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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Purification of Baddeleyite Concentrate by Alloying with Sulfuric Acid and Its Salts

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Abstract—The conditions for the sulfation of rough baddeleyite concentrate to remove impurity minerals were studied.

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Owing to presence of impurity minerals (pyrochlore, hatchettolite, zirkelite, and perovskite), baddeleyite concentrate (BC) can contain large content of radionuclides. The standard concentration methods used for separation of the above minerals are inefficient or result in a large loss of baddeleyite. The developed method of the sulfation purification of BC ensures selective decomposition of main impurities [1]. At the same time, a number of rough concentrates, especially of those separated from the residues of magnetic and gravity concentration, require very high sulfation temperatures. However, high sulfation temperature causes "cementation" of a sulfate mass, which impedes processing, increases energy expenditure, accelerates corrosion of equipment, and makes larger baddeleyite loss.

Therefore, we studied the effect of additives of sulfate salts on the degree of the sulfation purification of BC. The sulfation in the presence of sulfate salts is likely to give positive effect owing to the formation of less spongy sulfate cakes and the increase in the boiling temperature of sulfuric acid. The mixtures of sulfuric acid and ammonium sulfate were studied for the decomposition of titanoniobates and used in sulfuric acid technology of loparite [2, 3]. The use of the above mixtures ensures high degree of opening, providing a 98–99% extraction of components into solution. The obtained effect is accounted for by deceleration of the decomposition and by a lesser "setting" of the reagent mass. In extraction of tantalum and niobium into the solution, presence of ammonium sulfate is also favorable owing to the formation of mixed complexes. The only shortage of the method is a large consumption of sulfuric acid and ammonium sulfate. The sulfation of baddeleyite and eudialyte concentrates in the presence of ammonium sulfate was also studied. However, in the first case, the result was not so evident and in the second case, it was more likely negative [4,5].

EXPERIMENTAL

Rough baddeleyite concentrate used in the experiments was separated from the wastes of magnetic and gravitation concentration and contained (wt %): 87.4 ZrO_2, 1.5 SiO_2, 2.5 TiO_2, 0.51 Fe_2O_3, 1.6 CaO, 3.4 Nb_2O_5, 0.59 Ta_2O_5 (activity 1350 Bc g^{-1}). The sulfation was performed with a 93% sulfuric acid in the presence of ammonium, sodium, and potassium sulfates. The mixtures prepared were kept in glassy carbon crucibles in a thermostated desiccator. Sulfate mass was leached with water at 60°C for 1 h, baddeleyite was separated by gravitation method and washed off from sulfate ions. The specific radioactivity of the precipitates was determined by the radiometric and γ-spectrometric methods and the content of ZrO_2 in the solutions, by complexometric titration.

In the presence of sulfate salts, sulfation proceeded without foaming. The sulfate mass remains spongy even when 0.008 moles of ammonium sulfate per 1 mole of sulfuric acid is added and becomes viscous when 0.25 moles of ammonium sulfate are added. In the presence of the mixtures having nearly equimolar composition, pyrosulfates form a solid alloy. The results of the sulfation experiments are presented in Fig. 1.

It follows from the presented data that in the temperature range studied, the degree of the concentrate

Table 1. Effect of ammonium, potassium, and sodium sulfates on the purification degree and decomposition of the baddeleyite sample (50 g) in sulfation with 32.5 g of H_2SO_4 for 2.5 h at 250°C

Run no.	Reagent	Content		BC, Bc g^{-1}	Purification degree, %	Solution		Loss of ZrO_2, %
		g	mol·mol^{-1} H_2SO_4			*V*, ml	ZrO_2, g l^{-1}	
1	$(NH_4)_2SO_4$	0.82	0.02	202	85.0	265	2.8	1.77
2	"	3.3	0.08	121	91.0	265	2.9	1.87
3	"	9.7	0.24	90	93.3	280	3.8	2.3
4	"	19.5	0.49	86	93.7	272	2.8	1.8
5	"	39.8		1172	13.2	230	0.7	0.38
6	K_2SO_4	0.82	0.015	178	86.8	265	1.5	0.9
7	"	3.3	0.06	168	87.6	255	2.3	1.4
8	"	19.5	0.37	90	94.5	280	3.3	2.2
9	Na_2SO_4	1.6	0.037	98	92.7	260	2.7	1.67
10	"	3.3	0.076	69	94.9	260	3.3	2.05
11	"	6.6	0.15	70	94.8	260	5.7	3.5
12	"	19.5	0.45	65	95.2	325	4.7	3.6
13	"	43.3		iso	16.3	250	1.3	0.76

purification from radionuclides increases as the amount of the ammonium sulfate additive raises. Consequenly the sulfation to a required degree of purity may be performed at lower temperatures. The mechanism of the effect exerted by ammonium sulfate on the purification degree is unclear and cannot be explained solely by a deceleration of setting of sulfate mass and by tendency of components of decomposed minerals to form readily soluble double salts with ammonium. The sulfation with excess amount of sulfuric acid proceeds without setting but its efficiency is low. It was also established experimentally that sodium sulfate increases the purification degree to larger extent, though the solubility of double salts with sodium is considerably lesser than with ammonium [6]. The results of the sulfation experiments with different salts are given in Table 1.

