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Beneficiation of Eskişehir Beylikova Bastnasite Ore and Rare Earth Elements Recovery †

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Abstract: The unique magnetic, optical, and electrical properties of rare earth elements (REEs) have become essential in modern high technology. Considering the necessity of technology, efficient management and utilization of rare earth resources are of great importance. Even though there are more than 250 rare earth minerals around the world, the number of minerals that can be economically processed does not exceed three. Among these minerals, bastnaesite has a significant impact on scientific advancement and social progress. This project aims to contribute to the establishment of a sustainable supply chain for REE in Türkiye and Europe by conducting research and development activities to leverage the utilization of REEs found in our country. The primary objective of this project is to extract rare earth oxides from complex ore in the Eskişehir Beylikova region, which holds the largest reserve potential discovered in our country, and to refine these metal oxides to produce metals that can be used in magnet manufacturing. The project encompasses five main work packages over three years: project management, ore enrichment, solvent extraction-based purification, utilization of REOs and metals in additive materials, and magnet production.

Keywords: bastnasite; rare earth elements (REEs); ore benefication; hydrometallurgy

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1. Introduction

Rare earth elements (REEs) comprise a group of 15 lanthanides, along with yttrium and scandium, and they have been recognized as critical commodities by various international agencies and national governments because of their critical functions in clean energy, high-tech, and national defense industries and their inclusion in high-strength permanent magnets, such as catalysts in petroleum refining processes and as additives in metal and glass, highlighting their significance in technological advancements [1,2].

Since the lanthanides are not universally substitutable, each of the rare earth elements is needed for a different type of application. Ensuring supply security of these elements presents significant issues due to the disparities in demand for each REE and the variations in their abundance in the Earth's crust, as mentioned earlier [3]. For instance, manufacturers of terbium (Tb) and neodymium (Nd), which are among the least abundant REEs, will face greater challenges in terms of REE supply compared to manufacturers of catalysts for petroleum refining, who necessitate the use of lanthanum (La) and cerium (Ce), two orders of magnitude more abundant REEs [2]. While Nd, Pr and Dy are mainly used in magnetic applications, La, Ce, Pr and Nd are used in battery alloys, metal alloys, automotive catalysts, petroleum refining, polishing agents, phosphors and ceramics. Furthermore, Y is mostly used for luminescent materials and ceramics [4].

The main REEs containing minerals are bastnäsite, monazite, xenotime, and ion-adsorption clays. Various methods, including flotation, gravity, magnetic, and electrostatic separation, find extensive application in the beneficiation of rare earth minerals, and the ores are the primary resources that are considered for this intention [2,5].

Hydrometallurgical methods play a significant role in the processing of bastnazite ore and extracting rare earth elements (REEs) after the pre-enrichment stage. The leaching process has significant importance, as the effectiveness of leaching is the key factor that influences the entire procedure.

The project's objective is to produce rare earth concentrate from the complex bastnasite ore found in the Eskişehir Beylikova region, which is one of the largest rare earth reserves, extract rare earth oxides from the acquired concentrate, produce metals through a metal oxide refining process, and utilize these metals in the production of permanent magnets. Within the scope of this work, the ore sample collected from the site underwent a sequence of beneficiation and leaching procedures.

2. Results and Discussion

As China accounts for 88% of global rare earth production, other countries are exploring strategies to reduce their dependence on China by extracting rare earths from both primary and secondary sources. A variety of techniques, including ore beneficiation processes, leaching, and solvent extraction, are used in this quest. Figure 1 depicts a brief overview of the methods utilized in the beneficiation and purification of rare earth ores.

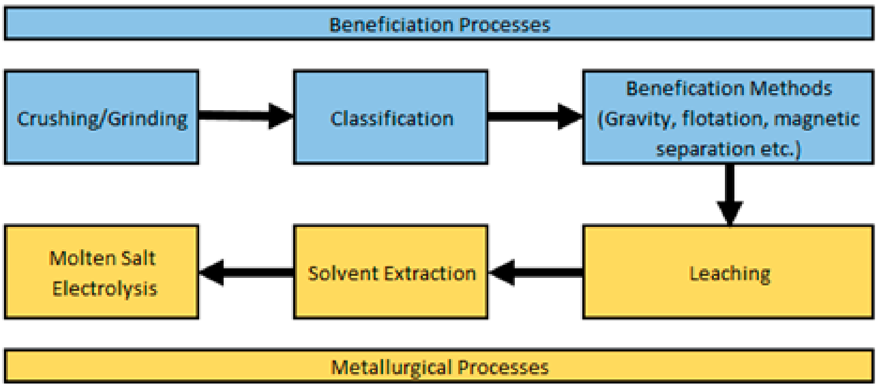

Figure 1. Overview of rare earth element (REE) production techniques.

