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EXTRACTION OF RARE EARTHS FROM A TURKISH ORE

In this study, the hydrometallurgical evaluation of a rare earth ore, that is located in mid-west Turkey, was investigated. It was found that the rare earths were contained in bastnasite mineral, the concentration of which was 10%. Other constituents of the ore were CaF_2 (55%), $BaSO_4$ (25.4%), $CaCO_3$ (2.8%) and minor amounts of ThO_2, Al_2O_3, Fe_2O_3, MnO, and SiO_2. The physical, chemical and mineralogical characterization of the ore were done and it was decided to carry out the experiments in three different routes:

i. Leaching of the ore samples in dilute H_2SO_4, HCl and HNO_3.
ii. H_2SO_4 curing of the ore that is followed by water leaching.
iii. After curing of the ore with H_2SO_4, roasting of the mixture at temperatures around 200°C and subsequent leaching of the roasted product with water.

The results of leaching experiments were found to be quite promising. Leach recoveries in the range of 80 to 90% were achieved. It is planned to continnue the studies to include the recovery of rare earths from the leach liquor obtained.

1. INTRODUCTION

Rare earths are a group of 15 chemically similar elements. Actually, rare earth is a misnomer simply because their relative abundance in the earth's crust is greater than that of copper, nickel, cobalt, etc (Spedding, 1978). The more common minerals containing rare earth elements are monazite, a phosphate mineral, and bastnasite, a carbonate mineral. There are also some other minerals of rare earths that are not encountered in conventional processing, e.g. xenotime, gadolinite, cerite, apatite, euxenite, samarskite, fergusonite, etc.

For over 25 years, the production of bastnasite has been the world's major source of rare earths. Previously, monazite was the principle source of rare earths (Mackey, 1986). The production of rare earths from monazite mineral is associated with several limitations due to radioactive waste disposal.

Production flowsheets in connection with the bastnasite mineral are generally accomplished by flotation, HCl leaching to remove any calcite present in the ore, roasting (to drive-off the carbon dioxide), and finally stronger HCl leaching to get all rare earths but cerium into a solution, which is followed by solvent extraction to recover the metal values (Moore, 1979).

Eskişehir, Beylikahır ore deposit, which is investigated in this study, is located in mid-west of Turkey. According to the chemical, physical and mineralogical analysis, the ore contained rare earths in bastnasite mineral ($LnFCO_3$). Total rare earth oxide (REO) reserve of the ore deposit was estimated to be 900000 tons with an average concentration of 3.75 % REO.

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2. EXPERIMENTAL

Representative samples from the ore deposit were taken as the first step in this study. Then chemical, physical and mineralogical analyses of the ore were done. Complete chemical analysis of the ore is given in Table 1. After the analysis of the ore by XRD, SEM and other mineralogical analysis techniques, it was found that there was no considerable localization of rare earths in any of the constituents and also the size of bastnasite grains was found to be below 5 microns.

Table 1. Chemical analysis of the ore

Element or compound	Percentage weight	Method of analysis	Element or compound	Percentage weight	Method of analysis
Ce	3.00%	ICP	SiO_2	1.30%	Gravity
La	2.70%	ICP	CaF_2	55.00%	Gravity
Nd	0.55%	ICP	$BaSO_4$	25.40%	Gravity
Pr	0.18%	ICP	Al_2O_3	4.00%	Gravity
Sm	220 ppm	ICP	Fe_2O_3	3.00%	AAS
Gd	120 ppm	ICP	ThO_2	0.07%	Colorimetric
Eu	60 ppm	ICP	SrO	0.60%	XRF
Tb	<25 ppm	ICP	MnO	0.54%	AAS
Dy	60 ppm	ICP	P_2O_5	1.00%	XRF
Ho	20 ppm	ICP	CO_2	1.16%	Volumetric
Er	40 ppm	ICP	S	3.60%	Volumetric
Tm	< 10 ppm	ICP	Pb	0.072%	AAS
Yb	25 ppm	ICP	Ag	0.003%	Optical spectrometer
Lu	< 10 ppm	ICP	Ti	0.07%	Optical spectrometer
Y	300 ppm	ICP	V	0.02%	Optical spectrometer
$CaCO_3$	2.80%	Gravity	Mg	0.20%	Optical spectrometer

