

HYDROMETALLURGICAL TREATMENT OF A RARE EARTH PRECONCENTRATE*Yavuz Topkaya, Mehmet Kul and İshak Karakaya*

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ABSTRACT

From a complex rare earth deposit, located in midwest of Turkey, which contained 1 million tons of REO, a preconcentrate was recovered by attrition scrubbing and cycloning. The grade of the very fine preconcentrate was 23.5%REO with a recovery of 77.5%. The major minerals present in the preconcentrate were bastnasite, fluoride and barite with minor amount of thorium. Various laboratory studies on the preconcentrate showed that the best way to recover the rare earth elements from the preconcentrate was to bake this material with concentrated sulphuric acid. After the optimisation of the baking parameters, the water leaching of the baked mass was investigated. Finally, the recovery of REE's from the pregnant leach solution by precipitation as double sulphate was studied. In this paper, the characterisation of the preconcentrate and the optimum conditions of baking, leaching and precipitation are presented.

INTRODUCTION

The term "Rare earths" denotes the group of chemically similar metallic elements which includes scandium, yttrium, and the lanthanides. The lanthanides (Ln) are the series of elements with atomic numbers 57 to 71, all of which, except promethium, occur in nature (Gupta et al., 1992). The rare earth elements, being chemically similar to one another, invariably occur together in the source minerals and behave as a single chemical entity. Among the rare earths the relative natural abundance varies widely, the most abundant being cerium and the least thulium. About 95% of the rare earths occur in only three minerals: bastnasite, a fluorocarbonate mineral (LnFCO_3); monazite, a phosphate mineral (LnThPO_4); and xenotime (YPO_4). The proportion of the heavier rare earths (Sm-Lu) content in bastnasite is considerably less than in monazite. 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. The production of rare earths from monazite is associated with the problem of disposal of radioactive waste (Jackson et al., 1993).

The bastnasite mined from Mountain Pass in the United States and the rare earths containing iron ores of Bayan Obo in China have to be crushed before they are concentrated by exploiting gravimetric, magnetic, or surface chemistry differences. At Mountain Pass, the ore contains 7-12% bastnasite and is obtained by open pit mining. Bastnasite is beneficiated by hot froth flotation and barite, calcite, quartz, etc. are separated from it and discarded as tailings. Bastnasite concentrate containing 60% rare earth oxides (REO) is obtained. For the production of rare earth elements (REE) from the bastnasite concentrate, HCl leaching to eliminate calcite present in the concentrate, roasting to drive-off CO_2 and to convert Ce^{3+} to Ce^{4+} , and finally stronger HCl leaching in order to put rare earths except cerium into leach solution, which is followed by solution purification and solvent extraction to recover the metal values (Mackey, 1986; Kaczmarek, 1980). An alternative process for "opening" bastnasite is used in China. The rare earth recovery from Bayan Obo deposit located in Inner Mongolia is as a by-product of iron-ore production. The lower grade bastnasite concentrate is taken into solution by sulphuric acid for further processing. This alternative process includes roasting with sulphuric acid, followed by an aqueous leach, to produce a solution with the full natural ratio of lanthanide elements. The Ln's are then precipitated either as a mixed sulphate or as hydroxide and eventually taken up in HCl. The initial cerium-containing product will be, when the valuable heavies have been removed, a light-lanthanide rare earth chloride (Koch, 1987; Kilbourn, 1993).

Eskişehir-Beylikoba ore deposit, which is investigated in this study, is located in mid-west of Turkey. The complex ore of hydrothermal origin contained rare earths in bastnasite mineral. The total rare earth oxide reserve of the ore deposit was estimated

to be 1 million tons with an average grade of 3.42%REO.

