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Solubility of Eskisehir thorium/rare earth ores in sulphuric and nitric acids

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Abstract: Nuclear energy is considered as one of the most important energy resources in the world. Thorium (Th) has a significant potential to be used in electricity production by nuclear energy since its existence is not depended on the presence of another radioactive elements, and it has larger potential reserves than uranium. Bastnaesite ((Ce, La)CO₃F) is one of the minerals from which Th can be economically extracted. In this study, solubility of bastnaesite containing ore obtained from Eskisehir, Turkey was investigated by leaching with H₂SO₄ and HNO₃ in terms of leaching performance of thorium and some rare-earth elements (Ce, Nd, La). In this context, 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 effects of several parameters such as the solid ratio, leaching time, acid amount and pulp temperature, on dissolution efficiencies of Th, Nd, Ce and La was investigated. The best results were obtained using 3.42 mol/dm³ HNO₃, solid-to-liquid ratio of 35%, 120 min leaching time and 60 °C temperature. Under these optimum conditions, the dissolution efficiencies of Th, Ce, Nd, and La were obtained as 94%, 82%, 77% and 70%, respectively.

Keywords: thorium, rare earth elements, bastnaesite, leaching, solubility

1. Introduction

Thorium exists in quite a prominent position especially in terms of nuclear energy. Thorium is a potential nuclear fuel because ²³²Th can be converted to ²³³U by absorbing slow neutrons. It is also considered as the cleanest nuclear power plant fuel as less plutonium and other trans-uranium elements are produced from the thorium fuel cycle compared to the uranium fuel cycle. Therefore, it is intended to be used as a substitute for uranium in nuclear reactors being more environmentally friendly compared to uranium. While thorium-based power plants have not yet been built industrially, thorium-based nuclear power research and development operations are ongoing in various countries as an alternative to uranium. Therefore, the interest in thorium as an energy source has been increased (Ipekoglu, 1983; Kaya and Bozkurt, 2003; Ali et al, 2007; Gui et al., 2014; Kursun et al., 2015; Kursun and Terzi, 2015; USGS, 2016).

Approximately sixty Th-bearing minerals are known in nature and the majority of these minerals have high ratios of rare earth elements (REE). Therefore, thorium is commonly associated with REEs which are very important in production of advanced materials for high technology industries, and mainly obtained as a by-product from distillation of monazite ((Ce, La)PO₄) and bastnaesite ((Ce, La)CO₃F). In 2013, exploration and development of rare-earth projects associated with thorium have been continued in Australia, Brazil, Canada, Greenland, India, South Africa, United States and Vietnam. The REEs are a unique group of elements, summarized as lanthanides plus scandium (Sc) and yttrium (Y), regarded as being among the most critical elements that are highly valued for their specialized applications in many modern technologies. Neodymium and dysprosium are used as magnets in wind turbines as well as electric vehicles and lanthanum, cerium, europium, terbium and yttrium for phosphors in energy efficient lights (Eyal and Olander, 1990a; Eyal and Olander, 1990b;

Eyal and Olander, 1990c; Ishikawa et al., 2002; Ali et al, 2007; Hingant et al., 2009; Gaiotte et al., 2011; Gok and Aytas, 2013; Lu et al., 2016; USGS, 2016).

There are several hydrometallurgical methods for extracting thorium and REEs from bastnaesite, which is the most industrially important rare earth mineral with the content of rare earth oxides (REOs) and Th equal to 67-73% and 0.2-0.3%, respectively. Presently, bastnaesite concentrates are obtained from gravity and flotation processes commonly treated by calcination-acid dissolution or directly by acid dissolution or alkaline roasting, including H_2SO_4 acid-roasting and water leaching, HCl acid leaching, HNO_3 acid leaching, Na_2CO_3 roasting and chlorination. The rare-earth extraction process uses either one or more reagents to decompose the minerals, and to leach the REEs into the solution. The commonly used acids include sulfuric acid (H_2SO_4), hydrochloric acid (HCl) and nitric acid (HNO_3). Bastnaesite can be decomposed into REOs and rare earth fluoride oxide at 400–560 °C, which can be dissolved by sulphuric, nitric and hydrochloric acids at room temperature. On the other hand, Th is soluble in HCl and H_2SO_4 but insoluble in water. Thorium compounds with fluoride, iodide, phosphate etc. ions are also slightly soluble in acids (Ipekoglu, 1983; Zhang and Saito, 1998; Ozbayoglu and Atalay, 2000; Kaya and Bozkurt, 2003; Yorukoglu et al., 2003; Zhang et al., 2004; Castor and Hedrick, 2006; Bian et al., 2011; Wang et al., 2013; Gui et al., 2014; Huang et al., 2014; ATSDR, 2016; Huang et al., 2016; Machacek and Kalvig, 2016; Ogata et al., 2016; Stone et al., 2016; USGS, 2016; Zhang et al., 2016).

