



Bulletin of the Mineral Research and Exploration

<http://bulletin.mta.gov.tr>



Production of rare-earth oxides from Eskişehir-Beylikova complex ores

Haydar GÜNEŞ^a, Hüseyin Eren OBUZ^a, Hasan AKÇAY^a, Çiğdem KARA^a and Ayşe ERDEM^{a*}

^aMaden Tetkik ve Arama Genel Müdürlüğü Maden Analizleri ve Teknoloji Dairesi, 06800 Ankara, Türkiye

Research Article

Keywords:

Rare Earth Elements,
Roasting, Leaching,
Solvent extraction,
Precipitation

ABSTRACT

In this study, the production technology of barite, fluorite, rare-earth elements, and thorium-bearing rare-earth oxides from the Eskişehir-Beylikova were investigated, and the processes that can be used in the production of thorium-free mixed rare earth oxides were tested. The applied processes are roasting, leaching, solvent extraction and precipitation methods, respectively. After all studies, the optimum roasting temperature and roasting duration are determined as 600 °C and 1 hour. In the extraction stage, the highest leaching efficiency is achieved with 5 M HCl, 1-hour leaching duration, 1/3 solid/liquid ratio and 35 °C leaching temperature. While methyl tri C8-C10 ammonium chloride (Adogen 464) is used for the removal of iron from produced solution, di-(2-ethylhexyl) phosphoric acid (D2EHPA) is used for the removal of thorium. As a result of solvent extraction studies, the solution containing rare earth elements is precipitated under optimum conditions. After precipitation, the product contains 99.65% rare earth oxides.

Received Date: 22.09.2021

Accepted Date: 19.09.2022

1. Introduction

Today, engineering studies in the fields of geology, mining, metallurgy and materials have accelerated to balance the supply and demand of rare earth elements (REE), which is one of the main sources of technological developments. Especially the development and usage of permanent magnets made of an alloy of neodymium, iron and boron NdFeB, providing better magnetic properties than the ones before them have had a big impact on improving this field. Due to the usage of these magnets in fields such as electric vehicles and wind turbines, the demand for REEs is constantly increasing. Today, the biggest supplier is China (Cheisson and Schelter, 2019). Considering the increasing worldwide demand and environmental problems caused by REE mines in China, in recent years, the trends towards recycling and alternative mineral resource has started (Sprecher et al., 2014;

Swain and Mishra, 2019). These trends also arise because of strategic reasons. For example, according to the European Commission and other studies, REE is classified as a critical raw material since the price fluctuations in 2011 (European Commission, 2020). The 11th Development Plan, set Türkiye's development vision, and used it as a basic roadmap, aims to develop projects for REEs to meet the raw material needs of the industry, and studies were started for this purpose. The primary REE resources are bastnaesite, monazite and xenotime. Although parisite mineral [Ca(Ce, La)₂(CO₃)₃F], contains lanthanum and cerium and is similar in structure to bastnaesite, cannot be used to produce REE (Obuz et al., 2018). In previous studies, the ore mineral observed in the Eskişehir-Beylikova area were mentioned as barite, fluorite and bastnaesite (Altaş et al., 2018). However, as a result of the recent mineral liberation analysis on the Eskişehir-Beylikova ore, it was determined that the REE-bearing main

Citation Info: Güneş, H., Obuz, H. E., Akçay, H., Kara, Ç., Erdem, A., 2023. Production of rare-earth oxides from Eskişehir-Beylikova complex ores. Bulletin of the Mineral Research and Exploration 170, 87-97. <https://doi.org/10.19111/bulletinofmre.1180222>

*Corresponding author: Ayşe ERDEM, ayse.erdem@mta.gov.tr

mineral is Th-parisite (Yeşilören Görmüş et al., 2021). For the evaluation and separation of REE-bearing ores, hydrometallurgy is one of the main methods (Erdem et al., 2021). For the separation and purifications to be carried out in the further stages, the REEs must be transferred to the solution. The process is solving of ores in different solvents such as acids and bases and getting the valuable elements into a solution is called leaching (Krishnamurthy and Gupta, 2015).

In the literature for REE extraction from solids, the soluble forms of REE-bearing minerals are formed by applying a roasting process at first. These processes can be classified as oxidising roasting (Zhao et al., 2018), heating with sulfuric acid (Kul et al., 2008) and chlorination roasting (Chi et al., 2004). In this step in the solution extracted from solid, other elements in the ore structure are also observed depending on ore type and extraction conditions. The solvent extraction technique is used in the separation and purification of the REEs by utilizing some characteristic chemical properties of them (Qi, 2018). This technique is carried out to ensure dispersion of the intended amounts of the required elements by creating two immiscible liquid phases. While one of the phases that are used, includes REE ions the other is the organic components that dissolved in an apolar solvent.

The mentioned organic components are structures that form complexes with metal ions, also called ligands. In this technique, the metal-ligand complexes that are produced by coordination bonds transfer to the organic phase and the desired separation are achieved (Choppin and Morgenstern, 2000; Rydberg et al., 2004; Lawrence, 2010). Sadri et al. (2017) obtained rare earth oxalates by roasting with sulfuric acid at 200 °C, taking to the solution with water, and precipitating with oxalic acid from monazite collected from Marvasat (Iran) placer deposit. Walawalkar et al. (2016), on the other hand, studied REE enrichments from phosphogypsum which is the main by-product of phosphoric acid the leaching by three different acids.

Although the best efficiency is with nitric acid, they argued that hydrochloric acid is more suitable due to the cost of extraction (Walawalkar et al., 2016).

