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Kazim Eşber ÖZBAŞ*, Cahit HIÇYILMAZ*

CONCENTRATION OF BARITE AND FLUORITE MINERALS OF ESKISEHIR-BEYLIKAHIR DISTRICT

In this study, concentration possibilities of barite and fluorite minerals of the Eskisehir-Beylikahir district were investigated. Concentration studies were carried out on composite samples obtained by mixing representative samples of Kücükhöyüklütepe and Devebagirtantepe in the ratio of 2 to 1. During the concentration studies, gravity concentration, flotation, and high intensity magnetic separation were applied to recover barite and fluorite. The best results, a fluorite concentrate assaying 91.85% CaF_2 with 51.98% recovery, and a barite concentrate assaying 87.45% $BaSO_4$ with 49.61% recovery, were obtained by the combination of gravity concentration–flotation–magnetic separation, respectively.

1. INTRODUCTION

The Eskisehir-Beylikahir complex ore body is one of the biggest known deposits in Turkey, not only in thorium content but also in rare earth elements content. On the other hand, barite and fluorite reserves of the ore body are also great. Totally, barite and fluorite reserve of the Eskisehir-Beylikahir area is more than 20 000 000 t (Ersecen 1989). Also, it was proved that 1 278 949 t (proved reserve) of rare earth elements assaying 3.52% (La + Ce + Nd) and 380 000 t of thorium assaying 0.20% ThO_2 exist in the ore body (Ciftci 1986).

The Eskisehir-Beylikahir complex ore was beneficiated by Kutluata and Özden (1985), Ciftci (1986), and Yüce et al. (1992). In order to obtain marketable barite and fluorite products with higher recoveries, such a study was carried out (Özbas 1993).

2. MATERIALS AND METHODS

1177 kg and 1086 kg of representative samples were taken from Devebagirtantepe and Kücükhöyüklütepe, respectively, and a composite sample was prepared by mixing them in the ratio of 1 to 2. The composite sample was then crushed to –8 mesh (–2.36 mm). The major ore minerals are: fluorite, barite, and rare earth minerals with minor amounts of calcite, quartz, mica, apatite, manganese minerals (pyrolusite, psilomelane, polianite), hematite, pyrite, and limonite. Chemical analyses of the

* Middle East Technical University, Mining Engineering Department, Ankara, Turkey.

composite ore are given in Table 1. Mineral distributions of composite sample in screen fractions are given in Table 2.

Table 1. The results of the chemical analyses of the composite sample (O.D.T.Ü. 1993)

Element or compound	Amount by weight, %	Method of analyses
Total rare earth elements	6.50	ICP
$CaCO_3$	2.80	Gravimetric
SiO_2	1.30	Gravimetric
CaF_2	52.47	Gravimetric
$BaSO_4$	25.40	Gravimetric
Al_2O_3	4.00	Gravimetric
Fe_2O_3	3.00	AAS

Table 2. Mineral distributions of composite sample in screen fractions

Screen fraction mesh	Screen fraction micron	wt. %	Barite		Fluorite		Calcite	
			$BaSO_4$ %	distribution, %	CaF_2 %	distribution, %	$CaCO_3$ %	distribution, %
-8 +28	-2362 +589	28.76	17.78	18.77	68.20	37.37	2.55	20.62
-28 +65	-589 +208	22.36	23.59	19.36	61.20	26.07	2.25	14.13
-65 +200	-208 +74	19.63	41.72	30.09	38.10	14.26	3.30	18.36
-200 +400	-74 +37	10.07	50.03	18.52	32.00	6.14	3.50	9.89
-400	-37	19.18	18.83	13.26	44.20	16.16	6.85	37.00

Flotation concentration studies were carried out by using the Denver Sub-A laboratory flotation machine with 2 dm^3 cell. The Deister shaking table was the gravity concentration equipment used for barite-fluorite concentration studies of Beylikahir complex ore. Magnetic separation tests were performed by using the Carpco model M127 high intensity induced roll magnetic separator.