In this study, solubility of bastnaesite containing ore obtained from Eskisehir, Turkey by leaching with H_2SO_4 and HNO_3 was investigated in terms of leaching performance of thorium and some REEs (Ce, Nd, and La).

2. Materials and methods

2.1 Materials

The samples subjected to the experimental studies were representatively taken from three different areas in Eskisehir-Kizilcaoren region. The results of preliminary characterization studies showed that the samples had similar features in terms of their mineralogical and chemical compositions. Therefore, some composite samples were prepared by mixing equal weight ratios of the samples to be used in the experiments. Subsequently, the characterization experiments were performed in order to determine the physical, chemical and mineralogical properties of the sample.

The results of chemical analysis obtained by inductively coupled plasma mass spectrometry (ICP-MS) indicated that La, Ce, Nd, Y, Th, and U contents of the sample were found to be 2.79%, 2.27%, 0.29%, 450 ppm, 0.69%, and 200.3 ppm, respectively. It was determined that the samples contained 0.14% of total moisture, and it can be removed after 90 min of drying in the oven at 105 °C. The samples were subjected to a size analysis after they were crushed in two stages by jaw and roll crushers in order to provide a suitable feed size for leaching. As a result of the sieve analysis, d_{50} and d_{80} of the sample were determined as 0.45 mm and 1.58 mm, respectively. Figure 1 shows the Th and REOs contents of the sample as a function of particle size.

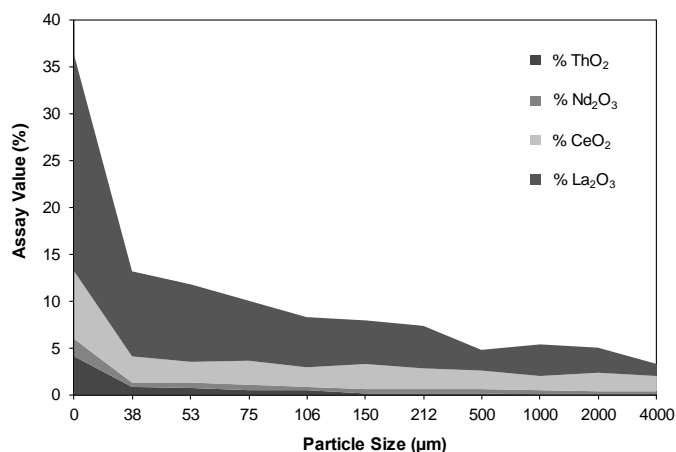


Fig. 1. Th and REOs content of sample according to sieve fractions

As seen in Fig. 1, Th and REE oxide contents in the sample were tended to increase inversely proportional to the particle size. The highest distribution was obtained in the $-38 \mu\text{m}$ size fraction, and the assay values of La_2O_3 , CeO_2 , Nd_2O_3 , and ThO_2 in this fraction were found as 23.11%, 7.17%, 1.90%, and 4.09%, respectively. The obtained results suggested that the liberation degree of bastnaesite, which was the dominant Th and REOs source in the sample, increased in finer particle sizes, thus, Th and REO contents tended to be concentrated in the finer fractions. The specific gravity of the sample was found as 3.29 g/cm^3 .

The pH change of the sample in the purified water depending on the time was analyzed in order to identify the electrokinetic properties of the sample. The pH profiles of the sample are shown in Fig. 2.

