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BENEFICIATION OF BEYLIKAHIR COMPLEX RARE EARTH DEPOSIT OF TURKEY

This study was devoted to the evaluation of the valuable mineral constituents of Beylikahir complex ore deposit which contains fluorspar, barite and bastnaesite. The mineralogical, chemical and screen analyses showed that fluorspar concentrated above 210 micron size while barite content increased below that size. The bastnaesite mineral occured either as cement material between the fluorspar and barite particles or was finely distributed within these minerals.
The application of gravity separation method alone by using shaking table produced fluorspar and barite concentrates assaying 72% CaF_2 and 80.95% $BaSO_4$ with recoveries of 84.68% and 60.14% respectively. Preliminary concentrations of rare earth elements (REE) were done by attrition scrubbing and desliming by cyclones. The preconcentrate obtained from cyclone overflow was upgraded by Mozley Multi-Gravity separator.
A REE concentrate was produced with 29.30% REE grade and 47.87% recovery. Three different metallurgical routes were followed for the extraction of REE from preconcentrate. Leach recoveries in the range of 75–80% were achieved.

INTRODUCTION

The International Union of Pure and Applied Chemistry defines the Rare Earth Elements (REE) as the lanthanides from lanthanum to lutetium (z = 71) together with yttrium (z = 39) and scandium (z = 21). Promethium (z = 61), a product of fission reaction, is not found in nature (Ohmer 1978). Rare earths do not occur in nature in the elemental state and except for scandium they do not occur in mineral as individual rare earth compounds. They are widely distributed in low concentrations throughout the Earth's crust. Although the rare earth elements are essential constituents of more than 100 minerals, only a few are of economic value. At the present time, the major minerals which make up most of the sources of Rare Earth Oxides (REO) world production are monazite, bastnaesite, euxenite and xenotime. Monazite is present in the beach sands around the coastal belt of India, Brazil, Australia, South Africa and USA. Baotou deposits in China, Dong Pao deposits in Vietnam and the Mountain Pass deposits in California are three of the largest

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deposits of bastnaesite. The main use of rare earth element is as catalyst in petroleum cracking operations (Vijayan et al. 1989). However, specific rare earth elements are rapidly gaining importance as ingredients in many applications.

Flotation is a standard method for recovering REO from finely grained igneous and hydrothermal deposits (Gerdel and Smith 1989; Morrice and Wong 1982; Fuerstenau and Pradip 1989) while physical methods such as gravity and magnetic/electrostatic separations are currently employed for the treatment of REO containing coarse beach sand and placer deposits (Aplan 1989; Dayton 1958).

BEYLIKAHIR COMPLEX RARE EARTH DEPOSIT OF TURKEY

Mineralogy of Ore

Beylikahir complex rare earth deposit is located in Middle-West of Turkey. Fluorspar, barite and bastnaesite are the main ore minerals. Bastnaesite is present in Beylikahir deposit either as cement material between the fluorspar and barite particles or it is intimately associated with these minerals (Çiftçi and Kumru 1985).

Table 1. Chemical analysis of sample (Akkurt et al. 1993)

Element or component	Weight %	Element or component	Weight %
Ce	% 3.00	Fe_2O_3	% 3.00
La	% 2.70	ThO_2	% 0.02
Nd	% 0.55	SrO	% 0.60
Pr	% 0.18	MnO	% 0.54
Sm	220 ppm	P_2O_5	% 1.00
Gd	120 ppm	CO_2	% 1.16
Eu	60 ppm	S	% 3.60
Tb	< 25 ppm	Pb	% 0.071
Dy	60 ppm	Sc	% 0.004
Ho	20 ppm	Ag	% 0.003
Er	40 ppm	Ti	% 0.07
Tm	< 10 ppm	V	% 0.02
Yb	25 ppm	Mg	% 0.20
Lu	< 10 ppm		
Y	300 ppm	calculated rare earth elements	: 6.5 %
$CaCO_3$	% 2.80	calculated rare earth oxides	: 7.9 %
SiO_2	% 1.30	calculated bastnaesite	: 10.2 %
CaF_2	% 52.47		
$BaSO_4$	% 25.40		
Al_2O_3	% 4.00		

Table 2. Distribution of barite, fluorspar and major rare earth elements (Özbaş,Hiçyilmaz 1994)

