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Sorption Conversion of Eudialyte Concentrate in Sulphuric Acid Medium

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Abstract

Thorough investigation of the decomposition of eudialyte concentrate by means of sorption conversion in low-concentration sulphuric acid solutions is carried out. The effect of process conditions on the efficiency of decomposition of acid-soluble minerals from the concentrate and sorption of valuable metals and natural radionuclides from the concentrate by the sorbent is studied. It is shown that the sorption of rare earth elements, manganese, uranium and thorium, which are rather stable against hydrolysis under experimental conditions, is achieved within a broad range of process parameters. The optimal conditions for the sorption of zirconium (hafnium), niobium (tantalum) and titanium by the sorbent differ due to different hydrolytic stability of these elements in low-concentration acid solutions. The choice of optimal process conditions should be determined by economic reasonability, because it is impossible to achieve a high recovery of all valuable components at the same time.

Keywords: eudialyte concentrate, acid processing, rare elements, recovery

INTRODUCTION

Traditional methods of the acid decomposition of eudialyte concentrate involve concentrated sulphuric acid solutions, which causes high consumption of the acid and, as a consequence, the formation of a large amount of salt wastes requiring utilization. An additional problem is utilization of silica, because calcium and strontium sulphates get into silica-containing wastes during decomposition with sulphuric acid. Because of this, attention to the development of technology for processing eudialyte concentrate through decomposition using low-concentration sulphuric acid solutions has increased [1, 2].

Leaching of rare earth elements (REE) and zirconium using a solution with pH 1.0 ($C_{H_2SO_4} \approx$ 0.65 wt. %) from the non-magnetic fraction obtained from eudialyte ore of the Norre Kärr deposit (Sweden) was investigated. Acid consumption rate, the composition of solutions, and the methods of recovery of REE and zirconium from these ores were not reported. Under conditions that are optimal in the opinion of the authors (temperature 50 °C, treatment time 4 h), the recovery of 86 % REE, 51 % zirconium was achieved. At a temperature of 75 °C, the recovery of REE and zirconium into the liquid phase increased, but the resulting silica gel was very difficult for subsequent processing [1].

With traditional approaches, the use of low-concentration solutions determines the necessity to use a large excess of the acid solution in order to prevent hydrolysis of metal ions of the III–V groups of the Periodic system. This causes a further increase in the amount of acid wastes containing silica to be utilized.

Acid consumption decreases substantially in the case if eudialyte concentrate is decomposed by means of sorption conversion [2]. The goal of the present work was to carry out a comprehensive investigation of the decomposition of eudialyte concentrate by means of sorption conversion using low-concentration sulphuric acid solutions.

EXPERIMENTAL

Eudialyte concentrate manufactured at the Lovozero mining and concentrating plant (Revda settlement, the Murmansk Region) was used in the work. The composition of this concentrate is, wt. %: 9.32 ZrO_2, 0.25 HfO_2, 1.85 Tr_2O_3, 0.61 Nb_2O_5, 0.03 Ta_2O_5, 2.06 TiO_2, 1.96 MnO, as well as 12.96 Na_2O, 1.32 K_2O, 0.98 MgO, 3.95 CaO, 2.02 SrO, 3.69 Al_2O_3, 3.95 Fe_2O_3, 41.83 SiO_2, 0.010 ThO_2 and 0.009 UO_2. The major minerals of the concentrate are readily acid-soluble eudialyte and nepheline, difficultly soluble lamprophyllite, insoluble albite and loparite. The content of minerals that were not decomposed during the process was about 15 wt. %, including approximately 1 wt. % of loparite. Lamprophyllite content was about 4.5 wt. %. The fraction of the middle and yttrium groups in the sum of REE oxides exceeds 43 %, which causes increased interest in this raw material.

The experimental procedure was mainly the same as that described in [3]. At large mass loss values, the solid residue was composed mostly of non-decomposed minerals. With a decrease in mass loss value, the residue contained not only minerals that are stable in acid solutions, but also partially decomposed eudialyte, often in the form of X-ray amorphous product enriched with silica. It was often difficult to assign it to the non-decomposed mineral residue or to silica gel.

