

UDC 661.682:549.657.7:66.081

DOI: 10.15372/CSD2023485

EDN: NMZKGE

Ways to Utilise Silica Sols – Wastes from Processing Eudialyte Concentrate

E. P. LOKSHIN, O. A. TAREEVA, S. V. DROGOBUZHSKAYA

*Tananaev Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials,
Kola Research Center, Russian Academy of Sciences,
Apatity, Russia*

E-mail: lokshin.ep@gmail.com

(Received 07.12.22; revised 01.03.23)

Abstract

The results of studies on the development of technologies for the utilisation of silica sols formed during eudialyte concentrate processing by means of sorption conversion are presented. As promising areas, the following directions have been proposed and studied: additional extraction of valuable metals from silica sols by sorption with sulphocationite; silica sol separation into silica-enriched silica gel and silica-depleted acid solution by successive freezing and thawing of the initial silica sol; the use of silica contained in silica sols to obtain wollastonite. The percentage of rare metals that can be absorbed by sulphocationite from silica sols obtained at a temperature of 80 °C – the optimum temperature for the decomposition of eudialyte concentrate by sorption conversion – is found to be (%) 58.6–70.3 Ti, 46–50 Zr, 24.7–29.9 Hf, 23.5–34.7 Nb, while sodium remains in silica sol. The low degree of filling of the sorption exchange capacity of the sulphonic cation exchanger allows it to be additionally saturated in the process of sorption conversion. It is shown that the concentration of SiO₂ reached 33.0 g/L in silica gels obtained by successive freezing and thawing of silica sols. The specific effective radioactivity of silica gels is low, which allows them to be used in the production of civil building materials. Acid solutions depleted in silica, the volume of which was 72.5–81.2 % of the volume of the initial silica sols, contain up to (%) 78.3 Ti, 56 Zr, 45.1 Hf, 76.4 Nb, 92.2 Na, 100 Th, 100 U, and only 1.1–3.6 SiO₂. Such solutions after additional strengthening are suitable for reuse for the decomposition of eudialyte concentrate. The possibility of obtaining wollastonite from silica sol based on nitric acid solution without the use of autoclave equipment has been experimentally proven. The ways of regeneration of the mother liquor obtained after precipitation of the wollastonite precursor are discussed.

Keywords: eudialyte concentrate, processing, liquid waste management

INTRODUCTION

Eudialyte concentrate is a polymetallic raw material containing valuable components, namely the elements of groups III–V of the Periodic Table: rare earth elements (REE), zirconium, hafnium, titanium, niobium, tantalum. The attention to eudialyte raw material as a source of REE is increasing during the recent years. Either in the Russian eudialyte concentrate [1] or in similar

products abroad [2, 3], the total content of rare elements does not exceed 14 wt. %.

The most promising hydrochemical methods are based on an acid decomposition of eudialyte and subsequent recovery of rare elements from the resulting solutions. In these processes, the major parts of silica and alkaline metals get into the acid solutions, and the total content of these components in the concentrates exceeds 50 wt. %. The major methods proposed in this area imply

substantial consumption of concentrated acids and, as a consequence, some other reagents, which in turn leads to a large amount of liquid salt wastes requiring utilization. The ways of their utilisation are not considered.

The sorption conversion of eudialyte concentrate has been proposed. This method involves mineral acids in low concentrations, taken in the amounts smaller than the stoichiometric level for eudialyte decomposition. During mineral decomposition, metal cations passing into solution are mainly absorbed by the sorbent, while a substantial part of sodium and major part of silica remain in the liquid phase in the form of silica sol or silica gel. The best results on the recovery of valuable rare metals are achieved when the liquid phase is obtained in the form of silica sol [4, 5].

The goal of the work was to search for the ways to utilise silica sols that are formed in the acid decomposition of eudialyte concentrate by sorption conversion. The tasks were put forward: to enhance the extraction of rare metals, to study the possibility of using silica contained in silica sols to obtain commercial products, to regenerate acid solutions in order to use them in circulation for the decomposition of eudialyte concentrate.

EXPERIMENTAL

To solve the formulated tasks, we studied:

- the possibility of additional sorption-based recovery of valuable metals from silica sols;
- silica concentrating by silica sol freezing-thawing;
- the application of silica present in silica sols to obtain wollastonite, which is a valuable commercial product [6].