Kursunoglu et al. (2021) used the sulfuric acid roasting technique on bastnaesite-bearing ore instead

of the direct acid leaching method. Then, they obtained rare earth oxalates by taking the obtained solid into a solution with water and precipitating it with oxalic acid directly. After the calcination of these oxalates, the obtained rare earth oxide (REO) product contains 6 % thorium (Th). It is known that this high thorium content will be a problem the matter such as operation and waste management, and so dangerous for human health (Judge and Azimi, 2020). The elements like Fe and Th that come from the mineral after the solution will affect the purity of the solution and may cause problems in the process and must be taken away. For thorium components to be by-products, iron which can display co-execution is emphasized. El Afifi et al. (2019) achieved the elimination of the Th and Fe from chloride solutions containing REE by applying direct precipitation with potassium sulfate and sodium sulfide. However, this technique was not able to provide enough explanation of the output of Th as a by-product. In the study done by Erdem et al. (2020), after the removal of Fe, U and Th from the solution by solvent extraction, the Th recovery process is started. REE solutions which are purified from impurities, can be evaluated by both direct solvent extraction and precipitation-dissolving. In this study, solving and precipitation steps are examined for the next studies in which REE separation will be made. After eliminating the Fe, U and Th impurities from the solution, using the solubility product values, a precipitation method is applied in which impurities that have high concentrations such as Al, Ca, Mn are not present.

2. Raw Material and Technique

2.1 Raw Material and Equipment

The raw ores taken from the Eskişehir-Beylikova area are first subjected to a beneficiation process in General Directorate of Mineral Research and Exploration laboratories. Because of the differences in the grain sizes of the minerals and abrasion resistance, the pre-concentrate production scrubbing method is used primarily. The -10 µm sample obtained as a result of abrasion was subjected to barite flotation and the samples to be used in metallurgical studies were prepared. The pre-concentrate produced as a result of these processes was used in roasting. After the processes, the concentration of fluorite-REE produced from raw minerals is determined

with the X-Ray Fluorescence Spectrometer (XRF) and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICPAES). The roasting temperatures of ore are determined by Differential Thermal Analysis-Thermal Gravity (DTA-TG). All of the acids and chemicals used and di-2-Ethylhexyl phosphoric acid (D2EHPA), tri octyl amine (Alamine 336), and decyl alcohol (1-Decanol) are of analytic quality. Kerosene is acquired from local sources. All of the solvents are directly used without any purification process.

Metal concentration in the solution is determined with the Agilent 725 Series ICP-OES. Concentrations in the solid material were determined with the Thermo Scientific ARL Perform'x 388 XRF. Energy and weight changes with the temperature were determined by SETARAM brand labSys evo model TG-DTA-DSC device.

2.2. Hydrometallurgical Processes

Before solving the solid sample, the roasting experiments are done by a rotary furnace at different temperatures, based on the data obtained from DTA analysis. In these experiments, 700g of sample for each temperature is fed into the preheated oven. By rotating the oven at 30 rpm, the sample was mixed homogeneously at the specified temperature. The sample is placed in a homogeneous temperature area inside the oven and does not overflow. The temperature in the homogeneous temperature area inside the furnace was measured by a thermocouple. After the roasting temperature was determined, experiments were carried out to determine the roasting time at the same temperature. To examine the effect of roasting temperature and time, the extraction time was kept constant for one hour with 5 M HCl with a 1/3 solid/liquid ratio. As a result of the experiments with sulphuric acid (H₂SO₄), hydrochloric acid (HCL) and nitric acid (HNO₃) at different concentrations, the most suitable acid and solid/liquid ratio (1/3,1/4,1/5), extraction time and temperature parameters are determined. The solids prepared at the determined roasting temperature and time were weighed in the required quantities. Then, the solids were slowly added to the acids prepared in the glass beaker placed on the magnetic mixer. After the addition of all the solids, the extraction process is commenced. During the extraction, a Teflon-coated magnetic mixer

was used to ensure that the suspension between the solid-liquid particles was homogeneous. The same diameter beakers and the same mixer were used for all experiments. All experiments were carried out in the same type of magnetic mixer and the mixing speed was kept constant at 550 rpm. When extraction was completed, samples were taken and filtered by using Whatman No: 3 filter paper, a Bühner funnel and Nuce flask. The solid remaining on the filter paper was washed with pure water. The volume of the solution produced from solid-liquid separation is determined and analysed in the ICP-OES device. The remaining solid was dried at 105 °C for 24 hours. The remaining solid was weighed and analysed by XRF. Solvent extraction experiments were carried out in a glass beaker and mixed with a Teflon propeller in a two-phase mechanical mixer. As a result of solvent extraction experiments performed with determined parameters (Erdem et al., 2020), inlet and outlet solutions were analysed and loading rates were determined.

For REE precipitation from the solution, 0,8 mole/l oxalic acid solution was used. REE/oxalate mole ratio, precipitation temperature and time parameters were investigated. As a result of the examination, the parameters with the most REE and the least impurity precipitated were determined. To determine the mixing time, the sample was taken and filtered by calculating the time elapsed since the oxalic acid was added. The filtrate was concentrated with nitric acid to prevent further precipitation.

2.3. Evaluation of the Data

The weight loss values observed in the roasting step are calculated by the formula in Equation 1. In this formula the m_{input} represents the mass entering the roasting and the m_{output} represents the mass of the final product.

$$\% \text{ weight loss} = \frac{m_{input} - m_{output}}{m_{input}} \quad (1)$$

The solving rate calculated over the metal concentration at the extraction stage is presented in Equation 2. In equation 2 C_{sol} represents the metal concentration as mg/l in the solution detected by ICP-OES, V_{stock} represents the volume of solution after washing as litre, C_{solid} represents the concentration of

the metal as mg/kg in the input solid which wishes to take into to solution, and m_{input} is the weight of input solid as kg.

$$\text{Solving rate (from liquid)} = \frac{C_{sol} - V_{stock}}{C_{solid} \times m_{input}} \quad (2)$$

The data obtained from the measurement XRF was evaluated in Equation 3.

