

Mechanoactivating Preparation of Bertrandite-Phenacite-Fluorite Concentrate to Vitriolic Disintegration

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Abstract

For the first time the authors have shown the possibility to disintegrate phenacite-containing flotation concentrate by 93 % solution of sulphuric acid, which provides transformation of ~92 mass % beryllium from the concentrate to water-soluble sulphate. The further enhancement of the completeness of the concentrate disintegration up to ~98 mass % is ensured by application of mechanoactivating preparation of the concentrate for sulphatization.

INTRODUCTION

Bertrandite-phenacite-fluorite concentrate that includes 4 mass % of beryllium is a relatively new, promising kind of raw material of beryllium chemical and metallurgical productions [1]. Its commercial application was first realized in Ul'ba Metallurgic Works (UMW) in the end of 20th century.

The traditional technology of processing the concentrate [2] is characterized by a multistage nature and it involves an expensive activating preparation of raw material for vitriolic disintegration, namely: a high-temperature melting of the mixture of high-grade bertrandite-phenacite-fluorite concentrate and low-grade beryllium concentrate (the beryllium content of 2 mass %) with soda ash and limestone in an ore-smelting furnace (melting temperature of ~1500 °C, the duration of the process ~4 h). The fusion cake resulting from melting of the above fusion mixture is granulated in cold water; the granules are subjected to wet grinding and classification. The aqueous pulp of the ground material prepared in this way is thickened and processed with 93 % solution of H₂SO₄ (the sulphatization is carried out within

~2 min at ~100 °C). The sulphatized product is subjected to leaching in water to form a solution of beryllium sulphate and difficultly soluble silica- and gypsum-containing sludge cake. Sulphate solution is neutralized by ammonium hydroxide with the result that difficultly soluble Be(OH)₂ precipitates.

This process is accompanied by the formation of significant amount of ecologically hazardous dump cake that contains beryllium, silicon dioxide, and gypsum from at the stage of vitriolic disintegration of the granulated fusion cake, by significant losses of beryllium with the cake and with waste mother solution at the Be(OH)₂ precipitation stage [1–3]. Large losses of beryllium with the cake (~2.5 mass %) are related to the application of limestone in melting the concentrates, which gives rise to gypsum at the stage of sulphatization and essentially increases a mass of the sludge cake. Significant losses of beryllium with mother solution (~2.5 mass %) are caused by a high content of fluorine in bertrandite-phenacite-fluorite concentrate (and, as a consequence, in the raw fusion mixture). Main part of fluorine passes into solution of beryllium sulphate later on and links beryllium into stable water-soluble com-

plexes at a stage of $\text{Be}(\text{OH})_2$ precipitation. For comparison, beryllium loss with mother solution is less than 1 mass % when first defluorinated concentrate is employed (that has been washed from fluorite with aluminium nitrate solution) [2]. However application of such washing of the concentrate is ineffective, for it leads to perceptible losses of beryllium with the nitrate solution.

This work investigates experimentally the potentiality to remove the noted limitations by direct vitriolic disintegration of bertrandite-phenacite-fluorite concentrate from Yermakovskoye deposit.

EXPERIMENTAL

Samples of bertrandite-phenacite-fluorite concentrate from Yermakovskoye deposit (Kazakhstan) which were selected from 23 various batches of the concentrate during the period from 1997 to 2004 have been used in the research.

The analysis of mineralogical composition of the concentrate samples was executed by the immersion method. Coarseness of concentrate particles was determined with the use of an optical microscope and a morphological method of the analysis. Beryllium content of the concentrate and of products of its processing was analysed by a photoneutron method (the methodical error was no more than 0.2 %). To make an estimate of impurity levels in the concentrate and in products of its processing, chemical and spectral methods of the analysis were applied (the error is no more than 0.03 %). X-ray diffraction analysis of initial and mechanoactivated concentrate was completed with the use of DRON diffractometer, CuK_α radiation.

Mechanoactivation of the concentrate was conducted in a planetary mill AIR-0.015M ("Gidrotsvetmet" Institute, Novosibirsk) under the following conditions: diameter of grinding balls of 5 mm, the mass ratio balls : concentrate = 50 : 1, three grinding barrels, the centripetal acceleration along the barrel axis of 350 m/s^2 , the volume ball loading of barrels comprised 60 %, and the duration of mechanoactivation was 20–60 min).