Metal and silica concentrations were determined by mass spectrometry with inductively coupled plasma with the help of an ELAN 9000 DRC-e mass spectrometer (Perkin Elmer, USA).

The phase composition of the samples was determined using a Dron-2 X-ray diffractometer (Russia).

RESULTS AND DISCUSSION

Sorption recovery of metals from silica sols

The content of metal oxides in silica sols is presented in Table 1. These data confirm the fact that silica sols contain substantial amounts of zirconium and niobium, while the fraction of sodium in the total amount of cations present in silica sols is 52.3–68.3 %.

Sulphocationite KU-2-8chS (GOST 20298-74) was introduced into the silica sol, the pulp was mixed for 1 h at 80 °C, then the liquid phase was separated from the sorbent by filtration and analysed. The volume ratio of the liquid phase (V_l) to the sorbent (V_s) was 25.0–66.7, which determined sorbent consumption (β) to be 55–59 % on the stoichiometric amount necessary for the sorption of metal cations Me^{n+} from silica sols. It was expected that in the case when there is a lack of the sorbent, the first cations to be sorbed will be polyvalent cations possessing higher ion potentials, while the major part of sodium will remain in the solution. The sorption amounts of components were calculated from the changes in their concentrations in silica sol.

The data on sorption efficiency are presented in Table 2.

According to the results, noticeable sorption was observed for rare earth elements, alkaline earth metals, thorium, aluminium, manganese; somewhat lower sorption was exhibited by zirconium, while sodium was almost non-sorbed for the chosen sorbent consumption. Though sorption was carried out at the same temperature, titanium and niobium were substantially lower sorbed from the silica sol obtained by decomposition in

TABLE 1
Concentrations of metal oxides in the studied silica sols, mg/L

Experiment	Medium	SiO ₂	ΣTr ₂ O ₃	TiO ₂	ZrO ₂	HfO ₂	Nb ₂ O ₅	Ta ₂ O ₅	ThO ₂	UO ₂
1	H ₂ SO ₄	9260	1.85	44.5	469	4.40	36.5	5.37	0.035	0.17
2	H ₂ SO ₄	4286	0.94	11.4	232	1.22	54.1	3.89	0.018	0.10
3	HNO ₃	5890	1.38	35.4	156	5.42	53.6	4.60	0.020	0.03
Experiment	Medium	Na ₂ O	K ₂ O	MgO	CaO	SrO	MnO	Al ₂ O ₃	Fe ₂ O ₃	
1	H ₂ SO ₄	1131	24.8	3.7	106.0	9.8	3.7	12.4	40.8	
2	H ₂ SO ₄	1130	58.1	4.34	128.1	14.1	28.1	7.6	12.5	
3	HNO ₃	1430	62.6	5.43	161.3	23.4	46.3	12.7	13.8	

TABLE 2

Recovery of metals from silica sols based on sulphuric and nitric acids into sulphocationite

Experiment	Medium	V_1/V_s	β , %	Sorption, rel. %							
				ΣTr	Ti	Zr	Hf	Nb	Ta	Th	U
1	H ₂ SO ₄	66.7	55	88.4	5.2	47.2	33.6	0.2	14.6	87.8	34.7
2	H ₂ SO ₄	33.3	58	90.8	70.3	46.0	24.7	23.5	3.9	63.6	69.7
3	HNO ₃	25.0	59	86.9	58.6	50.0	29.9	34.7	16.1	53.6	45.6

Experiment	Medium	V_1/V_s	β , %	Na	K	Mg	Ca	Sr	Mn	Al	Fe
1	H ₂ SO ₄	66.7	55	0.8	50.2	82.0	89.5	62.2	41.0	64.3	43.8
2	H ₂ SO ₄	33.3	58	0.9	49.9	65.7	69.9	88.7	82.2	75.4	31.4
3	HNO ₃	25.0	59	0.7	39.5	66.3	69.4	76.4	66.7	86.0	29.9

sulphuric acid at 20 °C (experiment 1) than from silica sols obtained at 80 °C (experiments 2 and 3). Therefore, titanium and niobium are not incorporated into the dispersion solution in silica sol obtained at 20 °C, it is possible that they form polymeric compounds with silicic acid. The extent of zirconium and niobium sorption from silica sols obtained at 80 °C was higher, however, in this case, too, a substantial part of these metals, especially niobium, was not absorbed by the sulphocationite. So, the strength of titanium and niobium containing polymers with silicic acid in silica sol obtained at 20 °C is higher than in silica sol obtained at 80 °C.