If the liquid phase contained a mixture of silica sol and silica gel, they were separated by centrifuging, followed by decanting of silica sol (solution). As a rule, silica sol formed gel during long-term exposure. At the liquid-to-solid ratio L/S = 5, the basis of the liquid phase was silica gel; its separation from the sorbent on a meshed filter proceeded with difficulty and required a large amount of water for washing.

Experimental conditions and their effect on mass loss values, the degree of filling (γ) the sorption exchange capacity of the sorbent, silica concentration in the liquid phase ($C^{l}_{SiO_2}$) and the nature of the formed liquid phase are summarized in Table 1. The consumption of the acid (α), which was determined by solution concentration and by the L/S ratio, was equal to 13–98 % of the stoichiometric amount. The ratio of the volume of acid

TABLE 1

Effect of process conditions on the characteristics of eudialyte concentrate decomposition

Exp.	Process temperature, °C	$C_{H_2SO_4}$, wt. %	Time, h	L/S	α, %	β, %	Mass loss, %	γ, %	$C^{l}_{SiO_2}$, mg/L	Liquid phase
1	20	2.0	4	15	39	69	54.5	72.3	H. a.	Ss
2	20	2.0	6	35	65	92	60.1	43.1	6030	Ss + Sg
3	20	2.0	10	15	39	115	68.2	56.5	20 080	Ss
4	20	2.0	10	35	65	115	70.6	54.3	9260	Ss
5	20	3.0	4	15	59	69	59.6	86.3	7185	Ss
6	20	3.0	12	5	13	100	78.8	72.4	15 430	Sg
7	30	2.0	4	15	39	69	64.0	87.7	10 040	Ss
8	40	2.0	4	15	39	69	66.2	90.8	12 160	Ss
9	40	2.0	10	20	52	115	78.4	58.4	15 215	Ss
10	60	1.5	4	15	29	69	31.2	64.6	7720	Ss
11	60	2.0	4	15	39	69	80.2	103.0	16 760	Ss
12	80	2.0	4	15	39	69	84.4	85.4	10 010	Sg + Ss
13	80	2.0	10	15	39	115	84.6	63.3	1430	Ss + Sg
14	80	2.0	10	25	65	115	71.2	51.4	11 520	Ss
15	80	2.0	6	35	65	92	62.6	40.0	5890	Ss
16	80	3.0	10	35	98	115	80.1	51.0	8800	Ss
17	80	3.0	12	5	13	100	72.3	68.4	1050	Sg + Ss
18	100	2.0	6	35	65	92	79.1	68.8	8380	Ss

Note. N. a. – not analyzed; Ss – silica sol; Sg – silica gel.

solution (L, mL) and the mass of eudialyte concentrate (S, g) L/S varied within the range from 5 to 35. The consumption of the sorbent (β) was estimated in per cent of the theoretically needed amount for sorption, assuming that cations were sorbed in the form of Me^{n+}.

The distribution of the most valuable and radioactive components of eudialyte concentrate between the products formed during sorption conversion is shown in Table 2. To evaluate the presented data, it should be taken into account that zirconium content in the concentrate is almost completely determined by eudialyte, but only about 88.2 % REE, 78.6 % Nb and 26.2 % Ti are related to eudialyte, while 11.5 % REE, 20.2 % Nb and 14.4 % Ti are present in loparite, and the major part of titanium (59.4 %) enters the concentrate with lamprophyllite.

The coefficients (K_d) of component distribution during sorption were calculated using experimental data according to equation:

$$K_d = \frac{m_c V_p}{m_p V_c}$$

where m_c and m_p are the masses of a component in the sorbent and in the solution, respectively; V_p, V_c are the volumes of solution and sorbent, respectively.

RESULTS AND DISCUSSION

It was assumed that the process carried out in the mode leading to the formation of silica sol would provide the high efficiency of the sorption of rare elements by the sorbent [2]. However, even at the high extent of concentrate decomposition, the formation of silica sol (experiments 9, 12, 17, 18) does not ensure the achievement of the high degree of recovery of valuable metals into the sorbent.

The sorption of most cations from weakly acidic solutions usually proceeds efficiently, increasing with an increase in process temperature. However, during the sorption conversion of eudialyte concentrate, the sorption efficiency of metals that pass into solution is determined not only by solution acidity and sorption temperature but also by other reasons.

