated" with fluorine.

In order to reduce the consumption of fluorine ion, the possibility of preliminary selective dissolution of the impurities contained in the initial concentrate was investigated. Leaching was carried out with 2 and 3 wt % HNO_3 solutions for 2 hours at a L:S ratio of 10:1, temperature 80°C and constant stirring. HNO_3 consumption was 67 and 100% of the stoichiometrically required amount, respectively.

A significant share of aluminum and calcium was leached already at 2 wt % HNO_3. Leaching of iron and titanium was difficult, and thorium was hardly leached at all. With an increase in the consumption and concentration of HNO_3 REE dissolution increased (1.6 % at $C_{HNO_3} = 2$ and 4.0 % at $C_{HNO_3} = 3$ wt %) and, while cerium leaching was poor (0.05–0.3 %), the leaching of other REEs, especially the medium and yttrium groups, was significant. Erbium was leached best: 10.1 % and 20.9 %, respectively, with 2 and 3 wt % HNO_3 solutions. Weight loss during treatment with 2 and 3 wt % HNO_3 amounted to 48.7 and 51.2 %, the content of $\sum Tr_2O_3$ in the concentrate increased from 12.2 to 23.4 and 25.6 wt %, and the total equivalent number of cations decreased from 7.39 to 4.76–4.34, respectively.

Up to 80 % of the leached REEs was recovered from the solution by sorption at a temperature of 20–80 °C and sorbent consumption 25 % of the stoichiometrically necessary for the sorption of the metal cations contained in the solutions, while most of the impurities were not sorbed.

Thus, pretreatment of the rare earth concentrate with low concentrated nitric acid solutions, including leaching and additional sorption from the leaching solution, allows a significant portion of aluminum and calcium to be removed with a relatively small loss of REEs, which under optimal conditions was as low as 0.32 rel %.

Our study of the possibility of reducing the fluorine consumption during the sorption conversion of the REE concentrate enriched with nitric acid treatment, carried out under the conditions described in [85], showed that thorium had lower absorption by the sorbent than REEs and most other impurities. The highest separation of REEs and thorium was observed at a fluorine consumption of 50–60 g per 1 kg of concentrate, regardless of the process temperature (20–80 °C). Increasing the consumption of fluorine ion to 100 g per 1 kg of concentrate did not improve the performance of thorium separation. There was no correlation between the amount of fluorine introduced and the separation performance of REEs and thorium, while the minimum value of A_{eff} of the REE oxides sum was not less than 1.7 $KBq \cdot kg^{-1}$.

A 2.5-fold decrease in the aluminum content in the concentrate practically did not affect the separation performance of REEs and thorium, which was estimated by the ratio of recoveries into the sorbent of REEs and thorium $\varepsilon_{\Sigma Tr} / \varepsilon_{Th}$. The recovery of aluminum and iron into the sorbent was quite high (the recovery of iron is comparable with the recovery of REE). This indicated the presence of aluminum and iron in the fluorine-containing nitric acid solution (at least a significant part of it) in cationic form, and not in the form of anionic fluorine-containing complexes.

Hence, it was concluded that the hypothesis that the separation of thorium during sorption conversion is due to the formation of poorly soluble thorium fluoride is inaccurate, and the achieved high separation degree of REEs and thorium is controlled by another mechanism.

Thus, in the process of sorption conversion of rare-earth phosphate concentrate, the introduction of fluoride-ion-containing compounds into a nitric acid solution allows the separation of REEs and thorium, while REEs are quantitatively sorbed by sulfocationite, and thorium mainly remains with phosphorus and fluorine in the mother slurry. The highest separation performance while maintaining a high degree of conversion is achieved using NH_4HF_2 and HF. Efficient separation of thorium from REEs can also be achieved using NaF, but the recovery of REEs from the concentrate into the sorbent is not high enough.

The mother slurry containing thorium formed as a waste of the sorption conversion process is not radioactive and can be disposed of at mineral fertilizer plants. The proposed approach eliminates the formation of radioactive waste requiring burial with a high content of thorium.

3.4.3 Decomposition using phosphoric acid solutions

It was shown above that separation of thorium is possible by sorption conversion of the phosphate concentrate in a nitric acid solution containing fluorine ion. The disadvantage of this approach is the high fluoride ion consumption, which under optimal conditions was 0.87 kg HF or 1.5 kg $NH_4F{\cdot}HF$ per 1 kg $\sum Tr_2O_3$ in the phosphate concentrate.

The reason for the decrease in the absorption of thorium by the cation exchanger was the formation of an anionic complex or a slightly dissociated molecule by it. In the process under study, fluorine and/or phosphate ions could be possible ligands promoting the formation of such thorium complexes.

In the sorption conversion of yttrofluorite concentrate, carried out in low concentrated nitric acid and hydrogen fluoride solutions, despite the high concentration of fluorine ion (up to 1 $mol{\cdot}l^{-1}$), the separation of REEs and thorium was not observed [86].

In phosphoric acid solutions during sorption conversion of apatite concentrate [87], on the contrary, there was a separation of REEs and thorium. The separation performance increased with increasing concentration of phosphoric acid from 5–10 to

38 wt %. In the sorption conversion of monazite concentrate, carried out at a temperature of 60 °C in a solution of 40 wt % phosphoric acid, the sorption of REEs 1.5 times exceeded the sorption of thorium (Table 44), and the thorium content in the mother liquor many times exceeded the content of REEs (Table 45). It was hypothesized that it was the concentration of phosphate ions in nitric acid solutions that affected the separation performance of REEs and thorium, and the different stability of phosphate complexes of REEs and thorium could be used to separate them.

We studied the sorption conversion of enriched phosphate rare earth concentrate in a 38 wt % H_3PO_4 solution. The concentrate contained (wt %): 23.4 $\sum Tr_2O_3$, 0.10 Me_2O, 3.46 CaO, 0.61 SrO, 0.80 Al_2O_3, 1.56 TiO_2, 6.32 Fe_2O_3, 0.058 ThO_2, $2\cdot10^{-4}$ UO_2, 37.3 P_2O_5, 1.44 F, 2.06 SiO_2 (the rest was water). L:S ratio was 15:1; in a number of experiments, fluorine ions in the form of NH_4F were additionally introduced into solutions. The experiments were carried out at a temperature of 20 °C, since during the sorption conversion of apatite concentrate in 38 wt % H_3PO_4 at a temperature of 80 °C, the amount of thorium absorbed by sulfocationite increases [87]. The experimental conditions and the key indicators of conversion performance are shown in Table 56.