CHARACTERIZATION AND MINERAL PROCESSING

At the start of this study, representative samples from the ore deposit were taken. Then, the physical, chemical and mineralogical characterisations of the ore were done using various techniques. The complete chemical analysis of the ore was as follows: 3.00%Ce, 2.70%La, 0.55%Nd, 0.18%Pr, 220ppm Sm, 120 ppm Gd, 60ppm Eu, <25ppm Tb, 60ppm Dy, 20ppm Ho, 40ppm Er, <10ppm Tm, 25ppm Yb, <10ppm Lu, 300ppm Y, 2.8%CaCO₃, 1.3%SiO₂, 52.5%CaF₂, 25.4%BaSO₄, 4.0%Al₂O₃, 3.0%Fe₂O₃, 840ppm Th, 0.6%SrO, 0.5%MnO, 1.0%P₂O₅. After the analysis of the ore sample by XRD, SEM, and other mineralogical analysis techniques, it was found that the bastnasite mineral was present in Beylikoba ore deposit as cement material between the fluor spar (CaF₂) and barite (BaSO₄) particles or as intimately associated with these minerals. The size of bastnasite was generally below 5 microns. The thorium content of the ore was mainly due to the presence of thoro-bastnasite and brockite (CaTh(PO₄)H₂O). Microscopic examination indicated that CaF₂ particles were present both in coarse and fine sizes, between 30 to 3000 microns, while BaSO₄ particles were mostly found in sizes finer than 500 microns. The other minerals in the matrix were calcite, quartz, biotite, muscovite, limonite, and minor amounts of manganese minerals, etc.

At the beginning of the experimental studies, the ore sample ground to -10 mesh (1.65mm) size was subjected to a sieve analysis, the results of which indicated that fluor spar was concentrated above 65 mesh (0.210mm) size while barite content increased below that size. The REE were enriched considerably in sub-sieve sizes. So, the classical concentration methods mentioned in the literature were not applicable alone for the production of marketable bastnasite concentrate. Attrition scrubbing of the original ore and desliming by cyclones was found to be the most promising method capable of concentrating the bastnasite. Therefore, the crushed ore 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. A preconcentrate with 28.0%REO grade and 72.6% recovery was obtained for 1.65mm top size. The REO grade and recovery were found to be 23.5% and 77.5%, respectively, for 1 cm size material. The preconcentrate having 28.0%REO was upgraded by using a Multi

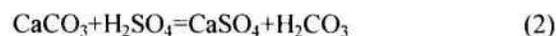
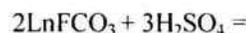
Gravity Separator. Finally, a concentrate with an average grade of 35.5%REO and recovery of 47.9% with respect to the original feed was obtained.

On the other hand, the beneficiation of fluorite and barite minerals was carried out by applying various physical concentration methods. The application of gravity separation method alone by using shaking table produced fluor spar and barite concentrates assaying 72.0%CaF₂ and 80.9%BaSO₄ with recoveries of 84.7% and 60.1%, respectively. Cleaning of gravity concentrates by flotation and magnetic separation methods upgraded the fluoride concentrate to 92.2%CaF₂ and barite to 90.0%BaSO₄.

HYDROMETALLURGICAL EXTRACTION OF RARE EARTH ELEMENTS

The hydrometallurgical experiments were planned and carried out with the preconcentrate. The preconcentrate having 23.5%REO and a top size of 37 microns was used without further grinding. The complete chemical analysis of the preconcentrate was as follows: 7.45%Ce, 8.78%La, 1.6%Nd, 0.53%Pr, 410 ppm Sm, 300ppm Gd, 160ppm Eu, <50ppm Tb, 120ppm Dy, 47ppm Ho, 85ppm Er, 24ppm Tm, 45ppm Yb, 10ppm Lu, 500ppm Y, 8.5%CaCO₃, 2.7%SiO₂, 41.4%CaF₂, 10.7%BaSO₄, 2.8%Al₂O₃, 4.2%Fe₂O₃, 2260ppm Th, 0.9%SrO, 0.3%MnO, 1.2%P₂O₅. In connection with Beylikoba preconcentrate baking of the preconcentrate with concentrated H₂SO₄ and subsequent water leaching was planned to be investigated.