One can see in Table 1 that, depending on process conditions, the resulting liquid phase was either silica sol or a mixture of silica gel with silica sol, or mainly silica gel. Because of the relatively low solubility of silica, eudialyte decomposition is mainly determined by the L/S ratio (see Table 1). For low L/S values, the solution gets saturated with silica rather rapidly, nevertheless, the mass loss is high. This is possible because of diffusion-driven leaching of cations from non-dissolved eudialyte and other silicates (nepheline, lamprophyllite), and non-dissolved silicate framework of the minerals is transformed into gel as a consequence of the substitution of metal ions in eudialyte crystals by hydroxonium cations according to reaction [4]:

$$-\overset{|}{\underset{|}{Si}}-O-K + H_3O^+ \rightarrow -\overset{|}{\underset{|}{Si}}-OH \cdot H_2O + K^+ \qquad (1)$$

$$K-O-\overset{|}{\underset{|}{Si}}-O-K + 2H_3O^+ \rightarrow$$

$$H_2O \cdot OH-\overset{|}{\underset{|}{Si}}-OH \cdot H_2O + 2K^+ \qquad (2)$$

At higher L/S values (for example, L/S = 35 in experiment 2, see Table 1), silica gel may be formed not as the product of diffusion-driven leaching of metal cations from the silica matrices of eudialyte and lamprophyllite but through polymerization of silica that passed into solution. This happens because silica sols containing silica are metastable, and their stability depends on silica concentration in the sol, temperature, pH of the medium, and the nature of mineral acid [5]. It is probable that silicon polymerization is also promoted by readily hydrolyzable metals that are present in silica sol.

An increase in the duration and temperature of the process causes an increase in the extent of concentrate dissolution, and therefore an increase in the amount of silica that passes into solution. As a rule, silica polymerization proceeded gradually during long-term storage of silica sols. However, in the experiments with L/S = 5–15, at a temperature of 80 °C and process duration 10–12 h, when the high extent of concentrate decomposition was achieved, silica polymerization was observed directly during decomposition because of a substantial increase in the concentration. In this situation, SiO_2 content in silica sols decreased to 1050–1430 mg/L (see Table 1, experiments 13 and 17), though for shorter process duration it reached 10 010 mg/L at 80 °C (experiment 12) and 20 080 mg/L at 20 °C (experiment 3).

Silica gels contained substantial concentrations of some metals; the products dried at 80 °C were determined to contain, wt. %: 42.6–55.3 SiO_2, 0.81–1.1 TiO_2, 4.48–6.60 ZrO_2, 0.11–0.14 HfO_2, 0.64–0.97 Nb_2O_5, 0.044–0.58 Ta_2O_5, 0.23–0.38 ΣTr_2O_3, 0.0015–0.006 ThO_2, 0.0012–0.0014 UO_2, 2.44–3.47 Na_2O, 0.16–0.59 K_2O, 0–0.14 MgO, 0.04–1.04 CaO, 0.15–0.42 SrO, 0.21–0.32 MnO, 0.34–1.35 Al_2O_3,

TABLE 2

Distribution of valuable and radioactive metals between the products of sorption conversion