In Equation 3, C_{input} represents the percent concentration of metal wished to calculate to solving rate in the input solid material, m_{input} weight of the input solid, C_{output} percent concentration of the metal wish to calculate to solving rate in the output solid material, m_{output} weight of the output solid.

$$\text{Solving rate ion (from solid)} = 1 - \frac{C_{output} - m_{output}}{C_{input} \times m_{input}} \quad (3)$$

The precipitation rate is calculated by Equation 4.

In Equation 4, C_{output} represents the metal concentration value in mg/l of remain in solution after precipitation, C_{input} metal concentration value in mg/l of solution before precipitation, V_{output} is the measured volume after precipitation, V_{input} is the volume of precipitated solution in litre.

$$\text{Precipitation rate} = 1 - \frac{C_{output} - V_{output}}{C_{input} \times V_{input}} \quad (4)$$

3. Experimental Results

3.1. Raw Material Categorization

The contents of the fluorite-REE pre-concentrate obtained from the Eskişehir-Beylikova complex ore determined by the XRF are presented in Table 1. The pre-concentrated ore contains a total of 8.55% rare earth oxide (TREO). DTA-TG analysis was carried out to determine the roasting temperature before the extraction experiments. The DTA-TG analysis result is presented in Figure 1.

Table 1- Composition of Fluorite-REE pre-concentrate obtained from Eskişehir - Beylikova region.

Oxide	CeO₂	La₂O₃	Nd₂O₃	Pr₆O₁₁	Y₂O₃	Er₂O₃	ThO₂	U₃O₈
Composition (%)	4.52	2.92	0.75	0.26	0.09	0.01	0.38	0.03
Oxide	BaO	Fe₂O₃	CaF₂	SiO₂	Al₂O₃	MnO	MgO	LOI
Composition (%)	5.81	9.84	31.8	14.2	6.6	1.66	1.08	12.6

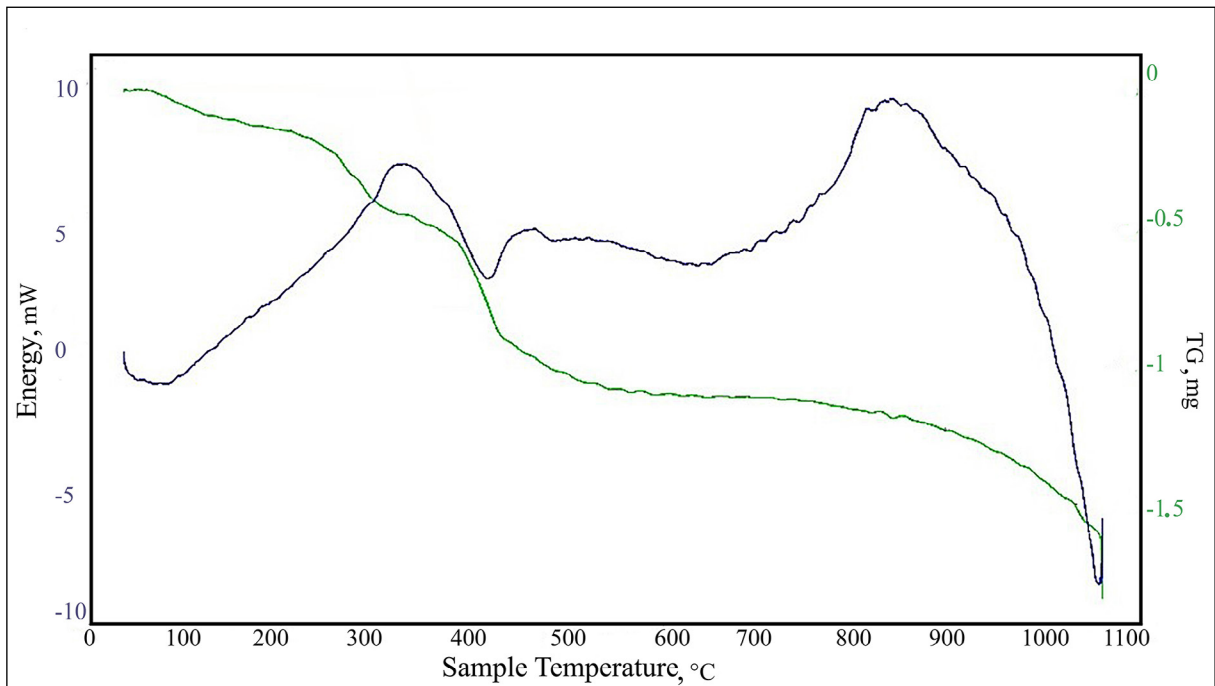


Figure 1- DTA-TG analysis of the Fluorite-REE pre-concentrate obtained from the Eskişehir - Beylikova region.

As a result of the DTA analysis, it was observed that an endothermic reaction happens at a temperature of 414°C. This reaction was compared with later X-Ray diffraction analysis (XRD) analyses and it was determined that the roasting process should be started at 400 °C. The weight loss data obtained in TG analysis is determined as 1.3% in the 210 - 330°C and 2% in the 365 - 470°C range.

3.2. Roasting and Extraction Optimisation

The ore samples were roasted for 1 hour at 400, 500 and 600°C, respectively, and then extracted with HCl. The results obtained with Equation 3 are presented in Figure 2.

As seen in Figure 2, the solving rate increases between the temperatures of 400-600°C, and the rate decreases when the temperature is increased further. The solving rate of total rare earth element (T-REE) increased to 89%, at 600 °C which is the maximum temperature in the roasting process. After, the roasting temperature is determined as 600 °C, at this temperature, with the same extraction parameters, the effect of roasting duration on solving rate was investigated. The results are presented in Figure 3.