Stoichiometric calculations were done using the reactions given below as the first step in hydrometallurgical studies. The stoichiometric amount of sulphuric acid (98%) needed for the baking experiments was calculated to be 45.0 g H₂SO₄ per 50 g preconcentrate:



Generally, the acid baking is applied to the treatment of monazite type rare earth ores or concentrates. But, several studies have been done in connection with acid baking of bastnasite type ores as well (Merker, 1986) This method as mentioned before is also used for low grade (30%REO) bastnasite concentrates in China .

As given above, the preconcentrate contains a substantial amount of CaF_2 which can be further processed to produce HF acid provided that its concentration is above a certain limit and the baking process is done at temperatures in excess of 200°C . So the experimental route followed in baking was planned not only to convert bastnasite to water soluble sulphate but also to produce a marketable HF acid by the dissociation of $41.4\%\text{CaF}_2$ that was present in the preconcentrate.

Samples weighing 50 g were mixed with calculated amount of concentrated H_2SO_4 in a Teflon beaker and a very fast reaction was observed causing formation of a hard mass after evolution of gases. Then, the beaker was placed in a muffle type furnace and the temperature was fixed at the desired level. A colour change was observed together with a weight loss as a result of baking. Finally, from the baked mass 40 g of sample was taken after grinding it to -1mm for water leaching. The leaching experiments were carried out in a 400 cc beaker, which was placed in a water bath for temperature control. The leaching experiments were done with water at 25°C for 2 hours at a solid to liquid ratio $\frac{1}{4}$ (g/cc) with the help of a mechanical stirrer at a constant stirring speed of 600 rpm. Among the experimental parameters investigated in baking were temperature, amount of sulphuric acid and duration of baking. Chemical analyses by ICP for the determination of leach recoveries were made by analysing the rare earth concentrations of the leach residues that were also washed with distilled water after leaching.

Effect of Baking Temperature

In the first series of experiments, the effect of baking temperature on the recovery of rare earth metals such as cerium and lanthanum was investigated. The other REE's were expected to behave in a similar manner to Ce and La. In these experiments, the amount of sulphuric acid added and the duration of baking were kept constant as stoichiometric amount and 2 hours, respectively. As it can be seen from Figure 1, up to about 100°C of baking temperature the recoveries of rare earth metals were limited. Beyond 150°C of baking temperature, the recoveries of cerium and lanthanum reached a level of about 85-90% and there was little change up to 550°C . Since for the production of HF acid, the minimum temperature of baking should be 200°C , the optimum temperature of baking for the Beylikoba preconcentrate was chosen to be 200°C and kept constant in the following baking experiments.

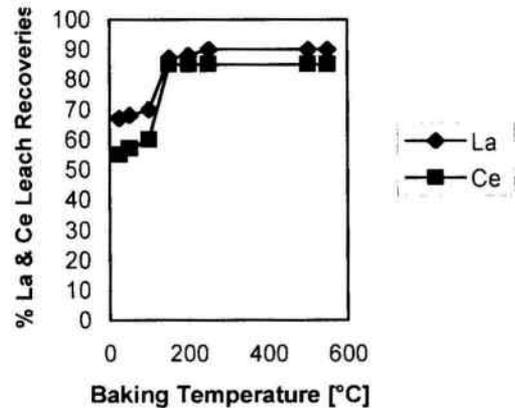


Figure 1: Effect of baking temperature on the leach recoveries of cerium and lanthanum.

Effect of Acid Addition

In the second set of experiments, while keeping the baking temperature at 200°C and the baking duration at 2 hours, the amount of concentrated sulphuric acid added was varied in the range of 22.5 and 90 grams per 50 grams of preconcentrate. These acid additions corresponded to $\frac{1}{2}$ and twice the calculated stoichiometric amount. The results of these second series of tests are given in Figure 2. As indicated by Figure 2, the minimum amount of sulphuric acid needed to obtain a rare earth recovery of the level of 85-90%, at least 45 grams of sulphuric acid (900 kg acid per ton of preconcentrate) was necessary, which corresponded to the stoichiometric amount.

