ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 4, pp. 537−544. © Pleiades Publishing, Ltd., 2009.
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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Sorption Extraction of Lanthanides from Phosphoric Acid Solutions

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Received June 30, 2008

Abstract— The possibility of sorption extraction of lanthanides from nitric-phosphoric and phosphoric acid solutions with inorganic sorbents based on hydrated titanyl hydrophosphate was studied. New technological solutions were suggested for lanthanide sorption from the products which are formed in processing of the Khibiny apatite concentrate on mineral fertilizers (frozen nitric-phosphoric acid extract, a product of nitric acid decomposition of apatite, and the production phosphoric acid from the dihydrate process).

DOI: 10.1134/S1070427209040028

A number of technological schemes is used in acid decomposition of the Khibiny apatite concentrate (hereinafter, apatite concentrate).

In the nitric acid method of decomposition, all lanthanides are transferred from the apatite concentrate into a nitric-phosphoric acid solution, potassium nitrate is crystallized from this solution by freezing to obtain a frozen nitric-phosphoric acid extract (FNPE), and sodium carbonate is introduced in a 110% excess above sodium fluorosilicate stoichiometry to cause it to precipitate.

Completeness of the lanthanide precipitation and their content in the concentrate depend on the degree of neutralization of the first proton of orthophosphoric acid. At high degree of the neutralization the lanthanide precipitation is virtually complete, but a large number of phosphates of other elements (mainly, of calcium) is coprecipitated from the solution, which markedly decreases the lanthanide concentration in the concentrate and yields precipitates in form of a hardly filterable gel.

Under the optimal conditions of the neutralization, the concentrates are enriched in lanthanides, whereas the most valuable lanthanides of the apatite concentrates (yttrium, heavy lanthanides) are precipitated to a considerably lesser extent than cerium-group lanthanides. Subsequent dephosphorization of the lanthanide concentrate is expensive.

In the dihydrate process of sulfuric acid decomposition of the apatite concentrate, as high as 20% of initial lanthanides pass into the wet-process phosphoric acid (WPPA) [2]. As a result, WPPA contains 0.1–0.12 wt % of the sum of lanthanides in terms of oxides (ΣLn_2O_3) [3], from 35 to 75% of yttrium of the apatite concentrate (according to different reports), 18.0–30.0 of europium, 20.0–22.6 of samarium, only 6.3–8.5 of lanthanum and 11.3–14.5 of cerium [4, 5]. The high content of the most valuable lanthanides in WPPA makes it interesting object for the lanthanide extraction.

Neutralization of WPPA, used in production of ammonium phosphates, with ammonium may cause precipitation of lanthanide phosphate concentrates containing (wt %): ΣLn_2O_3 1.73–2.30, TiO_2 2.1–2.2, Fe_2O_3 3.2–3.5, CaO 10.3–10.5, F 4.3–4.6, P_2O_5 46.4–46.7, and SO_4^{2-} 3.0–3.5m thereby the precipitation of lanthanide phosphates ceases after a pH 3 of the solution is attained [6]. This method reaches a reasonably complete precipitation of all lanthanides and aluminum [7].

Processing of the lanthanide phosphate concentrates of complex composition to remove a very low content of the net component is economically unreasonable.

The production WPPA from the dihydrate process is supersaturated with lanthanides, first of all, with cerium [3]. This suggested methods of the lanthanide crystallization on fluoride or phosphate seed grains in a heated WPPA flow [8, 9].