While examining the effect of roasting time on taking REEs into solution, while an increase in the solving amount between no roasted 0 points with the 1-hour roasting point in the roasting duration axis, after this, solving rate remained stable at the continued

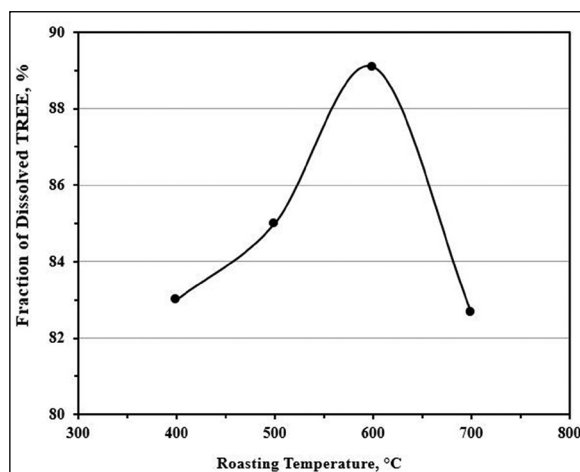


Figure 2- The effect of roasting at different temperatures on the solving rate (1-hour roasting time, 5M HCL, 1/3 solid/liquid ratio, 1-hour extraction time).

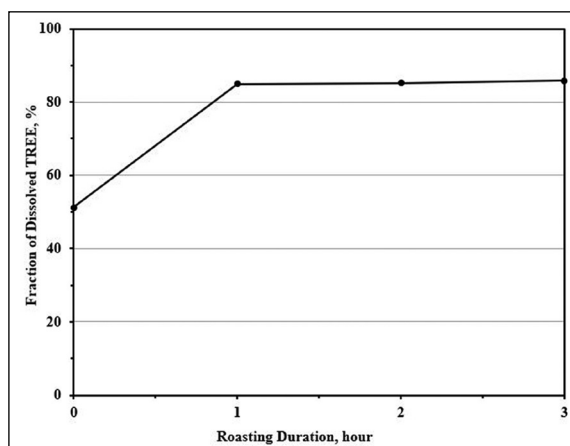


Figure 3- The effect of roasting time on REE dissolution (600 °C roasting temperature, 5 M HCL, 1/3 solid to liquid ratio, room temperature).

roasting after 1 hour. In this process, the weight loss is calculated as %6 on average.

Direct leaching and post-roasting leaching experiments were carried out to take REEs into solution. In these experiments, the most suitable roasting parameters are used that were determined in the previous steps. The obtained solving rates by extraction with three different acids are given in Figure 4.

In the leaching experiments performed with HCl (Figure 4a), a 40% difference is observed in the solving rate between the non-roasted and roasted samples. It wasn't observed any differences in solving rate after 5 mole/l in the extraction experiments with roasting. In the experiments performed with HNO₃ (Figure 4b), the difference is less between the non-roasted and roasted samples. The solving rate obtained from HNO₃ leaching on the roasted sample is not at the same level as HCl leaching even if used at 8 mole/l. The solving rate in the leaching experiments performed with H₂SO₄ (Figure 4c) sharply decreased after 4 mol/l concentration. The reason for this is the high calcium (Ca) ratio contained in the concentrate. Because of the Ca ratio, calcium sulphate (gypsum) is formed in sulphuric acid extraction.

The 5 M HCl concentration, which was determined as the most suitable parameter, negatively affects the hydrodynamic interactions between the acid and the concentrate during the extraction. As a result, a sharp

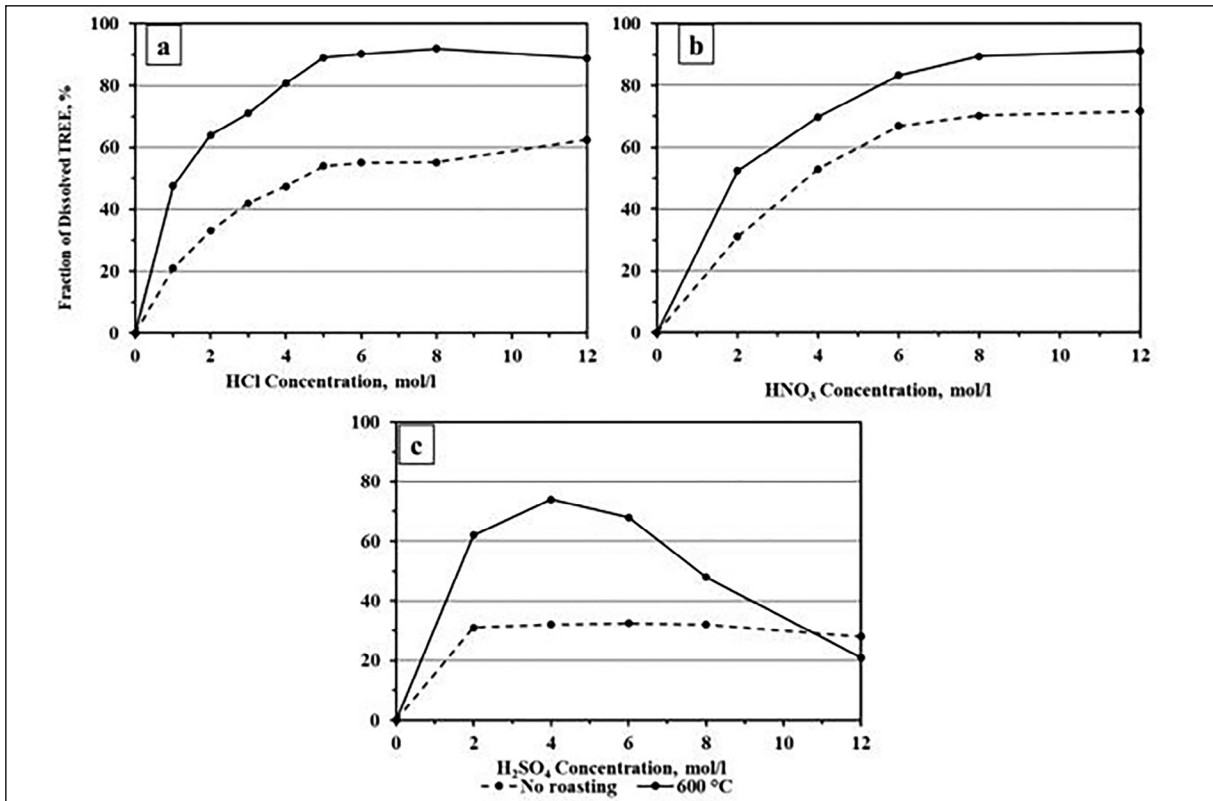


Figure 4- Extraction of unroasted (dashed line) and roasted samples with a) HCl, b) HNO₃, c) H₂SO₄ acids.

decrease is observed in the REE dissolution. According to the differences between these three acids, a higher solving rate with HCl at a lower concentration was determined. The parameters where the effect of 5 M HCl with solid/liquid is observed are tested. The results are presented in Figure 5.