The coverage of the sorption exchange capacity, calculated for the sorbent assuming the sorption of Me^{n+} cations, was 18.0, 26.3 and 16.1 % for experiments 1, 2 and 3, respectively.

So, the losses of zirconium and, to a smaller extent, niobium with the liquid phase may be decreased by treating silica sols with sulphocationite (the losses of rare earth elements with silica sols are low anyway).

Silica concentrating by silica sol freezing-thawing

To remove silica from the solutions with silicic acid containing up to 1 mol/L zirconium and 1–6 mol/L HNO₃ or HCl, it has been proposed to:

- coagulate silica by adding solid flocculants – organosilicon compounds on a macroporous silicon-containing carrier [7];
- coagulate silica by adding aqueous or aqueous-alcoholic solutions of the organosiliconates of alkaline metals or metal-organosiliconates of alkaline metals, or their mixtures [8, 9].

After the addition of 0.7–1.5 vol. % sodium methylsiliconate and 0.7–2.5 vol. % isopropanol, SiO₂ content in the solution decreased from 0.9–1.2 to 0.01–0.012 g/L. The precipitates were separated by filtering at a rate of 0.102–0.255 m³/(m² · h).

Humidity of the precipitate and the amount of zirconium getting into the precipitate are not reported [9]. The possibility to use this method for silica removal from the solutions obtained from sorption conversion, containing substantially higher concentrations of silica and especially sodium, is problematic.

The possibility to concentrate silica and separate silica from metals that are present in silica sol by silica sol freezing and subsequent thawing was investigated because under this kind of treatment silica sols were observed to decompose into silica gel enriched with silica, and a solution depleted in silica. Silica sols obtained in eudialyte concentrate decomposition by the solutions of 2 wt. % H₂SO₄, 2 wt. % HNO₃ and 1.14 wt. % HCl were used for experiments. The concentration of H⁺ in initial solutions was 0.314–0.343 g-ion/L.

Silica sols solidified when cooled to –2 °C. They were heated to the room temperature, the resulting emulsions were centrifuged, and the formed acid solution depleted in silica was separated by decanting from silica gel enriched in silica. Additional silica concentrating was not observed during repeated silica gel freezing. The volumes were measured, and the composition of resulting solutions and silica gels was analysed; the masses of silica gels were determined.

The composition of silica gels annealed at 800 °C and their characteristics are presented in Tables 3 and 4. The extraction of components into acid solutions obtained during silica sol freezing-thawing is shown in Table 5.

It follows from the data shown in Table 3 that SiO₂ recovery into silica gel was 96.4–98.9 %. The concentration of SiO₂ in silica gels reached 33.0 g/L. The concentration of SiO₂ in the products dehumidified by annealing silica gels at 800 °C was 91.8–95.0 wt. %, metal concentrations were comparable (see Table 4). The specific effec-

TABLE 3

Characteristics of the obtained silica gels

Silica sol	Volume fraction, rel. %		SiO ₂ concentration, g/L	Humidity, %	SiO ₂ extraction, %	A _{eff} *, Bq/kg
	Solution	Silica gel				
H ₂ SO ₄	73.6	26.4	33.0	95.3	98.8	52
HNO ₃	81.2	18.8	27.4	97.3	96.4	8
HCl	72.5	27.5	30.2	95.7	98.9	18

* Specific effective radioactivity of annealed silica gel.