Size fraction (micron)	Weight %	Barite		Fluospar		Cerium		Lanthanum	
		$BaSO_4$%	Dist, %	CaF_2 %	Dist, %	Ce%	Dist, %	La%	Dist, %
–1700 +600	28.76	17.78	18.77	68.20	37.37	1.70	14.89	1.40	14.14
–600 +200	22.36	23.59	19.36	61.60	26.07	1.60	10.94	1.50	12.01
–200 +75	19.63	41.72	30.09	38.10	14.26	2.90	17.33	2.80	19.43
–75 +38	10.07	50.09	18.52	32.00	6.14	3.60	19.45	3.50	12.37
–38	19.18	18.83	13.26	44.20	16.16	6.40	37.39	6.20	42.05
Total	100.00	27.22	100.00	52.47	100.00	3.29	100.00	2.83	100.00

Table 1 shows (Akkurt et al. 1993) the chemical analysis of sample and Table 2 (Özbayoğlu et al. 1993; Özbaş and Hiçyilmaz 1994) shows the distribution of barite, fluorspar and rare earth elements (cerium-lanthanum) in different size fractions.

Processing of Ore

The work presented in this paper was drawn from a comprehensive investigation of Beylikahir ore deposit (Özbayoğlu et al. 1993). The overall aim was to evaluate the potential reserve for the recovery of all valuable minerals namely barite, fluorspar and bastnaesite. Whilst the work presented here is focused on the recovery of REE, parallel investigations were undertaken to optimise the barite and fluorspar recovery. The application of shaking table produced fluorspar and barite concentrates assaying 72% CaF_2 and 80.95% $BaSO_4$ with recoveries of 84.68% and 60.14% respectively. The flowsheet is given in Figure 1.

Recovery of REE

As can be seen in Table 2, REE was concentrated in the –38 micron size fraction. The sub-sieve analysis showed that the sizes of bastnaesite grains were generally below 5 microns. Classical concentration methods are not applicable alone for production of marketable bastnaesite concentrate. Attrition scrubbing of original ore and desliming by cyclone seems to be a promising method capable of concentrating the bastnaesite. Therefore crushed ore (–1.65 mm) was subjected to attrition scrubbing for 1 hour at a solid concentration of 50% by weight. After dilution, the pulp was classified by a hydrocyclone. The overflow was collected as preconcentrate. Table 3 shows the results of attrition scrubbing and cycloning tests.

Recently developed multi-gravity separator (MGS) was used to increase the REE's grade of the cyclone overflow. MGS consists basically of a slightly tapered open ended drum that rotates in a clockwise direction and is shaken sinusoidally in an axial direction (Mozley 1991). Inside the drum is a scraper assembly which

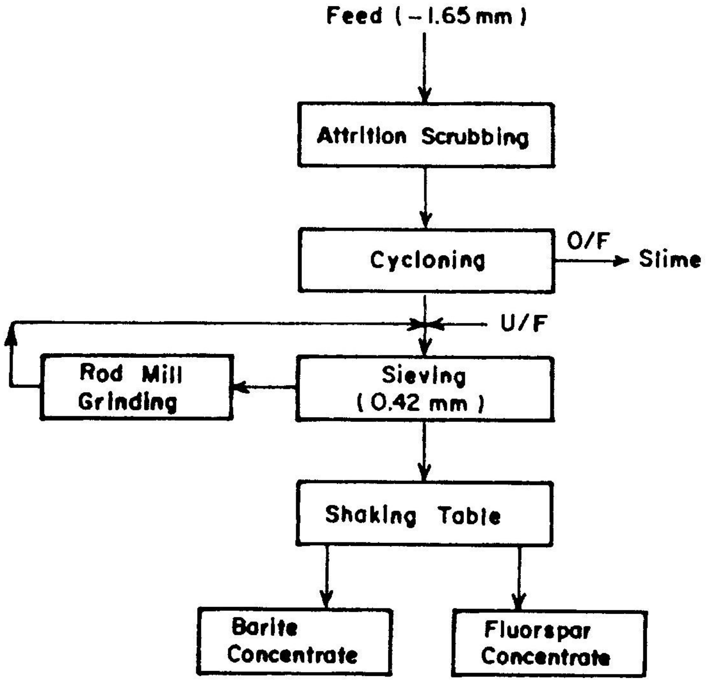

Fig. 1. Proposed flowsheet for the recovery of barite and fluorspar

rotates in the same direction but at a slightly faster speed. Feed slurry is introduced continuously midway onto the internal surface of the drum via an accelerator ring launder. Wash water is added via a similar launder positioned near the open end of the drum. As a result of the high centrifugal forces and the added shearing effect of the shake the dense particles migrate through the slurry film to form a semisolid layer against the wall of the drum. This dense layer is conveyed by the scrapers towards open end of the drum where it discharges into the concentrate launder. The less dense minerals are carried by the flow of washwater downstream to the rear of the drum to discharge via slots into the tailings launder (Figure 2). Washwater flowrate, shake amplitude, shake frequency, tilt angle, drum rotational speed are

