Artıbilim: Adana Alparslan Türkeş Bilim ve Teknoloji Üniversitesi Fen Bilimleri Dergisi 3(1), Haziran 2020, 34-40
Adana Alparslan Turkes Science and Technology University Journal of Science

Investigation of extraction of bastnaesite ore by alkaline leaching

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Geliş Tarihi:23.10.2019 **Kabul Tarihi:**26.06.2020

Abstract

In this study, a composite sample was prepared from the representative samples of the experiments taken from three different areas in Eskisehir-Kizilcaoren region, Turkey, and this composite sample was used for the leaching experiments. Considering the particle size analysis of the sample, the d_{50} and the d_{80} sizes of the sample were found to be 0.45 mm and 1.58 mm, respectively. It was determined from the fractional particle size analysis that the sample contained 2.79% La, 2.27% Ce, 0.29% Nd, 450 ppm Y, 0.69% Th, and 200.3 ppm U. The samples reduced to-38 µm were used for the leaching experiments. The leaching parameters, namely, 15-50% solids ratio, 30-320 min. of the leaching time, 25-500 kg/ton NaOH dosage, and 25-70°C pulp temperature were investigated in the leaching experiments. The optimum conditions for the leaching experiments for Th and REE (Ce, Nd, La) were obtained as 35% solids ratio, 500 kg/ton NaOH dosage, 120 min leaching time, and 50°C pulp temperature. As a result of the experiments carried out under these optimum conditions, 65.15% Th, 54.21% Cd, 45.44% Nd, and 54.01% La dissolution efficiencies were obtained.

Keywords: Alkaline leaching, Bastnaesite, Rare earth elements, thorium,

Bastnazit cevherinin alkali liçiyle ekstraksiyonunun araştırılması

Özet

Bu çalışmada, Eskişehir-Kızılcaören yöresindeki üç farklı bölgeden alınan temsili numuneler harmanlanarak kompozit bir numune hazırlanmış ve liç deneylerinde bu numune kullanılmıştır. Tane boyutu analizi sonuçlarına göre, numunenin d_{50} ve d_{80} boyutları sırasıyla 0,45 mm ve 1,58 mm olarak bulunmuştur. Fraksiyonel tane boyutu analizi sonuçlarına göre numunenin %2,79 La, %2,27 Ce, %0,29 Nd, 450 ppm Y, %0,69 Th ve 200,3 ppm U içerdiği tespit edilmiştir. Liç deneylerinde -38 µm tane boyutunda numuneler kullanılmıştır. Liç deneylerinde, %15-50 katı oranı, 30-320 dakika liç süresi, 25-500 kg/ton NaOH dozajı ve 25-70°C liç sıcaklığı parametrelerinin Th ve NTE çözünme verimleri üzerine etkileri araştırılmıştır. Deneylerde optimum koşullar, % 35 katı oranı, 500 kg/ton NaOH dozajı, 120 dakika liç süresi ve 50°C pülp sıcaklığı olarak elde edilmiştir. Bu optimum koşullar altında yapılan deneyler sonucunda %65,15 Th, % 54,21 Cd, % 45,44 Nd ve %54,01 La çözünme verimleri elde edilmiştir.

Anahtar Kelimeler: Alkali liçi, Bastnazit, Nadir toprak elementleri, Toryum,

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1. Introduction

Rare earth elements have unique chemical, catalytic, electrical, magnetic, and optical properties that make them essential in many high-tech components. The industrial applications of these elements have been extended to metallurgy, magnets, ceramics, electronics, chemical, optical, medical, agriculture, and nuclear technologies in the past century. The increasing demand for the rare earth elements in the world has required intensive studies for the extraction of rare earth elements from ores [1-5].