Exp.	Metal recovery, %															
	Zr				Hf				∑Tr				Nb			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
1	47.8	10.9	–	41.3	67.4	1.44	–	31.1	60.7	1.41	–	37.8	41.4	11.2	–	47.4
2	58.8	11.2	1.7	28.3	70.8	3.6	1.6	24.0	72.9	0.51	1.5	25.0	36.0	47.3	1.6	15.2
3	65.6	15.7	–	18.7	73.0	2.8	–	24.2	71.5	0.31	–	28.2	39.4	8.7	–	51.9
4	66.2	17.6	–	16.1	81.8	6.2	–	12.0	74.1	0.58	–	25.3	42.0	21.1	–	36.9
5	68.9	11.2	–	19.9	71.0	9.2	–	19.8	64.8	0.26	–	34.9	14.3	43.1	–	42.6
6	76.3	2.8	8.5	12.3	69.0	3.2	11.0	16.9	81.4	0.12	3.7	14.7	39.2	9.4	25.5	25.8
7	71.5	12.0	–	16.5	67.5	16.7	–	15.8	73.6	0.23	–	26.1	56.6	6.1	–	37.3
8	75.3	4.3	–	20.4	77.9	2.0	–	20.1	77.1	0.43	–	22.4	61.7	1.9	–	36.4
9	73.9	19.7	–	6.4	83.4	11.4	–	5.2	84.1	0.54	–	15.4	20.4	60.7	–	18.9
10	40.8	3.8	–	55.4	56.3	2.4	–	41.3	45.8	0.30	–	53.9	12.6	8.1	–	79.3
11	59.9	25.6	–	14.5	80.4	10.3	–	9.3	87.6	0.39	–	12.0	72.5	8.1	–	19.4
12	52.5	18.3	22.5	6.6	62.1	7.7	24.9	5.2	85.7	0.15	5.8	8.4	7.4	30.8	49.3	12.5
13	85.1	0.4	11.9	2.6	83.4	0.3	14.4	1.9	85.3	0.02	7.0	7.7	24.0	1.2	49.9	24.9
14	66.7	19.5	–	16.9	64.1	19.0	–	16.9	88.8	0.26	–	11.0	33.2	31.7	–	35.1
15	62.9	5.9	–	31.2	79.8	7.6	–	12.6	72.9	0.18	–	26.9	37.6	31.0	–	31.5
16	71.3	23.6	–	5.1	80.4	14.8	–	4.8	85.0	0.28	–	14.7	12.0	66.8	–	21.2
17	50.8	18.9	18.8	11.5	58.6	4.7	15.2	21.4	80.9	0.11	3.4	15.6	20.9	22.4	30.5	26.2
18	62.6	29.9	–	7.5	77.4	16.8	–	5.8	85.6	0.85	–	13.5	38.3	42.1	–	19.6
Exp.	Ti				Mn				Th				U			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
1	24.9	3.3	–	71.7	63.4	3.7	–	32.9	55.0	0.90	–	44.0	77.5	2.50	–	20.0
2	13.9	4.2	4.4	77.5	62.8	3.9	2.1	31.2	54.1	0.57	4.8	40.4	57.5	2.66	2.2	39.6
3	5.6	0.8	–	93.6	68.9	4.5	–	26.7	62.2	0.60	–	37.2	78.0	2.20	–	19.8
4	2.1	7.6	–	90.3	68.4	5.4	–	26.2	42.4	1.20	–	56.4	78.0	6.70	–	15.3
5	0.8	3.4	–	95.7	72.4	2.5	–	25.0	41.8	0.74	–	57.4	77.9	2.90	–	19.2
6	45.3	0.2	6.2	48.3	82.9	0.2	3.0	13.9	70.0	0.18	5.7	24.1	72.0	5.00	6.0	17.0
7	0.9	4.7	–	94.4	73.7	2.4	–	23.9	77.8	0.95	–	21.2	82.7	2.00	–	15.3
8	1.7	1.7	–	96.6	77.0	1.0	–	22.0	63.4	0.60	–	36.0	82.7	1.78	–	15.6
9	35.2	6.0	–	58.8	85.6	3.2	–	11.2	45.4	2.40	–	52.2	86.4	5.11	–	8.5
10	18.7	1.4	–	79.8	60.0	0.76	–	39.3	53.3	0.68	–	46.0	65.6	1.07	–	33.3
11	45.1	7.3	–	47.6	86.9	2.7	–	10.3	59.8	0.96	–	39.2	86.4	4.44	–	9.1
12	27.6	7.3	24.9	40.2	82.4	2.1	5.4	10.1	66.8	0.39	15.3	17.4	87.4	6.80	6.4	4.8
13	32.8	4.4	14.7	48.1	88.3	0.8	5.6	5.3	57.6	0.04	20.2	22.2	84.7	0.50	7.1	7.6
14	65.9	6.8	–	27.3	86.1	3.1	–	10.8	94.8	0.19	–	5.0	97.6	0.42	–	2.0
15	4.7	6.0	–	89.3	57.8	5.0	–	37.1	25.3	0.70	–	74.0	85.3	1.33	–	13.3
16	4.8	22.4	–	72.8	83.5	6.1	–	10.4	92.4	0.25	–	7.4	89.5	2.26	–	8.2
17	57.8	6.7	7.9	27.6	87.5	0.77	3.0	8.7	72.6	0.07	2.2	25.1	32.6	2.38	51.5	13.5
18	49.0	18.2	–	32.8	87.0	4.5	–	8.5	50.0	0.02	–	50.0	89.9	2.22	–	8.9

Note. 1. Products: 1 – sorbent; 2 – silica sol; 3 – silica gel; 4 – solid residue. 2. Dash means that silica gel was not formed.