Table 1. NPFE composition by manufacturers data (density at 25°C ~1.5 g cm^{-3})

Component concentration, wt %										
total HNO_3	free HNO_3	P_2O_5	Ca	Sr	Mg	Al	Fe	ZLn_2O_3	Si	F
26.55	12.7	22.5	3.41	0.25	0.031	0.20	0.13	0.48	0.30	1.8

Table 2. WPPA composition (H_3PO_4 concentration 38.5 wt %, density at 20°C g cm^{-3})

Component concentration, wt %									
TiO_2	ZLn_2O_3	F^-	SiO_2	Al	Fe	Na_2O	K_2O	CaO	SrO
1.31	1.291	16.5	8.56	2.66	1.76	1.24	0.39	0.92	0.15

It has been reported [10, 11] that the material of a seed determines the composition of crystallized lanthanide compounds. The product precipitated from the wet-process phosphoric acid (produced at Minudobreniya Balakovsky Open Joint-Stock Company) on phosphate seed contained (wt %): ΣLn_2O_3 50.67, P_2O_5 27.7, SO_3 5.13, F ≤ 0.1, CaO 2.59, MgO 1.24, Al_2O_3 2.14, Fe_2O_3 0.1, SiO_2 0.15, loss on calcinations at 700°C 5.91, and acid-insoluble residue 3.25. The precipitate obtained by the crystallization on fluoride seed contained (wt %): ΣLn_2O_3 66.7, F 24.8, P_2O_5 4.4, SO_3 0.37, CaO 2.59, SrO 0.56, loss on calcinations at 700°C 3.38.

The high concentration of lanthanides in these products, simple methods used for their preparation, and easy building of lanthanide separation apparatus into the technological process of WPPA production suggested a high efficiency for the method proposed. It has been found however [10, 11] that seeds are rapidly passivated and the precipitation of rare-earth products first becomes slower and then ceases at all. The experimental data [10, 11] show that the weight of the precipitates crystallized before the passivation of seed is only 4.5–6.25% of the initial seed. Because the preparation of seeds requires preliminary conversion of REE phosphates or fluorides into a water-soluble compound, which is expensive, the proposed method of REE separation from dihydrate WPPA will show promise only in the case, if a simple seed depassivation procedure not requiring complex chemical treatment of the obtained precipitates is available. In addition, the composition of the sum of lanthanides on seeds is unknown, with crystallization of yttrium compounds and yttrium-group lanthanides is unlikely.

It was suggested to use the thermal treatment of defluorinated WPPA in an autoclave at 200°C for 1 h [12]. This method is based on the fact that the solubility of lanthanide phosphates decreases as temperature is raised.

The precipitate formed contained, on washing with a fivefold amount of water and drying, (wt %) ΣLn_2O_3 15–24, P_2O_5 15, ThO 20.52 and was strongly contaminated with calcium. The recovery of lanthanides into the precipitate was as high as 98%. Industrial application of this technique is strongly impeded because of the high temperature and pressure.

Studies of the extraction separation of lanthanides from WPPA [13–15] have suggested no appropriate technological solution.

In this study, for separation of lanthanides from FNPE and WPPA we used a new technique including their sorption with mineral sorbents based on hydrated titanyl hydrophosphate.

EXPERIMENTAL

We used in the study FNPE from the Akron Open Joint-Stock Company (Novgorod). Production WPPA of the hydrate process from the VAZ Open Joint-Stock Company (Volkhov, Leningrad. region) was used without evaporation. A model solution used in the preliminary tests was close in composition to WPPA and contained (M): nitrate ions 2.6, phosphate ions 4.9, and calcium ions 1.2. Also it contained yttrium, lanthanum, cerium, and ytterbium ions in concentrations corresponding to their concentration in WPPA.

It was shown previously that the sorbents based on dehydrated titanyl hydrophosphate can effectively sorb cations of heavy, alkali and alkaline-earth metals, cobalt, lanthanides, uranium, and thorium from aqueous solutions containing as high as 32 g l^{-1} of the salts [16]

Table 3. Cation-exchange constants in lanthanide sorption

Constant	Y^{3+}	Gd^{3+}	Eu^{3+}	Sm^{3+}	Nd^{3+}	Ce^{3+}
log K_{ex} at 20°C at 50°C	−1.51	−1.45	−1.40 −0.98	−1.34	−1.22 −0.93	−1.16 −0.84

whose composition corresponds to their composition in the seawater.

