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Purification of Sphene Concentrate by Sorption Conversion

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

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

E-mail: lokshin.ep@gmail.com

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Abstract

A new method of purification of rough sphene concentrate from phosphorus impurities has been developed, based on its treatment with low-concentrated solutions of orthophosphoric or sulphuric acids in the presence of sulphocationite. It is shown that this method provides effective purification of sphene concentrate and makes it possible to increase the efficiency of the technology through significant reduction of the consumption of acids, elimination of the formation of liquid waste, and due to the possibility of using aluminium, which is formed during the decomposition of nepheline contained in the initial concentrate.

Keywords: sphene concentrate, chemical purification

INTRODUCTION

Rutile and ilmenite concentrates are used in the world practice to produce titanium compounds. In Russia, loparite concentrate is used to manufacture a small amount of titanium products, while the major needs are met by imported ilmenite [1].

During concentrating the apatite-nepheline ores from the Khibiny deposits, under development by the Fosagro-Apatit combine, sphene concentrate may be obtained from the foamy product of reverse nepheline flotation. Theoretically, sphene contains 40.8 wt. % TiO_2 and is of interest as a raw material source of titanium. This interest is even more substantial because sphene concentrates obtained from the ores of the Khibiny group of apatite deposits may contain the oxides of rare earth elements (REE) up to 0.56 wt. %, and $Nb_2O_5 + Ta_2O_5$ up to 0.37 wt. %.

The rough sphene concentrate obtained from concentrating the apatite-nepheline ore contained, wt. %: TiO_2 32.1, SiO_2 31.7, CaO 24.3, Al_2O_3 4.7, Fe_2O_3 4.5, P_2O_5 0.87 [2].

One of the important characteristics determining the quality of sphene concentrate is the content of phosphorus admixture, which causes titanium losses during hydrometallurgical processing because of the formation of poorly soluble titanium phosphates. For some areas of application, for example as a component for welding electrode coating, increased sulphur content is also harmful.

To purify the rough sphene concentrate from phosphorus, it was proposed to leach apatite present in the concentrate using various mineral acids: sulphuric, nitric, and hydrochloric [2, 3].

A substantial part of the rough concentrate was dissolved during purification, with the formation of solutions containing the anions of the used acid, as well as aluminium, calcium, phosphorus, and some other impurities.

The experimental-industrial production of purified sphene concentrate was organized at the

Fosagro-Apatit combine. According to TU 1715-069-00203938-2000, the concentrate contains not less than 35.0 wt. % TiO_2 and not more than 0.04 wt. % P_2O_5, 0.1 wt. % S, 2.5 wt. % (FeO + Fe_2O_3). The purified concentrate was obtained by sulphuric acid treatment of a non-magnetic fraction of the foamy product of reverse nepheline flotation [4]. The production rate was about 1500 t per year [5]. There is the possibility of multiple increase in the production of sphene concentrate.

The consumption of the acid, composition of the formed exhaust solutions and the methods of their utilization have not been reported [6]. With the low productivity of the experimental-industrial installation, these solutions were directed to the tailings dump of the combine, having no substantial effect on the composition of water involved in recirculating water supply. However, in the case of the production of substantial amounts of sphene concentrate, this approach may turn out to be unsuitable.

The goal of the work was to develop a method to obtain the purified sphene concentrate, to provide a sharp decrease in the amount of formed acid-containing liquid wastes.

EXPERIMENTAL

The possibility to purify sphene concentrate by means of sorption conversion was investigated [7]. Solutions with low concentrations of orthophosphoric acid (GOST 20298-74) and sulphuric acid (GOST 4204-77) were used as the working media.

The initial substance was the rough concentrate containing, wt. %: TiO_2 34.65, Al_2O_3 4.51, Fe_2O_3 2.28, Na_2O 2.36, K_2O 1.10 and P_2O_5 1.90. In addition to sphene, the concentrate also contains apatite and nepheline, which are readily decomposed with mineral acids, and practically undecomposable aegirine and feldspar.