0.75–1.35 Fe_2O_3. The concentrations of niobium and tantalum with respect to silica were usually higher than in initial eudialyte. Many metals are present in silica gels not in the dispersion solution but are chemically bound with silica matrix, which greatly hinders their recovery into the sorbent [4].

These polymers are also likely to be formed in silica sols, though in smaller amounts. The formation of polymers is caused by the partial hydrolysis of polyvalent metals in weakly acidic solutions with the formation of hydrate forms $Me(OH)_n^{m-n}$ where m is metal valence, n is the number of

hydroxyl groups [6] interacting with each other with the formation of polymeric ol compounds [7].

To provide the higher recovery of readily hydrolyzed elements of groups IV–V of the Periodic table into the sorbent, it is necessary to transfer them into a solution efficiently, preventing hydrolysis and hence the formation of non-sorbed polymers. An increase in acid concentration in the solution promotes leaching and prevents hydrolysis, but decreases sorption efficiency. An increase in process temperature promotes leaching and sorption of the majority of components but enhances hydrolysis. Finally, an increase in L/S promotes the dissolution of eudialyte but causes an increase in the losses with the liquid phase because of an increase in the amount of the formed silica sol and, as a consequence, the amount of the formed polymers. In addition, the consumption of the acid and the amount of mother solution for utilization increase.

The influence of process conditions on the efficiency of sorption of the most valuable metals of eudialyte concentrate by the sorbent was analyzed.

For the evaluation of REE distribution between the products of sorption conversion, it is necessary to take into account the fact that their recovery in the sorbent cannot exceed 88.5 %. For the concentration of 1.5 wt. % H_2SO_4, even at a temperature of 60 °C REE recovery into the sorbent was only 45.8 %, and at the concentration of 2 wt. % H_2SO_4 at a temperature within the range of 20–40 °C – 56.5–75.9 %, which points to insufficiently complete decomposition of eudialyte under these conditions. The high REE recovery into the sorbent (85.6–87.6 %) was achieved at a temperature of 60–100 °C and H_2SO_4 concentration 2 wt. %, though a substantial fraction of REE is lost with the silica residue during sulphuric acid decomposition of eudialyte because of the formation of poorly soluble double sulphates of the REE of cerium and middle groups with sodium and isomorphous cocrystallization with gypsum getting into the residue.

During the formation of silica gels, REE losses with them increased (see data in Tables 1 and 2), but they were relatively low. REE sorption from the solutions formed simultaneously with silica gel proceeded efficiently. As a rule, less than 1 %, frequently not more than 0.3 % of REE remained in mother solutions (see Table 2), while the major part of REE not sorbed by the sorbent passed into solid residues. Under any process conditions, K_d values for REE are large (K_d = 346–1770), this means that REE mainly did not form polymers with silica.

Because of the presence of loparite in the concentrate, recovery of the REE of cerium group into the sorbent is lower, and transition into the solid residue is higher than the corresponding values for REE of the middle and yttrium groups. Since the elements of yttrium group are almost completely bound with eudialyte in the concentrate, judging from the recovery of yttrium group REE into the sorbent and into the liquid phase, eudialyte decomposition under optimal conditions in sulphuric acid medium was not less than 94.5 %.

Zirconium and hafnium were leached rather efficiently (see Table 2). Decreased amount of zirconium in the solid residue, indicating the high extent of eudialyte decomposition, was obtained using solutions with $C_{H_2SO_4}$ = 2–3 wt. %, temperature within the range of 40–100 °C, and process duration 10–12 h. The high extent of eudialyte decomposition did not ensure high extent of recovery into the sorbent. At low temperatures (20–40 °C) and $C_{H_2SO_4}$ = 2–3 wt. %, recovery into the sorbent reached 68.9–71.5 %, but with an increase in temperature to 60–100 °C for process duration 4–6 h it decreased to 59.9–62.9 % for sol formation and to 52.5 % for gel formation. Accumulation of zirconium in the liquid phase increased in this situation: its concentration, calculated for ZrO_2, increased from 222 mg/L at 20 °C to 1589–1764 mg/L at 60–80 °C and L/S = 15, and to 796 mg/L at 100 °C and L/S = 35. However, with an increase in process duration from 4 to 10 h (see experiments 12 and 13) and sorbent consumption from 69 to 115 % at 80 °C and L/S = 15, the sorbent absorbed 85.1 % Zr and 83.4 % Hf, while zirconium concentration in the mother solution was only 25.8 mg/L.