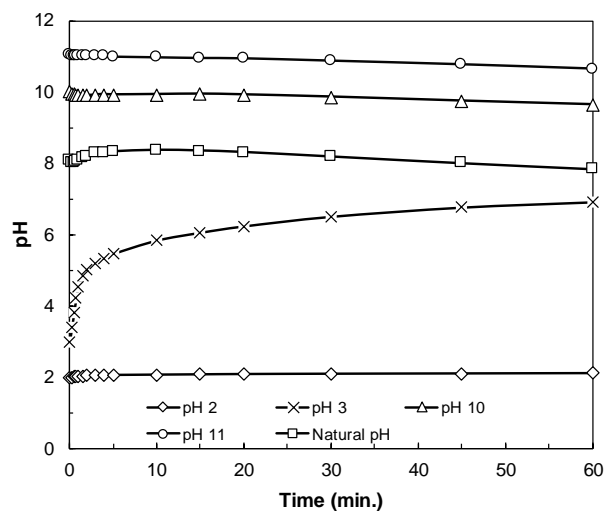


Fig. 2. pH profile of the sample

As seen from Fig. 2, the pH value of the sample at pH 3, 8, 10 and 11 started reaching a buffer pH value in the alkaline regions after a certain time. No change depending on the time was observed at pH 2 which was the highest acidic pH value analyzed in the experiments. The reason of this can be explained by the limited amount of the anions formed by dissolving from the sample in a high acidic medium.

In order to determine the mineralogical composition of the sample, the X-ray diffraction analysis (XRD) was performed (Fig. 3). The results of XRD analysis showed that the sample contained high rates of fluorite- CaF_2 and plumbian-barite ($\text{Ba, Pb})\text{SO}_4$. Bastnaesite and some other minerals, which exist within the mineralogical composition in the sample, could not be seen by XRD due to the detection limits of the method.

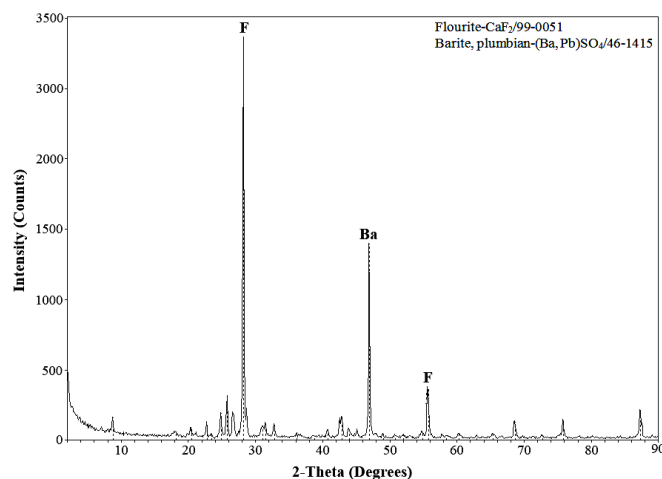


Fig. 3. XRD diffraction pattern of the sample

2.2 Methods

The leaching experiments were carried out in Erlenmeyer flasks using a shaking water bath (Witeg, Germany), and the shaking speed, pH, and pulp temperature were controlled periodically during the experiments. The values of pH and pulp temperature were controlled periodically during the experiments. In the leaching processes, H₂SO₄ at 96-98% purity (Tekkim, Turkey) and HNO₃ at 55-57% purity (Tekkim, Turkey) were used. The particle size of the feed samples was 106 μm, which were obtained from the closed circuit grinding in a steel ball mill. After the leaching process, solid-liquid separation was carried out using filter papers with pores size of 4 μm. The obtained filter cake was washed in 2 steps with 1% (w/w) acid solution, then Th and REE contents were analyzed by the ICP-MS method. The dissolution efficiency (D.E.) was calculated according to formula:

$$D.E. \% = \frac{Th,REE \text{ in the feed} - Th,REE \text{ in the f.cake}}{Th,REE \text{ in the feed}} \cdot 100. \quad (1)$$

The effects of several parameters such as the solid-to-liquid ratio, leaching time, acid amount and pulp temperature on dissolution efficiencies of Th, Nd, Ce, and La were investigated under different conditions of 15-50% solid ratio, 30-320 min leaching time, 0.137-4.38 (H₂SO₄), 0.214-6.85 (HNO₃) mol/dm³ concentration, and 25-90°C leaching temperature.

3. Results and discussion

3.1 Effect of solid-to-liquid ratio

The dissolution efficiency of Th, Ce, Nd, and La as a function of solid-to-liquid ratio for H₂SO₄ and HNO₃ leaching are shown in Fig. 4. The dissolution efficiencies of all investigated elements increased up to 35% solid ratio in a similar manner with both H₂SO₄ and HNO₃. After this point, the solubility of Th, Ce and La significantly decreased especially for H₂SO₄ leaching. On the other hand, the dissolution efficiencies followed a relatively stable trend after this point for HNO₃ leaching. This was probably due to the relative decrease in the amount of solvent per unit of solids due to the increase in the solid ratio and the lack of sufficient solvent amount to dissolve the target contents in the aqueous media in the high solids ratio.