TABLE 4

The composition of silica gels annealed at 800 °C, obtained during silica sol freezing-thawing

Silica sol	Content, wt. %							
	Na ₂ O	K ₂ O	CaO	SrO	Al ₂ O ₃	Fe ₂ O ₃	ΣTr ₂ O ₃	SiO ₂
H ₂ SO ₄	3.42	0.30	0.50	0.05	0.01	0.54	0.016	91.8
HNO ₃	2.86	0.32	0.58	0.015	0.04	0.008	0.014	95.0
HCl	3.98	0.25	0.86	0.05	0.05	0.24	0.012	91.8
Silica sol	TiO ₂	ZrO ₂	HfO ₂	Nb ₂ O ₅	Ta ₂ O ₅	MnO	ThO ₂	UO ₂
H ₂ SO ₄	0.35	1.93	0.12	0.78	0.047	0.10	0.0001	0.0005
HNO ₃	0.08	0.87	0.04	0.13	0.042	0.04	0.0001	0.00005
HCl	0.18	1.80	0.085	0.49	0.050	0.11	0.00009	0.00016

TABLE 5

Extraction of the components into acid solutions obtained by silica sol freezing-thawing, %

Silica sol	Na ₂ O	K ₂ O	CaO	SrO	Al ₂ O ₃	Fe ₂ O ₃	ΣTr ₂ O ₃	SiO ₂
H ₂ SO ₄	76.7	46.0	60.3	66.7	81.5	13.8	20.8	1.2
HNO ₃	92.2	100	62.0	95.7	81.2	23.0	65.8	3.6
HCl	85.8	32.0	38.2	68.8	12.3	60.1	52.1	1.1
Silica sol	TiO ₂	ZrO ₂	HfO ₂	Nb ₂ O ₅	Ta ₂ O ₅	MnO	ThO ₂	UO ₂
H ₂ SO ₄	77.9	80.0	23.7	44.6	3.2	66.2	21.0	21.6
HNO ₃	78.3	56.0	45.1	76.4	6.6	87.3	100	100
HCl	65.1	12.0	4.8	22.7	0.6	72.3	26.9	49.2

tive radioactivity (A_{eff}) is so low (see Table 3) that the obtained silica gels may be used in the production of building materials for civil purposes.

The volume of acid solutions obtained in the process accounted for 72.5–81.2 % of the volume of initial silica sol, and it decreased with an increase in SiO₂ concentration in silica sols. Not only silicon but also metals that were present in silica sols were observed to get distributed between the solution and silica gel. The fraction of metals that passed into the solution depended on metal kind, and for some metals it depended on silica sol forming acid. A substantial decrease in the fraction of some metals that passed from silica sols into the acid solution (see Table 3) pointed to the processes taking place in silica sols: the formation of poorly soluble double sulphates of rare earth elements and sodium in silica sol obtained after

decomposition in sulphuric acid, the formation of polymers of some metals with silicic acid in all silica sols, enhancing in hydrochloric acid.

The process flow scheme for silica sol processing with silica concentrating by freezing-thawing is presented in Fig. 1.

The use of silica present in silica sols to obtain wollastonite

It has been assumed that silica present in silica sols is promising to synthesise wollastonite, which is widely used in many technological areas. Calcium carbonate CaCO₃ was introduced into silica sol, obtained by eudialyte concentrate decomposition with nitric acid, in the stoichiometric amount necessary for the synthesis of CaSiO₃. The formed solution was neutralised with sodium bicarbonate

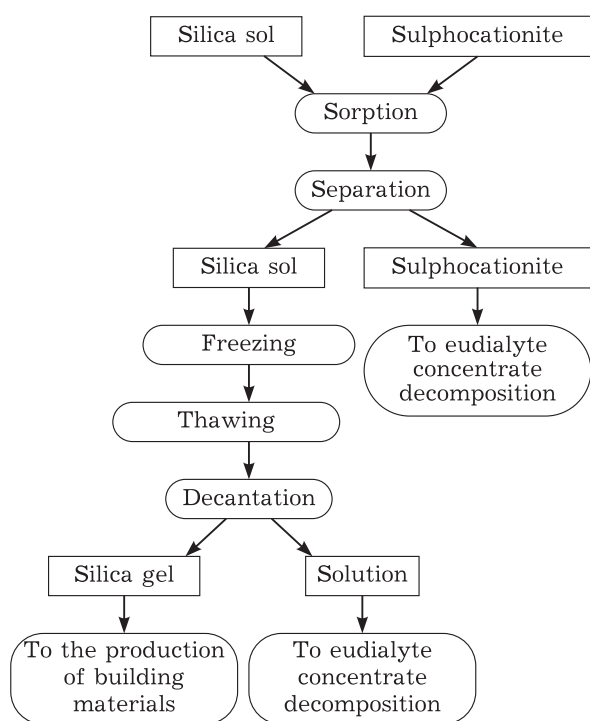


Fig. 1. The process flow scheme of silica sol processing with silica concentrating by freezing-thawing.