Table 56

Experimental conditions and key indicators of conversion performance (ε – extraction)

Experiment	Fluorine, g/kg of concentrate	β, %	t, °C	Time, h	Mass of residue rel %	$\varepsilon_{\Sigma Tr}$, %	ε_{Th}, %	$\varepsilon_{\Sigma Tr}/\varepsilon_{Th}$
1	0	123	20	4	41.4	61.6	14.6	4.22
2	15	123	20	4	57.6	59.4	4.47	13.3
3	50	123	20	4	58.0	52.7	3.34	15.8
4	0	200	20	4	45.0	61.0	6.70	9.1

From the data in Table 56, it can be seen that the conversion performance in phosphoric acid significantly decreased compared with the conversion performance in nitric acid. Moreover, as the data in Table 57 shows, the decrease in REE recovery into the sorbent was mainly controlled by cerium, whose sorption did not exceed 24.3 rel %. Alkaline earth metals were well absorbed by the sorbent. In contrast to the conversion in a nitric acid medium, titanium, aluminum, iron, and thorium, as can be seen from the data in Tables 57 and 58, accumulated in solution. A relatively small amount of thorium that got into the sorbent determined a satisfactory degree of REE and thorium separation for practical applications. A_{eff} of the solutions did not exceed 0.125 $KBq\cdot kg^{-1}$, i.e. these can be handled without restrictions in an industrial environment.

Table 57

Recovery of the components into the sorbent

Experiment	Recovery, rel %									
	Y	La	Ce	Pr	Nd	Sm	Eu	Gd		
1	88.0	96.0	24.3	93.1	92.9	89.2	90.2	82.1		
2	87.7	94.5	20.8	92.0	92.1	88.6	88.2	81.14		
3	86.7	94.7	6.8	91.6	91.3	87.6	87.0	78.8		
4	95.5	97.8	18.9	97.1	96.9	96.0	95.7	87.0		
	Tb	Dy	Ho	Er	Tm	Yb	Lu	∑Tr		
1	87.2	88.2	87.9	87.6	86.4	81.4	79.6	61.6		
2	86.6	87.7	87.2	87.0	85.8	82.0	82.0	59.4		
3	85.2	86.6	85.6	85.4	84.0	80.0	81.1	52.7		
4	93.6	95.5	95.4	95.2	94.7	93.0	93.2	61.0		
	Na	K	Mg	Ca	Sr	Al	Ti	Fe	Th	U
1	66.4	59.8	72.8	95.6	96.1	37.4	0.94	29.5	14.6	17.6
2	53.7	60.2	24.2	94.6	94.2	36.6	1.21	25.5	4.45	29.4
3	27.3	14.4	40.4	94.6	94.3	28.7	0.53	22.6	3.34	28.7
4	40.5	63.2	76.4	98.6	97.1	49.5	3.30	29.1	6.69	19.6

Increasing ß up to 200 % (experiment 4) led to a slight increase in the recovery of all REEs, except cerium. Adding fluorine ion in the form of NH_4F to the phosphoric acid solution, other conditions being equal, caused a decrease in the recovery of both REEs and thorium into the sorbent, but the separation performance of REEs and thorium improved. This suggests the formation of thorium fluorophosphate complexes in such solutions.

The resulting residues compared with the initial concentrate were characterized by (Table 59):

— increased cerium content, especially in experiments without the use of NH_4F where the content of Ce_2O_3 in $\sum Tr_2O_3$ amounted to 93.7 – 95.4 wt %,

— reduced, although rather high, concentration of ThO_2 relative to $\sum Tr_2O_3$,

— reduced titanium and iron content.

Table 58

Concentration of the components in the mother liquors

Experiment	Concentration, mg·l^{-1}							
	Y_2O_3	La_2O_3	$Ce_2O_3^*$	Pr_2O_3	Nd_2O_3	Sm_2O_3	Eu_2O_3	Gd_2O_3
1	30.22	75.73	296.0	29.35	120.6	27.17	8.54	24.77
2	31.52	80.37	346.4	30.89	118.6	28.04	8.82	25.97

End of table 59

3	33.41	87.96	226.6	33.66	143.4	30.48	9.60	28.0
4	9.78	24.88	181.6	8.15	33.7	8.32	2.72	7.86
	Tb_2O_3	Dy_2O_3	Ho_2O_3	Er_2O_3	Tm_2O_3	Yb_2O_3	Lu_2O_3	ΣTr_2O_3
1	3.03	11.73	1.52	2.82	0.24	1.36	0.14	633.2
2	3.16	11.74	1.55	2.81	0.25	1.25	0.14	691.7
3	3.42	13.20	1.75	3.21	0.26	1.38	0.15	616.6
4	0.99	3.81	0.50	0.895	0.074	0.42	0.043	283.8

	Na_2O	K_2O	MgO	CaO	SrO	Al_2O_3	TiO_2	Fe_2O_3	ThO_2	UO_2
1	17.30	8.76	3.56	106.4	12.11	284.5	908	3483	39.62	0.071
2	19.49	6.17	3.76	134.7	13.34	282.2	878	3648	38.35	0.117
3	28.35	16.34	3.64	130.7	14.45	301.5	730	3524	34.22	0.054
4	24.13	6.25	3.37	37.10	5.42	223.7	973	3464	31.60	0.073

** — the concentration of cerium in the solution is conventionally calculated for* Ce_2O_3*, although the bulk of cerium is present in the form of* Ce^{4+}.

Table 59

Properties of the residues

Experiment	Mass, Rel %	Content, wt %									
		CaO	SrO	Al_2O_3	TiO_2	Fe_2O_3	ThO_2	Ce_2O_3	ΣTr_2O_3	P_2O_5	F
1	41.4	0.06	0.03	0.12	1.03	0.51	0.03	21.6	22.6	26.9	0.78
2	57.6	0.036	0.04	0.10	0.81	0.47	0.026	16.1	17.1	20.0	0.49
3	58.0	0.05	0.04	0.15	1.21	1.18	0.038	19.3	20.3	29.5	0.56
4	45.0	0.005	0.03	0.11	0.96	0.60	0.052	21.7	22.3	23.8	0.50

Thus, conversion in a phosphoric acid environment supports the separation of REEs and thorium, and REEs, in addition to cerium, are effectively absorbed by the sorbent, and thorium accumulates in the phosphoric acid solution in a form that is not sorbed by the cation exchanger — an anionic complex or an almost undissociated molecule. Adding a small amount of fluorine ion improves the separation performance of REEs and thorium.

We hypothesized that the most likely cause of the “abnormal” behavior of cerium was the gradual oxidation of Ce^{3+} to Ce^{4+} atmospheric oxygen when storing the phosphate concentrate in an air atmosphere. To verify this, cerium-enriched residues from experiments 1–4 were combined and treated with a phosphate solution containing hydrogen peroxide at 20 °C in the presence of sulfocationite (β = 123 %, L:S = 15:1, time 4 hours). Formation of oxygen bubbles was observed as described by the reaction:

$$Ce_4 + + H_2O_2 \rightarrow Ce_3+ + H_2O + 0.5O_2\uparrow. \qquad (21)$$

The recovery of REEs, including cerium, into the sorbent amounted to 93.8 %. The residue was a hydrated silica product containing (wt %): 2.95 $\sum Tr_2O_3$, 0.72 TiO_2, 0.12 Al_2O_3 and 0.12 Fe_2O_3, ≤ 0.05 each oxides of alkaline and alkaline earth elements, 0.016 ThO_2 and 0.0002 UO_2. REE loss with the solid residue amounted to ≈ 4 %. Only 2.7 % of thorium reached the sorbent, and the bulk (80.2 %) passed into the mother liquor. The value of $\varepsilon_{\Sigma Tr}/\varepsilon_{Th}$ amounted to 34.7, i.e. separation of thorium from REEs performed well. A_{eff} of the residue was about 0.525 $KBq\cdot kg^{-1}$, i.e. this can be handled without restrictions in a production environment.