It was also observed that the diffusion and mixing problems began to arise as the viscosity of the pulp increased. The obtained results showed that the solid ratio had no positive effect on the dissolution efficiency after a certain level. According to the results, 35% of solid ratio was found to be optimum for the dissolution efficiency of Th, Ce, Nd, and La.

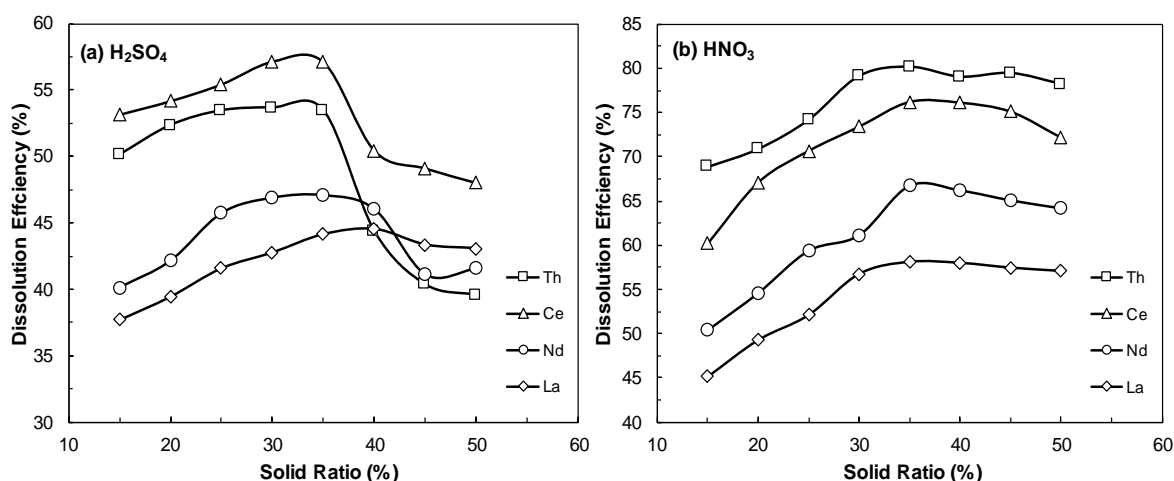


Fig. 4. Dissolution efficiency of Th, Ce, Nd, and La as a function of solid ratio in (a) H₂SO₄ (25 °C pulp temperature, 2.19 mol/dm³ acid dosage, 240 min leaching time) and (b) HNO₃ (25 °C pulp temperature, 2.57 mol/dm³ acid dosage, 240 min leaching time)

3.2 Effect of leaching time

The dissolution efficiency of Th, Ce, Nd, and La as a function of leaching time in H_2SO_4 and HNO_3 is given in Fig. 5. According to the results, it was observed that the leaching time showed a considerable effect on the dissolution efficiency for all elements for both H_2SO_4 and HNO_3 leaching. In H_2SO_4 the dissolution efficiency of 20% at 30 min increased to about 47% for Th and 35% for Ce after 150 min.

A non-linear increase in the dissolution efficiencies was obtained up to 220 min of leaching time, and then no significant increase was observed in H_2SO_4 leaching. On the other hand, the dissolution efficiencies showed an almost linear increase up to 120 min of leaching time, and then they reached a plateau after this point in HNO_3 leaching. The lack of further increase after the certain point was due to completion of dissolution reactions in terms of H_2SO_4 and HNO_3 soluble Th and REE contents. The optimum leaching time in H_2SO_4 and HNO_3 was 220 min and 120 min, respectively.