3. EXPERIMENTAL RESULTS

1. Flotation studies

Flotation studies were performed on composite ore ground to –65 mesh (–208 μm) size. Flotation of barite and fluorite minerals was studied separately.

1. Flotation of fluorite. In this group of studies, barite was subjected to depressing, and fluorite was floated. The first experiment was performed at pH 9 by using 400 g/t of $AlCl_3$, 400 g/t of Na_2SiO_3 as depressants, 600 g/t of A723 type collector (Cyanamid company), and 65 g/t of MIBC as frother. Conditioning times were 10 min. for depressants, and 5 min. for collectors. Fluorite concentrate obtained at the end of 5 min. flotation time was cleaned by adding 180 g/t of $AlCl_3$ and 180 g/t of Na_2SiO_3. No collector was used at this stage. The results are given in Table 3 and Fig. 1.

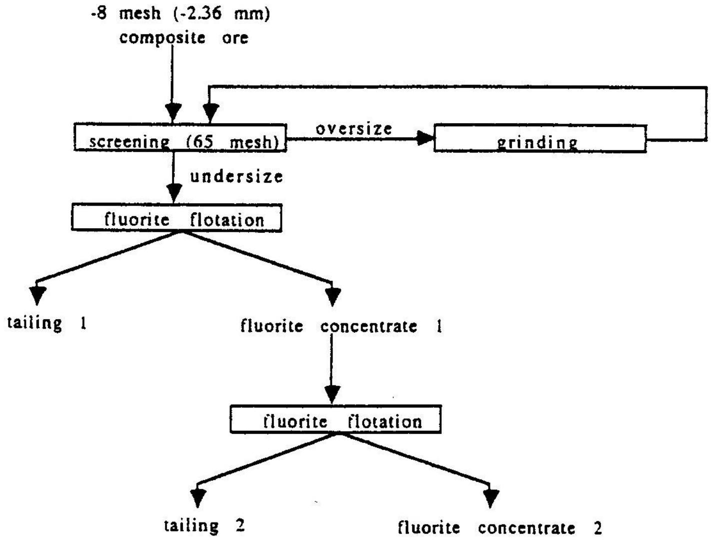

Fig. 1. Flotation of fluorite from composite ore

The same experiment was repeated by using hot flotation pulp (50 °C) which is common for fluorite flotation (Genctan 1967; Pryor 1979; Ciftci 1986; Schubert 1990). Cleaning stage was not applied. The results are given in Table 4 and Fig. 2.

The results of both the tests showed that the grades of fluorite and barite in their respective concentrates did not increase sufficiently, and reagents used for the selective flotation of fluorite were unsuccessful in providing the selectivity between fluorite and barite minerals.

Table 3. Results of fluorite flotation from composite ore

Product	wt.	Grade		Recovery	
	%	$BaSO_4$ %	CaF_2 %	$BaSO_4$ %	CaF_2 %
Tailing 1	41.84	24.94	40.78	41.08	32.50
Tailing 2	22.25	11.22	69.64	9.83	29.56
Fluorite conc. 2	35.91	34.73	55.44	49.09	37.94
Feed	100.00	25.40	52.47	100.00	100.00

Table 4. Results of fluorite flotation from composite ore (hot pulp)

Product	wt.	Grade		Recovery	
	%	$BaSO_4$ %	CaF_2 %	$BaSO_4$ %	CaF_2 %
Tailing	40.12	17.64	47.63	27.86	36.42
Fluorite conc.	59.88	30.60	55.71	72.14	63.58
Feed	100.00	25.40	52.47	100.00	100.00