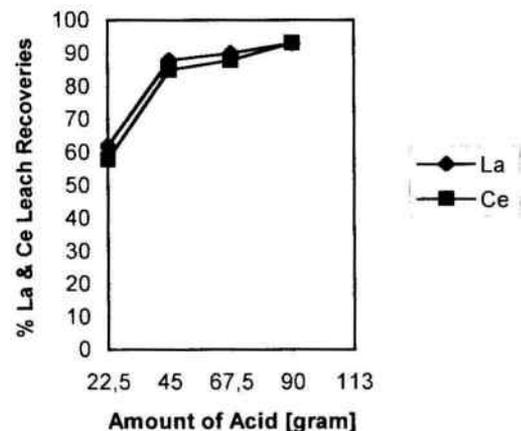


Figure 2: Effect of amount of sulphuric acid added in baking on the leach recoveries of cerium and lanthanum

Effect of Baking Duration

In the last set of experiments, the duration of baking was optimised while keeping the baking temperature and amount of acid added constant at 200°C and 45 g H₂SO₄ per 50 g preconcentrate, respectively. In these experiments, the baking duration was increased up to 24 hours and the results obtained are shown in Figure 3. From the figure, it can be seen that a baking duration of about 1 hour was more than enough in order to obtain cerium and lanthanum leach recoveries of about 85-90%.

So, the optimum conditions of baking for the Beylikoba preconcentrate was found to be 200°C baking temperature, 45.0 g H₂SO₄ per 50 g preconcentrate and 1 hour of baking duration. Under these optimum conditions, the amount of thorium leached from the preconcentrate was determined to be 86% by means of XRF analysis. The pH of the pregnant leach solution obtained under the optimum conditions of baking was 2.6. XRD analysis of the leach residues indicated the presence of mainly gibbsite, barite, etc.



Figure 3: Effect of baking duration on the leach recoveries of cerium and lanthanum.

Optimisation of Leaching and Precipitation

Later the optimisation of leaching parameters were done. The leaching optimisation results showed that the recovery of REE's increased with decreasing leaching temperature and leaching duration as short as ½ hour was enough in order to put the rare earth metals into leach solution. Changes in solid to liquid ratio and stirring speed did not seem to effect the leach recoveries substantially within the ranges studied.

As soon as the experiments for the optimisation of leaching parameters were completed, a stock pregnant

leach solution was prepared under the optimum baking and leaching conditions determined. The rare earths were then precipitated as double lanthanide sulphate Na₂SO₄·Ln₂(SO₄)₃·2H₂O with sodium sulphate addition, which was followed by caustic digestion of the double lanthanide sulphate to obtain Ln(OH)₃.

The optimum conditions found for the precipitation of mixed rare earths as double sulphate were 1.25 times of the stoichiometric amount of sodium sulphate addition at 50°C. In a very short precipitation time, like 5 minutes, it was possible to obtain a relatively pure rare earths with little amount of thorium contamination. Under the stated optimum conditions, the efficiency of precipitation of lanthanides was more than 98%.

In the coming months, the initial separation of cerium from Ln(OH)₃ after drying and oxidation of Ce³⁺ to Ce⁴⁺ and HCl leaching in order to separate the rare earths by solvent extraction will be carried out with the aim of separating light and heavy rare earth elements.

CONCLUSIONS

Beylikoba ore deposit was found to contain rare earths in the form of bastnasite mineral. The mineralogical studies revealed that bastnasite was extremely small in size being mostly in a few microns size range. A preconcentrate was produced in bulk contained 23.5%REO by attrition scrubbing and cycloning but this was not a marketable product.

The sulphuric acid baking and water leaching experiments carried out on the preconcentrate indicated that 85 to 90% of the REE's could be taken into leach solution as well as producing HF acid as by-product. Almost complete precipitation of rare earths from the pregnant leach solution as double sulphate with sodium sulphate was found to be possible.

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