Zirconium sorption worsened as a consequence of the formation of silicon-zirconium polymers: silica sols from experiments 3, 4, 11, 12, 18 were observed to contain at the same time increased concentrations of silica and zirconium, and decreased K_d (<10), while in the case of zirconium sorption from the solutions in which there was no substantial formation of silicon-zirconium polymers, K_d could exceed 40 (experiments 1, 2, 13, 15). As a rule, hafnium was sorbed more efficiently than zirconium.

Estimating niobium distribution between the products of sorption conversion, it is necessary to take into account the fact mentioned above: maximal possible extent of niobium recovery is approximately 80 %, because about 20 % of niobium is incorporated into loparite, which is not

decomposed during sorption conversion. In the solution of 2 wt. % H_2SO_4, an increase in temperature to 60–100 °C provided substantial efficiency of its leaching, while the concentration 1.5 wt. % was insufficient. Similarly to the case of zirconium, efficient leaching did not ensure niobium absorption by the sorbent, because its substantial fraction was retained by the liquid phase. The maximal recovery of niobium into the sorbent, equal to 61.7 %, was obtained at a temperature of 40 °C, L/S = 15, sorbent consumption 69 % of the stoichiometric amount (experiment 8). At a temperature of 80–100 °C, the fraction of non-sorbed niobium increased substantially. This fraction was especially low if gel was formed. Process conditions had a substantial effect on K_d of niobium and tantalum. The low values of this parameter (frequently $K_d < 1$) point to the formation of polymers with silica, enhancing with a temperature increase to 80–100 °C.

The major part of titanium was not leached usually (see Table 2). This fact points to a more difficult decomposition of lamprophyllite in comparison with eudialyte. Temperature rise to 80–100 °C promoted decomposition of lamprophyllite. Titanium sorption from silica sols proceeded efficiently, as a rule. In the case of gel formation, a substantial fraction of titanium that passed into the liquid phase was not sorbed (experiments 12, 13). Higher titanium recovery into the sorbent was observed at a temperature of 60 °C (experiment 11) with the solution 2 wt. % H_2SO_4. A decrease in H_2SO_4 concentration (experiment 10), an increase in process temperature (experiment 18) caused a decrease in titanium sorption in the sorbent.

The major part of manganese not sorbed by the sorbent was present in the insoluble residues. Manganese sorption was rather efficient. The values of K_d for manganese are high (10^2–10^3), that is, this element, similar to REE, alkaline and alkaline earth metals, aluminium, iron, did not form polymers with silica. Retention of manganese by the liquid phase increased at a temperature of 80–100 °C and L/S = 35, reaching 4.5–7.5 % of the initial amount. Nevertheless, since temperature rise caused an increase in the extent of concentrate decomposition, manganese recovery into the sorbent at increased temperatures is rather high – up to 87 %.

In comparison with the initial concentrate, residues of unreacted minerals are depleted of REE (to 0.99 wt. % ΣTr_2O_3), zirconium (to 2.38 wt. % ZrO_2) and uranium (to 0.002 wt. % UO_2), enriched with iron (to 8.06 wt. % Fe_2O_3), titanium (to 7.36 wt. % TiO_2), niobium (to 1.45 wt. % Nb_2O_5), tantalum (to 0.07 wt. % Ta_2O_5), thorium (to 0.03 wt. % ThO_2) because of the accumulation of aegirine, lamprophyllite and loparite in them. So, the major part of uranium present in the concentrate is bound either with eudialyte or with readily decomposable accessory minerals.

The cations of multiply charged metals are sorbed more efficiently than the cations of alkaline metals, so it was assumed that in the case of the lack of sorbent alkaline metals would be accumulated in the solution, and the sorbent would be enriched with the cations of multiply charged metals, which would simplify its subsequent processing. However, at the high mass loss and β = 69 % (experiments 11 and 12) the sorbent absorbed 75.4 and 47.6 % of sodium that was present in the concentrate, as well as 59.0 and 82.6 % of potassium, respectively. An increase in sorbent consumption created more favourable conditions for the sorption of all cations, but at β = 115 % a substantial fraction of alkaline metals, especially sodium, also was not sorbed. This could lead to an almost 2-fold decrease in γ, which caused definite difficulties for desorption to be carried out. The arrangement of the counter-flow process will provide more efficient use of the sorption capacity of the sorbent.