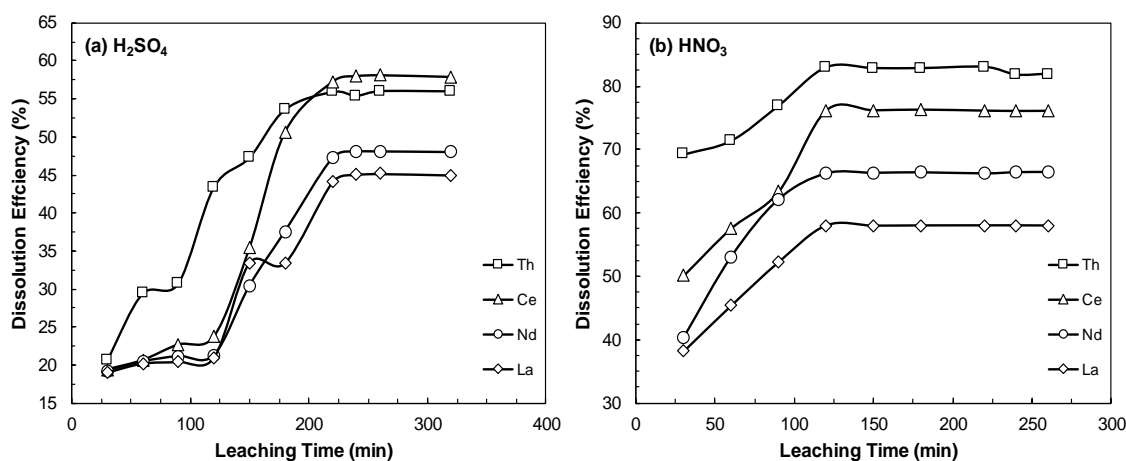


Fig. 5. Dissolution efficiency of Th, Ce, Nd, and La as a function of leaching time in (a) H_2SO_4 (35% solid ratio, 25 °C pulp temperature, 2.19 mol/dm³ acid dosage) and (b) HNO_3 (35% solid ratio, 25 °C pulp temperature, 2.57 mol/dm³ acid dosage)

3.3 Effect of acid dosage

The dissolution efficiency of Th, Ce, Nd, and La as a function of acid amount in H_2SO_4 and HNO_3 is given in Fig. 6. When the effect of acid dosage in H_2SO_4 was examined, it was observed that the dissolution efficiency of Th was more affected by the acid dosage compared to HNO_3 leaching. The dissolution efficiencies of Th and REEs increased up to the acid dosage of 2.19 mol/dm³, and after this point, no significant change was observed. On the other hand, a rapid increase in the REE dissolution efficiencies up to acid dosage of 1.71 mol/dm³ was observed in HNO_3 . Subsequently, even the slope of the dissolution curves reduced, the increase continued up to a plateau point at 3.42 mol/dm³. According to these results, it can be concluded that the investigated range of acid amounts was sufficient to dissolve Th and REE, and any further increase in the acid amount would not have significant positive effect. Therefore, the optimum amount of H_2SO_4 and HNO_3 were found to be 2.19 mol/dm³ and 3.42 mol/dm³, respectively.

3.4 Effect of pulp temperature

The dissolution efficiency of Th, Ce, Nd, and La as a function of pulp temperature in H_2SO_4 and HNO_3 is shown in Fig. 7. As clearly seen from Fig. 7, the temperature showed no significant effect on the dissolution efficiencies of REEs for leaching with both acids. However, considering its positive effect on the dissolution efficiency of Th, the optimum pulp temperature was determined as 70 °C in H_2SO_4 , at which Th, Ce, Nd and La dissolved with rates of 66.67, 51.04, 43.22 and 40.29%, respectively. Similarly, the increase at the rate of 8% was observed in the dissolution efficiency of Th in H_2SO_4 . Furthermore, the optimum pulp temperature was determined as 60 °C due to the legible differences between the dissolution efficiencies obtained at 60 and 70 °C in HNO_3 leaching experiments.