Table 60 shows the content of the metals in the phosphoric acid solution. The main impurities in the mother liquor were cerium, titanium, and iron. The sufficiently high cerium content is probably due to the partial presence in the form of Ce^{4+} which, similarly to thorium, forms a poorly sorbed form. The solution contained ($mg\cdot l^{-1}$) 12.36 ThO_2 and 0.006 UO_2 which determined an A_{eff} of ≈ 0.035 $KBq\cdot kg^{-1}$, i.e. the solution can be handled carried out without restrictions.

Table 60

Concentration of components in the mother liquor obtained by sorption conversion of cerium-enriched phosphate residues

<table>
<tr><th colspan="10">Concentration, $mg\cdot l^{-1}$</th></tr>
<tr><td>Y_2O_3</td><td>La_2O_3</td><td>Ce_2O_3</td><td>Pr_2O_3</td><td>Nd_2O_3</td><td>Sm_2O_3</td><td>Eu_2O_3</td><td colspan="3">Gd_2O_3</td></tr>
<tr><td>1.11</td><td>2.89</td><td>242.5</td><td>0.97</td><td>4.12</td><td>0.95</td><td>0.27</td><td colspan="3">2.57</td></tr>
<tr><td>Tb_2O_3</td><td>Dy_2O_3</td><td>Ho_2O_3</td><td>Er_2O_3</td><td>Tm_2O_3</td><td>Yb_2O_3</td><td>Lu_2O_3</td><td colspan="3">$\sum Tr_2O_3$</td></tr>
<tr><td>0.14</td><td>0.50</td><td>0.05</td><td>0.12</td><td>0.01</td><td>0.06</td><td>0.006</td><td colspan="3">256.3</td></tr>
<tr><td>Na_2O</td><td>K_2O</td><td>MgO</td><td>CaO</td><td>SrO</td><td>Al_2O_3</td><td>TiO_2</td><td>Fe_2O_3</td><td>ThO_2</td><td>UO_2</td></tr>
<tr><td>95.6</td><td>1.1</td><td>4.3</td><td>0.25</td><td>0.29</td><td>21.2</td><td>414.2</td><td>144.4</td><td>12.36</td><td>0.006</td></tr>
</table>

The effect of phosphoric acid concentration and temperature on the separation performance of REE and thorium during the sorption conversion of rare earth phosphate concentrate was studied. Experimental conditions: sorbent consumption in a H^+- form ß=132 %, hydrogen peroxide in the form of a 30 wt % solution 650 % of the stoichiometrically necessary, $C_{H_3PO_4}$ = 15–38 wt %, temperature 20–60 °C, treatment time 4 hours. Experimental results are shown in Tables 61–63.

Table 61

Concentration effect of phosphoric acid on the recovery of components into the sorbent at 20 °C

Experiment	$C_{H_3PO_4}$, wt %	Recovery, rel %							
		Y	La	Ce	Pr	Nd	Sm	Eu	Gd
1	15	99.1	99.6	99.4	99.4	99.4	99.0	99.1	99.1
2	20	96.9	99.0	98.7	98.6	98.5	97.3	97.4	97.7
3	25	95.4	98.6	98.0	97.8	97.7	95.9	96.2	96.7
4	38	86.1	95.8	94.1	93.3	92.8	87.7	89.0	90.5
		Tb	Dy	Ho	Er	Tm	Yb	Lu	∑Tr
1	15	99.1	99.0	99.0	98.9	98.8	98.6	99.1	99.4
2	20	97.6	97.0	97.2	97.0	97.0	96.3	96.8	98.6
3	25	96.5	95.8	96.0	95.6	95.5	94.4	95.1	97.9
4	38	90.8	89.0	88.9	88.6	87.6	85.5	87.5	93.8

		Na	K	Mg	Ca	Sr	Al	Ti	Fe	Th	U
1	15	80.0	49.9	79.6	84.4	98.6	64.0	1.43	44.0	43.2	26.8
2	20	78.5	47.9	74.0	80.8	97.9	53.7	2.03	16.1	11.5	14.8
3	25	74.5	37.6	68.4	75.3	97.4	48.0	1.90	20.1	9.31	19.1
4	38	83.9	54.1	81.8	86.6	95.8	53.3	1.77	24.3	6.40	30.6

Table 62

Concentration of the components in the mother liquors

Experiment	Concentration, mg·l^{-1}							
	Y_2O_3	La_2O_3	Ce_2O_3	Pr_2O_3	Nd_2O_3	Sm_2O_3	Eu_2O_3	Gd_2O_3
1	2.43	8.72	20.9	2.04	8.46	2.34	0.69	2.20
2	9.89	31.9	77.9	8.61	34.4	8.51	2.45	7.58
3	14.7	50.8	126	13.7	57.7	13.2	3.72	11.4
4	51.4	191	492	53.0	216	46.3	12.5	38.5
	Tb_2O_3	Dy_2O_3	Ho_2O_3	Er_2O_3	Tm_2O_3	Yb_2O_3	Lu_2O_3	$\sum Tr_2O_3$
1	0.25	1.06	0.13	0.23	0.018	0.092	0.008	49.5
2	0.86	3.57	0.43	0.80	0.061	0.30	0.027	187
3	1.29	5.14	0.63	1.20	0.092	0.47	0.048	300
4	3.89	15.7	1.95	3.57	0.297	1.43	0.132	1128

	Na_2O	K_2O	MgO	CaO	SrO	Al_2O_3	TiO_2	Fe_2O_3	ThO_2	UO_2

End of table 62

1	12.6	2.57	1.09	62.5	3.87	147	1070	2701	28.3	0.074
2	14.9	3.56	1.87	141	8.11	209	1097	4177	43.2	0.088
3	17.8	4.13	1.72	161	9.86	228	1087	3597	44.4	0.081
4	15.3	6.74	4.50	312	20.6	236	1220	4225	52.1	0.067

Table 63

Properties of the residues

Experiment	Mass, Rel %	Content, wt %									
		CaO	SrO	Al_2O_3	TiO_2	Fe_2O_3	ThO_2	UO_2	$\sum Tr_2O_3$	P_2O_5	F
1	19.0	2.93	0.024	0.27	0.93	1.42	0.004	$7\cdot10^{-5}$	0.42	9.8	1.29
2	17.0	3.45	0.022	0.22	0.73	1.21	0.014	$7\cdot10^{-5}$	0.51	2.7	1.47
3	15.0	5.24	0.032	0.36	0.95	1.50	0.015	$11\cdot10^{-5}$	0.68	2.6	1.36
4	14.0	0.95	0.028	0.26	0.92	0.92	0.005	$2\cdot10^{-4}$	0.96	12.0	1.14

It is seen that the addition of hydrogen peroxide ensured the transition of cerium into the sorbent and, as a result, the high performance of sorption conversion, which gradually decreased with increasing acidity of the solution. The value of $\varepsilon_{\Sigma Tr}/\varepsilon_{Th}$ on the contrary, with an increase in the acidity of the solution, increased from 2.3 at $C_{H_3PO_4}$ = 15 wt % to 14.6 at $C_{H_3PO_4}$ = 38 wt %.