This study involves investigations of both the beneficiation and leaching of rare earth ore found in Eskisehir-Beylikova. The ore consists of 40.80% CaF_2, 35.35% $BaSO_4$, 2.01% Ce, 1.50% La, 0.39% Nd, and 0.10% Th, and the reserve is estimated to be 694 million tons. Ozbayoglu and Atalay suggested that rare earth minerals are accumulated in finer size fractions (−5 microns) and proposed the attrition scrubbing method for ore beneficiation [6]. Basturkcu et al. performed MLA analysis on the −38 and +38 micron fractions of the attrition scrubbing product in order to examine the effect of attrition scrubbing in detail and compared these results with MLA analysis on the −38 and +38 micron fractions of the ore [7]. As a result of this study, rare earth yields in the −38 micron fraction of the attrition scrubbing product reached 70%. Two approaches are employed in this study: one of these approaches is attrition scrubbing–sieving, while the second is grinding–flotation, both of which are explained in the subsequent sections. In the scrubbing–sieving method, the ore was fractionated and crushed with a jaw crusher prior to the attrition scrubbing. The attrition scrubbing products were sieved with a mesh size of 45 microns; the −45 microns fraction was obtained as the product, and the flow chart is given in Figure 2. The behavior of the ore in various fractions has also been analyzed utilizing this approach. As depicted in Table 1, the highest rare earth grade was found in the product at −45 microns subsequent to attrition scrubbing of the −3 + 0.075 mm fraction, which was obtained from the −3 mm fraction of the ore and leaching process.