At the beginning of the experimental studies, Beylikahır samples ground to -10 mesh size were subjected to a sieve analysis the results of which indicated an enrichment of rare earths at finer size fractions. In order to produce a salable concentrate with at least 60% REO, concentrating by attrition scrubbing followed by hydrocycloning was employed, but the concentration of REO in the cyclone overflow did not go up beyond 25% with a recovery of less than 70%. Keeping all this information in mind, the initial hydrometallurgical experiments were planned to make use of the original ore itself at a size of -200 mesh (74 microns).

In connection with Beylikahır rare earth ore, three different processing routes were planned:

i. Leaching of the ore directly in acid solutions by using H_2SO_4, HCl and HNO_3.
ii. Curing of the ore with H_2SO_4 and water leaching.
iii. Curing of the ore 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.

Stoichiometric calculations were done as the first step in hydrometallurgical studies. The stoichiometric amount of acid needed for the dissolution of rare earths and calcite by direct leaching was calculated for H_2SO_4, HCl and HNO_3 as:

3.79 g H_2SO_4/40 g ore
7.61 g HCl/40 g ore
4.96 g HNO_3/40 g ore

In the case of H_2SO_4 curing experiments, the amount of acid requirement was taken to be the same as that utilized in direct leaching. But, when roasting the cured mixture at temperatures around 200°C, the amount of acid was calculated so that CaF_2, Fe_2O_3 and MnO would also react with H_2SO_4 (i.e. the stoichiometric acid requirement was taken as 42.3 g H_2SO_4/50 g of ore).

2.1. Direct Leaching

All direct leaching experiments were made by using 40 g of ore samples ground to -200 mesh. In each run 40 g of sample was leached with acid in a 400 cc glass beaker which was placed in a constant temperature water bath. These direct leaching experiments were performed at a solid to liquid ratio of 1 to 4, at constant stirring speed, at room temperature for 3 hours. Increasing amounts of acids were added in order to examine the amenability of ore to dissolution in highly acid solutions. As the results were examined, it was found that the rare earths dissolved by 86% when 8 fold excess of HCl was added to the leachant and by 82% when 8 fold excess of HNO_3 was added. In the case of H_2SO_4, the results obtained were very low even after 16 fold excess acid addition.

2.2. Acid Curing and Water Leach

After having observed that leaching of the ore directly in H_2SO_4 solution did not give satisfactory leach recoveries, acid curing experiments were planned. One advantage of acid curing was that the ore came in contact with a concentrated acid (98% H_2SO_4) providing easier sulfation. It was quite important to wait for a certain time period for the curing simply because the sulfation was known to take place some time. Then, the reacted mixture was placed in a 400 cc glass beaker and the leaching was done at room temperature for 3 hours at a solid to liquid ratio of 1 to 4 in a constant temperature water bath with the help of a mechanical stirrer. Stirring speed was kept constant in each run.

In a series of experiments the effect of the amount of acid addition, waiting time and particle size were examined. The results of all these acid curing experiments are given in Table 2 and Figures 1, 2. Chemical analyses by ICP for the determination of leach recoveries were made by only analyzing the rare earth percentages of the leach residues that were also washed by distilled water amounting to more than twice the volume of leach solution.