Thorium oxide content in eudialyte concentrate with respect to ΣTr_2O_3 is 0.54 wt. %, uranium – 0.49 wt. %. Since radionuclides are usually concentrated together with REE during mineral raw processing, we analyzed the behavior of radionuclides during the sorption conversion of eudialyte concentrate in sulphuric acid medium.

Specific effective radioactivity (A_{ef}) of the studied eudialyte concentrate is equal to 1.2 KBq/kg, that is, this concentrate relates to the II class of materials with increased content of natural radionuclides [8]. The major portion (≈74 %) of radioactivity of eudialyte concentrate is determined by uranium.

Under the optimal conditions of the acidic decomposition of eudialyte concentrate (60–80 °C), a substantial part of thorium and the major part of uranium are absorbed by the sorbent (see Table 2). The A_{ef} value of saturated sorbents did not exceed 0.205 KBq/kg at β = 69 % and 0.135 KBq/kg at β = 115 %, that is, works with the sorbents may be carried out without restrictions. Thorium and uranium were usually well sorbed (see Table 2), sorption efficiency decreased only in separate experiments at decreased temperature. The re-

sulting silica sols and silica gels are even less radioactive.

The radioactivity of unreacted mineral residues is mainly due to non-decomposed loparite, so thorium content is much higher than uranium content in the residues from experiments in which high mass loss was achieved, and A_{ef} of these products may exceed 0.740 KBq/kg.

At 20 °C, desorption of radionuclides with 5 M NaCl solution proceeds by one or two orders of magnitude worse than REE desorption. For this reason, even at the stage of desorption the probability of obtaining rare earth concentrate with increased radioactivity decreases sharply. However, if radionuclides from the eluate get into rare earth concentrate, its A_{ef} value may exceed 740 KBq/kg. The conditions for hydrolytic precipitation of radioactive cake to be buried, and then non-radioactive REE concentrate from these eluates have been determined [9].

CONCLUSIONS

1. The parameters of sorption conversion of eudialyte concentrate in sulphuric acid solutions affect the nature and results of the process in a complicated and often contradictory manner. Lamprophyllite is most stable among the minerals to be decomposed.

2. The degree of concentrate decomposition depends on acid concentration, L/S ratio, process duration and temperature. The optimal concentration of sulphuric acid solution is 2 wt. %. In the case of 2.0 wt. % H_2SO_4 is used, the mass loss increased slightly at a temperature of 40 °C and sharply increased at a temperature of 60–80 °C or with an increase in process duration to 10–12 h.

3. The mechanism of eudialyte decomposition depends first of all on L/S value. At the high values of L/S ratio and process duration, the high extent of the dissolution of eudialyte and some accompanying minerals is possible. At lower L/S values, after saturation of the solution with silica, eudialyte dissolution becomes impossible, and its decomposition proceeds through diffusion-driven leaching of metals from eudialyte crystals with the formation of silica gel on the basis of silica frameworks of eudialyte and lamprophyllite.

4. Silica polymerization proceeds in the formed solutions, with the capture of leached metals that are prone to hydrolysis, and the process leads to the formation of silica sols or silica gels, depending on process conditions.

5. Efficient sorption of REE, manganese, uranium and thorium, which are rather stable against hydrolysis under experimental conditions, was achieved within a broad range of parameters. The maximal recovery of zirconium (hafnium), niobium (tantalum) and titanium is achieved under different conditions. The high extent of eudialyte decomposition does not ensure high recovery of the metals of IV–V groups into the sorbent.

7. The optimal conditions for the sorption of zirconium (hafnium), niobium (tantalum) and titanium differ from each other because these metals possess different stability against hydrolysis, which determines the formation of non-sorbed polymers with silica. Hydrolysis degree depends on solution acidity, process temperature, and the order of reagents introduction.

8. During sorption conversion of eudialyte concentrate in sulphur acid solutions, it is principally impossible to provide at the same time the maximal recovery of all valuable components, so the optimal process conditions will be determined by the economic reasonableness.

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