Thorium, a radioactive element with very high mobility, is also an important source, especially for nuclear researches. Thorium metal and its compounds are not used in structural engineering due to low tensile strength, low elasticity, high density, and corrosion resistance; but their alloys are solid, durable, and often unsupported materials, especially thorium-magnesium alloys are very rugged and heat resistant. Thorium oxide (ThO_2) is used in gas lamps, aerospace research, the production of pot and ceramic parts, televisions, electronic devices, special optical glasses, and scientific instruments [6-10].

Bastnaesite is a principal commercial rare earth ore mineral as rare earth fluorocarbonate, $RECO_3F$, which primarily contains light rare earth elements and slightly includes thorium. Bastnaesite is one of the most important mineral resources containing rare earth elements especially La and Ce. There are several hydrometallurgical methods for extracting rare earth elements and thorium from bastnaesite. They can be classified into two process methodologies: One is the acidic method and the other one is the alkali method using sodium hydroxide (NaOH) [11-16].

The leaching process is one of the most important steps of hydrometallurgical methods which are used for the extraction of thorium and rare earth elements. Inorganic acids, especially in recent years, organic acids have been commonly used as the leach reagents. Additionally, alkaline leaching has also started to be used in the extraction of thorium and rare earth elements. Barbosa et al. (2001) studied the effect of the main operational parameters such as temperature (150°-300° C), concentration of NaOH (50-75%), time of reaction (1-6 h), particle size of the concentrate (< 0.149 mm and <0.053 mm), and solid/liquid ratio (1/4 and 1/8). The results showed the technical viability of the alkaline leaching process with a rare earth extraction reaching values over 90%. Kandil and El Faramawy (2009) studied the leaching behaviour of Egyptian monazite in alkaline treatment in reflux instead of the pyrometallurgical process using mechanochemical treatment where grinding was carried out in the presence of sodium hydroxide and followed by pressure leaching in an autoclave that gave an incongruent result. It was found that the monazite was effectively decomposed in 2 h at~130°C using 600 g/l NaOH in the reflux. The recovery of thorium by this method under these conditions was about 98.1% [3, 17-19].

In this context, this study was aimed to investigate the recovery of thorium and rare earth elements from bastnaesite ore by NaOH leaching under the several leaching parameters.

2. Materials and methods

2.1. Materials

The representative samples were taken from three different areas in Eskisehir-Kizilcaoren region, and a composite sample was prepared to be used for the leaching experiments. The samples were classified in various sizes by way of size reduction with a roll crusher followed by sieving, and the particle size less than 38 µm was used for the leaching experiments in order to obtain the highest dissolution efficiency. The particle size analysis of the sample (Figure 1) showed that the d_{50} and the d_{80} sizes of the sample were found to be 0.45 mm and 1.58 mm, respectively. As a result of the chemical analysis of the sample, the sample contained 2.79% La, 2.27% Ce, 0.29% Nd, 450 ppm Y, 0.69% Th, and 200.3 ppm U (Table 1).

As a result of the thin and polished section studies for the sample, it was observed that the ore had a brecciated structure, and the main minerals forming mineralization in the sample were fluorite, barite, and bastnaesite (bound to Th and REE (Ce, Nd, La)). Bastnaesite mostly existed as a filling material between barite and fluorite minerals. Occasionally, it was observed to be nested in phases with fine fluorite and barite minerals. Fluorite and barite particles were observed to be partially distributed in each other, especially in fine sizes.