When the effect of the solid/liquid ratio was examined, only a 0.2% increase was observed after the 1/4 ratio. For this reason, 1/4 of the solid/liquid ratio is used for the following steps. Then, the experiments were carried out to examine the effect of leaching temperature on solving rate and the results given in Figure 6.

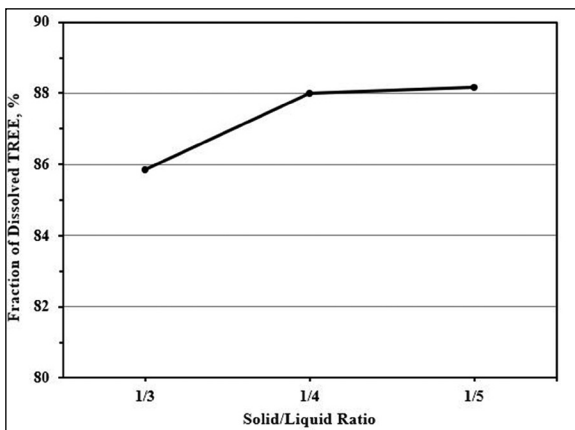


Figure 5- The effect of solid/liquid ratio on the solving ratio in the pre-concentrate sample that was roasted at 600 °C for 1 hour and extracted with 5 M HCl acid for one hour at room temperature.

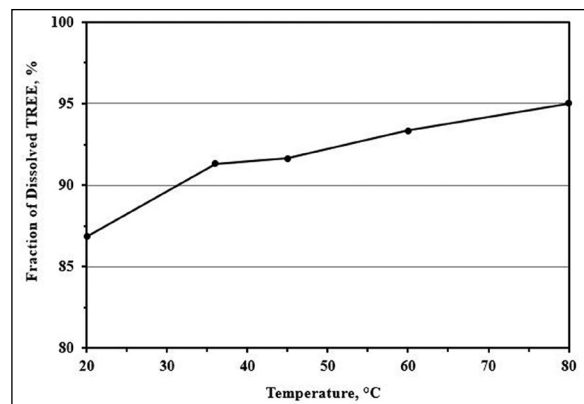


Figure 6- The effect of leaching temperature on solving rate on the pre-concentrate sample which is 1 hour roasting at 600 °C and, one hour leached with 5 M HCl acid and 1/4 solid/liquid ratio.

When the extraction temperature was increased from room temperature to 35 °C, 6% increase was observed in solving rate. Subsequently, as the extraction temperature was increased lower increases were observed in the solving rate. Even though the solving rate was increased in the extraction at 80 °C, because of heating costs for keeping extraction at high temperatures, it is evaluated as disadvantageous. For this reason, it was concluded that the optimum extraction temperature is 35 °C. To examine the effect of the extraction time on the determined optimum parameters, the solving rates obtained in the experiments carried out between 15-120 minutes are presented in Figure 7.

When the extraction time was increased from 15 minutes to 60 minutes, an increase of 10% was observed in the solving rate, while an additional 2% increase in the solving rate was observed when the extraction time was increased from 60 minutes to 120

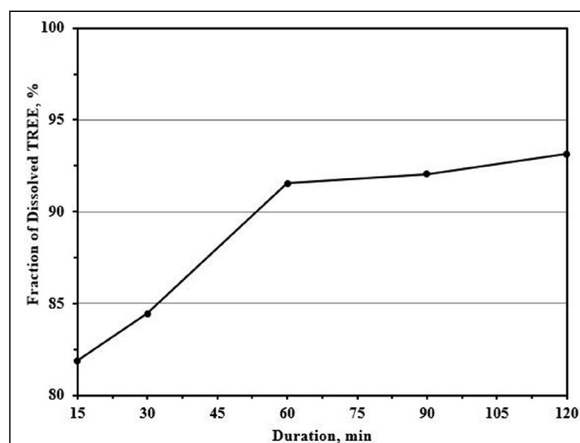


Figure 7- The effect of extraction time to take REE into solution from pre-concentrate under the determined optimum parameters (1 hour roasting at 600 °C, 5 M HCl, 1/4 solid/liquid ratio, 35 °C extraction temperature).

minutes. Considering these data, it was determined that the extraction time of 60 minutes was sufficient for the rate of taking REEs into solution. The concentrations of waste products of input, roasted and extraction solids are presented in Table 2.

The extraction was done in three repetitions under optimum conditions which are 1 hour roasting at 600 °C temperature, and then 1/4 solid/liquid ratio, 35 °C temperature for 60 minutes with 5 M HCl. During these repetitive extractions, different stock volumes are acquired. Concentrations varying according to stock volumes were determined with the ICP-OES. The mean and standard deviations of these values were calculated. The results are presented in Table 3.

Table 3- The content of the solution obtained as a result of roasting and extraction under optimum conditions, determined by ICP-OES.

Element	Average concentration (g/l)	Standard deviation (g/l)
TREE	22.00	0.68
Al	5.30	0.46
Ba	0.67	0.10
Ca	5.09	0.35
Fe	10.58	1.60
Mn	3.91	0.09
Si	0.16	0.01
Th	0.63	0.01

3.3 Solvent Extraction Studies

For REO production from the solution obtained by roasting and extraction of the above-mentioned pre-concentrate, the oxalic acid was added until precipitated all REEs, at first. The precipitation rate of

Table 2- XRF results of concentrate, roasted concentrate and residue samples.