Experiments were carried out as follows. A weighted portion of the concentrate and the required amount of sulphocationite KU-2-8chS (GOST 20298-74) were placed in a solution prepared by diluting the chosen acid with distilled water to the necessary concentration.

The pulp was kept at room temperature for a definite time under permanent mixing. Then the sorbent was separated through a mesh filter from the pulp, which was composed of a solid residue and acidic solution, and the solid residue was separated from the solution. The solid residue was washed with water on a paper filter or by means of repulping (twice at L/S = 10) and dried at a temperature of 80 °C.

Sorbent consumption (β = 210 %) was evaluated in per cent of theoretically necessary amount for the sorption of cations (Me^{n+}) of alkaline metals and aluminium, as well as calcium which is present in apatite: these ions may pass into solution during the purification of sphene concentrate. We neglected the fact that a portion of aluminium may be present in the concentrate not in the form of nepheline but as feldspar, which is insoluble under the process conditions. The chosen sorbent consumption ensured efficient sorption of metal cations that passed into the solution.

The products were analyzed by means of atomic absorption (metals), spectrophotometry (phosphorus), and potentiometry (fluorine).

RESULTS AND DISCUSSION

The efficiency of treatment was evaluated from an increase in titanium concentration and from the residual content of phosphorus in the concentrate, in the case if orthophosphoric acid was used, or phosphorus and sulphur in sulphuric acid was used.

Though sphene is noticeably decomposed with the transition of calcium into solution and the formation of titanium phosphates under the action of hot 40–80 wt. % H_3PO_4 solutions [8], calcium is not leached from sphene under soft conditions of acid treatment (low temperature and low acidity of the solution).

Decomposition of apatite and nepheline by orthophosphoric and sulphuric acids is described by the reactions:

$$Ca_5(PO_4)_3F + 7H_3PO_4 \rightarrow 5Ca(H_2PO_4)_2 + HF \quad (1)$$

$$(Na,K)AlSiO_4 + 4H_3PO_4 \rightarrow (Na,K)H_2PO_4 + Al(H_2PO_4)_3 + H_2SiO_3 + 2H_2O \quad (2)$$

$$Ca_5(PO_4)_3F + 5H_2SO_4 + 2H_2O \rightarrow 5CaSO_4 \cdot 2H_2O + 3H_3PO_4 + HF \quad (3)$$

$$(Na,K)AlSiO_4 + 4H_2SO_4 \rightarrow (Na,K)_2SO_4 + Al_2(SO_4)_3 + SiO_2 \cdot nH_2O + 4H_2O \quad (4)$$

$$H_2SiO_3 + 6HF \rightarrow H_2SiF_6 + 3H_2O \quad (5)$$

Calculating the amount of cations that passed into solution, we have admitted that aluminium is incorporated only in nepheline, while the source of calcium passing into solution is fluoroapatite. In addition, during the dissolution of nepheline, its components sodium and potassium will pass into the solution in the amount proportional to the aluminium content. With these assumptions, the total amount of cations that passed into solution during

the treatment of 1 g of the concentrate is estimated to be approximately 4.4 mg-equiv.

Rare-earth elements (Tr) in apatite provide isomorphic substitution of calcium, and decomposition in phosphoric acid solutions leads to the formation of poorly soluble compounds – $Tr(H_2PO_4)_3$, while in sulphuric acid solutions the compounds with limited solubility are formed – $NaTr(SO_4)_2$. The formation of even less soluble fluorides of REE does not occur because fluorine, which is liberated during apatite decomposition, is bound into a fluorosilicate complex.

The content of the sum of REE oxides in apatite from the Khibiny deposits under development is about 1 wt. %. REE phosphates are poorly soluble in solutions with low acid concentrations. It was not excluded that apatite dissolution could be hindered in these solutions, which would lead to an increase in residual phosphorus content in the purified concentrate. We determined the solubility of calcium and REE from apatite in low-concentration solutions of phosphoric acid. For this purpose, 1 g of the Khibiny apatite concentrate (GOST 22275-90) was placed in 50 mL of phosphoric acid solution (S/L = 1:50) with the necessary concentration ($C_{H_3PO_4}$), and kept under periodic mixing for 14 days. The concentrations of calcium and REE of the cerium group in the resulting solutions are presented in Table 1.