It was suggested that lanthanide sorption from phosphoric acid solutions can occur and is described by the same regularities as selective sorption of cerium and strontium radionuclides [16]. Then, according to the law of mass action, the distribution constant K_d in an acid solution should increase as pH of the solution increases to pH ≤ 4–5. This suggestion is also confirmed by variations with the solution pH of K_d of the sum of these cations in their sorption with hydrated titanyl hydrophosphate (Fig. 1). At the same time, as was mentioned previously, the lanthanide precipitation from phosphoric acid solutions even at pH 3 is complete. Therefore, the sorption must be performed from the solutions of a considerably larger acidity.

Solutions used in studying the sorption were preliminarily neutralized with ammonium hydrocarbonate to pH ~1.5–1.7 and a dilution resulted from the introduction of ammonium hydrocarbonate into the solutions was taken into account in estimate of the lanthanide extraction. We used two types of the synthesized sorbents: hydrated titanyl hydrophosphate (sorbent 1) and zirconium-modified sorbent characterized by higher acidity (sorbent 2). Both sorbents used in the tests were in the form of 0.3–0.7-mm granules. The specific content of the cation-exchange hydrophosphate groups in sorbent 2 was larger by 14.8% than in sorbent 1.

Preliminarily, the cation exchange constants of protons of the sorbent for cations of some lanthanides in the nitric acid solutions were determined for sorbent 2 (Table 3). The determination of the thermodynamic constants for cation exchange has been described previously [17]. It was established that increasing temperature increases sorption efficiency.

The sorption was performed at 70°C for 1 h. At this temperature the production phosphorus-containing solutions are used in technological processes. The sorption of lanthanides from a model solution and FNPE containing about 8 g l^{-1} ΣLn_2O_3 was performed at $\alpha = 20$ and that from WPPA, at $\alpha = 100$ (α is the ratio of the volume of a liquid to the mass of a sorbent. In sorption from WPPA $\alpha = 100$.

Table 4. Data on lanthanide sorption from a model solution

Solution	Concentration in solution, g l^{-1}				
	CeO_2	La_2O_3	Y_2O_3	Yb_2O_3	SrO
Sorbent 1					
Initial	5.56	2.64	0.13	0.0063	1.8
Mother	5.45	2.64	10.08	0.003	0.92
Extracted from solution, %	2.0	–	38.5	52.4	48.9
Sorbent 2					
Mother	1.15	1.14	0.01	0.0001	0.90
Extracted from solution, %	79.3	56.8	92.3	98.4	50

The sorbent was separated and washed with water. The concentration of the individual lanthanides in the initial and mother solutions was analyzed by the atomic emission spectrometry with inductively coupled plasma on a Perkin Elmer Plasma 400 instrument.

Results obtained in studying the sorption from the model solution are collected in Table 4. As seen, under conditions of examination sorbent 1 sorbed badly cerium-group lanthanides, whereas it sorbed markedly yttrium and ytterbium. Sorbent 2 ensured higher sorption efficiency for all the lanthanides studied. Both sorbents sorbed strontium markedly and to the same extent. The sorption efficiency for lanthanides increased in the order of decreasing the ionic radius (Å): La^{3+} (1.061), Ce^{3+} (1.034), Y^{3+} (0.93), and Yb^{3+} (0.858) [18].

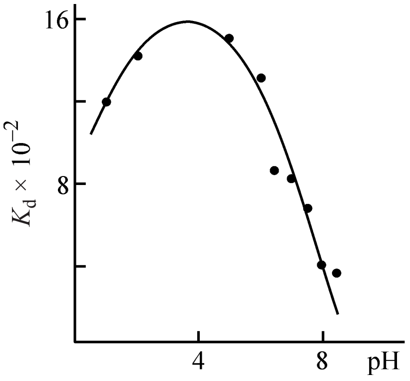


Fig. 1. Distribution constant K_d (cm^3 g^{-1}) vs. pH of the suspension on hydrated titanyl hydrophosphate [16].