Table 3. Results of attrition-scrubbing and cycloning test

Product	Weight, %	Grade, %		Recovery, %	
		Ce	La	Ce	La
Cyclone overflow	26.82	9.25	9.20	73.40	87.18
Cyclone underflow	73.18	1.22	0.50	26.60	12.82
Feed	100.00	3.38	2.83	100.00	100.00

critical variables which are effective on the concentrate grade and recovery. The success of concentration with MGS depends on the selection of suitable parameters. The optimization of these parameters necessitates too many tests. The total number of experiments required can be reduced by employing factorially designed series by the use of the Yates technique (Özbayoğlu et al. 1985; Hoover 1979). These test series provide an indication of optimum parameters. The first step involved in this technique is selection of reasonable levels for parameters which require some preliminary tests. In the light of preliminary tests the rotational drum speed, and tilt angle were kept constant, at 240 rpm and 8° respectively. Shake frequency, shake amplitude and washwater flowrate were chosen as the major variables to be considered. The Yates technique for 2^3 experiments (3 being the number of parameters) was used for statistical design and analysis of the test results. Table 4 shows the experimental conditions and the grade and recovery responses for each experiment. The experimental conditions were arranged in the so-called Yates order.

Table 5 and Table 6 combines the Yates technique with ANOVA (analysis of variance) to simplify the decision on the significancy of parameters being investigated. The procedure for preparing the table is as follows:

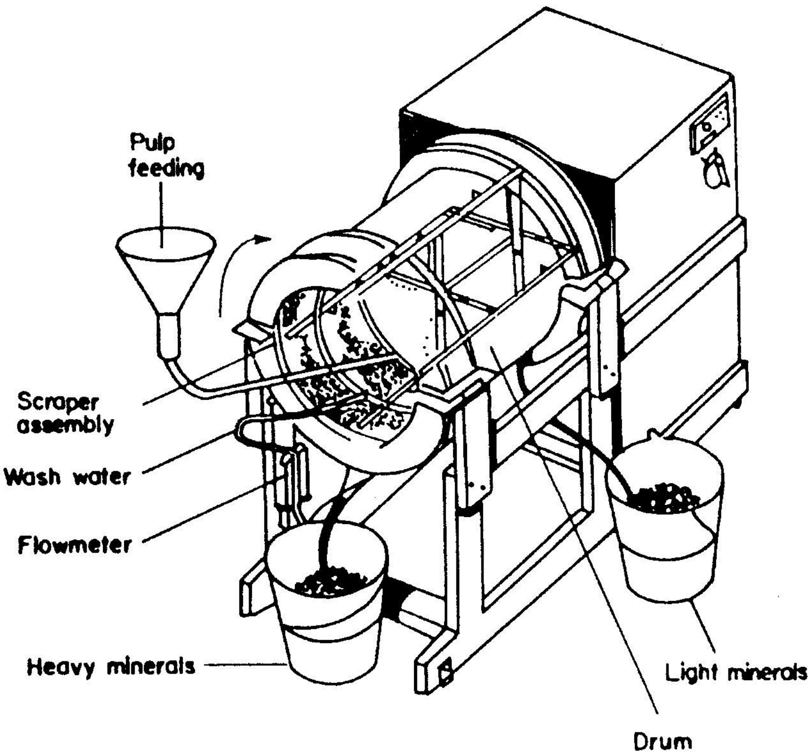

Fig. 2. Multi-gravity separator

Table 4. Experimental conditions and responses

Test No	Code	Shake frequency (cycle/min)	Wash water flow (dm^3/min)	Shake amplitude (mm)	Grade Ce, %	Recovery %
1	(1)	4	4	10	12.11	83.01
2	a	5.6	4	10	12.88	71.02
3	b	4	8	10	12.18	79.69
4	ab	5.6	8	10	12.50	77.59
5	c	4	4	20	13.11	72.69
6	ac	5.6	4	20	12.54	77.27
7	bc	4	8	20	12.52	76.87
8	abc	5.6	8	20	12.54	76.87

i. In the column (3), the upper half is obtained by adding successive pairs responses, and the lower half is obtained by subtracting successive pairs. Columns (4) and (5) are calculated in the same way as mentioned above.
ii. Tests are repeated 3 times at center points to estimate the error associated with the determination of an individual response, which is required for the test statistical significance.
iii. ANOVA procedure is applied.
iv. Table value of F (1,2) for a = 0.05 is compared with the calculated F value.