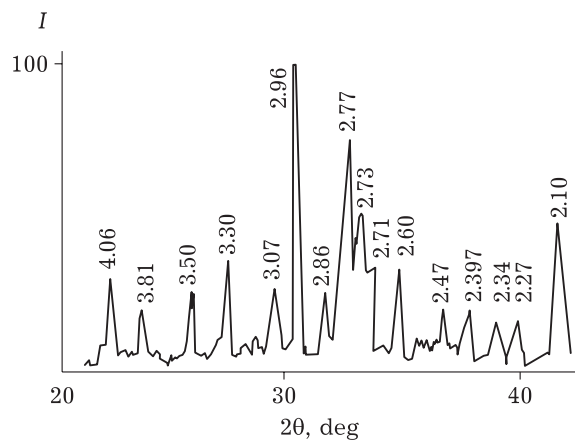


Fig. 2. X-ray diffraction patterns of wollastonite obtained from silica sol formed in the decomposition of eudialyte concentrate with nitric acid. Numbers in the spectrum indicate interplanar spacing, Å.

(NaHCO_3) to pH 6, heated for 2 h at 80 °C under permanent mixing. The formed precipitate was separated by filtering and annealed at 800 °C. According to the data of X-ray diffraction analysis, the obtained product was wollastonite (Fig. 2).

The composition of initial and stock solutions is shown in Table 6. It follows from these data that the major part of metal components except sodium passed into the precipitate.

The stock solution was treated in the static mode with KU-2-8chS sorbent under the conditions: $V_1/V_s = 5$, temperature 20 °C, duration 0.5 h, mixing. The concentrations of components in the obtained solution decreased to, mg/L: 2270 Na_2O , 20 K_2O , 0 CaO , 9.9 Al_2O_3 , 23.0 TiO_2 . So, the acid solution may be recovered. The content of Na_2O in the sorbent was 28.1 g/L, and it may be increased by carrying out the sorption process in the dynamic mode, so that the residual sodium content in the solution, mainly determining the degree of nitric acid neutralisation, will be decreasing.

Silica sols obtained through the decomposition of eudialyte concentrate with sulphuric acid, may be also used for the synthesis of wollastonite, however, because of the formation of poorly soluble calcium sulphate as an intermediate product, it is necessary to use autoclave equipment in this case [10].

Rare metals that are present in silica sols are almost completely passing into wollastonite during its synthesis (see Table 6), so it is reasonable to extract them preliminarily by sorption with sulphocationite.

The process flow scheme of silica sol processing with the synthesis of wollastonite and utilisation of the stock acid solution is presented in Fig. 3.

On the basis of the results obtained in the studies, two versions of utilisation may be proposed for the acid solutions formed in the sorption conversion of eudialyte concentrate, which are silica sols containing a number of metals from eudialyte concentrate.

According to the first version, silica sol is frozen at a temperature of <2 °C. After thawing, the initial product is decomposed into silica gel enriched with silicic acid, and silica-depleted acid solution. This silica gel is a promising raw material for the production of highly efficient heat insulating foam silicate materials [11]. Judging from metal concentrations in silica-depleted acid solutions (see Tables 1 and 5), the acids present in them were neutralised only by 12–15 %. Taking into account also low concentrations of silicic acid in the solutions, after additional strengthening they are suitable for use in the sorption conversion of eudialyte concentrate. A noticeable part of rare metals get into these solutions (see Table 5), which leads to a decrease in the losses of these metals.