Sample	CeO₂	La₂O₃	Nd₂O₃	Pr₆O₁₁	Y₂O₃	Er₂O₃	ThO₂	U₃O₈
Concentrate (%)	4.52	2.92	0.75	0.26	0.09	0.01	0.38	0.03
Roasted (%)	4.82	3.18	0.80	0.26	0.10	0.02	0.40	0.03
Waste (%)	0.78	0.44	0.05	<0.01	0.04	0.02	0.14	0.01
Sample	BaO	Fe₂O₃	CaF₂	SiO₂	Al₂O₃	MnO	MgO	LOI
Concentrate (%)	5.80	9.80	31.80	14.20	6.60	1.70	1.10	12.60
Roasted (%)	5.90	10.50	32.60	15.50	7.30	1.80	1.20	7.70
Waste (%)	6.10	10.60	44.00	18.30	4.20	0.60	1.20	5.30

REE oxalates is much higher than that of impurities. The reason of this, the differences solubility product among metal-oxalate salts. Therefore, the solubility of the formed REE oxalates in water is much lower than the oxalates of other elements. For this reason, when the pH value of the solution was 0, the oxalate product obtained from the precipitation with the addition of 30% oxalic acid was calcined until it was completely oxidized and XRF analysis was carried out. The results of the XRF analysis are shown in Table 4.

Table 4- XRF analysis of the final REO concentrate obtained when the pH value is 0, with the addition of 30% oxalic acid direct precipitation from the pre-concentrate obtained by roasting and extraction, under determined optimum conditions.

Element	Composition (%)
TREO	96.20
CeO ₂	53.04
La ₂ O ₃	28.9
Nd ₂ O ₃	9.02
Pr ₆ O ₁₁	3.69
Sm ₂ O ₃	0.52
Y ₂ O ₃	0.53
Al ₂ O ₃	0.15
CaO	0.79
Fe ₂ O ₃	0.40
MnO	0.06
SiO ₂	0.24
ThO ₂	1.85
Minor Oxides	0.80

The solubility product values of the compounds formed by the oxalate ions of Fe, Ca, Al, Th and Mn elements, which have high concentrations in the solution content, cause precipitation, albeit to some extent. When Fe and Th elements are removed from the solution, the REO contents of the obtained solid material will increase. During the Fe and Th removal process, applied optimum parameters determined by Erdem et al. (2020). While 20% in volume Adogen 464 in kerosene with 1/1 organic/aqueous ratio at the -0,58 pH was used for Fe removal, for Th removal was used 30% D2EHPA, solved in kerosene, with the 1/3 organic/aqueous ratio. The contents of the Fe and Th removed solution are given in Table 5.

Table 5- Contents of the Fe and Th removed solution which used the parameters determined by Erdem et al. (2020), from the final concentrate mentioned in Table 4.

Element	Average concentration (g/l)
TREE	22.50
Al	4.91
Ba	0.74
Ca	4.38
Fe	<0.001
Mn	4.24
Si	0.14
Th	0.01

3.4 Precipitation Studies

After oxalate precipitation, directly from the extraction solution, the major impurity was determined to be Th, followed by Ca and Fe. Fe and Th removal provide obtaining valuable by-products, and higher purity REO concentrate. For this reason, from the Fe and Th free solution, oxalic acid precipitation studies were carried out. The effects of different initial pH values and different oxalic acid adding ratio are presented in Figure 8.

The acquired data shows that oxalic acid mol ratios cause precipitation in all pH values. In these parameters, where fixed 30 minutes mixing time, and at -0.3 pH and 0 pH values, it is observed that as the oxalic acid mol ratio increases T-REE precipitation ratio also increases rapidly.

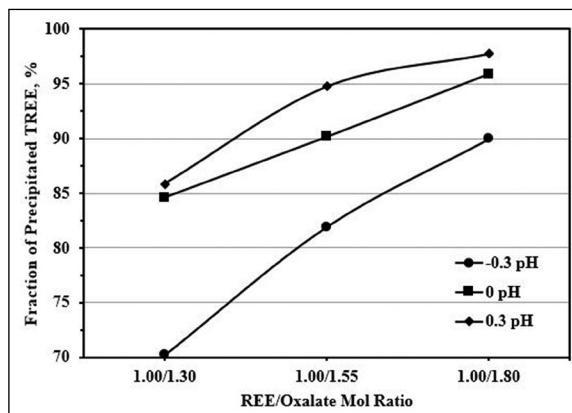


Figure 8- The effect of REE/oxalate mol ratio in different pH values on precipitation ratio of REE in the final REO concentrate (30 minutes of mixing time, 20 °C precipitation temperature).

If at the 0.3 pH, between 1.00/1.55 and 1.00/1.80 REE/oxalate mole ratios, the precipitation ratio increasing speed is decreased. The effect of time parameters, which was getting the maximum precipitation ratio when adding 1.00/1.80 REE/oxalate mole ratio at 0.3 pH value, are observed and presented in Figure 9.

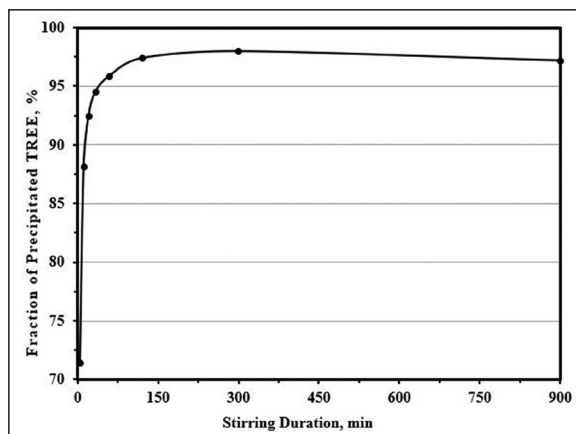


Figure 9- The effect of mixing time of the obtained solution on the REE precipitation ratio (1.00/1.80 REE/oxalate mol ratio, 20 °C precipitation temperature).