In the presence of sulfate salts, the equivalent amount of sulfuric acid converts to disulfates. In the sulfation experiments, as high as 49% of the acid was bound and the equimolar mixtures were used:

$$H_2SO_4 + M_2SO_4 = 2MHSO_4.$$

Since it seems unlikely that under the given conditions sodium or ammonium disulfates are more active than sulfuric acid, we may suggest that for the increase in the purification degree are responsible pyrosulfates formed on heating to 150–200°C.

$$2MHSO_4 \rightleftarrows M_2S_2O_7 + H_2O.$$

Decomposition in the presence of sodium and potassium pyrosulfates is performed by alloying at 650–700°C and that in the presence of ammonium pyrosulfates, by alloying at 400–450°C [7]. SO_3 separated at 450°C is believed to be the active component:

$$M_2S_2O_7 \rightleftarrows M_2SO_4 + SO_3\uparrow.$$

Apparently, the above reaction begins at lower temperatures. The equimolar mixtures (runs nos. 5, 13) decompose baddeleyite to small degree and, probably, this value of the purification degree is the contribution of pyrosulfates into the decomposition. The participation of pyrosulfates in the decomposition is indirectly confirmed by the fact that the effect exerted by ammonium, potassium, and sodium sulfates on the purification from

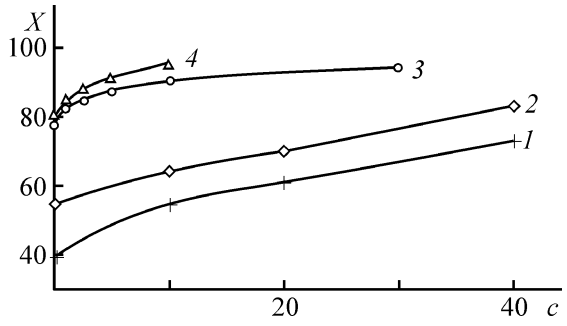

Fig. 1. Purification degree *X* (%) of the wastes vs. the amount of ammonium sulfate *c* (% in relation to H_2SO_4) at constant consumption of H_2SO_4 (65 g per 100 g of the concentrate). Sulfation time (h): (*1, 2*) 3 and (*3, 4*) 2.5. Temperature (°C): (*1*) 200, (*2*) 230, (*3*) 250, and (*4*) 260.

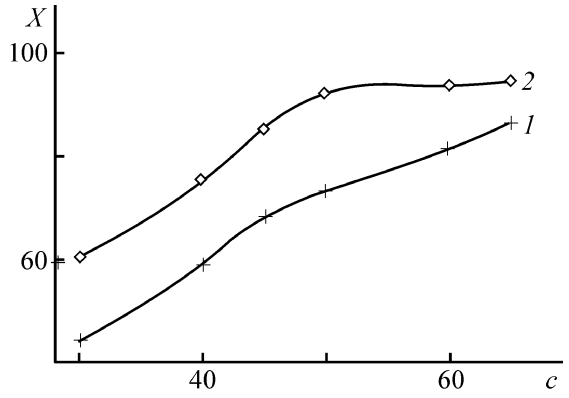

Fig. 2. Effect of the consumption of sulfuric acid *c* (g/100 g BC) on the BC purification from radionuclides at the sulfation temperature 250°C. (*X*) Purification degree (%). (*1*) Without and (*2*) with $(NH_4)_2SO_4$ (0.16 moles per 1 mole of H_2SO_4).

radionuclides and on the baddeleyite decomposition is different. This is because potassium and sodium pyrosulfates decompose minerals to various degrees [7]. The degree of the baddeleyite decomposition markedly increases only in the presence of sodium sulfate, whereas ammonium sulfate does not virtually affect it.

In leaching the sulfate cake, a great bulk of radionuclides with the sludges is removed from baddeleyite by gravitation method. The sludges contain incompletely decomposed minerals and gypsum with a codeposited radium(II) sulfate. Removal of sludges is more complete in the case of ammonium sulfate additive, which increases density and viscosity of the leaching solution. Therefore, this fact can be to some extent responsible for the better purification degree. At the same time, introducing ammonium sulfate into the pulp for leaching a sulfate cake in amounts ensuring the maximum effect in sulfation does not yield the same result, purification degree increases only slightly.

Use of the ammonium sulfate and sulfuric acid mixture makes it possible to somewhat decrease the consumption of sulfuric acid. When a 20% acid, instead of the equivalent amount of ammonium sulfate, is used in sulfation, the purification degree decreases insignificantly (Fig. 2).

CONCLUSIONS

(1) Introduction of ammonium, potassium, and sodium sulfates into sulfuric acid in sulfation of coarse baddeleyite concentrate makes it possible to increase the degree of purification from radionuclides, decrease consumption of sulfuric acid by 20%, and decrease the sulfation temperature.

(2) The purification degree increases with addition of sulfate salts in the following order: $Na_2SO_4 > (NH_4)_2SO_4 > K_2SO_4$. This is due to the contribution of forming pyrosulfates into the decomposition.

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