As can be seen from Table 2 and Figure 1, the acid additions up to 8 fold of stoichiometric amount brought about an increase in the leach recoveries of rare earth elements, while further acid additions did not provide higher leach recoveries. Therefore, 8 fold of the stoichiometric amount was chosen as the technical optimum acid amount to be added. From Table 2, it can be observed that the leach recoveries of rare earths stayed almost the same at around 90% levels at all waiting times that were in the range of 5 to 40 hours. This indicated that the acid curing process proceeded reasonably fast. In connection with the effect of particle size of the sample on the leach recoveries, a series of experiments were carried out. The results are presented in Table 2 and Figure 2. It was observed that the particle size did not have a considerable effect on the leach recoveries of rare earths except at sizes finer than 100 mesh.

After the completion of acid curing and water leaching experiments, it could be concluded that Beylikahir samples as coarse as -10 mesh size could be sulfated with 8 fold of stoichiometric amount of acid. After mixing the acid and sample, a waiting time of about 5 hours could be sufficient for effective sulfation of bastnasite. In addition, it should be noted that the production of HF acid as a by-product by this process was not possible.

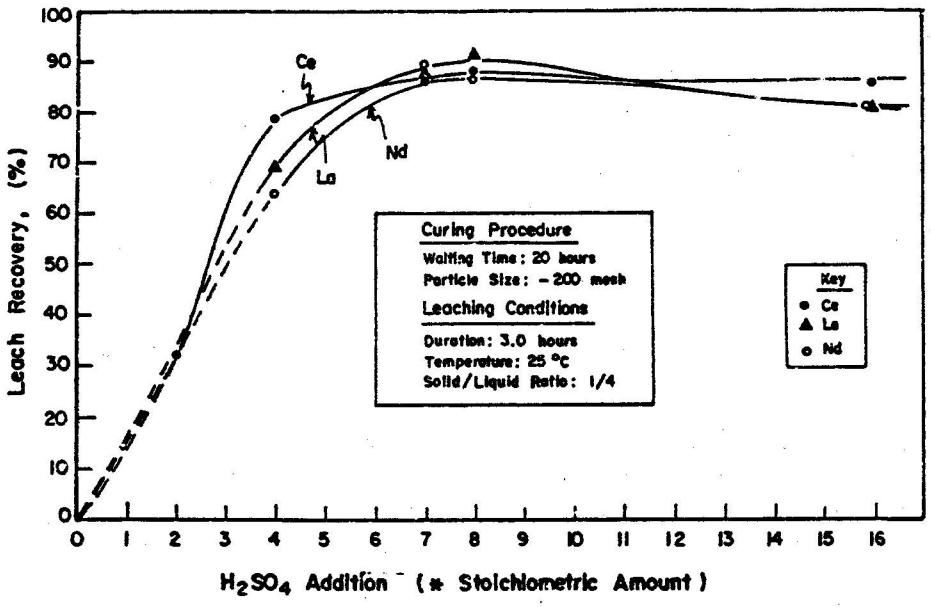

Fig. 1. Effect of the amount of H_2SO_4 addition in acid curing on the leach recoveries of rare earths