It follows from the data shown in Table 1 that the solubility of fluoroapatite $Ca_5(PO_4)_3F$ increased with an increase in the concentration of phosphoric acid, so that, judging from calcium concentration, the solubility at 20 °C was 1.44, 4.81 and 8.67 g/L at $C_{H_3PO_4}$ equal to 0.94, 3.15 and 5.03 wt. %, respectively.

In apatite, the fraction of REE oxides in their sum is approximately equal to, wt. %: La_2O_3 29, Ce_2O_3 41, Pr_2O_3 4.4, Nd_2O_3 15 [9]. With the determined apatite solubility in the studied phosphoric acid solutions, REE concentration should be, mg/L: La_2O_3 4.1–24.0, Ce_2O_3 6.0–35.4, Pr_2O_3 0.6–3.6, Nd_2O_3 2.0–11.8. For $C_{H_3PO_4}$ = 0.94 wt. %, REE of the cerium group, comprising the major part of REE present in apatite, were not transferred into the solution. At $C_{H_3PO_4}$ = 3.15–5.03 wt. %, the amount of lanthanum and cerium in the solution is also smaller than their amount in dissolved apatite. Praseodymium and neodymium did not pass into the solution because of the lower solubility of their phosphates in phosphoric acid in comparison with the solubility of lanthanum and cerium phosphates.

So, the low solubility of REE phosphates may hinder purification of sphene concentrate from phosphorus admixture. However, due to the high efficiency of REE sorption from phosphoric acid solutions at room temperature (the distribution coefficient during sorption from 5 wt. % H_3PO_4 reaches 714 [10]), we supposed that the solubility of REE in low-concentration solutions of phosphoric acid would be sufficient for their efficient sorption, and the necessary completeness of purification from phosphorus would be achieved during sorption conversion.

TABLE 1

Dependence of the content of calcium and REE of the cerium group on the concentration of phosphoric acid ($C_{H_3PO_4}$) at 20 °C

$C_{H_3PO_4}$, wt. %	Content in solution, mg/L				
	CaO	La_2O_3	Ce_2O_3	Pr_2O_3	Nd_2O_3
0.94	798	≤0.005	≤0.005	≤0.002	≤0.005
3.15	2674	14.1	16.4	≤0.002	≤0.005
5.03	4816	18.8	19.9	≤0.002	≤0.005

TABLE 2

Effect of the conditions of rough sphene concentrate sorption conversion in phosphoric acid solutions on the content of titanium and phosphorus in the obtained concentrates

$C_{H_3PO_4}$, wt. %	L/S	Time, h	Content, wt. %	
			TiO_2	P_2O_5
0.5	40	2	H. a.*	0.67
1	20	0.5	37.0	1.08
1	20	1	38.0	0.82
1	20	2	38.2	0.46
3	20	3	39.8	0.095

* Not analyzed.

The dependence of the content of titanium and phosphorus oxides in the obtained concentrates on the conditions of sorption conversion is shown in Table 2.

One can see that noticeable dissolution of apatite is observed with the solution 0.5 wt. % H_3PO_4. However, even in the solution of 1 wt. % H_3PO_4 the content of P_2O_5 in the purified concentrate decreased within 2 h only to 0.46 wt. %. The high level of purification from phosphorus admixture was achieved through the treatment in a 3 wt. % H_3PO_4 solution for three hours. The purified concentrate, accounting for about 85 % of the mass of the initial concentrate, contained 0.68 wt. % Al_2O_3, 0.43–0.55 wt. % Na_2O, 0.53 wt. % K_2O and did not contain sulphur.