Table 5. Separation coefficients for lanthanides in their sorption from a model solution

Sorbent	$K_{Y/La}$	$K_{Yb/La}$	$K_{Y/Ce}$	$K_{Yb/Ce}$
1	9.1	47.1	31.0	54.5
2			3.1	16.2

Table 6. Lanthanide concentration in initial and mother solutions

Lanthanide	Concentration in solution, mg l^{-1}		
	initial	1	2
Y_2O_3	286	185	145
La_2O_3	1810	477	134
Ce_2O_3	3120	560	73.3
Pr_2O_3	357	71.0	17.2
Nd_2O_3	1700	352	66.3
Sm_2O_3	193	54.7	14.8
Eu_2O_3	23.1	7.37	5.45
Gd_2O_3	122	50.4	25.4
Tb_4O_7	17.2	n.d.[a]	5.22
Dy_2O_3	51.2	26.7	16.9
Ho_2O_3	6.63	4.43	3.12
Er_2O_3	23.2	н.о.	7.76
Yb_2O_3	10.2	6.16	5.22
ΣLn_2O_3	7687.2	1794.8	517.2

[a] Not determined; the same for Tables 7–9.

The separation coefficients were calculated by equation:

$$K_{1/2} = \frac{N_1C_2}{N_2C_1} , \tag{1}$$

(N_1, N_2 and C_1, C_2 are the concentrations of components 1 and 2 in the equilibrium solid and liquid phases, respectively, in any similar units (Table 5). As seen, all sorbents under examination, especially more basic sorbent 1, may be promising for selective extraction of yttrium and heavy lanthanides from the complex solutions containing large excess of cerium-group lanthanides.

In study of the sorption separation of lanthanides from FNPE we took into account that the concentration of lanthanides and concurrent cations (mainly strontium and calcium) in it is high and a large consumption of the sorbent will be required. Therefore, we studied the possibility of separating preliminarily a majority of lanthanides in the form of double sulfates with sodium (hereinafter, double sulfates). The use of sodium compounds for sulfate precipitation required preliminary precipitation of sodium fluorosilicate, because its presence in the concentrate considerably decreased the concentration of lanthanides.

As known, double sulfates of many lanthanides are difficultly soluble in aqueous solutions [19]. In sulfuric acid and phosphoric-sulfuric acid solutions, their solubility is low [20, 21]. Data on the possibility of preparation of double sulfates and their solubility in nitric-phosphoric acid solutions have not been found. The solubility of double sulfates in nitric acid solutions is higher [22]. Therefore, it was suggested that free nitric acid must be neutralized prior to the precipitation of lanthanides as double sulfates.

Fluorine was precipitated by the known procedure. In this case, sodium carbonate was consumed in a 105% amount above stoichiometry of the reaction and a widely accepted assumption that fluorine precipitates as Na_2SiF_6 was used. It should be noted however that the concentration of silicon dioxide in the initial solution is small to bind all fluorine, whereas correlates well with the total concentration of silicon and aluminum. Consequently, it may be suggested that not only SiF_6^{2-} complex but also AlF_6^{3-} complex is present in the solution, with about 40% fluorine bound into the second complex.

The residual content of fluorine in the solution was 6 g l^{-1}, which corresponded to the precipitation of 77.8% fluorine. The attained degree of the fluorine precipitation also warrants a conclusion that fluorine precipitates not only as Na_2SiF_6, but also as Na_3AlF_6.

Into a defluorinated solution, a prescribed amount of sodium sulfate was introduced and the solution was neutralized without precipitation of lanthanide phosphates. This was made possible if the total consumption of sodium carbonate and ammonium hydrocarbonate was sufficient to neutralize free nitric acid and 70% and less of the first proton of phosphoric acid. Into a neutralized solution, sodium sulfate was introduced in a tenfold amount above the stoichiometric composition of double lanthanide sulfates $NaLn(SO_4)_2$. Double sulfates were crystallized for 2 h and a crystalline precipitate was easily separated by filtration. The residual concentration of lanthanides in the solution is given in Table 6 (solution 1).