Table 5 and 6 indicated that the selected parameters have no significant role on the grade and recovery responses of the concentration process. As it is seen in Table 4, the concentrates grades and recoveries were almost the same within the given operating conditions. In order to increase the grade of the product, the rougher concentrate was cleaned in MGS and finally a concentrate with an average grade of 29.30% REE (35.50% REO) and recovery of 47.87% with respect to original feed was achieved. Table 7 shows the contents of major REE in the cleaned concentrate.

Hydrometallurgical Extraction of Rare-Earth Elements

Besides beneficiation studies, hydrometallurgical recovery of REE was investigated. Three different routes were followed for the extraction of REE from the preconcentrate (Akkurt et al. 1993)

i. Leaching of the preconcentrate in acid solutions by using H_2SO_4, HCl and HNO_3.
ii. Curing of the preconcentrate with H_2SO_4 and then water leaching.
iii. Curing of the preconcentrate with H_2SO_4, roasting of the mixture in a muffle furnace at temperatures around 200 °C and subsequent leaching of the roasted product with water.

Table 5. Yates technique combined with ANOVA for recovery response

Yates order (1)	Recovery Ce, % (2)	Column (3)	Column (4)	Column effects total (5)	$(5)^2/2^3$ (6)	Degree of freedom (7)	F Calculated (6) / (7) Se^2 (8)	F Table (1,2, 0.05)	Decision
1	83.01	154.03	311.31	615.01	–	–	–	–	not significant
a	71.02	157.28	303.7	–9.51	11.31	1	3.47	18.51	not significant
b	79.69	149.96	–14.09	7.03	6.18	1	1.89	18.51	not significant
ab	77.59	153.74	4.58	5.31	3.52	1	1.07	18.51	not significant
c	72.69	–11.99	3.25	–7.61	7.23	1	2.22	18.51	not significant
ac	77.27	–2.10	3.78	18.67	43.57	1	13.36	18.51	not significant
bc	76.87	4.58	9.89	0.53	0.05	1	0.02	18.51	not significant
abc	76.87	0.00	–4.58	–14.47	26.17	1	8.03	18.51	not significant
Column total		605.5	617.84	614.96					
Alternative total		308.92	307.48	0.0					

Center points responses 1) 78.58 % 2) 75.52 % 3) 75.31%

Frequency (a) : 4.8 cycle/min

Wash water flow (b) : 6 liter/min

Amplitude (c) : 15 mm

Average recovery 76.47 %

$$Se^2 = \sum_{i=1}^{3} \frac{(R_i - R_{average})^2}{2}$$

$Se^2 = 3.26$

Table 6. Yates technique combined with ANOVA for grade response

Yates order (1)	Grade Ce, % (2)	Column (3)	Column (4)	Column effects total (5)	$(5)^2/2^3$ (6)	Degree of freedom (7)	F Calculated (6) / (7) Se^2 (8)	F Table (1,2, 0.05)	Decision
1	12.11	24.99	49.67	100.38	–	–	–	–	not significant
a	12.88	24.68	50.71	0.54	11.31	1	1.89	18.51	not significant
b	12.18	25.65	1.09	–0.90	6.18	1	5.31	18.51	not significant
ab	12.50	25.06	–0.55	0.14	3.52	1	0.10	18.51	not significant
c	13.11	0.77	–0.31	1.04	7.23	1	7.10	18.51	not significant
ac	12.54	0.32	–0.59	–1.64	43.57	1	17.68	18.51	not significant
bc	12.52	–0.57	–0.45	–0.28	0.05	1	0.52	18.51	not significant
abc	12.54	0.02	0.59	1.04	26.17	1	7.36	18.51	not significant
Column total		100.92	100.16	100.32					
Alternative total		50.08	50.16	0.08					