Within the second version, additional sorption treatment of silica sols with sulphocationite is carried out at first, and this operation involves

TABLE 6

Metal content in the initial and stock solutions, mg/L

Solution	Y ₂ O ₃	La ₂ O ₃	Ce ₂ O ₃	Pr ₂ O ₃	Nd ₂ O ₃	Sm ₂ O ₃	Eu ₂ O ₃	Gd ₂ O ₃
Initial	0.420	0.142	0.295	0.037	0.186	0.056	0.018	0.048
Final	0.0005	0.0019	0.0027	0.00027	0.0010	<1 · 10 ⁻⁵	<1 · 10 ⁻⁵	<1 · 10 ⁻⁵
Solution	Tb ₂ O ₃	Dy ₂ O ₃	Ho ₂ O ₃	Er ₂ O ₃	Tm ₂ O ₃	Yb ₂ O ₃	Lu ₂ O ₃	ΣTr ₂ O ₃
Initial	0.010	0.070	0.013	0.041	0.0060	0.041	0.0051	1.380
Final	<1 · 10 ⁻⁵	<1 · 10 ⁻⁵	<1 · 10 ⁻⁵	<1 · 10 ⁻⁵	<1 · 10 ⁻⁵	<1 · 10 ⁻⁵	<1 · 10 ⁻⁵	0.006
Solution	Na ₂ O	K ₂ O	MgO	CaO	SrO	Al ₂ O ₃	TiO ₂	SiO ₂
Initial	1430	62.6	5.4	161.3	23.4	12.7	62.0	7660
Final	7890	29.3	2.3	26.1	0.51	15.5	33.6	320
Solution	Fe ₂ O ₃	Nb ₂ O ₅	Ta ₂ O ₅	ZrO ₂	HfO ₂	MnO	ThO ₂	UO ₂
Initial	13.8	59.7	5.84	197.7	7.23	46.3	0.0028	0.046
Final	<0.001	0.033	0.0036	0.031	0.001	0.22	0.00017	0.0042

the absorption of a part of zirconium and niobium from silica sol by the sorbent, while sodium remains quantitatively in the liquid phase (see

Table 2). The sorbent is used in the decomposition of eudialyte concentrate by sorption conversion, while silica sol is directed to obtaining the pre-