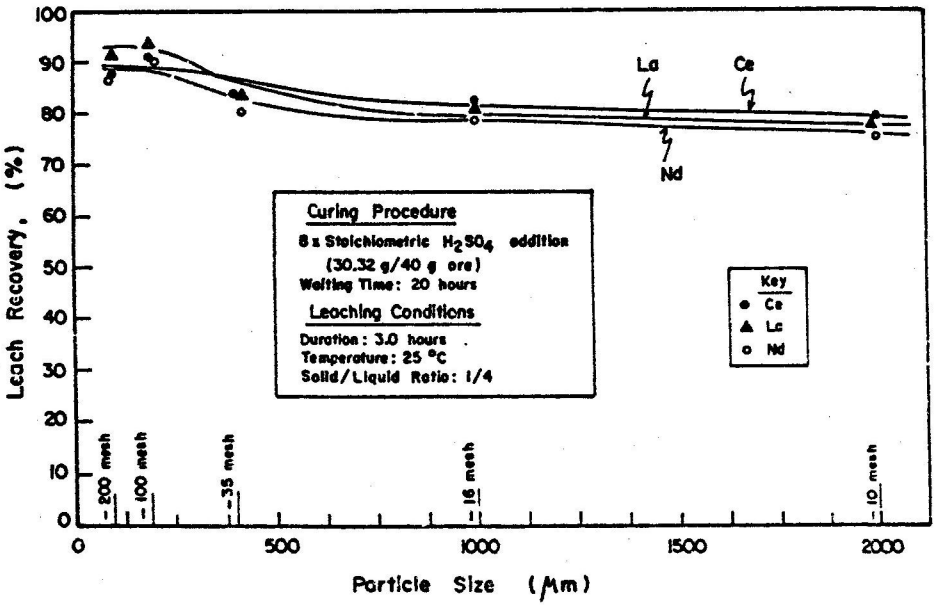

Fig. 2. Effect of the particle size of the sample on the leach recoveries of rare earths

Table 2. Results of acid curing experiments

Exp. code	Waiting time after mixing (hrs)	Amount of H_2SO_4 added (g / 40 g ore)	Particle size (mesh)	Leach recovery (%)		
				Ce	La	Nd
1	20	7.58 (2)	-200	32.0	NA	NA
2	20	15.16 (4)	-200	78.5	68.9	64.1
3	20	26.53 (8)	-200	85.9	87.4	89.1
4	20	30.32 (8)	-200	87.6	91.4	86.5
5	20	60.64 (8)	-200	85.4	80.7	80.9
6	5	30.32 (8)	-100	90.4	91.1	89.5
7	20	30.32 (8)	-100	90.9	93.3	90.1
8	40	30.32 (8)	-100	89.4	92.4	92.4
9	20	30.32 (8)	-35	84.0	83.5	80.5
10	20	30.32 (8)	-16	82.3	80.3	79.0
11	20	30.32 (8)	-10	79.4	78.7	75.9

*NA: not analyzed.
**Numbers in parentheses represent the excess of acid in relation to stoichiometric amount.

2.3. Acid Curing, Roasting and Water Leach

Generally, acid curing is applied to the treatment of monazite type rare earth ores (Parker et al., 1971). But, several studies have been also recorded in connection with the acid curing treatment of bastnasite type ores (Merker, 1985).

As it is given in Table 1, the ore is reported to contain a substantial amount of CaF_2 which can be further processed to produce HF acid provided that its concentration is above some certain limit and the curing process is done at temperatures in excess of 200 °C. So, the experimental route followed in this part was planned not only to convert bastnasite to water soluble sulfate but also to produce a marketable HF acid by the dissociation of CaF_2.

Samples weighing 50 grams were mixed with calculated amount of concentrated H_2SO_4 in a porcelain crucible and a very fast reaction was observed causing the formation of a hard mass after the evolution of gasses. Then, the crucible was placed in a muffle type furnace and the temperature was fixed at the desired level. A color change was observed together with a weight loss in the range of 30 to 40% of the weight of ore sample as a result of roasting. Finally, from the reacted mass 40 grams of sample was taken for leaching. Leaching conditions were kept constant in each run. As before the temperature of leaching was taken as room temperature (a constant temperature water bath was employed for this purpose), the solid to liquid ratio was chosen 1 to 4 and the duration of leaching was taken as 3 hours. The leaching experiments were done in 400 cc glass beakers with the help of a mechanical stirrer operating at a constant speed.

Among the experimental parameters investigated in roasting were:
- amount of H_2SO_4 addition,
- temperature of roasting,
- duration of roasting,
- particle size of the sample used

All pertinent data for the acid curing and roasting experiments are given in Table 3 and Figures 3 and 4. As can be seen from Table 3 and Figure 3, the effect of the amount of H_2SO_4 addition was quite important from the point of view of acid consumption. In other words, the leach recoveries of Ce and La increased up to the stoichiometric acid addition, while there was no