The preliminary tests showed that when sodium sulfate is introduced into the solution without neutralization, about 10 % lanthanides is precipitated. Upon neutralization of free nitric acid and 40% of the first proton of phos-

Table 7. Extraction of lanthanides into solid products

Lanthanide	Extracted, % of the initial		
	into double sulfates	in sorption	total
Y_2O_3	23.0	15.2	38.2
La_2O_3	68.6	22.4	91.0
Ce_2O_3	78.6	18.5	97.1
Pr_2O_3	76.3	17.8	94.1
Nd_2O_3	75.4	19.8	95.2
Sm_2O_3	66.3	24.3	90.6
Eu_2O_3	62.0	9.3	71.3
Gd_2O_3	50.8	23.8	74.6
Tb_4O_7	n.d.	n.d.	63.0
Dy_2O_3	37.9	21.9	59.8
Ho_2O_3	20.5	22.2	42.7
Er_2O_3	n.d.	n.d.	59.3
Yb_2O_3	12.2	25.5	37.7
ZLn_2O_3	72.2	19.6	91.7

phoric acid at sodium sulfate consumption in 800–1500% amount relative to the stoichiometry, no precipitation of lanthanides in the form of double sulfates was attained. The degree of lanthanide extraction into the precipitate was (%): 20.4, 21.9, and 34.4 % at the sodium sulfate consumption of 800, 1000, and 1500%, respectively.

The mother liquor (solution 1) was neutralized to pH ~1.7, sorbent 2 was introduced into it, and sorption was performed in static mode for 60 min. In the course of the sorption, the solution was additionally neutralized with phosphoric acid to prevent a marked pH decrease caused by released protons of hydrophosphate groups. The residual content of lanthanides in the solution is given in Table 6 (solution 2).

The data of Table 6 were used to calculate the lanthanide precipitation into the solid product (Table 7). In the calculation, allowance was made for the change in the solution concentration in the presence of water formed by reaction of ammonium hydrophosphate with phosphoric acid.

As seen from Table 7, the precipitation of ΣLn_2O_3 into the double sulfate concentrate, which, according to XPA, contains sodium fluorosilicate as major impurity, is high ((72.2% of its content in the initial solution). The content of sodium fluorosilicate in this concentrate may be decreased, whereas extraction of fluorine into the fluorine-containing product may be increased in the case of the joint introduction of sodium compounds (carbonate or sulfate) at the stage of defluorination. This is because a large excess of sodium cations forming therewith in the solution will increase the crystallization degree of difficultly soluble fluorine-containing compounds, sodium fluorosilicate and fluoroaluminate.

Table 8. Concentration of individual lanthanide oxides in the sum of lanthanides of the separated products (ΣLn_2O_3 = 100%)

Lanthanide	Concentration, %			
	in initial solution	in sulfate concentrate	sorbed	total
Y_2O_3	3.71	1.19	2.86	1.83
La_2O_3	23.45	22.38	26.58	23.21
Ce_2O_3	40.42	44.20	37.93	42.64
Pr_2O_3	4.62	4.91	4.18	4.73
Nd_2O_3	22.02	23.08	22.23	22.71
Sm_2O_3	2.50	2.30	3.10	2.49
Eu_2O_3	0.30	0.26	0.14	0.24
Gd_2O_3	1.58	1.12	1.91	1.36
Tb_4O_7	0.22	n.d.	n.d.	n.d.
Dy_2O_3	0.66	0.35	0.73	0.49
Ho_2O_3	0.086	0.0245	0.097	0.06
Er_2O_3	0.30	n.d.	n.d.	0.19
Yb_2O_3	0.13	0.052	0.064	0.06

At the same time, precipitation of yttrium and heavy lanthanides was insufficient. This is due to the high solubility of their double sulfates or due to the fact that some lanthanides form no double sulfates under these conditions. Apparently, in the latter case, their cocrystallization may be explained by isostructural substitution. This is because lanthanide sulfates and double lanthanide sulfates have similar structures. Similar cocrystallization was also observed in precipitation of the double lanthanide sulfate concentrate from phosphoric-sulfuric acid solutions [23].