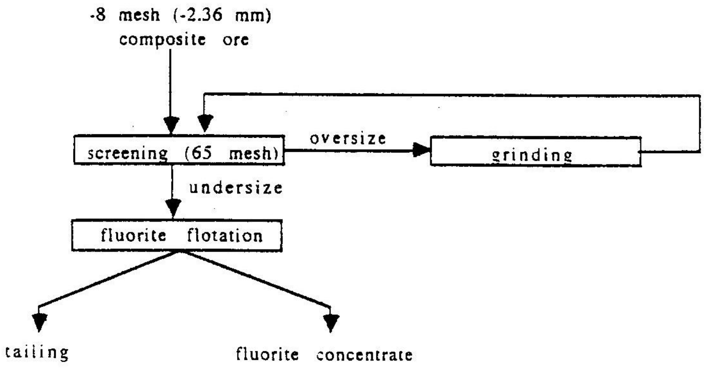

Fig. 2. Flotation of fluorite from composite ore (hot pulp)

2. Flotation of barite. In order to obtain the selectivity between barite and fluorite minerals, barite flotation tests were carried out. In the first experiment, 400 g/t of Na_2SiF_6 as fluorite depressant, and 200 g/t of A845 as collector (Cyanamid company) for barite were used at pH 9.3. Frother was 65 g/t of MIBC. Conditioning times for depressant and collector were 10 and 5 minutes, respectively. Flotation time was 5 minutes. The results are given in Table 5 and Fig. 3.

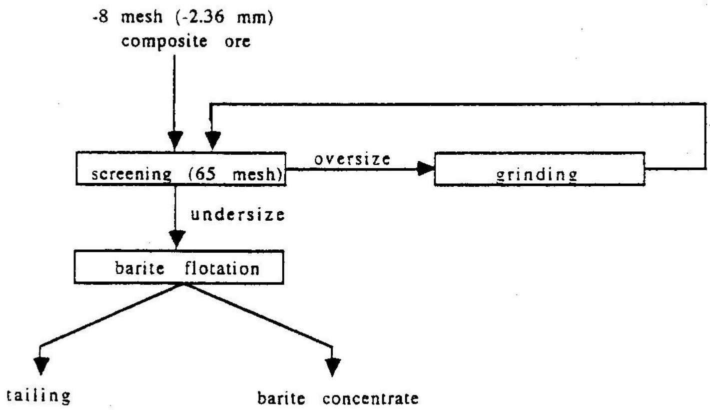

Fig. 3. Flotation of barite from composite ore

To increase the grade and recovery of the flotation concentrates, the above experiment was repeated by increasing the amount of Na_2SiF_6 to 600 g/t, and the amount of A845 to 400 g/t. The grade of fluorite was increased to 70.54% CaF_2 with a lsmall decrease of recovery to 68.22%.

The results of both the experiments showed that more selective fluorite concentrates with higher recoveries were obtained by reverse flotation than direct flotation. Drilling mud grade barite was not obtained during fluorite and barite flotation studies. However, the fluorite concentrates obtained by barite flotation was suitable for metallurgical uses (Fig. 3 and Table 5).

Table 5. Results of barite flotation from composite ore

Product	wt. %	Grade BaSO$_4$ %	Grade CaF$_2$ %	Recovery BaSO$_4$ %	Recovery CaF$_2$ %
Tailing	58.39	8.00	65.46	18.37	72.84
Barite conc.	41.61	49.83	34.25	81.63	27.16
Feed	100.00	25.40	52.47	100.00	100.00

2. Concentration studies performed by gravity, magnetic separation, and flotation

During this study, –8 mesh (–2.36 mm) composite ore was sieved through 65 mesh (208 μm) screen to treat the fractions separately. Screen oversize (–8 +65 mesh fraction) was ground to –35 mesh under close control, and fed to hydrocyclone to remove –400 mesh fraction. Cyclone underflow which was –35 +400 mesh fraction was concentrated by shaking table. Fluorite concentrate obtained from shaking table was upgraded by high intensity magnetic separation and flotation.

Screen undersize (–65 mesh fraction) was again fed to hydrocyclone to remove –400 mesh fraction. Cyclone underflow (–65 +400 mesh fraction) was again concentrated by shaking table. To increase the grade of fluorite concentrate obtained from shaking table, high intensity magnetic separation followed by flotation was applied (Fig. 4 and Table 6).