Exploratory experiments into direct sulphatization of 12 batches of the Yermakovskoye

concentrate were performed with the use of a glass-graphite cup of capacity 2.5 l that was covered with fluoroplastic cap. Samples of concentrate (the -0.045 mm fraction or without screening) were mixed with the required quantity of 93 % H_2SO_4 in the glass-graphite cup that was put on an electric hot plate. The reaction mixture represented a jelly-like mass that was held at the preset temperature and duration of sulphatization. The reaction mixture was periodically agitated with a spatula.

After completion of the process, sulphatized concentrate that represented a semidry mass with lumps was processed with water with the aim of leaching the soluble sulphates. The leached pulp was neutralized by ammonium hydroxide and filtered; silicon-sulphate cake was subjected to aqueous washing from water-soluble beryllium in a standard regime.

With the aim of an additional increase of the beryllium extraction degree from the tested concentrate and with the aim of cutting the duration of power-consuming sulphatization, this work investigates the effect of mechanoactivation of beryllium raw material used on the completeness of its disintegration by sulphuric acid. We have made experiments on mechanoactivation of Yermakovskoye bertrandite-phenacite-fluorite flotation concentrate and on the subsequent sulphatization of the activated material (the $-27.6 \text{ }\mu\text{m}$ coarseness, the average size of particles of $2.1 \text{ }\mu\text{m}$).

In the first stage of the work Yermakovskoye concentrate was mechanoactivated in a laboratory planetary mill. In this series of experiments, weighed samples of the mechanoactivated concentrate (20.0–38.1 g) were processed with the calculated quantity of 93 % H_2SO_4 (the consumption of H_2SO_4 comprised 1.6 ml/g of the concentrate). The reaction mass was let to stand during a preset time at the temperature of $(275 \pm 25)^\circ\text{C}$ in a glass-graphite cup; the mass of sulphates was stirred every 15 min. Upon termination of the high-temperature standing of the reaction mass, it was processed in a standard regime (leaching of the sulphate mass: S : L = 1 : 5, $t = 95^\circ\text{C}$, $\tau = 30 \text{ min}$; neutralization up to pH 3.5 (with 8–10 % solution of ammonia); the 1st washing of the cake: the solution of ammonium sul-

TABLE 1

Mineralogical and granulometric composition of Yermakovskoye concentrate

Sample number	Content, mass % (the coarseness of minerals, mm)			
	Bertrandite	Phenacite	Fluorite	Quartz, calcite, micas, feldspars
1	6.5 (-0.04)	12.0 (-0.014)	222	593
2	8.0 (-0.04)	9.5 (-0.104)	192	633
3	3.5 (-0.04)	15.0 (-0.104)	195	620
4	14.0 (0.10-0.12)	4.8 (0.04-0.06)	-	-
5	4.8 (0.06-0.08)	12.3 (0.06-0.08)	-	-
6	8.0 (-0.08)	17.0 (-0.05)	20.0 (0.02-0.10)	55.0 (0.02-0.07)
7	16.0 (-0.10)	8.0 (-0.05)	26.0 (0.01-0.06)	50.0 (0.01-0.06)
8	10.0 (-0.05)	12.0 (-0.064)	24.0 (0.01-0.07)	54.0 (0.01-0.06)
9	15.0 (-0.07)	8.0 (-0.04)	30.0 (0.01-0.07)	47.0 (0.01-0.06)
Average	9.5	11.0	230	-

phate (50 g/l) acidified with H₂SO₄ up to pH 3.5; T : L = 1 : 7 with respect to the initial concentrate, $t = 80$ °C, $\tau = 15$ min; the 2nd washing of the cake: the solution of ammonium sulphate (50 g/l) acidified with sulphuric acid up to pH 3.5; see the washing 1).

RESULTS AND DISCUSSION

The results of investigations of the mineralogical composition of the concentrate are presented in Table 1. The data on the chemical composition of 19 batches of the concentrate are given in Table 2.