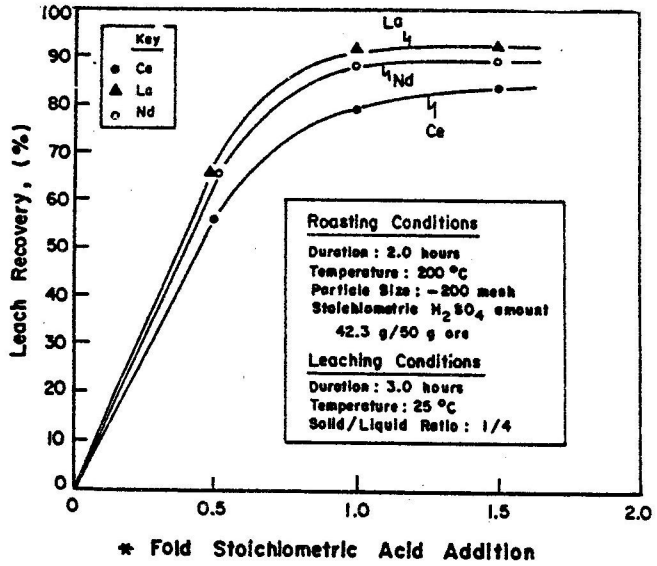

Fig. 3. Effect of the amount of acid addition in curing and roasting on the leach recoveries of rare earths

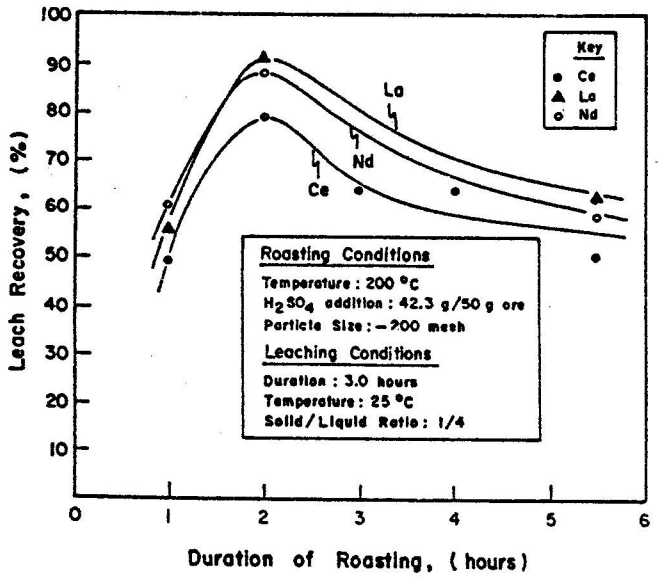

Fig. 4. Effect of the duration of roasting on the leach recoveries of rare earths

considerable increase in the leach recoveries with acid additions in excess of the stoichiometric amount. From Table 3, the temperature of roasting was observed not to affect the leach recoveries of rare earths to a large extent. But, at this point it must be emphasized that the temperature of roasting was chosen as 200°C in order to be able to collect HF gas as a valuable by-product. The effect of the duration of roasting was observed to be quite interesting simply because the leach recoveries of rare earths decreased after roasting for more than 2 hours. This tendency of the ore can be seen from Table 3 and Figure 4. It was thought that some sort of an insoluble compound formed in excessive roasting periods. Further experiments are planned to find out the reason for this drop. Effect of the particle size of the sample used on the leach recoveries of rare earths was also examined and the results are given in Table 3. The results indicated that the particle size of the sample did not have a considerable effect on the leach recoveries. So a particle size of -10 mesh could be employed for acid curing, roasting and water leaching process.