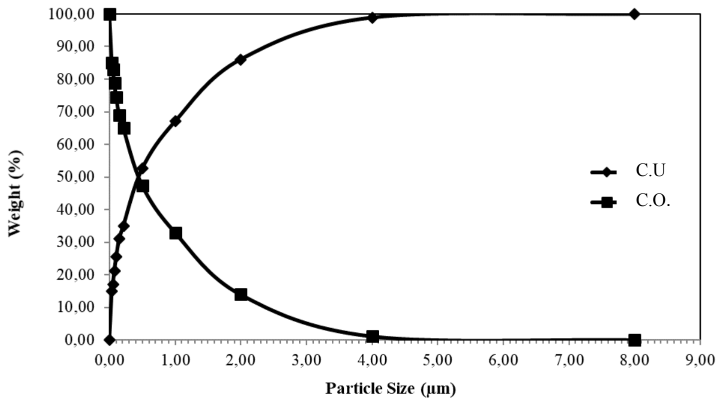


Figure 1. Oversize-undersize graphs of sample

Table 1. Result for chemical analysis of sample

C*	C (%)*	C	C (%)	C	C (ppm)*	C	C (ppm)	C	C (ppm)	C	C (ppm)
Ba	30.72	Al	0.66	Nb	21340	**U**	**200.3**	Rb	26.7	Hg	4.3
Ca	21.78	**Nd**	**0.29**	Mn	3127	As	150	Cu	13	Lu	4.3
F	13.78	Na	0.14	Sr	2620	Gd	69	Cr	12	Tm	3.7
S	4.21	Pr	0.11	Pb	712	Be	57	Bi	10	Sn	2.7
SiO_2	3.21	Mg	0.04	Zn	620	Dy	53	Ho	9.3	Cd	2.1
La	**2.79**	Ti	0.02	V	456	Mo	46	W	8.9	Cs	1.3
Ce	**2.27**	Sc	0.013	**Y**	**450**	Eu	31.3	Tb	7.7	Ni	1.22
K	0.85	LOI**	8.33	Sm	210,6	Zr	30.3	Co	5	Hf	0.6
Th	**0.69**										

C: Constituent;C (%): Content (%); C (ppm): Content (ppm)

**LOI: Loss on ignition

2.2. Methods

In this study, the effect of the NaOH leaching process on the dissolution efficiencies of Th, and REE (Ce, Nd, and La) was investigated to obtain from the bastnaesite samples. In this context, the solutions prepared with a ratio of 20% and 30% NaOH were used in the NaOH leaching experiments. In the experiments, the several leaching parameters, 15,20,25,30,35,40,45,50% solids ratio, 30,60,90,120,150,180,220,240,260,320 min leaching time, 25,50,100,200,300,400,500 kg/ton NaOH dosage, and 25,30,40,50,60,70^oC pulp temperature were experimented, and the effect on Th and REE dissolution efficiencies of NaOH leaching was investigated. When the leaching of bastnaesite with NaOH is in progress, the following reactions occur (Equation 1-2):

$$RECO_3F + 3NaOH = RE(OH)_3 + NaF + Na_2CO_3 \quad (1)$$

$$ThO_2 + 4NaOH = Th\,(OH)_4 + 2Na_2O \quad (2)$$

In Equation 1, rare earth hydroxide, sodium fluoride, and sodium carbonate liberated by the reaction of bastnaesite mineral and sodium hydroxide. In Equation 2, thorium dioxide and sodium hydroxide react, and thorium hydroxide and sodium oxide liberated (Zhang et al., 2016).