As seen from data of Tables 6, 7, about 20% lanthanides were additionally precipitated by sorption from the initial solution. In this case, contrary to the case of double sulfate precipitation, when cerium-group lanthanides precipitated to larger extent than yttrium and elements from the middle and yttrium groups, the sorption efficiencies of some lanthanides, except for europium, differed slightly. Why sorption efficiency for europium is different and requires additional verification.

Note, in a phosphoric acid solution the sorbent is hydrolytically stable and cannot degrade after repeated use.

Table 8 compares the relative content of individual lanthanides in the apatite concentrate (initial solution) and in

Table 9. Sorption efficiency of individual lanthanides by sorbents 1 and 2

Lanthanide	Residual concentration of oxide in solution, mg l^{-1}		Sorbed, %
	initial	mother	
Sorbent 1			
Y_2O_3	173	150	13.3
La_2O_3	132	105	20.4
Ce_2O_3	416	348	16.3
Pr_2O_3	84.0	37.5	55.4
Nd_2O_3	311	185	40.5
Sm_2O_3	59.5	47.5	20.2
Eu_2O_3	16.1	15.5	3.7
Gd_2O_3	47.7	42.5	10.9
Tb_2O_3	n.d.	n.d.	n.d.
Dy_2O_3	27.0	23	14.8
Ho_2O_3	5.3	4	24.5
Er_2O_3	n.d.	n.d.	n.d.
Yb_2O_3		n.d.	n.d.
ZLn_2O_3	1291	979.5	24.1
Sorbent 2			
Y_2O_3	173	108	37.6
La_2O_3	132	53.8	59.1
Ce_2O_3	416	186.9	55.1
Pr_2O_3	84.0	40.8	51.4
Nd_2O_3	311	114	63.3
Sm_2O_3	59.5	29.0	51.3
Eu_2O_3	16.1	7.86	51.2
Gd_2O_3	47.7	38.0	20.3
Tb_2O_3	4.9	2.9	40.8
Dy_2O_3	27.0	15.3	43.3
Ho_2O_3	5.3	0.75	85.8
Er_2O_3	9.9	5.55	43.9
Yb_2O_3	5.1	3.85	24.5
ZLn_2O_3	1291	606.7	53.0

Table 10. Coefficients of sorption separation of lanthanides with respect to lanthanum for sorbents 1 and 2

Sorbent	$K_{Y/La}$	$K_{Ce/La}$	$K_{Pr/La}$	$K_{Nd/La}$	$K_{Sm/La}$
1	0.60	0.76	4.8	2.65	0.98
2	0.41	0.84	0.73	1.19	0.72

the obtained products. As seen, in the separated sum, the content of cerium-group lanthanides (La, Ce, Pr, Nd, Sm) is close, whereas that of yttrium and heavy lanthanides, especially of yttrium, is lower than in the “apatite” sum. Nonetheless, the content of both yttrium and ytterbium in the precipitated products is considerable.

The optimization of the solutions proposed must make precipitation of yttrium and heavy metals more complete.

Data on the lanthanide sorption from WPPA are given in Table 9. The data of Table 9 show that both sorbents under examination are capable of sorbing lanthanides from a partially neutralized WPPA solution, but the degree of their sorption is different. Under the examination conditions the efficiency of lanthanide sorption, reasonably high for search experiments (53% lanthanides sorbed), was attained for sorbent 2. Sorbent 1 showed considerably lower results (about 24.1%). The higher sorption efficiency of sorbent 2 is due to its higher acidity, and possibly, somewhat higher (by 14.8%) specific content of the cation-exchange groups. It is especially important that sorption extraction makes difference in the efficiences of all lanthanides lower.