At 20 °C and $C_{H_3PO_4}$ = 20–25 wt %, a high degree of conversion was achieved (recovery of the REE sum into the sorbent 97.9–98.6 %, including recovery of yttrium group REEs ≥ 94.4–96.3 %) and a sufficient degree of separation ($\varepsilon_{\Sigma Tr}/\varepsilon_{Th}$= 8.55 — 10.5). In the sorbent, the thorium content relative to $\sum Tr_2O_3$ will be 0.024 — 0.029 wt %, which, with its subsequent processing, will make it possible to produce rare earth materials with $A_{eff} \leq 0.74$ KBq·kg^{-1}, since the contribution of uranium to A_{eff}, as measurements show, does not exceed 1 rel %.

Under optimal conditions, 1 liter of the sorbent contained following metals in terms of oxides (g): 28.75 $\sum Tr_2O_3$, 0.075 Na_2O+K_2O Me_2O, 3.4 CaO, 0.75 SrO, 0.5 Al_2O_3, 0.038 TiO_2, 1.42 Fe_2O_3, 0.0072 ThO_2, 0.000042 UO_2.

In the sorption conversion step, not only thorium was separated, but also titanium, as well as a significant share of iron and aluminum. These impurities accumulated in the mother liquors (Table 62) due to the formation of anionic complexes or undissociated molecules. Under optimal conditions, 1 liter of the sorbent contained following metals in terms of oxides (g): 28.75 $\sum Tr_2O_3$, 0.075 Na_2O+K_2O

Me_2O, 3.4 CaO, 0.75 SrO, 0.5 Al_2O_3, 0.038 TiO_2, 1.42 Fe_2O_3, 0.0072 ThO_2, 0.000042 UO_2.

The non-decomposed residues were non-radioactive products based on hydrated silica (Table 63). Their disposal is not a problem.

During conversion in a 20 wt % H_3PO_4 environmnt, increasing the temperature to 40–60 °C provided a high conversion performance (REE recovery into the sorbent 98.4–98.9 %), but thorium separation dropped: the $\varepsilon_{\Sigma Tr} / \varepsilon_{Th}$ ratio was 2.06 at 40 °C and 1.86 at 60 °C. The increase in the sorption of thorium with increasing temperature is associated with the destruction of its forms not sorbed by sulfocationite and formed at 20 °C.

Thus, the possibility has been shown of separating thorium from REEs in the process of sorption conversion in phosphoric acid solutions of the rare earth phosphate concentrate produced by the nitric acid processing of apatite. The optimal conditions for sorption conversion in phosphoric acid solutions, which ensure high thorium separation performance, are an H_3PO_4 concentration in the solution of 20–25 wt % and a temperature of 20 °C. In the process, no intermediate and final products with an increased concentration of naturally occurring radionuclides are formed.

Increasing the concentration of phosphoric acid to 38 wt % improves the separation performance of REEs and thorium, but reduces the recovery of REEs into the sorbent. Increasing the process temperature to 40 °C dramatically reduced the separation performance of REEs and thorium. In addition to thorium, silica and the bulk of titanium, iron, aluminum, and uranium enter the mother slurry.

The introduction of small amounts of fluorine ion into the phosphate solution improves the separation performance of rare earth elements and thorium, but is not considered necessary to obtain a non-radioactive rare earth product.

3.5 Concentration of the REEs in the fluorophosphate concentrate precipitated from the phosphoric acid extracted in a dihydrate process

REEs can be recovered from the extraction phosphoric acid of the dihydrate process by the sorption method [4, 8]. At the same time, thorium can be separated [12]. To implement the sorption separation of REEs, an extensive set of process equipment is required, which has to be accommodated by the existing production site. This makes the practical implementation of the sorption separation of REEs from extraction phosphoric acid in functioning plants problematic.

It was found that when fluoride reagents ($NH_4F \cdot HF$, NH_4F) are added to extraction phosphoric acid, ≥ 95 % REEs precipitate [88]. To implement this method, a significantly more limited scope of equipment is required, which greatly simplifies the implementation of such a process on existing production sites. Processing of precipitated concentrates is possible on a separate site.

The resulting fluorine-phosphate precipitates contain ≈ 7 wt % $\sum Tr_2O_3$. The increased relative content in the sum REE yttrium and lanthanides of the medium and yttrium groups (Table 64), the possibility of producing these on existing production sites explain the high relevance of this anthropogenic product.

Table 64

Approximate ratio of individual REEs in commercial extraction phosphoric acid ($\sum Tr_2O_3$ = 100 %)

Content, wt%							
Y_2O_3	La_2O_3	Ce_2O_3	Pr_2O_3	Nd_2O_3	Sm_2O_3	Eu_2O_3	Gd_2O_3
12.7-13.4	10.2-18.6	32.2-36.2	4.2-6.5	15.9-24.1	3.0-4.6	1.0-1.25	3.7-3.8
Tb_2O_3	Dy_2O_3	Ho_2O_3	Er_2O_3	Tm_2O_3	Yb_2O_3	Lu_2O_3	
0.38-0.42	2.1	0.34	0.88	0.09	0.49	0.06	

The specifications of the fluorophosphate concentrate used in this study are given in Table 65.

Table 65

Composition of the fluorophosphate concentrate

Major components											
Na_2O	MgO	CaO	Al_2O_3	SiO_2	TiO_2	Fe_2O_3	$\sum Tr_2O_3$	ThO_2	UO_2	F	P_2O_5
Content, wt %											
4.39	8.07	8.28	17.65	16.45	0.097	0.53	7.295	0.10	0.00016	28.5	9.8
Relative content in the total gEq of concentrate cations, rel %											
7.04	20.04	14.68	51.49	–	–	0.15	6.60	–	–	–	–

We investigated the possibility of decomposition of this concentrate by sorption conversion. Sulfate solutions were used as the liquid phase, since it was believed that the mother sulfur-phosphorus-fluorine-containing liquors obtained in the process would be utilized in the production of mineral fertilizers.