Table 3. Results of acid curing, roasting and water leaching experiments

Exp code	Roasting conditions				Percent leach * recovery		
	Temp. (°C)	Time (hrs)	H_2SO_4 ** addition (g/50g ore)	Particle size (Tyler mesh)	Ce	La	Nd
12	200	2.0	21.15 (0.5)	-200	56.5	65.4	65.6
13	200	2.0	42.30 (1.0)	-200	79.6	91.2	88.4
14	200	2.0	63.45 (1.5)	-200	83.9	92.0	89.1
15	100	2.0	42.30 (1.0)	-200	79.0	92.5	NA
16	250	2.0	42.30 (1.0)	-200	77.6	89.6	NA
17	300	2.0	42.30 (1.0)	-200	77.7	92.2	NA
18	200	1.0	42.30 (1.0)	-200	49.3	55.8	60.5
19	200	3.0	42.30 (1.0)	-200	63.8	NA	NA
20	200	4.0	42.30 (1.0)	-200	64.1	NA	NA
21	200	5.5	42.30 (1.0)	-200	50.6	62.2	58.8
22	200	2.0	42.30 (1.0)	-200	78.6	90.9	86.5
23	200	2.0	42.30 (1.0)	-35	82.3	90.4	80.6
24	200	2.0	42.30 (1.0)	-16	80.3	89.9	81.7
25	200	2.0	42.30 (1.0)	-10	80.7	88.9	81.4
26	200	2.0	42.30 (1.0)	-1 cm	77.4	NA	NA

*Laching Conditions: Temperature: 25°C, duration: 3.0 hours, solid/liquid ratio: 1/4
**Numbers in parentheses represent excess of acid in relation to stoichiometric amount

In addition, an acid curing, roasting and water leaching experiment was performed using a cyclone overflow concentrate containing 23% REO and similar results were obtained as those of the original ore. Further experiments with the concentrate are continued. Recovery of rare earths from solution are also being planned. .

3. CONCLUSIONS

Eskişehir, Beylikahır rare earth ore deposit was found to contain rare earths in bastnasite mineral. The mineralogical studies revealed that bastnasite was extremely small in size being mostly in a few microns size range. A semi-concentrate containing about 23% REO was produced by physical separation techniques but this was not a salable product.

Among the three experimental routes examined, it was found that each route had its own advantages and disadvantages. As far as the direct leaching with H_2SO_4 is concerned the results were not promising at all. But if direct leaching with HCl or HNO_3 is considered more than 85% of leach recoveries could be accomplished. In connection with the acid curing and leaching experiments, the results indicated quite promising leach recoveries. More than 80 to 90% of each rare earth could be taken into solution. One important finding was that the process was nearly independent of the particle size of the sample used. Acid curing, roasting and leaching experiments were found to be a possible means of taking rare earths into solution in the range of 70 to 90% as well as producing HF acid as a by-product.

It is planned to continue of the experiments to include the optimization of leaching experiments in each case and the recovery of individual rare earths from the leach liquor obtained.

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Akkurt S., Topkaya Y., Özbayoglu G., (1993), Ekstrakcja ziem rzadkich z rudy tureckiej, *Fizykochemiczne Problemy Mineralurgii*, 27, 69-76, (English text)

Badano hydrometalurgiczne właściwości tureckiej rudy ziem rzadkich. Stwierdzono, że ziemie rzadkie zawarte są w bastnezycie, którego zawartość wynosiła 10%. Pozostałymi składnikami są CaF_2, (55%), $BaSO_4$ (25,4%), $CaCO_3$ (2,8%) oraz mniejsze ilości ThO_2, Al_2O_3, Fe_2O_3, MnO i SiO_2. Na podstawie fizykochemicznej i mineralogicznej charakterystyki rudy zdecydowano się na prowadzenie eksperymentów trzema sposobami: i) ługowanie rudy rozcieńczonym kwasie siarkowym, solnym i azotowym, ii) traktowanie rudy kwasem siarkowym, po czym następowało ługowanie wodą, iii) traktowanie rudy kwasem siarkowym, a następnie prażenie rudy w temperaturze około 200 °C i ługowanie produktu prażoną wodą. Wyniki ługowania były zachęcające. Uzyski ługowania wynosiły od 80 do 90%. Planuje się kontynuowanie badań i ich rozszerzenie na odzyski ziem rzadkich z roztworów po ługowaniu.