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Purification of Sphene Concentrate to Remove Phosphorus Impurity with Dilute Mineral Acids

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Abstract—Methods of crystal-optic, X-ray phase, chemical, and IR spectroscopic analyses were used to study the interaction of sphene and fluorapatite concentrates with dilute mineral acid solutions. The conditions under which the sphene concentrate can be purified to remove admixtures of phosphorus-containing compounds were found.

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Sphene (CaTiSiO_5) is a rock-forming mineral in apatite-nepheline ores of the Khibiny deposits. The sphene concentrate obtained in dressing of these ores is regarded as a promising raw material for production of titanium pigments and for use in coatings of welding electrodes [1]. Presence of phosphorus in the concentrate intended for manufacture of the titanium dioxide pigment leads to a pronounced decrease in the yield of titanium into the final product [2] and precludes direct use of the concentrate in coatings of welding electrodes. According to technical specifications for the sphene concentrate for welding electrodes [TU (Technical specification) 1715-069-00 203 938-2000], the content of phosphorus should not exceed 0.1% in terms of P_2O_5 . The presence of phosphorus is due to the fact that the sphene concentrate contains an admixture of a fluorapatite mineral, $\text{Ca}_5(\text{PO}_4)_3\text{F}$, both as aggregations with sphene and separately.

Phosphorus compounds cannot be removed to the required extent in the dressing stage. Therefore, chemical purification methods based on decomposition of fluorapatite with dilute solutions of mineral acids (sulfuric acid, for the most part) have been suggested [3]. In this process, sphene remains unchanged.

The content of phosphorus in the initial sample of the sphene concentrate used to develop the purification procedure was 1.88% in terms of P_2O_5 .

The conditions of the given process require an additional study to substantiate the choice of an acid

and minimize its expenditure at satisfactory purification parameters. The mineralogical¹ and chemical compositions of the starting sphene and fluorapatite concentrates used in this study are listed in Tables 1 and 2, respectively.

Chemical purification to remove fluorapatite can be performed not only with sulfuric acid, but also with hydrochloric and nitric acids [3]. With H_2SO_4 used,

Table 1. Mineralogical composition of sphene and fluorapatite concentrates

Mineral	Sphene concentrate	Apatite concentrate
	content, wt %	
Sphene	86.0	0.4
Fluorapatite	4.5	95.1
Nepheline	3.2	1.8
Aegirine	4.5	0.8
Feldspars	1.5	
Microcline		0.1
Hydromicas	0.5	0.1
Titanomagnetite		0.1

¹ Mineralogical analysis was made by V.F. Fedchenko at the Central laboratory of Apatit Open Joint-Stock Company.

Table 2. Chemical composition of sphene and apatite concentrates

Concentrate	Content, wt %							
	TiO ₂	SiO ₂	CaO	Fe ₂ O ₃	P ₂ O ₅	MgO	Na ₂ O	F
Sphene	35.9	30.4	25.1	1.7	1.88	0.6	0.7	0.4
Fluorapatite	0.4	2.3	49.6	0.4	39.2	0.2	0.2	3.1

the purified sphene concentrate is contaminated with an additional impurity to be controlled, sulfur. Nevertheless, use of this acid can be justified by the simpler utilization of spent sulfuric acid solutions, compared with those of hydrochloric and nitric acids. To choose rational purification conditions, the behavior of fluorapatite and sphene concentrates in their interaction with dilute mineral acids was studied.

Samples of apatite and sphene concentrates, taken from the dressing stage, were treated with acids of various concentrations and subjected to chemical, crystal-optic, X-ray phase, and IR spectroscopic analyses. The behavior of aegirine, feldspars, and nepheline was not studied because they contain no phosphorus. In addition, the first two of these minerals are stable against dilute acids and the decomposition of nepheline has been studied in sufficient detail [4].

Because it is fluorapatite that is the source of phosphorus impurity limited in the sphene concentrate, its interaction with mineral acids was studied separately.

To determine the behavior of fluorapatite under sphene concentrate purification conditions, experiments on fluorapatite decomposition with dilute sulfuric, hydrochloric, and nitric acids were performed at room temperature and s : 1 = 1 : 3. The chosen expenditure of the acids was lower than the stoichiometric value even for 5% solutions. The interaction of fluorapatite with dilute mostly occurs under the chosen conditions by the reactions



The degree of apatite decomposition was judged from the increase in the phosphorus concentration in solutions in the course of time. The results obtained (Table 3) characterize the kinetics of fluorapatite decomposition. It follows from these data that the decomposition of fluorapatite by sulfuric and hydro-

chloric acids occurs at approximately equal rates exceeding that for nitric acid. The choice of nitric acid is also undesirable because of the more difficult utilization on nitrate waste solutions.