The concentrate and sorbent were placed in a 4 wt % H_2SO_4 (L:S = 8.7÷25) solution, stirred for 1 hour at a temperature of 20 °C. The selected cation exchanger consumption supported sorption of only 71.4 % of the Na, Mg, Ca, Al, and REE cations contained in the concentrate, which made it possible to hope that at the sorption conversion stage, the sorbent would be enriched in the more easily adsorbed REEs.

We investigated the effect on the conversion performance of the L:S ratio. The results of the experiments are presented in Tables 66 and 67.

Table 66

Element distribution between the products of sorption conversion at L:S = 25

Product	Recovery into the product, %							
	Na	Mg	Ca	Al	Ti	Fe	Th	U
Sorbent	31.7	54.6	72.4	13.5	-	19.0	74.1	16.3
Solution	64.9	44.1	24.3	85.0	99.0	79.2	13.0	81.2
Suspension	3.4	1.3	3.3	1.5	0.7	1.8	12.9	2.5
	Recovery into the product, %							
	Y	La	Ce	Pr	Nd	Sm	Eu	Gd
Sorbent	84.0	90.2	89.7	89.1	88.2	89.5	88.8	88.9
Solution	12.1	6.0	6.5	7.0	7.9	6.7	8.7	8.7
Suspension	3.9	3.8	3.8	3.9	3.9	3.8	3.5	3.4
	Recovery into the product, %							
	Tb	Dy	Ho	Er	Tm	Yb	Lu	∑Tr
Sorbent	86.7	86.3	86.0	85.8	85.7	85.3	74.1	88.4
Solution	10.3	11.1	11.6	11.9	12.2	12.5	24.0	7.8
Suspension	3.0	2.6	2.4	2.3	2.1	2.2	1.9	3.8

Table 67

Component distribution between the products of sorption conversion at L:S = 8.7

Product	Recovery into the product, %							
	Na	Mg	Ca	Al	Ti	Fe	Th	U
Sorbent	57.4	64.6	77.4	55.8	30.3	54.1	61.5	33.5
Solution	19.9	10.3	8.0	24.2	64.5	27.9	5.8	54.1
Suspension	22.7	25.1	14.6	20.0	5.2	18.0	32.7	12.4
Product	Recovery into the product, %							
	Y	La	Ce	Pr	Nd	Sm	Eu	Gd
Sorbent	82.8	85.0	84.8	84.9	85.0	84.4	85.0	84.8
Solution	4.9	2.6	2.8	3.0	3.1	3.6	3.7	3.8
Suspension	12.4	12.4	12.4	12.2	11.9	12.1	11.3	11.4
Product	Recovery into the product, %							
	Tb	Dy	Ho	Er	Tm	Yb	Lu	∑Tr
Sorbent	84.3	84.3	84.1	84.0	84.1	83.3	83.4	84.6
Solution	4.6	5.0	5.5	5.6	5.8	5.9	5.7	3.3
Suspension	11.1	10.7	10.4	10.4	10.1	10.8	10.9	12.1

Analysis of the data in Tables 66 and 67 shows that in this case too, sorption conversion allows to concentrate REEs in the sorbent, while the bulk of the many impurity cations remain in the sulfuric acid solution. Silica, fluorine and phosphorus-containing anions also remain in the slurry. REE loss with the mother liquor is likely to decrease with a decrease in the concentration of sulfuric acid. The degree of proton substitution in sulfocationite for metal cations with a decrease in L:S in the studied interval increased from 51.4 to 87.8 %.

The decrease in the volume of sulfate solution used in the conversion slightly reduced the degree of REE concentration in the sorbent, but it led to a significant increase in the sorption of sodium, aluminum, titanium, iron, and uranium. The degree of concentration in the cation exchanger of various REEs is quite close, although for the REEs of the cerium group it is slightly higher than for the others, which is determined by the small difference in their acid-base properties. Under optimal conditions, the content of REE oxides in the sorbent relative to the sum of oxides of sorbed metals exceeded 31 wt %. Of the impurities, the sorbent contained a significant amount of magnesium, calcium and aluminum. It seems advisable to develop methods for the preliminary chemical concentration of REEs in fluorophosphate concentrate.

The relative amount of suspensions, which, compared with the initial concentrate, are slightly enriched in thorium, increases with a decrease in L:S, apparently due to an increase in the concentration in the mother liquor of fluorine and phosphorus anions that bind thorium into slightly soluble compounds. Suspension can be reduced by increasing the consumption of the sorbent, or the suspensions can be recycled.

Thus, the possibility of sorption conversion of a fluorophosphate concentrate in a sulfuric acid environment has been shown with the recovery of REEs into sulfocationite and their separation from silicon, phosphorus, fluorine, and the bulk of impurity cations.

4. LIST OF REFERENCES

1. Lokshin E.P., Tareeva O.A., Sedneva T.A. Processing of apatite concentrate by sorption conversion: preprint // Apatity: FRC KRC RAS, 2018. 64 p. ISBN 978-5-91137-372-6. [In Russian].
2. Nikonov V.N., Mikhlin E.B., Norina T.M., Afonina T.A. A study of REE sorption from sulfate environments // Chemical, sorption, and extraction-based methods for the concentration and treatment of rare metals: Collected papers. Moscow: Giredmet, 1978. Vol. 83. Pp. 52-61. [In Russian].
3. Lokshin E.P., Tareeva O.A., Elizarova I.R. Desorption of metals from sulfocationite with concentrated solutions of sodium salts // Chemical Industry Today. 2018. No. 2. Pp. 31-36. [In Russian].
4. Sibilev A.S., Shestakov S.V., Kozyrev A.B., Nechaev A.V., Polyakov E.G., Falchik Yu.A., Shibnev A.V. REE recovery from extraction phosphoric acid at PhosAgro-Cherepovets // Chemical Technology 2015. No. 4. Pp. 201-205. [In Russian].
5. Lokshin E.P., Tareeva O.A., Elizarova I.R. Isolation of Rare Earth Elements from Ammonium Salts Solutions // Theoretical Foundations of Chemical Engineering. 2015. V. 49. N 4. P. 555-559. DOI 10.1134/S0040579515040144.
6. Claim 2020101164 Russian Federation. IPC C01F 17/00, C22B 59/00 (2006.01). A method for the recovery of rare earth concentrate / E.P. Lokshin, O.A. Tareeva. Priority date 10.01.2020. [In Russian].
7. Lokshin E.P., Tareeva O.A. Development of processes for the recovery of rare earth elements during the sulfuric acid processing of the Khibiny apatite concentrate into mineral fertilizers. Apatity: KRC RAS, 2015. 268 p. [In Russian].
8. Patent 2465207 RF, IPC C01F17/00, C22B59/00, C01B25/222 (2006.01). A method for the recovery of lanthanides from extraction phosphoric acid / E.P. Lokshin, O.A. Tareeva. Claim 11.07.2011. Publ. 27.10.2012. Bull. 30. Pat. 2525947 RF, IPC C 22 B 59/00, 3/24, C 01 F 17/00 (2006.01).
9. Patent 2525947 RF, IPC C 22 B 59/00, 3/24, C 01 F 17/00 (2006.01). A method for the recovery of rare earth elements from extraction phosphoric acid / E.P. Lokshin, O.A. Tareeva, V.T. Kalinnikov. Claim 03.07.13. Publ. 20.08.14. Bull. No. 23. [In Russian].
10. Sibilev A.S., Shestakov S.V., Kozyrev A.B., Nechaev A.V., Polyakov E.G., Falchik Yu.A., Shibnev A.V. REE recovery from extraction phosphoric acid at PhosAgro-Cherepovets // Chemical Technology. 2015. No. 4. Pp. 201-205. [In Russian].
11. Patent 2443630 RF, IPC C 01 F 17/00, C 22B 59/00, C 01 B 25/222 (2009.01). A method for the recovery of lanthanides from extraction phosphoric acid / E.P.