When the effect of mixing duration is observed, it is revealed that there is an increment until the 120th second. Between 120-300 seconds there is a 2% increase in the REE precipitation ratio but there is not increasing in the further times. For this reason, 300 seconds is determined as the most suitable for mixing time for precipitation. Then, the parameters were tested to examine the effect of temperature on precipitation, and the results are presented in Figure 10.

The increase of less than 1% was observed between 40-60 °C. After that, precipitation rate is decreased. Since the temperature changes have not been significantly different in the REE precipitation rate, it is decided that the room temperature is the optimum parameter for the experiment. Rare earth oxides were obtained by calcining the rare earth oxalates obtained from the precipitation process using these parameters. The obtained REO was analysed by the XRF and presented the results in Table 6.

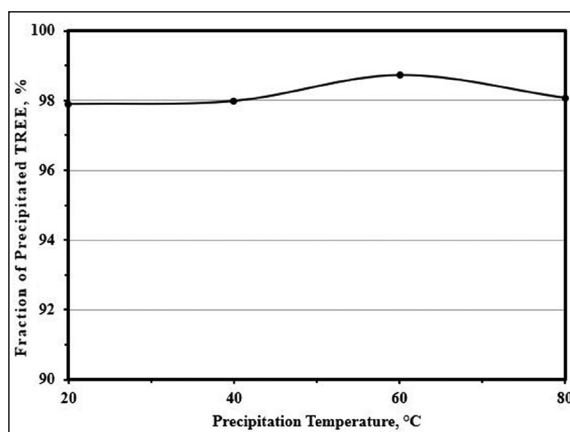


Figure 10- The effect of temperature on REE precipitation ratio (1,00/1,80 REE/oxalate mol ratio, 300 seconds mixing duration). The study of the effect of precipitation temperature revealed a change between 20-40 °C.

Table 6- XRF analysis of REO solid obtained by precipitation after solvent extraction

REOs	Composition (%)
TREO	99.65
CeO ₂	53.91
La ₂ O ₃	29.09
Nd ₂ O ₃	11.59
Pr ₆ O ₁₁	4.31
Sm ₂ O ₃	0.44
Y ₂ O ₃	0.31
Minor Oxides	0.35

4. Discussion

As a result of the DTA analyses on the concentration obtained from the Eskişehir-Beylikova complex mineralization in the ore dressing laboratory of MTA, the reaction at 400 °C was taken as a basis and the roasting temperatures were studied at 400-700 °C. After roasting, extraction was done with 5 M HCl at 1/3 solid/liquid ratio for 1 hour. According to the test results, the highest solubility rate was determined at 600 °C. In the roasting time tests carried out at 600 °C, it was determined that sufficient solubility rate was achieved in 1 hour roasting time. In the experiments performed with HCl, H₂SO₄ and HNO₃ at the determined roasting temperatures, it was understood that roasting was necessary to increase the solubility rate. Compared to other acids, it has been observed that a higher solubility rate is achieved at lower concentrations in studies with HCl acid. As a

result of increasing in the concentration by studies with H_2SO_4 , the free sulphate ions in the environment combine with the Ca^{+2} ions to form gypsum. Thus, it causes insufficient dissolution of REEs in the environment. Cost and high concentrations are disadvantages of the solution to be made with HNO_3 . 5 M is preferred as the HCl concentration, and in the experiments performed with this constant parameter, it is determined that the most effective parameter is temperature. After the solution experiments, the optimum parameters are determined as 5 M HCl, 1/4 solid/liquid ratio and 35 °C extraction temperature. The solubility rate for the whole REE is calculated as %91.55. As a result of the serial experiments, solution contains 22 g/l REE, 10 g/l Fe^{+n} and 0.63 g/l Th^{+4} . When oxalate precipitation and calcination are made directly from the solution, it is determined that only Th, Ca and Fe elements among the impurities in the solution caused large impurities in the final product. From these impurities, Fe and Th are removed from the solution because of they may affect the price and marketability of the final product.

Kursunoglu et al. (2021) used the roasting technique with sulfuric acid on the ore-bearing bastnaesite, which they obtained from this region. Then, this solid material is dissolved in water, precipitated with oxalic acid directly, and obtained rare earth oxalates. Rare earth oxide (REO) product obtained as a result of the calcination of these oxalates contain 6% Th (thorium). It is known that high Th contents will be problem for operation and waste management, and very dangerous for human health (Judge and Azimi, 2020).

A purified solution was obtained by applying the optimum parameters used in previous studies for Th and Fe removal (Erdem et al. 2020). The precipitation parameters from the purified solution were tested. After the appropriate REE/oxalate mole ratio was determined, it is understood that the precipitation took place in a quick time. When precipitation was made with the determined optimum parameters, just 0.35% non-REE oxides were determined in the final product. In this study, parasite has been detected in addition to bastnaesite in complex mineralization (Yeşilören Görmüş et al., 2021). Contrary to known,

REO recovery from parasite-bearing complex ore has been demonstrated in the laboratory application.

5. Conclusion

This study examined the production of REO from fluorite concentration obtained from barite, fluorite, and REE-bearing Eskişehir-Beylikova complex ore. The concentration is firstly roasted and the optimal roasting temperature is determined as 600 °C for extraction. In this temperature, the extraction tests with three different acids showed that most suitable acid for extraction is HCl. The optimal HCl concentration is determined as 5 M mol/l.

After this stage, the optimum conditions obtained with 5 M HCl are 1/3 solid/liquid ratio, 35°C extraction temperature and 60 minutes extraction time. With these parameters, the solubility rate of TREE is determined as 91.55%. T-REE concentration in the solution is measured at 22 g/l. At these stages, obtained REO purity after direct oxalate precipitation and calcination is determined as 96.20%. In this step, ThO_2 is a greatest impurity.