Table 6. Results of concentration of composite ore by gravity concentration, magnetic separation, and flotation

Product	wt. %	Grade BaSO$_4$ %	Grade CaF$_2$ %	Recovery BaSO$_4$ %	Recovery CaF$_2$ %
Slime 1	19.43				
Slime 2	16.68				
Barite pre-conc. 1	15.28	88.68		42.95	
Barite pre-conc. 2	2.82	80.76		8.97	
Final barite conc.(comb.)	18.10	87.44		51.92	
Fluorite pre-conc. 1	14.26		61.34		16.67
Magnetic tailing 1	6.82		41.63		5.41
Fluorite conc. 1	7.44		79.41		11.26
Fluorite pre-conc. 2	31.53		71.13		42.75
Magnetic tailing 2	7.83		39.81		5.94
Fluorite conc. 2	23.70		81.48		36.81
Final fluorite conc.	5.32		83.93		8.51
Feed	100.00	25.40	52.47	100.00	100.00

The results of the flotation tests showed that easily depressed mineral fluorite during the previous experiments (Fig. 3 and Table 5) became flotable after the removal of magnetic impurities. So that fluorite flotation was applied to upgrade the fluorite concentrate. Fluorite flotation experiment shown in Figure 4 was the best among one set of flotation tests (Özbas 1993). In this flotation test, 500 g/t $BaCl_2$, 500 g/t citric acid were used as barite depressants, and 150 g/t sodium oleate was used as fluorite collector at pH 9.5.