Lokshin, O.A. Tareeva. Claim 02.08.10. Publ. 27.02.2012. Bull. No. 6. [In Russian].
12. Patent 2509169 RF, IPC C01F17/00, C22B59/00, C01B25/222 (2009.01). A method for the recovery of lanthanides from extraction phosphoric acid / E.P. Lokshin, O.A. Tareeva. Claim 11.07.11. Publ. 27.10.12. Bull. 30.
13. Preston J.S., Cole P.M., Craig W.M., Feather A.M. The recovery of rare earth oxides from a phosphoric acid by-product // Hydrometallurgy. 1996. V. 41. № 1. P. 1-19.
14. Bushuev N.N., Levin B.V. Fundamentals of a new process for the separation of rare earth elements from extraction phosphoric acid // Chemical Technology. 2014. No. 1. Pp. 52-58. [In Russian].
15. Lokshin E.P., Ivanenko V.I., Tareeva O.A., Korneykov R.I. Recovery of lanthanides from phosphoric acid solutions using sorption methods // Journal of Applied Chemistry. 2009. Vol. 82. No. 4. Pp. 544-551. [In Russian].
16. Patent 2559476 RF. IPC C01F 17/00, C22B 59/00 (2006.01). A method of the recovery of rare earth metals from a nitrophosphate solution during nitric acid processing of apatite concentrate / Osmak A.V., Nikolaeva I.I., Bazyukina T.V. Maklashina E.A. Claim 04.06.2014. Publ. 10.08.2015. Bull. No. 22. [In Russian].
17. Goldinov A.L., Kopylev B.A., Abramov O.B., Dmitrievsky B.A. Integrated nitric acid processing of phosphate mineral feeds. Leningrad: Chemistry, 1982, 208 pp. [In Russian].
18. Patent 2458863 RF, IPC C01F7/00 (2006.01). A method for the recovery of rare earth concentrate from apatite / M.V. Tauk, I.I. Nikolaev, A.V. Osmak, N.V. Gorshkova, L.V. Spakhova // Claim 14.02.2011. Publ. 20.08.2012. Bull. No. 23. [In Russian].
19. Moiseev S.D., Semenov V.A., Shelekhova T.A. Extraction treatment of rare earth phosphate concentrate obtained by processing apatite // Chemical Industry. 1981. No. 8. [In Russian]. Pp. 472-475. [in Russian].
20. Patent 2532773 RF, IPC C22B 59/00, C22B 3/06, C22B 3/26 (2006.01). A processing method for phosphate rare earth concentrate / M.V. Tauk, I.I. Nikolaeva, E.A. Maklashina, G.V. Saldaeva. Claim 25.07.2013. Publ. 10.11.2014. Bull. No. 31.
21. Patent 18456 DDR. Verfahren zur Gewinnung von Phosphorsäure aus apatithaltigen Mineralien und Gesteinen / E. Thilo, F. Wodtske. Publ. 01.04.1960.
22. Brevet 1474086 Fr. IPC C 01 b. Perfectionnement aux procédés de fabrication d’acide phosphorique / P. Dumont. Claim 04.02.1966. Publ. 13.02.1967. Bull. No. 12.

23. Patent 1285466 BRD. IPC C 01 b. Verfahren zur Herstellung von Phosphorsäure / L.W. Cochran. Anmeldetag 17.05.1967. Auslegetag 19.12.1968.
24. Patent 1287054 BRD. IPC C 01 b. Verfahren zur Herstellung von Phosphorsäure / L.W. Cochran. Anmeldetag 16.11.1967. Auslegetag 16.01.1969.
25. Khafizov R.Kh., Krachak A.N., Gruzdeva A.N., Bolotkov A.A., Khafizov S.Kh., Smirnov A.A., Zhiguleva T.I. Sorption concentration and separation of REEs from extraction phosphoric acid // Proceedings of the international research and practice workshop “Processing and disposal of associated fluoride compounds and the recovery of rare earth metals in the production of mineral fertilizers.” Moscow: NIUIF, 2011. Pp. 180-197. [In Russian].
26. Norwood M.V., Kohler J.J. Characterization of fluorine-, aluminum-, silicon-, and phosphorus-containing complexes in wet-process phosphoric acid using nuclear magnetic resonance spectroscopy // Fertilizer Research. 1991. V. 28. P. 221-228.
27. Kulba F.Ya., Nikolaeva S.A., Gavryuchenkov F.G., Reshetnikova Z.V. Potentiometric study of complexation in Me (III) - HF - H_3PO_4 systems (Me - Fe, Al) using a glass electrode // Journal of Applied Chemistry. 1975. Vol. 48. No. 11. Pp. 2547-2549. [In Russian].
28. Gorelov A.M., Shtin A.P. Investigation of the properties of phosphoric acid solutions of titanium // Transactions of the Institute of Chemistry, UF USSR Academy of Sciences. 1970. Issue 20. Pp. 106-110. [In Russian].
29. Zherin I.I., Amelina G.N. Chemistry of thorium, uranium, plutonium. Tomsk: TPU, 2010.147 p. [In Russian].
30. Kobets L.V., Umreiko D.S. Uranium phosphates // Advances in Chemistry. 1983. Vol. 52. No. 6. Pp. 897-921. [In Russian].
31. Patent 2467949 RF, IPC C01B 25/234 (2006.01). A defluorination method for extraction phosphoric acid / N.M. Brizitskaya, N.V. Buccolini, M.N. Tsikin, V.V. Dolgov, A.M. Norov, A.S. Malyavin. Claim 29.06.2011. Publ. 27.11.2012. Bull. No. 33. [In Russian].
32. Lokshin E.P., Tareeva O.A., Elizarova I.R. Obtaining a rare earth concentrate from sulfocations saturated with rare earth metals from sulfate solutions of phosphogypsum leaching // Chemical Technology. 2014. Vol. 15. No. 12. P. 738-745. [In Russian].
33. Lokshin E.P., Tareeva O.A., Elizarova I.R. Isolation of rare earth elements from solutions of ammonium salts // Chemical Technology. 2014. No. 4. Pp. 222-226. DOI 10.1134/S0040559515040144. [In Russian].
34. Lokshin E.P., Tareeva O.A. Treatment of phosphogypsum - a process waste of sulfuric acid processing of the Khibiny apatite concentrate - to remove phosphorus impurities // 4th international conference "Issues of rational management of the natural and anthropogenic mineral resources of the Barents

region in the building materials industry." Presentation. Arkhangelsk, 2010. Pp. 83-86. [In Russian].