More efficient purification of sphene concentrate from phosphorus admixture was achieved by means of sorption conversion in 2 wt. % H_2SO_4.

The data on the effect of treatment time (room temperature, L/S = 20) on the content of phosphorus and titanium in the purified concentrate are shown in Fig. 1. With the chosen modes of washing from the mother solution, sulphur content in the purified concentrate was 0.1 wt. %.

The mass loss by the initial concentrate during purification was about 15 %. Unlike for the known methods of chemical purification of sphene concentrate, during purification by means of sorption conversion, the major part of cations from dissolved minerals are absorbed by the sorbent. The anions of these minerals are accumulated in the acid solution. The concentrations of admixtures in mother solutions were, mg/L: TiO_2 ≤0.003, Al_2O_3 ≤0.004, Na_2O 67–102, K_2O 17–20, F 14–19. At L/S = 20, the concentration of phosphoric acid in mother solutions increased by 0.13 wt. % per cycle, provided that apatite present in the initial concentrate was completely decomposed. The concentration of the most difficultly sorbed alkaline metals did not exceed 3.7 mg-equiv/L,

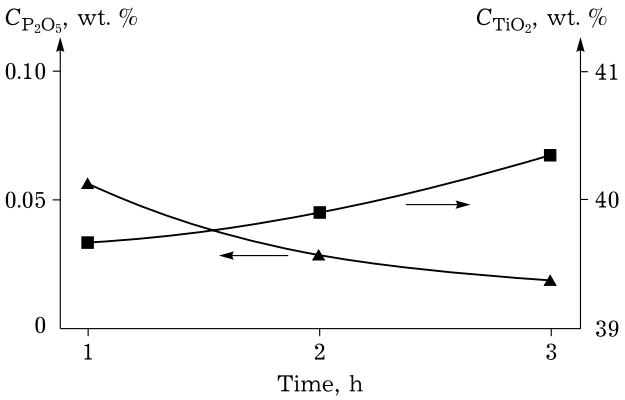

Fig. 1. Dependence of the efficiency of sphene concentrate purification from the time of treatment in the solution of 2 wt. % H_2SO_4.