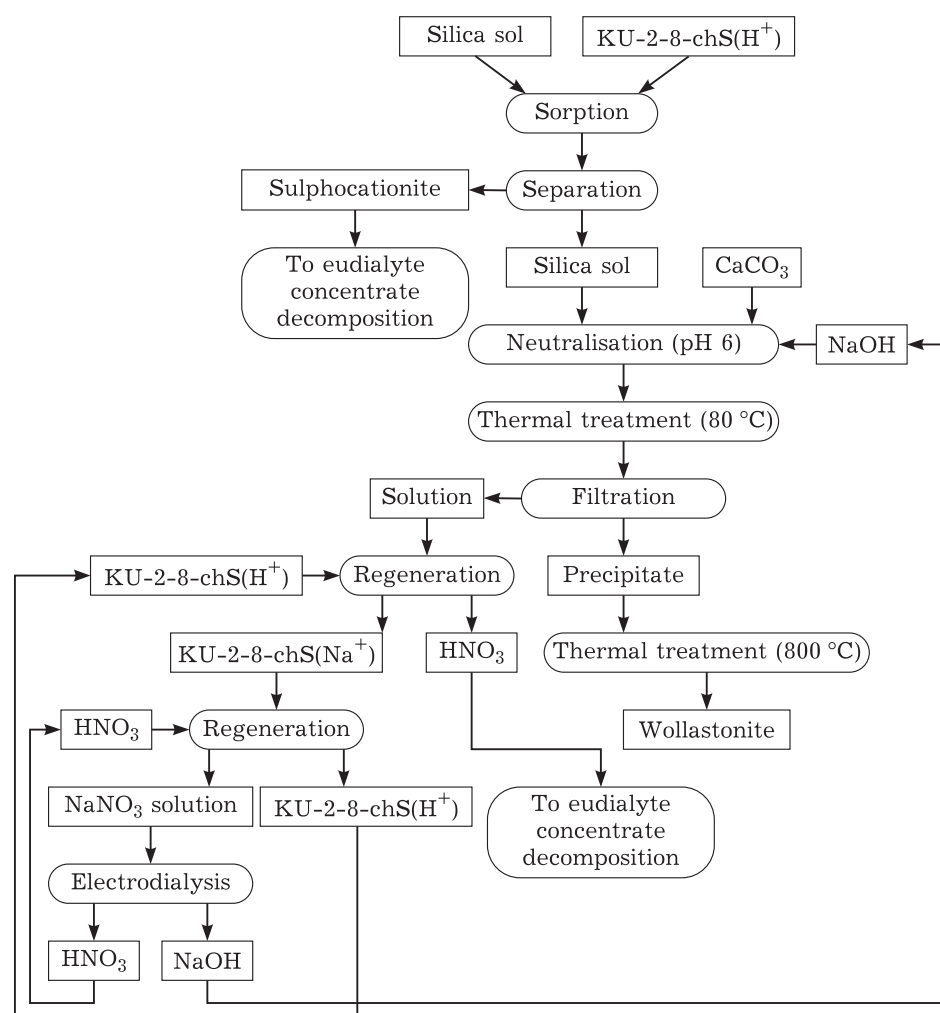


Fig. 3. The process flow scheme of silica sol processing to obtain wollastonite with utilisation of the stock acid solution.

cursor of wollastonite. Sodium is recovered with sulphocationite from the stock solution obtained after separating the precursor of wollastonite, to obtain the acid solution suitable for re-use in the sorption conversion of eudialyte concentrate. The sorbent saturated with sodium is reactivated by acid treatment from Na^+ - into H^+ -form, while sodium hydroxide and the acid for use in the technology are prepared from the resulting solution by means of electrodialysis [12].

CONCLUSIONS

1. For the purpose of completing the development of eudialyte concentrate technology through sorption conversion, two versions have been proposed for processing silica sols formed during acid decomposition of eudialyte concentrate by sorption conversion.

2. The technologies provide additional extraction of valuable methods from silica sols by sorption with sulphocationite, different versions of silica use for manufacturing valuable products, regeneration of acid solutions for their re-use in the decomposition of eudialyte concentrate.

3. Utilisation of silica sols formed in eudialyte concentrate processing by sorption conversion ensures almost complete exclusion of the formation of liquid wastes.

REFERENCES

- 1 Lokshin E. P., Elizarova I. R., Ryskina M. P., Tareeva O. A., On the composition of eudialyte concentrate, *Nonferrous Metals*, 2018, No. 2, P. 10–14. (In Russ.).
- 2 Davis P., Stopic S., Balomenos E., Panias D., Paspaliaris I., Friedrich B., Leaching of rare earth elements from eudialyte concentrate by suppressing silicon dissolution, *Minerals Engineering*, 2017, Vol. 108, P. 115–122.
- 3 Ma Y., Stopic S., Friedrich B., Hydrometallurgical treatment of a eudialyte concentrate for preparation of rare earth carbonate, *Johnson Matthey Tech.*, 2019, Vol. 63, No. 1, P. 2–13.
- 4 Lokshin E. P., Tareeva O. A., Drogobuzhskaya S. V., Sorption conversion of eudialyte concentrate in sulphuric acid medium, *Chem. Sustain. Dev.*, 2022, Vol. 30, No. 3, P. 266–272.
- 5 Lokshin E. P., Tareeva O. A., Decomposition of an eudialyte concentrate with nitric acid by sorption conversion, *Russian Metallurgy (Metally)*, 2020, No. 9, P. 964–970. (In Russ.).
- 6 Tyulnin V. A., Tkach V. R., Eyrikh V. I., Starodubtsev N. P., Wollastonite as a Unique Multi-Purpose Mineral Raw Material, *Ruda i Metally*, Moscow, 2003. (In Russ.).
- 7 Pat. RU 2034797 C1, 1995. (In Russ.).
- 8 Pat. RU 2077506 C1, 1997. (In Russ.).
- 9 Pat. RU 2526546 C2, 2014. (In Russ.).
- 10 Akatyeva L. V., Development of chemical technological foundations for raw material processing to obtain calcium silicates and composite materials, Thesis for Dr. Sci. in Technology, Moscow, 2014. (In Russ.).
- 11 Manakova N. K., Suvorova O. V. Mining wastes of the Murmansk Region for the production of block foam silicates, *Proceedings of the Fersman Scientific Session of the GI KSC RAS*, 2017, No. 14, P. 243–245. (In Russ.).
- 12 Lokshin E. P., Tareeva O. A., Sedneva T. A., Processing of Apatite Concentrate by Sorption Conversion, Federal Research Center of the Russian Academy of Sciences, Apatity, 2018. (In Russ.).