The experiment showed that sorbents under examination are stable in solutions of both orthophosphoric and nitric acids and lanthanides can be partially desorbed with a 1 M NHO_3 solution and completely desorbed with a 3 M HNO_3 solution.

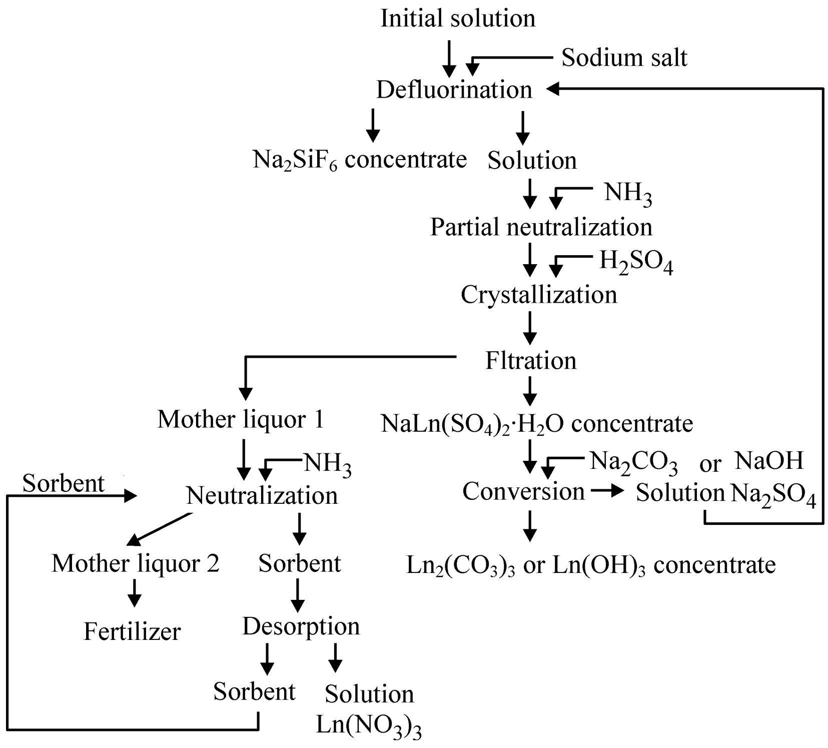
The separation constant for lanthanides, whose concentration in the initial solution exceeded 50 mg l^{-1} in terms of oxides, was calculated from data of Table 9 (see Table 10). The separation constants for other lanthanides were not calculated, because the relative errors of determination in a complex solution and at low concentration might be large.

The data of Table 10 show that, like in sorption from a model solution, a more basic sorbent 1 sorbs lanthanides more selectively than a more acidic sorbent 1.

With the use of a technological scheme, the total extraction of lanthanides from NPFE in laboratory tests was 91.8%. A majority of lanthanides was precipitated into the well processable concentrate of double sulfates of lanthanides with sodium [24]. The remaining lanthanides were separated in the form of a nitric acid solution. Consequently, the method studied by us does not require processing of phosphate concentrate, contrary to the known methods [1] suggesting its precipitation.

The sorption is also the promising process in separation of lanthanides from the production wet-process phosphoric acid, if the processing of the latter involves the stage of neutralization (as it is done in production of

A principal technological scheme of lanthanide separation from FNPE



mono- and diammonium phosphate and sodium polyphosphate detergents).

CONCLUSIONS

(1) Inorganic sorbents based on hydrated titanyl hydrophosphate can effectively sorb lanthanides from the products of the acid decomposition of the Khibiny apatite concentrate on mineral fertilizers.

(2) The sorbent modification increasing its acidic properties increases the sorption efficiency for all lanthanides.

(3) A principal technological scheme of lanthanide separation from the frozen extract of nitric-phosphoric acid solution was suggested instead of the known method concerning the lanthanide precipitation into the hardly processable phosphate concentrate.

ACKNOWLEDGMENTS

The study was financially supported by the Russian Foundation for Basic Research (projects 06-08-00223-a and 06-08-00144-a).

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