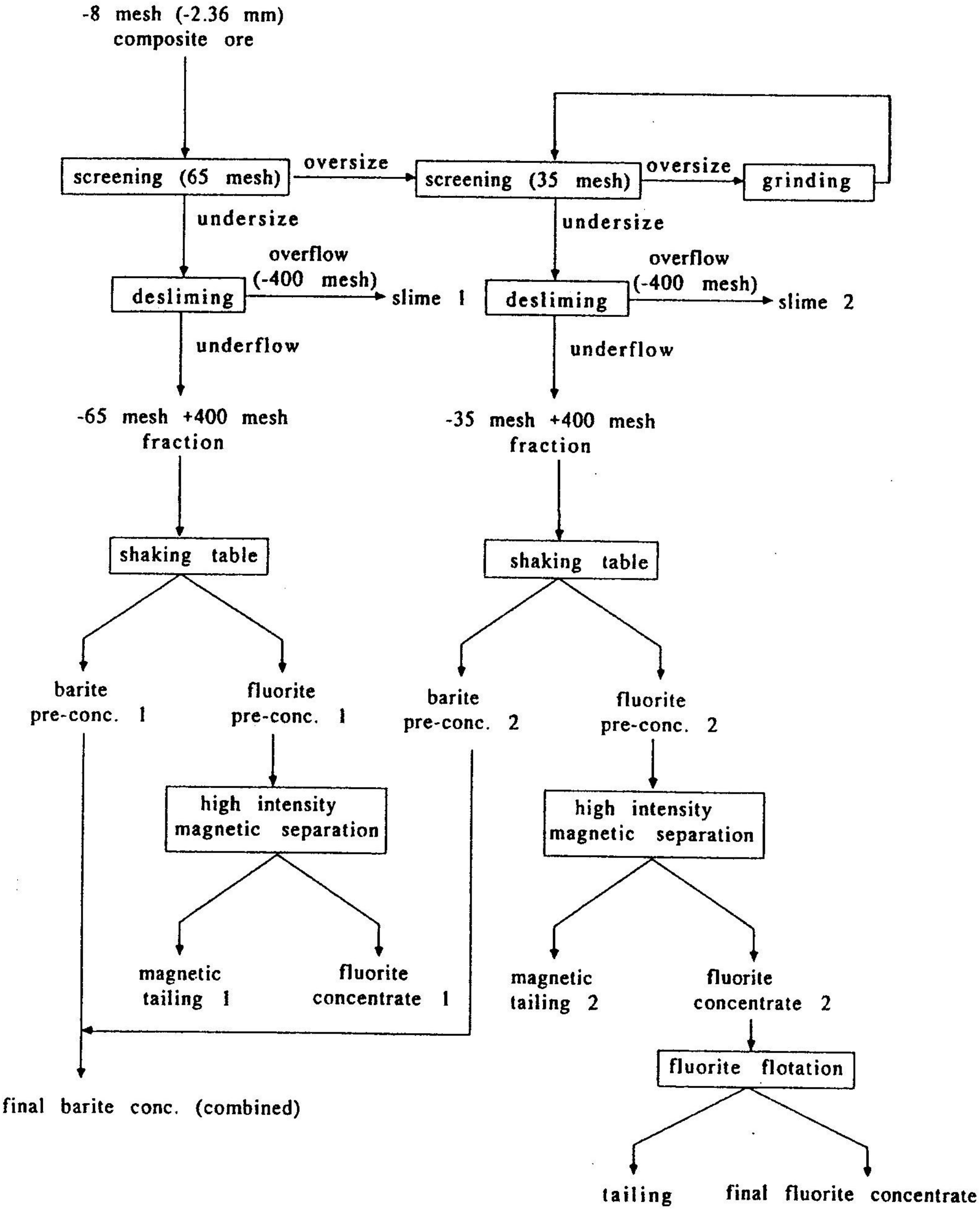

Fig. 4. Concentration of composite ore by gravity conentration., magnetic separation, and flotation

3. Concentration studies performed by gravity, flotation, and magnetic separation

The flowsheet shown in Fig. 4 was followed by two differences:

a) The screen oversize (–8 +65 mesh; –2.36 mm +208 μm) which was ground to –35 mesh (–417 μm) was treated by means of shaking table with closed sized fractions; that is, –35 +400 mesh fraction was separated as –35 +65 mesh and –65 +400 mesh to treat by means of shaking table. The purpose of feeding closed sized fractions to shaking table is the higher performance of gravity concentration equipments with closed sized materials. The results of gravity concentration were given in Table 7 and Fig. 5.

b) The previous study given in part 2. showed that separation of magnetic impurities prior to barite flotation increased the difficulty of fluorite depression and hence decreased selectivity. So that, the sequence of concentration methods was changed as gravity concentration, flotation, and magnetic separation.

Fluorite pre-concentrates 1, 2, and 3 were flotated using several combinations of reagents such as Na_2SiF_6, Na_2CO_3 as fluorite depressants and A845, and S3903 as barite collectors in different dosages (Özbas 1993). However, the best results were obtained by barite flotation from combined fluorite pre-concentrates 1 and 2 at pH 7.6 using 1250 g/t Na_2SiF_6, 750 g/t Na_2CO_3, and 900 g/t of S3903. Conditioning times were 40 and 20 minutes for depressants and collector, respectively. The concentrate obtained after high intensity magnetic separation contained 92.71% CaF_2 with 19.11% recovery.

Table 7. Results of concentration of composite ore by gravity concentration, flotation, and magnetic separation

Product	wt. %	Grade		Recovery	
		$BaSO_4$ %	CaF_2 %	$BaSO_4$ %	CaF_2 %
Slime 1	21.73	10.82	36.20	9.26	14.99
Slime 2	10.06	13.36	40.55	5.29	7.77
Barite pre-conc. 1	8.85	91.60		31.91	
Barite pre-conc. 2	3.48	85.96		11.78	
Barite pre-conc. 3	2.08	72.29		5.92	
Final barite conc. 1+2+3	14.41	87.45		49.61	
Fluorite pre-conc. 1	15.85		51.53		15.57
Fluorite pre-conc. 2	12.49		67.70		16.12
Fluorite pre-conc. 3	25.46		73.58		35.70
Fluorite pre-conc. 1+2	28.34		58.65		31.69
Final fluorite conc. 1	10.81		92.71		19.11
Final fluorite conc. 2	18.88		91.35		32.87
Final fluorite conc.(comb.)	29.69		91.85		51.98
Feed	100.00	25.40	52.47	100.00	100.00