For the minimize ThO_2 and other impurities, the solvent extraction technique is applied. After the extraction with the optimum parameters determined in the previous studies, the precipitation parameters are optimized. To that, optimisation of the precipitation experiments is done. After this optimization, the most suitable precipitation parameters are determined as 1.00/1.80 REE/oxalate mol ratio with a mixing time of 300 seconds at room temperature. REE oxalates obtained with these parameters are calcined and REO concentration is produced. The TREO content of the concentration is determined as 99.65%.

Acknowledgements

This study was supported within the scope of the scientific research project titled “Technological Evaluation of Eskişehir Beylikova Complex Ore and Development of Production Process” of MTA General Directorate with the code 2020-35-16-01-8. The authors thank to Zümür ALKAN and Ayşe KOYUNCU for their assistance with the analyses.

References

- Altaş, Y., Tel, H., İnan, S., Sert, Çetinkaya, B., Sengül, S., Özkan, B. 2018. An experimental design approach for the separation of thorium from rare earth elements. *Hydrometallurgy* 178, 97–105.
- Cheisson, T., Schelter, E. J. 2019. Rare earth elements: Mendeleev's bane, modern marvels. *American Association for the Advancement of Science* 363 (6426), 489–493.
- Chi, R., Zhang, X., Zhu, G., Zhou, Z. A., Wu, Y., Wang, C., Yu, F. 2004. Recovery of rare earth from bastnaesite by ammonium chloride roasting with fluorine deactivation. *Minerals Engineering* 17(9–10), 1037–1043.
- Choppin, G. R., Morgenstern, A. 2000. Thermodynamics of solvent extraction. *Solvent Extraction and Ion Exchange* 18(6), 1029–1049.
- El Afifi, E. M., Borai, E. H., Shahr El-Din, A. M. 2019. New approaches for efficient removal of some radionuclides and iron from rare earth liquor of monazite processing. *International Journal of Environmental Science and Technology* 16(12), 7735–7746.
- Erdem, A., Babuçoğlu, Y., Güneş, H., Obuz, H. E., Özdemir, E., Kara, Ç., Diktepe, Ş., Akgül, M. B., Özen İlik, B., Akçay, H. 2021. Nadir Toprak Minerallerinin Fiziksel Ayrılması ve Flotasyonu. Derleme. *International Journal of Pure and Applied Sciences* 7(2), 321-345.
- Erdem, A., Güneş, H., Kara, Ç., Akçay, H., Gülmez, A., Alkan, Z. 2020. Production of high purity thorium oxide from complex ores leach liquor. *Bulletin of the Mineral Research and Exploration* 164, 1–7.
- European Commission. 2020. Communication from the commission to the European parliament, the council, the European economic and social committee and the committee of the regions.
- Judge, W. D., Azimi, G. 2020. Recent progress in impurity removal during rare earth element processing: A review. *Hydrometallurgy* 196, 105435.
- Krishnamurthy, N., Gupta, C. K. 2015. *Extractive Metallurgy of Rare Earths*. CRC Press, United State of America.
- Kul, M., Topkaya, Y., Karakaya, I. 2008. Rare earth double sulfates from pre-concentrated bastnaesite. *Hydrometallurgy* 93(3–4), 129–135.
- Kursunoglu, S., Hussaini, S., Top, S., Ichlas, Z. T., Gokcen, H. S., Ozsarac, S., Kaya, M. 2021. Production of mixed rare earth oxide powder from a thorium containing complex Bastnaesite ore. *Powder Technology* 379, 641–654.
- Lawrance, G. A. 2010. *Introduction to Coordination Chemistry*. John Wiley and Sons Ltd., United Kingdom.
- Obuz, H. E., Güneş, H., Kara, A., Ugurluer, D., Babuccuoglu, Y., Alkan, M. 2018. Leaching Kinetics of Rare-Earth Elements from Complex Ores by Acidic Solutions. *Extraction* 2391–2398.
- Qi, D. 2018. *Hydrometallurgy of Rare Earths: Extraction and Separation*. Elsevier, 1-797.
- Rydberg, J., Choppin, G. R., Musikas, C., Sekine, T. 2004. *Solvent Extraction Equilibria. Solvent Extraction Principles and Practice, Revised and Expanded*. CRC Press 121–217.
- Sadri, F., Rashchi, F., Amini, A. 2017. Hydrometallurgical digestion and leaching of Iranian monazite concentrate containing rare earth elements Th, Ce, La and Nd. *International Journal of Mineral Processing* 159, 7–15.
- Sprecher, B., Xiao, Y., Walton, A., Speight, J., Harris, R., Kleijn, R., Visser, G., Kramer, G. J. 2014. Life cycle inventory of the production of rare earths and the subsequent production of NdFeB rare earth permanent magnets. *Environmental Science and Technology* 48(7), 3951–3958.
- Swain, N., Mishra, S. 2019. A review on the recovery and separation of rare earths and transition metals from secondary resources. *International Journal of Cleaner Production* 220, 884–898.
- Walawalkar, M., Nichol, C. K., Azimi, G. 2016. Process investigation of the acid leaching of rare earth elements from phosphogypsum using HCl, HNO₃ and H₂SO₄. *Hydrometallurgy* 166, 195–204.
- Yeşilören Görmüş, N., Gürtekin, G., Erdem, A., Gülmez, A. 2021. Kızılcaören (Sivrihisar) bölgesi nadir toprak element (NTE) içeren minerallerin mineral serbestleşme analiz (MLA) yöntemi kullanılarak tayini. *International Journal of Pure and Applied Sciences* 7(2), 251-264.
- Zhao, L., Wang, L., Shuai, G., Long, Z., Cui, D., Huang, X. 2018. Thermal decomposition and oxidation of bastnaesite concentrate in inert and oxidative atmosphere. *Journal of Rare Earths* 36(7), 758–764.