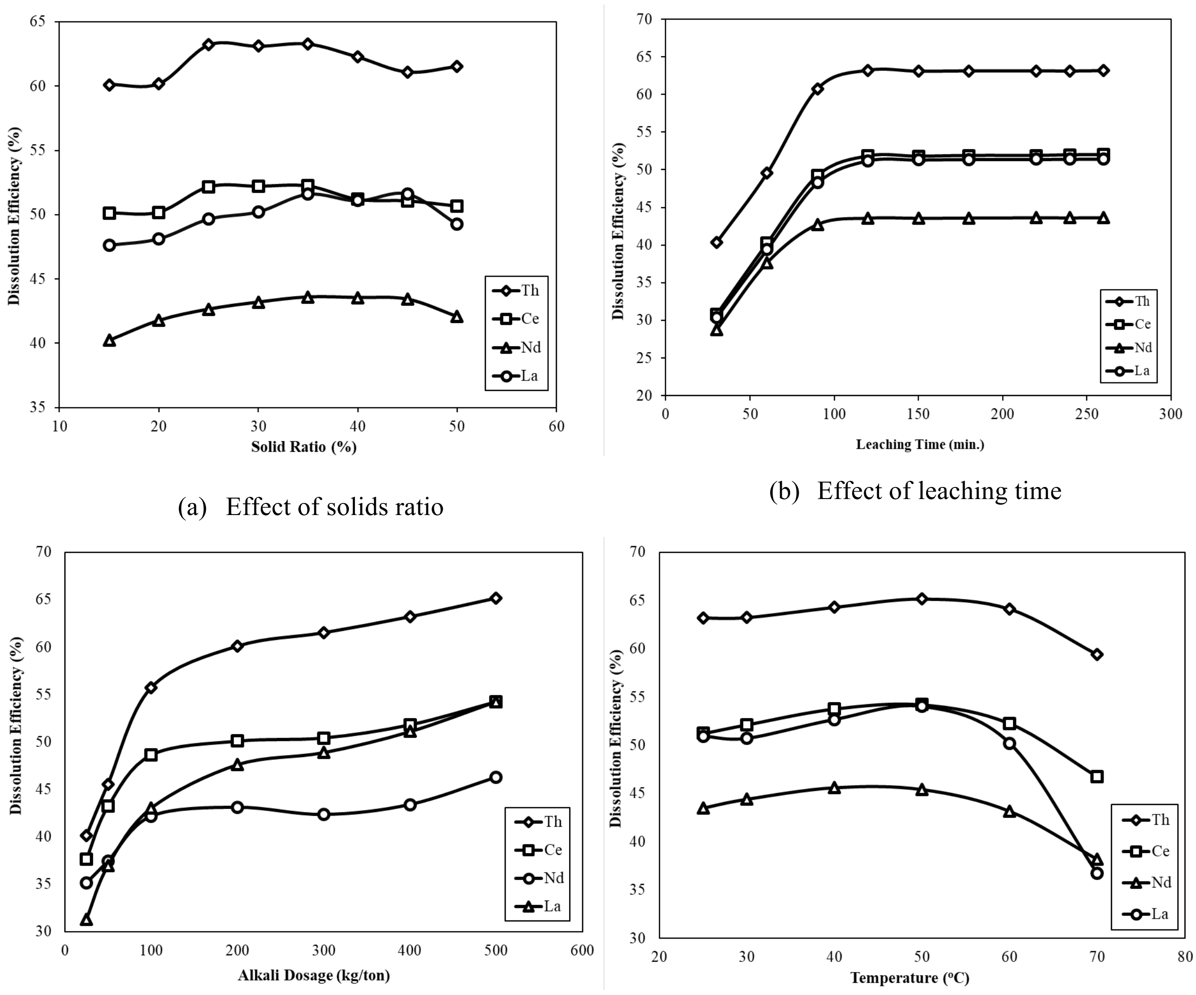
3. Results and discussion

3.1. Effect of solids ratio

As seen in Figure 2-a, the dissolution efficiencies for Th, Ce, Nd, and La increased to a certain point depending on the increase of solids ratio. The highest Th, Ce, Nd, and La dissolution efficiencies were obtained at 35% solids ratio as 63.29%, 52.24%, 43.61%, and 51.61%, respectively. Since no significant change was observed in the dissolution efficiencies depending on the solids ratio after this point, and due to the probability of a decrease in viscosity owing to a higher solid/liquid ratio, the optimum solids ratio was determined as 35%.

3.2. Effect of leaching time

The dissolution efficiency of Th increased up to a certain point depending on the leaching time (Figure 2-b). The highest dissolution efficiency of Th was obtained at 120 min of leaching time as 63.22%. The highest Ce, Nd, and La dissolution efficiencies were obtained at 260 min of leaching 51.99%, 43.64%, and 51.45%, respectively. The dissolution efficiencies of Ce, Nd, and La were obtained at 120 min of leaching time as 51.83%, 43.59%, and 51.22%, respectively. The optimum leaching time was chosen as 120 min because of the following two reasons: The first one was that the leaching time is an important parameter in terms of time/multi-efficiency principle in both experimental and plant-based studies, and the second one was the fact that there was no significant change in the dissolution efficiencies of Ce, Nd, and La after 120 min of the leaching time.