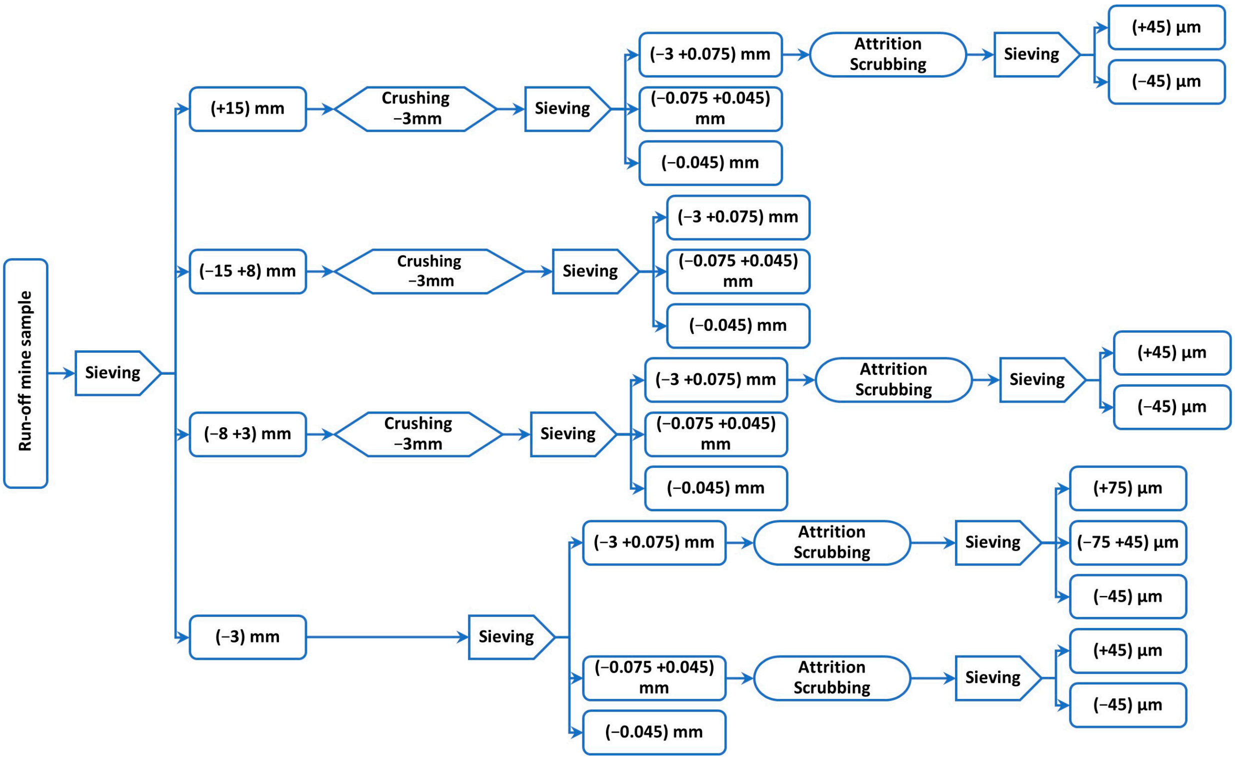

Figure 2. Preparation flowsheet of Sample 1.

Table 1. Major rare earth contents of the Sample 1 and Sample 2.

	La (ppm)	Ce (ppm)	Nd (ppm)	Pr (ppm)	U (ppm)	Th (ppm)
Sample 1	26,627.00	24,679.00	4290.00	2022.00	257.00	446.00
Sample2	50,526.72	59,596.40	3473.59	8404.22	370.07	1251.58

The second sample was prepared through fine grinding of ore to −150 microns, followed by a flotation test, as shown in Figure 3.

Periodic dosing with H_2SO_4 was used to ensure a pH level between 4.5 and 5.0 in tests using the modified fatty acid so that it did not drop below 4.5 and did not exceed 5.0. The test parameters for flotation are given in Table 2.

The results in Table 1 show that a 7% REO content is achieved by simple attrition scrubbing and sieving, and ~17% REO is achieved with grinding, sieving, and flotation. Also, the REO content reaches up to 13.25% when grinding and sieving are applied. Analysis of the product with a 13.25% rare earth content and the product with ~17% rare earth content shows that the recovery of rare earth ore is 89.39%. In this regard, the rare earth analysis and the XRF analysis for the flotation concentrate and slime are shown in Tables 3 and 4.

Leaching tests were performed for both prepared samples utilizing two different approaches, and chemical beneficiation processes of the enriched Eskisehir Beylikova bastnazite complex ore involved acid leaching prior to solvent extraction techniques. The effects of various parameters, including the S/L (solid/liquid) ratio, temperature of reaction medium (temperature of solution), reaction time, and oxidizing agent additives, on the leaching efficiency were investigated in detail. ICP (OES) and XRF analyses were performed for the characterization of rare earth element oxides.