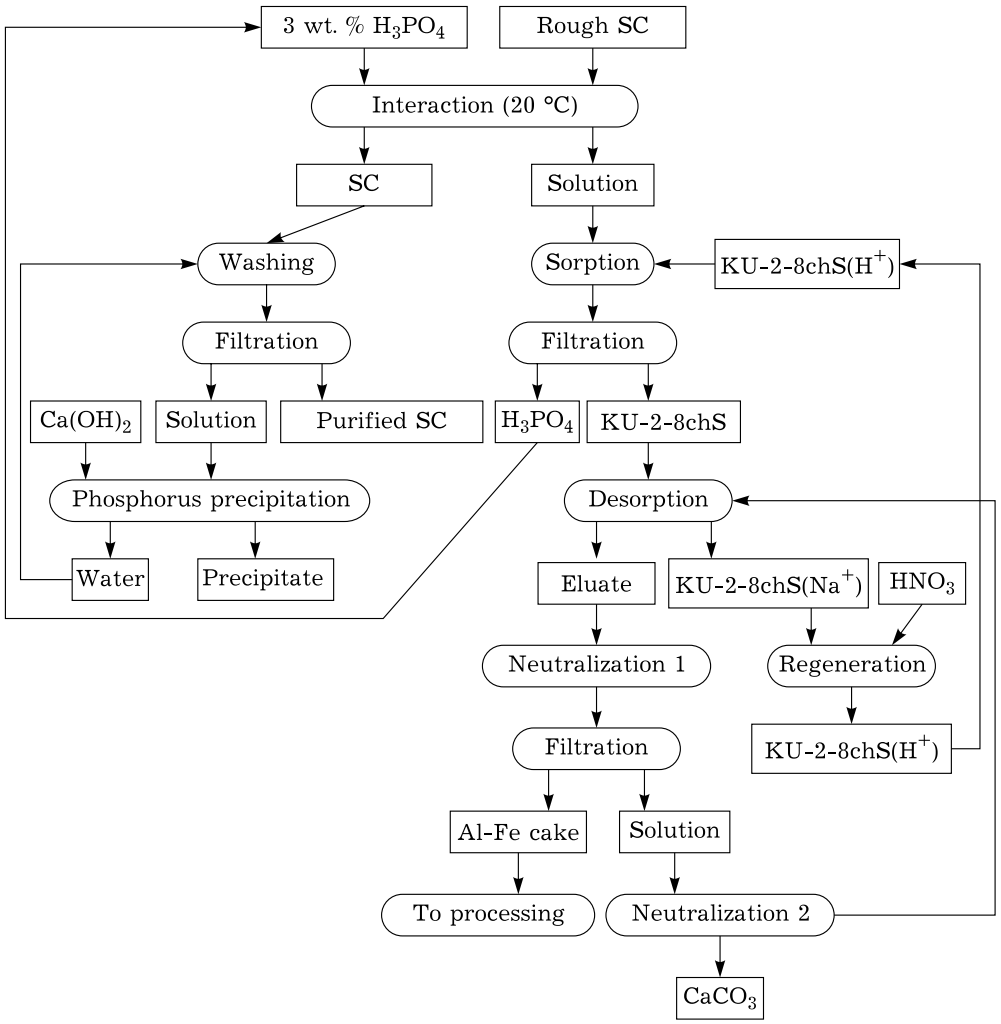

Fig. 2. Technological flowchart of the phosphoric acid purification of sphene concentrate (SC).

and this caused almost no decrease in solution acidity. This determines the possibility of multiple usage of acid solutions for recycling to treat the new portions of rough sphene concentrate.

The number of cycles of the use of acid solutions may be limited by the accumulation of silica formed during nepheline decomposition. Taking into account the initial and final Al_2O_3 content in sphene concentrate, we calculated that about 11 % of the mass of initial concentrate was connected with nepheline. Therefore, the amount of SiO_2 that may pass from nepheline into solution is 4.7 % of the mass of initial concentrate. For L/S = 20, silica concentration in the solution, calculated for SiO_2, will be 2.35 g/L per cycle. As the experience suggests, acid solutions are gelated if SiO_2 concentration increases to 12–16 g/L, which does not allow using these solutions for recycling. Therefore, they may be used for not less than 5 cycles of concentrate purification.

Thus, the consumption of acids for sphene concentrate purification by means of sorption conversion may be decreased substantially. For example, if the process is carried out using 2 wt. % H_2SO_4, it will be less than 50 % of the stoichiometric amount required for nepheline and apatite dissolution according to reactions (3) and (4).

Aluminium and calcium cations are desorbed from the sulphocationite by the solutions of sodium salts, and then the sorbent is transformed into the H^+-form through the acid treatment. Aluminium hydroxide and the carbonates of alkaline earth metals, mainly calcium, are precipitated from the eluate into separate products [10].

Aluminium hydroxide may be used to prepare aluminium sulphate or chloride to be used as coagulants.

Neutralization of the phosphoric acid or sulphuric-phosphoric acid solution enriched with silica allows using water for recycling to prepare acid solution excluding the formation of liquid acid wastes requiring utilization. Utilization of the carbonates of alkaline earth metals removed from the sorbent becomes possible.

A technological flowchart of phosphoric acid purification of the rough sphene concentrate is shown in Fig. 2.

The flowchart remains almost unchanged for sulphuric acid purification, but sulphuric-phosphoric solution is obtained, and a mixture of gypsum and calcium phosphate is precipitated.

CONCLUSION

The possibility of efficient purification of rough sphene concentrate by means of sorption conversion using 3 wt. % H_3PO_4 or 2 wt. % H_2SO_4 solutions is demonstrated. This allows a substantial reduction in acid consumption and excludes the formation of liquid wastes, opening the possibility to use aluminium, which is formed in the decomposition of one of the major admixture minerals – nepheline.

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