(a) Effect of solids ratio

(b) Effect of leaching time

(c) Effect of alkali dosage

(d) Effect of pulp temperature

Figure 2. Effects of (a) solids ratio, (b) leaching time, (c) alkali dosage, and (d) pulp temperature on dissolution efficiencies of Th and REE (Ce, Nd, La).

3.3. Effect of NaOH dosage

According to the results seen in Figure 2-c, the dissolution efficiency of Th increasesd in proportion to alkaline dosage. After this point, both Th, and Ce, Nd, and La dissolution efficiencies started to decrease dramatically. The highest Th dissolution efficiency was obtained as 65.19% under the conditions of 500 kg/ton of NaOH dosage. The highest Ce, Nd, and La dissolution efficiencies under the conditions of 500 kg/ton of NaOH dosage were obtained as 54.23%, 46.27%, and 54.26%, respectively. The increasing the concentration of solution directly affected the speed of the leaching reaction. On the other hand, a very high concentration of the solution may adversely affected the reaction speed in some leaching processes. In this case, it is necessary to select an optimum concentration of reagents that will maximize the leaching process. Considering the highest dissolution efficiencies of both Th and REE (Ce, Nd, La), the optimum NaOH dosage was determined as 500 kg/ton.

3.4. Effect of pulp temperature

The dissolution efficiency of Th increased up to a certain point depending on the pulp temperature. The highest dissolution efficiency of Th at 50°C pulp temperature was obtained as 65.15%. The highest Ce and La dissolution efficiencies were obtained as 54.21% and 54.01%, respectively under 50^{o}C, while the highest Nd dissolution efficiency was obtained as 45.63% at 40^{o}C. The dissolution efficiency of Nd was obtained as 45.44% at 50^{o}C (Figure 2-d). Because of the possibility of excessive dissolution of undesirable substances or destruction of solid at high temperature, the optimum pulp temperature was determined as 50°C.

4. Conclusion

In this study, the leaching experiments with NaOH; 15-20-25-30-35-40-45-50 solids ratio, 30-60-90-120-150-180-220-240-260-320 min leaching time, 25-50-100-200-300-400-500 kg/ton NaOH, and 25-30-40-50-60-70^{o}C pulp temperature parameters were tested; and the best results for Th and REE (Ce, Nd, La) were obtained under the conditions of 35% solids ratio, 500 kg/ton NaOH, 120 minleaching time, and 50^{o}C pulp temperature. The optimum values were selected because of following reasons: The probability of decrease in the viscosity owing to higher solid/liquid ratio, the significance of leaching time in terms of time/multi-efficiency principle in both experimental and plant-based studies, the possibility of the effect of the very high concentrated solution on the reaction speed in some leaching processes, and the possibility of excessive dissolution of undesirable substances or destruction of solid at high temperature. As a result of the experiments carried out under these optimum conditions, 65.15% Th, 54.21% Cd, 45.44% Nd, and 54.01% La dissolution efficiencies were obtained.

The reason for the relatively low dissolution efficiencies of Th and REE versus the high reagent amounts of alkaline leaching was that it caused an excessive reactive consumption of the silicates. According to Celep (2011), the alkaline leaching has also some distinct advantages over either the acid leaching processes or the pyrometallurgical processes: the solid residues are considerably less toxic, and most of the heavy metals can be leached. But since the rare earths play a significant role in economics, and thorium is a strategic element, alkaline leaching can also be an alternative method and can be interactively used in the recovery of rare earths and thorium from bastnaesite.

Acknowledgments

This paper was first submitted at the 16th International Mineral Processing Symposium (IMPS 2018).

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