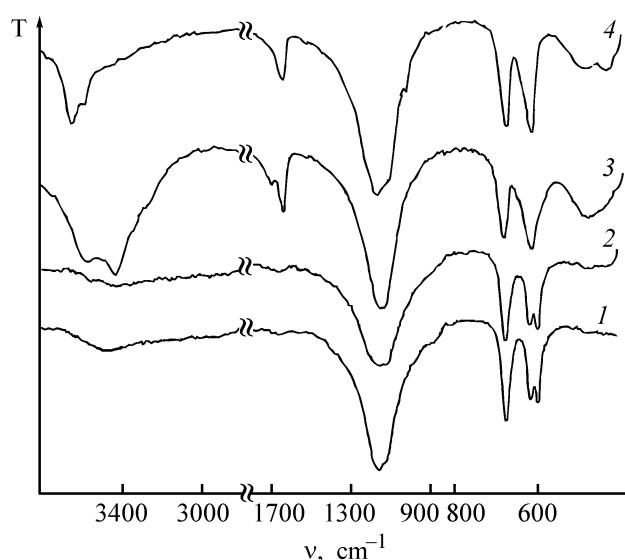
The data furnished by chemical, crystal-optic, X-ray phase, and IR spectroscopic analyses of precipitates formed in decomposition of fluorapatite with dilute H₂SO₄ at an acid expenditure exceeding the stoichiometric value show that these precipitates are composed of anhydrite, CaSO₄. The IR spectra of precipitates not washed to remove the mother liquor and dried at room temperature and at 90°C also coincide with the spectrum of anhydrous calcium sulfate [5] (see figure, curves 1 and 2).

At the same time, the spectra of the precipitates washed with water and dried at room temperature show that anhydrite is converted into gypsum in the course of washing. The IR spectrum reveals the appearance of a doublet of absorption bands in the ranges of both stretching (3400–3600 cm⁻¹) and deformation vibrations (1630–1690 cm⁻¹) of water molecules (see figure, curve 3).

In drying of washed precipitate at 90°C, gypsum loses 1.5 molecules of water and is converted into a semihydrate CaSO₄ · 0.5H₂O. This is indicated by the disappearance of splitting in the region of deformation vibrations and a shift of the absorption bands

Table 3. Decomposition of fluorapatite with dilute acids

Treatment time, h	P ₂ O ₅ concentration, g l ⁻¹ , in treatment with indicated acid, wt %					
	H ₂ SO ₄		HCl		HNO ₃	
	2	5	2	5	2	5
1	8.1	25.2	8.8	26.5	5.1	14.9
2	8.4	26.5	9.2	27.6	5.6	15.6
3	8.5	26.8	9.3	28.4	6.5	20.5



IR spectra of calcium sulfates. (v) Wave number. (1) CaSO_4 not washed to remove the mother liquor with water and dried at room temperature, (2) CaSO_4 not washed to remove the mother liquor with water and dried at 90°C , (3) $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ washed to remove the mother liquor with water and dried at room temperature, and (4) $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ washed to remove the mother liquor with water and dried at 90°C .

in the range of stretching vibrations of water to higher frequencies (see figure, curve 4).

The methods used in this study did not reveal any content of calcium phosphate in the precipitates.

Similarly to experiments on apatite decomposition with dilute acid solutions, the purification of the sphene concentrate to remove phosphorus (fluorapatite) was studied. The results obtained are listed in Table 4.

Table 4. Kinetics of purification of the sphene concentrate to remove fluorapatite ($s : 1 = 1 : 3$)

Treatment time, h	Residual content of P_2O_5 , wt %, upon treatment with indicated acid, wt %					
	H_2SO_4		HCl		HNO_3	
	2	5	2	5	2	5
1	1.1	0.25	0.9	0.18	1.15	0.17
2	0.41	0.09	0.38	0.083	0.51	0.10
3	0.24	0.056	0.19	0.042	0.27	0.061
4	0.14		0.12		0.16	
5	0.094		0.081		0.11	

The results of purification of the sphene concentrate to remove the phosphorus impurity confirm the data obtained in fluorapatite decomposition and demonstrate that nitric acid is less effective than hydrochloric and sulfuric acids. The efficiency of the acids decreases in the order $\text{HCl} > \text{H}_2\text{SO}_4 > \text{HNO}_3$. In the same order grows the overstoichiometric expenditure of the acid for fluorapatite decomposition. At equal percentage concentrations of the acids, nitric acid has the lowest concentration in gram-equivalents. Nevertheless, the characteristics obtained with any of the three acids can give a sphene concentrate satisfying the requirements of TU 1715-069-00 203 938-2000 to the content of phosphorus (less than 0.1% in terms of P_2O_5).

From the ecological standpoint, use of nitric acid for purification of the sphene concentrate to remove phosphorus is less attractive because the maximum permissible concentration (MPC) of nitrate ions is lower than that for sulfate and chloride ions. The MPC is most simply provided in purification of waste solutions containing sulfate ions. Use of H_2SO_4 solutions leads to contamination of the concentrate with calcium sulfate having low solubility, and the technical specification for welding materials does not limit the content of sulfur. It is necessary to take into account that the expenditure of water for washing of the purified sphene concentrate to remove mother liquor containing sulfate ions is approximately 2–3 times that for washing to remove chloride ions. The real expenditure of water for purification to remove phosphorus is at a minimum for hydrochloric acid.