35. Lokshin E.P., Tareeva O.A., Elizarova I.R., Kalinnikov V.T. Recovery of rare earth elements from extraction phosphoric acid // Journal of Applied Chemistry. 2015. Vol. 88. No. 1. Pp. 3-14. DOI 10.1134/S1070427215010012. [In Russian].
36. Frayret J., Castetbon A., Trouve G., Potin-Gautier M. Solubility of $(NH_4)_2SiF_6$, K_2SiF_6 and Na_2SiF_6 in acidic solutions // Chemical Physics Letters. 2006. V. 427. P. 356–364.
37. Nikolaeva N.M. Chemical equilibrium in aqueous solutions at elevated temperatures. Novosibirsk: Nauka, Siberian Branch of the USSR Academy of Sciences, 1982. 230 p. [In Russian].
38. Papkova M.V., Saykina O. Yu., Mikhaylichenko A.I., Konkova T.V. Desorption of REEs from the sulfocationite KU-2 with hydrochloric acid and ammonium nitrate // Advances in Chemistry and Chemical Technology. 2015. Vol. 29. No. 3. Pp. 83-85. [In Russian].
39. Lokshin E.P., Tareeva O.A., Elizarova I.R. Processing of phosphodihydrate to recover rare earth elements and obtain phosphate- and fluoride-free gypsum // Journal of Applied Chemistry. 2011. Vol. 84. No. 9. Pp. 1409-1417. [In Russian].
40. Patent 2000141 RF, 01 J 39/00. A method of ion exchange extraction of metal ions from solutions / E.G. Drozhko, R.A. Penzin, V.V. Milyutin, V.M. Gelis, A.I. Bardov. Claim 05.02.92. Publ. 07.09.93. Bull. No. 33-36. [In Russian].
41. Semin B.D., Kushnirov Yu.F. To the question of fractional separation of metal hydroxides // Metallurgy of Non-Ferrous Metals. Transactions of the Krasnoyarsk Institute of Non-Ferrous Metals. 1971. No. 4. Pp. 190-196. [In Russian].
42. Solubility Handbook. Vol. 2. Book 2. Leningrad: Nauka, 1969. 1170 p. [In Russian].
43. Alemrajabi M., Rasmuson Å.C., Korkmaz K., Forsberg K. Upgrading of a rare earth phosphate concentrate within the nitrophosphate process // Journal of Cleaner Production. 2018. V. 198. P. 551-564.
44. Riley E., Dutrizac J.E. The behaviour of the rare earth elements during the precipitation of ferrihydrite from sulphate media // Hydrometallurgy. 2017. T. 172. C. 69-78.
45. Spitsyn V.I., Martinenko L.I. Coordination chemistry of rare earth elements. Moscow: Moscow State University, 1979. 254 p. [In Russian].
46. Wasserman I.M. Chemical precipitation from solutions. Leningrad: Chemistry, 1980. 208 p. [In Russian].

47. Patent 2104938 RF, IPC^6 C01F 17/00. A method for the recovery extraction of rare earth elements from phosphogypsum / Valkov A.V., Valkov D.A. Claim 26.09.96. Publ. 20.02.98. Bull. No. 5. [In Russian].
48. Mudruk N.V., Korovina Yu.V., Elizarova I.R., Nikolaev A.I. Isolation of thorium iron cake from process solutions after nitric acid unlocking of perovskite concentrate // Non-Ferrous Metals. 2017. No. 6. Pp. 63-68. DOI: 10/17580/tsm.2017.06.10. [In Russian].
49. Kosynkin V.D., Makarov V.D., Shatalov V.I. Treatment of loparite rare earths to remove radioactive impurities // Development of the Loparite Rare Metal Industry in Russia. Proceedings of the 4th scientific conference. St. Petersburg: Alice St. Petersburg, 2001. Pp. 153-158. [In Russian].
50. Posypayko V.I., Alekseeva E.A., Vasina N.A. Fusibility diagrams of salt systems. Part 3. Binary systems with a common cation. Moscow: Metallurgy, 1978. 204 p. [In Russian].
51. Patent 2070426 RF, IPC B 01 D 61/44 (2006.01). A method of producing cesium or rubidium hydroxide and acid / T.A. Sedneva, I.P. Tyulyunov, I.A. Fedina, V.A. Masloboev, E.P. Lokshin, N.B. Voskoboinikov. Claim 23.02.93. Publ. 20.12.96. Bull. No. 35. [In Russian].
52. Kochetkov S.P., Smirnov N.I., Ilyin A.P. Concentration and purification of extraction phosphoric acid: a monograph. GOUVPO, Ivanovo. State University of Chemical Engineering: Ivanovo, 2007. 304 p. [In Russian].
53. Postnikov N.N. Thermal phosphoric acid. Chemistry: Moscow, 1970. 304 p. [In Russian].
54. Lokshin E.P. Obtaining orthophosphoric acid of high purity // Proceedings of the international research and practice conference "Phosphate mineral feeds: production and processing". 17.05.2012. Moscow. NIUIF. Pp. 87-96. [In Russian].
55. Yu Z., Mamoun M. An integrated process for the treatment of apatite obtained from dephosphorization of iron ore // J. Chem. Tech. Biotechnol. 1990. V. 47. P. 47-60.
56. Jin Yong-shi, Jiang Tao, Yang Yong-bin, Li Qian, Li Guang-hui, Guo Yu-feng. Removal of phosphorus from iron ores by chemical leaching // J. Cent. South. Univ. Technol. 2006. V. 13. N 6. P. 673-677. DOI: 10.1007/s11771-006-0003-y.
57. Patent Application № 2017/0028410 A1 USA, Int. Cl. B03D 1/008, B03C1/033 (2006.01). Beneficiation of rare earth elements bearing ancylite / Anderson C.G., Hao Gui. Заявл. 01.08.2016.
58. Gupta C.K, Krishnamurthy N. Extractive Metallurgy of Rare Earths. London, New York, Washington: CRC Press, 2005, 522 p.