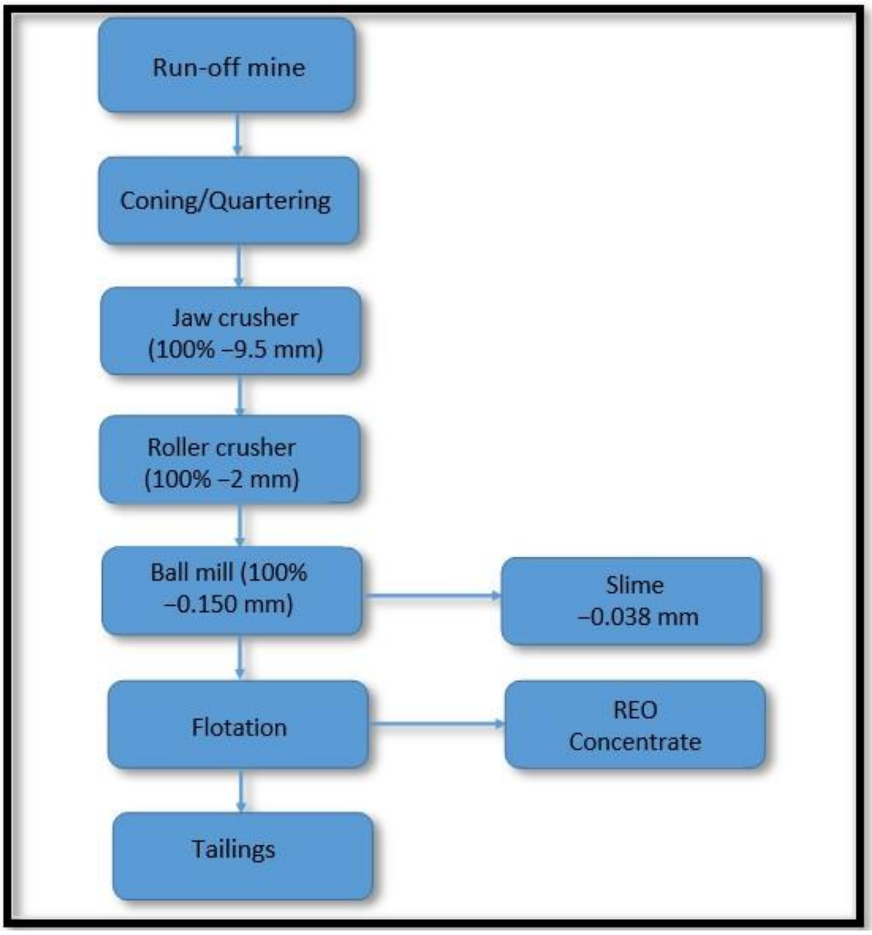

Figure 3. Preparation flowsheet of Sample 2.

Table 2. Major rare earth contents of the prepared samples.

Flotation Reagents	Amount
Modified Tall Oil Fatty Acid	5000 g/t
MIBC	20 g/t
pH	4.5–5.0

Table 3. Rare earth analysis of flotation products.

Content	Flotation Concentrate	Slime	Content	Flotation Concentrate	Slime
	ppm	ppm		ppm	ppm
Sc	2.40	1.50	Gd	452.19	231.03
Y	284.54	220.25	Tb	82.08	50.59
La	50,526.72	33,966.67	Dy	92.07	64.51
Ce	59,596.40	35,023.86	Ho	15.28	10.91
Pr	3473.59	2376.28	Er	42.50	31.19
Nd	8404.22	5769.60	Tm	4.84	3.13
Sm	426.76	297.84	Yb	32.05	23.95
Eu	155.28	117.35	Lu	4.45	3.20
U	370.01	218.46	Th	1251.57	893.33

Table 4. XRF analysis of flotation products.

Content	Flotation Concentrate (%)	Slime (%)	Content	Flotation Concentrate (%)	Slime (%)
CaF_2	38.78	56.18	ZnO	0.21	0.13
$BaSO_4$	20.96	17.24	MgO	0.32	0.43
CaO	32.20	46..40	PbO	0.35	0.12
La_2O_3	7.75	5.32	Cs_2O	0.50	0.40
CeO_2	7.70	4.34	Cl	0.09	-
Fe_2O_3	7.39	5.16	Nb_2O_5	0.07	0.03
SiO_2	4.20	4.42	Al_2O_3	0.72	0.70
MnO	5.21	1.46	Y_2O_3	0.16	0.14
P_2O_5	2.27	1.35	MoO_3	0.04	-
Nd_2O_3	1.52	0.98	Rh	0.06	-
U	-	0.47	K_2O	0.09	0.14
Pr_2O_3	0.43	0.37	Ga_2O_3	0.09	0.09
Na_2O	0.30	-	CuO	0.04	0.04
ThO_2	0.36	0.26	NiO	0.06	0.08
TiO_2	0.33	0.22			

3. Conclusions

The bastnazite ore sourced from the Eskisehir, Beylikova region, was characterized in order to assess the ore structure. The rare earth oxide content in the ore is raised from 3% to 7% with a recovery of 50.66% using attrition scrubbing–classification, 3% to 13.25% with a recovery of 56.7% using grinding–classification, and 3% to ~17% using grinding–flotation. When 13.25% rare earth-containing products and ~17% rare earth-containing products are studied together, the recovery of rare earth ore is calculated as 89.39%. Subsequent to the physical beneficiation processes, chemical purification procedures were implemented to further enhance and purify REEs. As part of the classification tests, the slime was eliminated after grinding the ore below a grain size of -150 µm, ensuring sufficient liberation for subsequent flotation tests. Simple closed-circuit milling–classification achieves a classification product with a higher grade and recovery of rare earth oxides (REOs) compared to multiple stages of attrition scrubbing. The product contains a total of 13.25% REOs (Ce, La, Nd, and Pr oxides), with a recovery of 56.7% in the classification overflow that can be readily attained. Compared to attrition scrubbing, the milling–classification system is an industrially more feasible option prior to solvent extraction.

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