It follows from the data in Table 4 that purification to remove fluorapatite is sufficiently effective and the content of phosphorus in the target product decreases to the required level already in 3–5 h, depending on the acid concentration.

Starting from the assumption that there exist aggregations of sphene and fluorapatite [3], it was decided to check the effectiveness of the purification conditions for a finely ground sphene concentrate, in which the content of aggregations is virtually zero. The sphene concentrate was ground in a ball mill to grain size of $-28 \mu\text{m}$ and treated with 2% hydrochloric acid. The choice of the acid was due to its higher efficiency, compared with sulfuric and nitric acids.

The reactivity of sphene in its interaction with the acid grows with the grinding fineness, and the higher the acid concentration, the stronger the interaction. Simultaneous decomposition of sphene and fluorapatite may lead to formation of a poorly soluble

titanium phosphates, i.e., to lower degree of purification to remove phosphorus. Therefore, 2% hydrochloric acid was taken for the treatment in order to reduce the degree of sphene decomposition. The finely ground sphene concentrate was processed using the procedure described above. The results of the experiments are presented below

Treatment time, h	1	2	3
Residual content of P_2O_5 , wt %	0.14	0.029	0.024

Comparison with the data in Table 4 shows a considerably higher efficiency of purification to remove phosphorus for the finely ground sphene concentrate.

The final stage in preparation of the sphene concentrate is its washing with water to remove the mother liquor. Because of the low solubility of the precipitated calcium sulfate ($\sim 2 \text{ g l}^{-1}$), its removal by washing requires a water volume exceeding that of the acid by a factor of 6–8. At the same time, the expenditure of water to removal of chloride and nitrate ions by washing is 2–3 times smaller than that for calcium sulfate.

The problem of utilization of solutions formed in decomposition of fluorapatite and washing solutions requires an additional analysis. One of suggestions is to purify the sphene concentrate in fluidized-bed apparatus, which will enable fuller consumption of the acid and lower expenditure of water for washing of the purified concentrate. In this case, the acid will be consumed nearly completely. With hydrochloric acid used for purification, the waste solution will be a solution of $CaCl_2$, which can be utilized, e.g., by electrodialysis [6, 7].

With sulfuric acid used for purification to remove phosphorus, the forming finely crystalline $CaSO_4$ will be carried away from the apparatus by the washing solution and then can be separated by hydroclassification, which was confirmed in the stage of pilot industrial tests at Apatit Open Joint-Stock Company.

CONCLUSION

The efficiencies of purification of the sphene concentrate to remove a phosphorus impurity with hydrochloric and sulfuric acids are close, but preference should be given to hydrochloric acid, which rules out any contamination of the concentrate with sulfur impurity and makes it possible to reduce the expenditure of water for washing by a factor of 2–3.

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REFERENCES

1. Fedorov, S.G., Nikolaev, A.I., Brylyakov, Yu.E., et al., *Khimicheskaya pererabotka mineral'nykh kontsentratorov Kol'skogo poluostrova* (Chemical Processing of Mineral Concentrates from Kola Peninsula), Apatity: Kola Nauch. Tsentr Ross. Akad. Nauk, 2003.
2. Gerasimova, L.G., *Pigmenty i napolniteli iz prirodnogo titansoderzhashchego syr'ya i tekhnogennykh otkhodov* (Pigments Produced from Natural Titanium-containing Raw Materials and Technological Wastes), Apatity: Kola Nauch. Tsentr Ross. Akad. Nauk, 2001.
3. Motov, D.L. and Maksimova, G.K., *Sfen i ego khimicheskaya pererabotka na titanovye pigmenty* (Sphene and Its Chemical Processing To Give Titanium Pigments), Leningrad: Nauka, 1983.
4. Kalinnikov, V.T., Nikolaev, A.I., and Zakharov, V.I., *Gidrometallurgicheskaya kompleksnaya pererabotka netraditsionnogo titano-redkometall'nogo i alyumosilikatnogo syr'ya* (Integrated Hydrometallurgical Processing of Unconventional Titanium–Rare-Earth and Aluminosilicate Raw Materials), Apatity: Kola Nauch. Tsentr Ross. Akad. Nauk, 1999.
5. Plyusnina, I.I., *Infrakrasnye spektry mineralov* (IR Spectra of Minerals), Moscow: Mosk. Gos. Univ., 1977.
6. RF Patent 2174561.
7. Todorov, S.A., Lainer, Yu.A., and Medvedev, A.S., *Izv. Vyssh. Uchebn. Zaved., Tsv. Metall.*, 2004, no. 3, pp. 37–39.