59. Handling of mineral feeds and materials with a high natural content of radionuclides. Public health rules and standards SP-2.6.1.798-99. Moscow: Ministry of Health of Russia, 2000. 11 p. [In Russian].
60. Kruesi P.R., Duker G. Production of rare earth chloride from bastnesit // J. Metals. 1965. V. 17. P. 847-849.
61. Belikov M.L., Ivanenko V.I., Lokshin E.P., Sedneva T.A. Distillatio of HF from acid fluoride-sulfate solutions // Chemistry for Sustainable Development. 2017. Vol. 25. No. 5. Pp. 473–478. DOI: 10.15372/ KhUR20170501. [In Russian].
62. Kim W., Bae I., Chae S., Shin H. Mechano-chemical decomposition of monazite to assist the extraction of rare earth elements // J. Alloys and Compounds. 2009. V. 486. N 1-2. P. 610-614.
63. Abdel-Rehim A M. An innovative method for processing Egyptian monazite // Hydrometallurgy. 2002. V. 67. P. 9-17.
64. Kuzmin V.I., Pashkov G.L., Lomaev V.G., Voskresenskaya E.N., Ruzmina V.N. Combined approaches for comprehensive processing of rare earth metal ores // Hydrometallurgy. 2012. V. 129-130. N 11. P. 1-6.
65. Merritt R.R. High temperature methods for processing monazite: 1. Reaction with calcium chloride and calcium carbonate // J. Common Met. 1990. V. 166. N 2. P. 197-212.
66. Patent 2242528 RF, IPC C01F 17/00, C01G 56/00, C22B 59/00, C22B 60/02. A method of unlocking the monazite concentrate / V.P. Kosenko, V.T. Zhukov, G.F. Pekhov, V.N. Kazantsev. Claim 08.04.2002. Publ. 20.12.2004. Bull. No. 35. [In Russian].
67. Patent 2331681 RF, IPC C22B 59/00, C22B 60/02. A method of decomposition of monazite / V.A. Nizov, N.V. Obabkov, A.L. Smirnov, A.A. Mikheev, G.D. Terentyev, V.P. Smetannikov, V.D. Kosynkin, V.F. Leontiev. Claim 30.04.2004. Publ. 20.08.2008. Bull. No. 23. [In Russian].
68. Tananaev I.V., Vasilyeva V.P. On the solubility of lanthanum phosphate in phosphoric acid solutions // Journal of Inorganic Chemistry. 1964. Vol. 9. No. 9. Pp. 213-214. [In Russian].
69. Vasilenko N.A., Chepelevetsky M.L. Solubility of lanthanum phosphate in aqueous solutions of phosphoric acid at 80° // Journal of Inorganic Chemistry. 1957. Vol. 2. No. 10. Pp. 2486-2489. [In Russian].
70. Sergeeva N.M., Kuzmenkov M.I. A study of the La_2O_3–H_3PO_4–H_2O system // Journal of Inorganic Chemistry. 1983. Vol. 28. No. 8. Pp. 2157-2159. [In Russian].
71. Ulyanov A.I., Kazakova T.I. A study of the $CePO_4$–H_3PO_4–H_2O system at 25° // Bull. USSR Academy of Sciences. Chemistry series. 1963. No. 7. Pp. 1157-1164. [In Russian].

72. Sveshnikova V.N., Ginzburg V.L. A study of the ternary system cerium phosphate - phosphoric acid - water at 70ºC // Journal of Inorganic Chemistry. 1962. Vol. 7. No. 5. Pp. 1169-1173. [In Russian].
73. Kijkowska R. Preparation of lanthanide orthophosphates by crystallisation from phosphoric acid solution // Journal of Materials Science. 2003. V. 38. P. 229-233.
74. Information and analysis resource: http://www.monazite.ru/monazite
75. Vulikh A.I. Ion exchange synthesis. Moscow: Chemistry, 1973. 232 p. [In Russian].
76. Lokshin E.P., Tareeva O.A. The interaction of cations of aluminum, iron (III) and titanyl with SiF_6^{2-} in sulfuric and nitric acid environments // Journal of Applied Chemistry. 2015. Vol. 88. No. 9. Pp. 1364-1368. DOI 10.1134/S1070427215090268. [In Russian].
77. Patent 2148019 RF, IPC^7 C01F 17/00, C22B 3/06. A method of processing a phosphate rare earth concentrate isolated from apatite / V.N. Lebedev, S.D. Sergeeva, V.A. Masloboev, E.P. Lokshin. Claim 23.11.1998. Publ. 27.04.2000. Bull. No. 12. [In Russian].
78. Lokshin E.P., Lebedev V.N. Isolation of phosphorus from phosphate-containing rare earth materials by carbon thermal reduction // Journal of Applied Chemistry. 1999. Vol. 72. No. 2. Pp. 184-190. [In Russian].
79. Lokshin E.P., Tareeva O.A. Features of sulfuric acid leaching of lanthanides from phospho-hemihydrate // Journal of Applied Chemistry. 2008. Vol. 81. Vol. 1. Pp. 10-15 [in Russian].
80. Kuzina T.I., Slivko T.A., Zimina G.V., Komissarova L.N. On the solubility of rare earth orthophosphates in nitric acid // University Bull. Non-Ferrous Metallurgy. 1994. No. 1 - 2. Pp. 68-70. [In Russian].
81. Makhmadmurodov A., Juraev H.Sh., Komilova G., Karimov V. Determination of the solubility product of yttrium fluoride // Transactions of the Tajik SSR Academy of Sciences. 1972. Vol. 15. No. 9. P. 40-43. [In Russian].
82. Ikrami D.D., Komilova G., Khaitova M. On the solubility of lanthanum and scandium fluorides in nitric acid // Transactions of the Tajik SSR Academy of Sciences. 1973. Vol. 16. No. 3. Pp. 65-69. [In Russian].
83. Lokshin E.P., Tareeva O.A., Elizarova I.R. Sorption conversion of phosphate concentrates of rare earth metals // Journal of Applied Chemistry. 2014. Vol. 87. No. 8. Pp. 1038-1043. [In Russian].
84. Patent 2590796 RF, IPC C22B 3/08, 59/00 (2006.01). A method of processing phosphogypsum / E.P. Lokshin, O.A. Tareeva. Claim 01.04.15. Publ. 10.07.16. Bull. No. 19.

85. Patent 2612244 RF, IPC C22B 59/00, 3/06, 3/24 (2006.01). A method of processing REE phosphate concentrate / E.P. Lokshin, O.A. Tareeva. Claim 11.11.15. Publ. 03.03.17. Bull. No. 7. [In Russian].
86. Lokshin E.P., Tareeva O.A., Elizarova I.R. Defluorination of fluorinated rare earth materials // Chemical Technology. 2019. Vol. 20. No. 2. Pp. 76-81. [In Russian].
87. Lokshin E.P., Tareeva O.A., Elizarova I.R. A new approach to the processing of apatite concentrate // Journal of Applied Chemistry. 2016. Vol. 89. No. 7. Pp. 887-893. [In Russian].
88. Lokshin E.P., Tareeva O.A., Elizarova I.R. Precipitation of rare earth elements from extraction phosphoric acid by fluorine compounds // Journal of Applied Chemistry. 2011. Vol. 84. No. 5. Pp. 743-751. [In Russian].

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