TABLE 2

Chemical composition of Yermakovskoye concentrate

Sample number	Concentration, mass %							
	Be	F	Al	Ca	Si	Fe	Mn	Cr
1	3.97	10.80	-	17.40	13.80	-	-	-
2	4.12	9.35	-	10.89	10.51	3.00	0.48	0.003
3	3.97	9.49	-	11.42	11.87	2.96	0.50	0.003
4	3.67	12.00	2.55	22.80	11.99	5.40	0.49	0.004
5	4.13	14.12	1.89	24.15	8.80	3.33	0.23	<0.001
6	3.77	9.37	3.14	19.05	14.08	4.55	0.44	<0.001
7	3.88	13.75	2.55	21.90	12.52	4.93	0.39	0.006
8	3.82	12.87	2.52	19.24	11.78	4.85	0.44	0.008
9	3.35	14.00	2.77	23.00	10.10	4.35	0.27	0.011
7*	3.12	12.00	1.58	22.30	10.05	4.24	1.30	0.005
12*	3.78	10.75	2.52	19.85	12.67	5.13	0.74	0.008
35*	4.04	10.00	2.00	24.60	10.71	4.13	0.46	0.006
55*	4.55	12.40	1.76	22.50	10.80	3.85	0.74	0.005
173*	3.03	-	-	-	-	3.13	0.43	-
197*	3.49	5.20	1.83	13.60	15.48	5.78	1.63	0.008
201*	3.84	9.30	1.78	19.90	12.60	4.56	1.04	0.006
212*	4.22	10.50	2.04	19.15	12.51	4.75	0.72	0.006
214*	3.65	10.75	2.52	20.90	12.37	4.45	1.00	0.008
217*	3.99	9.65	2.41	20.90	12.65	4.65	0.73	0.008
Average	3.81	10.91	2.27	19.64	12.00	4.13	0.67	0.005

*The number of the warehouse batch.

TABLE 3

Results of the direct vitriolic disintegration of Yermakovskoye concentrate with 93 % H_2SO_4 . The sulphatization conditions: the weighed portion of the concentrate of 50–100 g; leaching: S : L = 1 : 5 (by initial concentrate), $\tau = 20$ min, $t = 95$ °C, $V = \text{const}$; pulp neutralization with 8 % NH_3 solution up to pH 3.5; the 1st washing of the cake: 5 % solution of $(NH_4)_2SO_4$ acidified with H_2SO_4 up to pH 3.5; S : L = 1 : 7 (by initial concentrate), $\tau = 15$ min, $t = 95$ °C, $V = \text{const}$; the 2nd washing of the cake: 5 % solution of $(NH_4)_2SO_4$ that has been acidified by H_2SO_4 to reach the pH 3.5 (see the 1st washing)

Experiment number	Sulphatization			Extraction degree, mass %	
	Consumption of 93 % H_2SO_4 , ml/g of the concentrate	t , °C	τ , h	of beryllium into sulphate solution (by cake)	of fluorine into the gas phase ^a
<i>Batch No. 1 (initial concentrate without sifting of the -0.045 mm fraction)</i>					
1	80	225 ± 25	1	50.9	92.0
2	80	225 ± 25	2	52.2	87.8
3	80	225 ± 25	3	56.5	—
4	160	275 ± 25	1	82.1	—
5	160	275 ± 25	8	90.2	97.3
6	160	275 ± 25	11	90.0	95.9
7	160	250 ± 25	14	91.5	92.5
8	250	250 ± 25	1	82.0	—
9	250	250 ± 25	3	84.1	—
10	250	250 ± 25	11	94.6	—
11	250	325 ± 25	4	87.4	—
12	250	325 ± 25	7	90.9	98.0
13	250	325 ± 25	10	93.0	—
<i>Batch No.1 (-0.045 mm fraction of the concentrate)</i>					
14	160	275 ± 25	1	91.9	91.6
15	160	275 ± 25	6	93.1	96.4
<i>Batch No. 7*</i>					
16	160	275 ± 25	1	96.1	91.2
17	160	275 ± 25	1	94.2	—
18	160	275 ± 25	1	94.2	—
19	160	275 ± 25	1	95.5	—
20	160	275 ± 25	1	91.7	—
21	160	275 ± 25	1	92.3	—
22	160	275 ± 25	1	93.6	—
23	160	275 ± 25	1	95.5	—
24	160	275 ± 25	1	96.2	—
25	160	275 ± 25	1	95.5	—
26	160	275 ± 25	1	94.2	—
Average				94.5	—
<i>Batch No. 12*</i>					
27	160	275 ± 25	1	93.7	93.3
28	160	275 ± 25	1	87.3	—
29	160	275 ± 25	1	89.4	—
30	160	275 ± 25	1	86.8	—
Average				89.3	—