On the other hand, the grade of fluorite pre-concentrate 3 was upgraded to 91.35% CaF_2 with 32.87% recovery by using 1250 g/t Na_2SiF_6, 2750 g/t Na_2CO_3, and 600 g/t S3903 collector at pH 8.9 when the conditioning times were 30 minutes for depressants and 20 minutes for collector. When these fluorite concentrates were combined, the

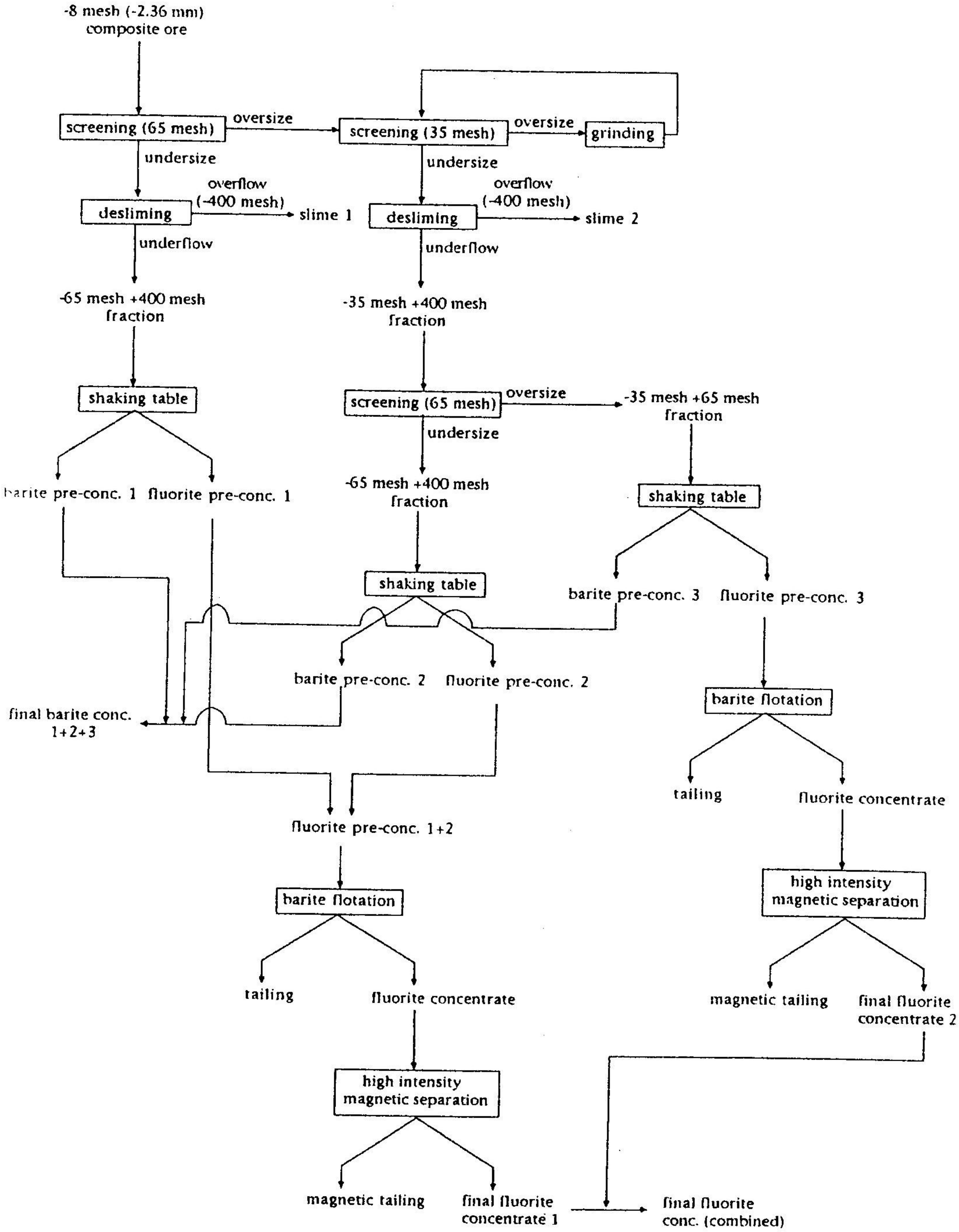

Fig. 5. Concentration of composite ore by gravity concentration, flotation, and magnetic separation

grade of the final concentrate reached to 91.85% CaF_2 with 51.98% recovery (Fig. 5 and Table 7).