Center points responses 1) 12.20 % 2) 12.47 % 3) 12.38%

Frequency (a) : 4.8 cycle/min

Average "Ce" grade 12.35 %

Wash water flow (b) : 6 liter/min

$$Se^2 = \sum_{i=1}^{i=3} \frac{(grade_i - grade_{average})^2}{2}$$

Amplitude (c) : 15 mm

$Se^2 = 0.019$

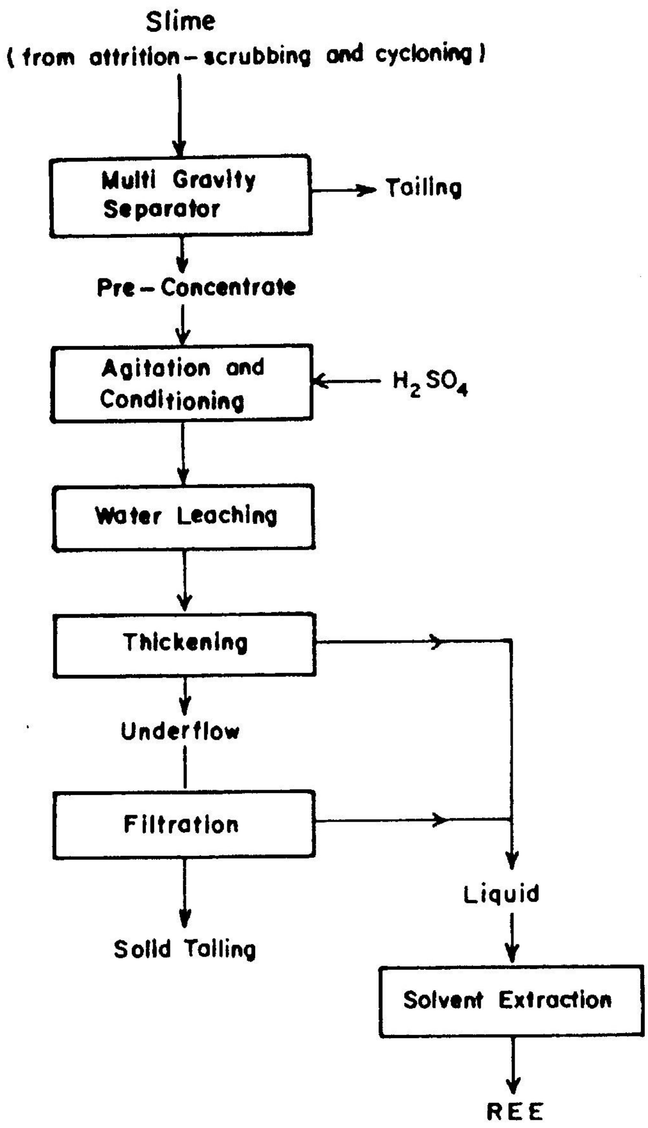

Fig. 3. Proposed flowsheet for the extraction of REE

It was found that each route had its own advantages and disadvantages. In connection with the acid curing and water leaching experiments, it was concluded that 75 to 80% of REE could be leached from preconcentrate by using 585 kg H_2SO_4/Mg of concentrate. The final flowsheet for the recovery of REE is given in Figure 3.

CONCLUSIONS

Beylikahir complex ore deposit contains REE in the form of bastnaesite mineral. The mineralogical analysis revealed that bastnaesite was found mostly in a few micron size range. A preconcentrate containing 29.30% REE (35.50% REO) was produced with the combination of attrition scrubbing and cycloning followed by multi gravity separator treatment. Operating variables such as wash water flow shake frequency, and amplitude were not so effective on the grade of concentrate within the given operation ranges. Barite and fluorspar concentrates were produced with marketable grades by the treatment of deslimed ore by shaking tables. The bastnaesite preconcentrate was leached by water after H_2SO_4 curing; more than 75% of REE were taken into solution.

Table 7. Rare-earth elements grades of final concentrate

Elements	%
Ce	13.75
La	11.81
Nd	2.30
Pr	1.00
Sm	0.15
Y	0.064

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Dokonano oceny użytecznych składników kompleksowej rudy z Beylikahir, która zawierała fluoryt, baryt i bastnaesyt. Analiza mineralogiczna, chemiczna i sitowa wykazały, że fluoryt koncentruje się w ziarnach o rozmiarze większym niż 210 mikrometrów, podczas gdy zawartość barytu wzrasta w klasie ziarn poniżej 210 mikrometrów. Stwierdzono także, że bastnaesyt występuje zarówno jako lepiszcze pomiędzy ziarnami fluorytu i barytu, jak i w formie drobnych ziarn zawartych w tych minerałach. Zastosowanie separacji grawitacyjnej na stole koncentracyjnym dostarczyło koncentratów fluorytu i barytu zawierających 72% CaF_2 i 80.95% $BaSO_4$ z uzyskiem odpowiednio 84.68% i 60.14%. Wstępnego wzbogacania pierwiastków ziem rzadkich (REE) dokonano przez ocieranie i odszlamianie w cyklonach. Koncentrat wstępny, otrzymany w przelewie cyklonu, był dalej wzbogacany za pomocą separatora Mozley'a. Otrzymano koncentrat zawierający 29.3% REE z uzyskiem 47.87%. Zastosowano trzy różne metody hydrometalurgiczne dla wydzielenia REE ze wstępnego koncentratu. Osiągnięto 75-80% wyługowania REE.