TABLE 3 (Final)

Experiment number	Sulphatization			Extraction degree, mass %	
	Consumption of 93 % H ₂ SO ₄ , ml/g of the concentrate	t, °C	τ, h	of beryllium into sulphate solution (by cake)	of fluorine into the gas phase ^a
<i>Batch No. 20*</i>					
31	160	275 ± 25	1	96.0	–
32	160	275 ± 25	1	96.6	–
33	160	275 ± 25	1	96.3	–
34	160	275 ± 25	1	99.1	–
35	160	275 ± 25	1	92.4	–
Average				96.1	–
<i>Batch No. 35*</i>					
36	160	275 ± 25	1	95.1	–
37	160	275 ± 25	1	91.1	–
38	160	275 ± 25	1	85.1	96.0
39	160	275 ± 25	1	89.1	97.0
40	160	275 ± 25	1	88.1	–
Average				89.7	96.5
<i>Batch No. 55*</i>					
41	160	275 ± 25	1	93.4	97.1
42	160	275 ± 25	1	93.4	–
Average				93.4	–
<i>Batch No. 173*</i>					
43	160	275 ± 25	1	98.3	–
44	160	275 ± 25	1	95.4	–
45	160	275 ± 25	1	96.0	–
Average				96.6	–
<i>Batch No. 201*</i>					
46	160	275 ± 25	1	93.8	94.8
47	160	275 ± 25	1	92.7	–
Average				93.3	–
<i>Batch No. 212*</i>					
48	160	275 ± 25	1	91.0	–
49	160	275 ± 25	1	92.9	–
Average				92.0	–
<i>Batch No. 214*</i>					
50	160	275 ± 25	1	94.0	95.6
51	160	275 ± 25	1	90.7	–
Average				92.4	–
<i>Batch No. 217*</i>					
52	160	275 ± 25	1	93.0	–
53	160	275 ± 25	1	83.9	–
54	160	275 ± 25	1	82.9	–
Average				86.6	–
Average value over the exp. 16–54				92.4	94.8

^aThe exp. 1–15 – by the basic solution and the cake; the exp. 16–54 – by the basic solution, the washing water 1, and the cake.

* The number of the warehouse batch.

It is evident from the data of Table 1 that the content of fluorite, bertrandite, and phenacite varies in different parties of the concentrate. An examination of the granulometric composition of nine samples of the concentrate has demonstrated that it is completely presented by particles with the coarseness of 0.12 mm and less (the coarseness of the bulk of the particles comprises ~ 0.064 mm), which form fragile conglomerates 1–4 mm in size (the fraction of conglomerates comprises $\sim 50\%$ of the mass of the concentrate).

It follows from results of exploratory experiments on direct vitriolic disintegration of Yermakovskoye concentrate (Table 3) that the tested technology provides the statistically average extraction of beryllium from the concentrate into sulphate solution at a level of 92.4 mass % ($\tau_s = 5$ h). Completeness of beryllium precipitation from the sulphate solutions received in this way approaches 100 mass %, since commercially acceptable defluorination of the concentrate is achieved in these experiments (see Table 3) (by an average of 94.8 mass %). Nevertheless, the overall yield of beryllium from the raw material into $\text{Be}(\text{OH})_2$ is insufficiently high (~ 92 mass %), although a significant cutting down of the expensive technological operations of the process of obtaining $\text{Be}(\text{OH})_2$ from mineral raw material has been attained.

Interaction of bertrandite and phenacite with H_2SO_4 at the optimum temperature of the process that is equal to $(275 \pm 25)^\circ\text{C}$ proceeds presumably according to the equations of the reactions

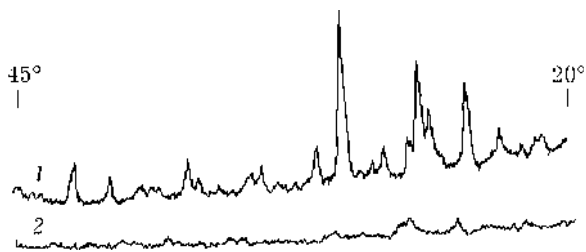
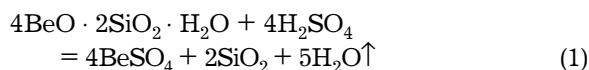
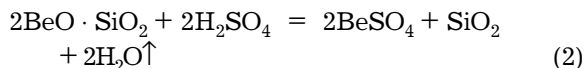
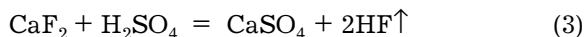