barite pre-concentrates 1, 2, and 3 On the other hand, there was no attempt to upgrade barite pre-concentrates 1, 2, and 3 by flotation and magnetic separation in order to prevent recovery losses. Three pre-concentrates were combined and a final concentrate assaying 87.45% $BaSO_4$ with 49.61% recovery was obtained (Fig. 5 and Table 7).

Final concentrates are marketable as no. 2 ceramic grade fluorite and drilling mud grade barite.

4. DISCUSSION

According to the results of the flotation studies, in order to obtain more selective fluorite concentrates with higher recoveries, reverse flotation of fluorite is more successful than direct flotation. On the other hand, only metallurgical grade fluorite could be obtained by reverse flotation of fluorite. Drilling mud grade barite could not be obtained by flotation from the Eskisehir-Beylikahir complex ore.

During the gravity concentration parts of the studies, it was observed that due to their specific gravities, mica minerals (e.g. biotite) were concentrated generally with fluorite, while iron minerals (e.g. hematite, limonite) were concentrated with barite. The removal of these impurities was necessary to increase the grades of both barite and fluorite concentrates. Therefore, high intensity magnetic separation followed by flotation was applied after gravity concentration. But during the flotation tests some unexpected results were obtained. The depression of fluorite, which was easy before, became impossible after magnetic separation. As a result, it can be claimed that the magnetic impurities in the ore were playing an important role in the depression of fluorite mineral by giving some ions to the flotation pulp. Not only reverse flotation but also direct flotation of fluorite were not selective after high intensity magnetic separation.

Therefore, it was decided to apply high intensity magnetic separation after flotation, and concentration studies were performed by the combination of gravity concentration, flotation, and magnetic separation. By using this combination, no. 2 ceramic grade fluorite and barite suitable for drilling mud additive were obtained.

5. CONCLUSIONS

1. It is possible to obtain barite concentrate suitable for drilling mud additive from the Eskisehir-Beylikahir complex ore.

2. It is also possible to obtain metallurgical grade and/or no. 2 ceramic grade fluorite concentrate from the Eskisehir-Beylikahir complex ore.

3. More selective fluorite concentrates were obtained with reverse flotation of fluorite.

4. A fluorite concentrate assaying 70.54% CaF_2 with 68.22% recovery was obtained by reverse flotation of fluorite, whereas the grade of the barite concentrate was very low.

5. High intensity magnetic separation is necessary to remove magnetic impurities such as biotite obtained with fluorite, and hematite obtained with barite in gravity concentration.

6. To provide the depression of fluorite during its reverse flotation, high intensity magnetic separation must be applied after flotation, not before.

7. A fluorite concentrate assaying 91.85% CaF_2 with 51.98% recovery, and a barite concentrate assaying 87.45% $BaSO_4$ with 49.61% recovery were obtained by the combination of gravity concentration–flotation–magnetic separation.

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Özbaş K.E., Hiçyilmaz C., (1994), Wzbogacanie rudy barytowo-fluorytowej z rejonu Eskisehir-Beylikahir (Turcja), *Fizykochemiczne Problemy Mineralurgii*, 28, 65–74, (English text)

Badano możliwość wzbogacania rudy barytowo-fluorytowej metodą flotacji, wzbogacania grawitacyjnego i separacji magnetycznej w polu magnetycznym o wysokim natężeniu. Celem badań było rozdzielenie barytu od fluorytu. Najlepsze wyniki osiągnięto za pomocą kombinacji wymienionych metod i otrzymano koncentraty: barytowy zawierający 87,45% barytu z uzyskiem 49,6% oraz fluorytowy zawierający 91,85% fluorytu przy jego uzysku wynoszącym 51,98%.