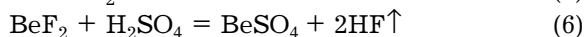
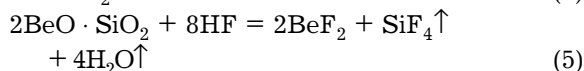
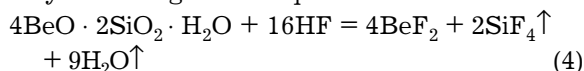
Fig. 1. Results of X-ray diffraction analysis of the concentrate in the range of reflection angles of $20\text{--}45^\circ$: 1 – the initial, 2 – the concentrate (31 g) ground in a planetary mill ($\tau_{gr} = 50$ min).



The defluorination mechanism of the Yermakovskoye concentrate is based on the sulphatization reaction of its fluorite component:



The evolving gaseous fluorine hydride intensifies the process of disintegration of bertrandite-phenacite component of the concentrate presumably according to the equations of the reactions



Hence, an assumption can be made that fluorite that is available in the tested concentrate has a positive effect on the extraction degree of beryllium from the concentrate into the water-soluble sulphate.

Figure 1 and Table 4 display the results of studying the effect of the concentrate mechanoactivation on the completeness of its disintegration with sulphuric acid (the batch No. 3, see Tables 1, 2).

X-ray diffraction analysis of the concentrate has shown (see Fig. 1) that destruction of crystal lattices of the minerals that are the constituents of the concentrate occurs during mechanoactivation of the concentrate in a planetary mill, and an X-ray amorphous product is formed.

As suggested by data of Table 4 (exp. 2–8), mechanoactivation that is applied to Yermakovskoye concentrate ensures thereafter a deep extraction of beryllium into sulphate solution (97.2–99.2 mass %) with the duration of sulphatization for just 30 min. During the sulphatization process a fairly high defluorination of the concentrate is achieved. Thus, it was equal to 82.7–91.9 mass % in exp. 1–8. Owing to this circumstance beryllium can be extracted virtually completely (by 99.9 mass %) from sulphate solution into $\text{Be}(\text{OH})_2$ at the following stage of the process, and extraction degree of beryllium from raw material into beryllium hydroxide is as large as 97–98 mass %.

The comparison analysis of data of Table 4 (exp. 6–8) and Table 3 demonstrates that preliminary mechanoactivation of Yermakovskoye concentrate makes it possible to enhance the

TABLE 4

Results of experiments on mechanical activation of Yermakovskoye concentrate and sulphuric acid disintegration of the activated product

Experiment number	Duration of the process, min		Extraction degree, mass %	
	Mechanoactivation	Sulphatization	of beryllium into sulphate solution (by cake)	of fluorine into the gas phase (by sulphate solution and cake)
1	20	60	97.3	91.9
2	40	30	97.2	90.2
3	50	30	99.2	83.6
4	50	30	98.9	85.6
5	50	30	98.6	84.7
6	55	30	98.8	82.7
7	60	30	98.2	84.9
8	45	30	97.7	88.6

Note. Fluorite (~95 mass % CaF_2) has been additionally blended at a rate of 5 mass % to the concentrate in the exp. 1–5 before the mechanoactivation; in exp. 6–8, the concentrate was mechanoactivated without admixture of fluorite.

completeness of its disintegration by sulphuric acid from ~92 mass % (the completeness of disintegration of the nonactivated concentrate) to ~98 mass %. Application of mechanoactivation of the concentrate makes it possible to reduce the duration of the high-temperature sulphatization from 5 h to 30 min.

CONCLUSION

The results of the present study testify that the applied mechanoactivation of bertrandite-phenacite-fluorite concentrate makes it possible to reduce a number of preparatory operations prior to its sulphatization from six (mixing of raw material and fluxes, melting of mixture, granulation of the fusion cake, wet grinding of the granulate, classification of the ground granulate, and thickening of the aque-

ous pulp of the ground granulate) to one and to do away with the application of expensive fluxes. The presented technology of sulphatization of the mechanoactivated concentrate allows the yield of beryllium from raw material into $\text{Be}(\text{OH})_2$ to be raised from ~95 to 97–98 mass %.

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