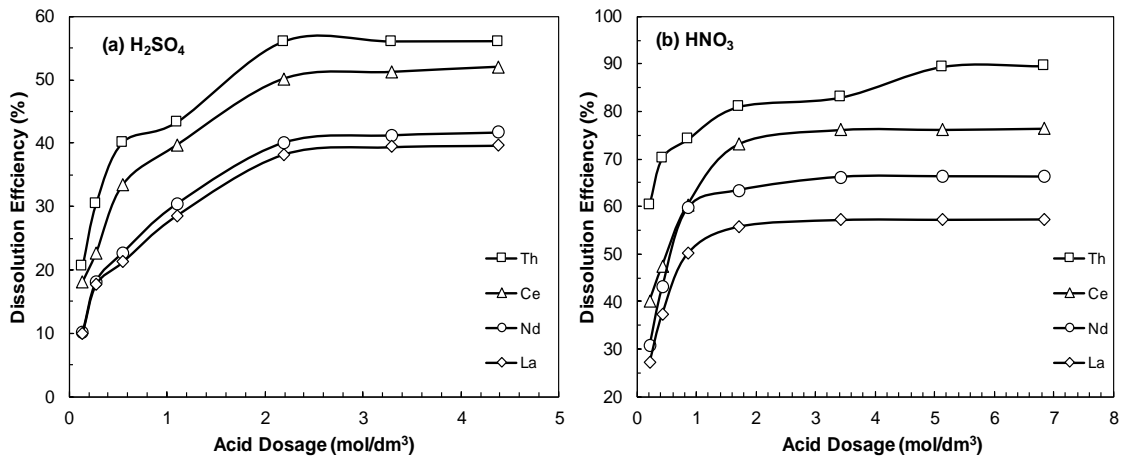


Fig. 6. Dissolution efficiency of Th, Ce, Nd and La as a function of acid dosage in (a) H₂SO₄ (35% solid ratio, 25 °C pulp temperature, 220 min leaching time) and (b) HNO₃ (35% solid ratio, 25°C pulp temperature, 120 min leaching time)

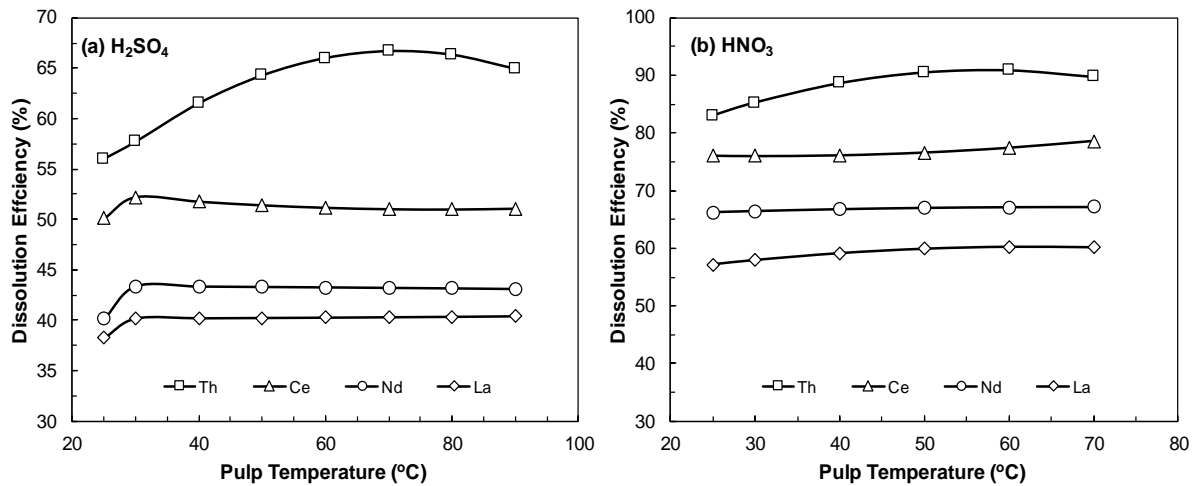


Fig. 7. Dissolution efficiency of Th, Ce, Nd, and La as a function of pulp temperature in (a) H₂SO₄ (35% solid ratio, 2.19 mol/dm³ acid dosage, 220 min leaching time) and (b) HNO₃ (35% solid ratio, 3.42 mol/dm³ acid dosage, 120 min leachig time)

4. Discussion and conclusions

In this study, the solubility of a bastnaesite containing ore by leaching with H₂SO₄ and HNO₃ were compared in terms of dissolution efficiencies of Th, Ce, Nd, and La. According to the results, the highest Th dissolution efficiency was obtained as 90.88% and 66.67% in HNO₃ and H₂SO₄, respectively. The highest dissolution efficiencies for Ce, Nd, and La were obtained as 51.04%, 43.22%, and 40.29% for H₂SO₄ leaching, and 77.45%, 67.15%, and 60.22% for HNO₃ acid leaching, respectively. The dissolution efficiencies of the elements by using both acids were obtained from the highest to the lowest as Th, Ce, Nd, and La, respectively. The difference between dissolution efficiencies of Th, Ce, Nd and La can be attributed to the fact that part of these elements might be contained in different species of bastnaesite group and other trace REE minerals in the sample, which all differs in their acid solubility properties, as well as to the fact that REE fluorides have different solubility constants as it was presented by Migdisov et al. (2009).

The results obtained in this study are consistent with the results of studies on the dissolution REEs from bastnaesite containing ores for H₂SO₄ and HNO₃ leaching in literature. Feng et al. (2013) performed series of experiments with H₂SO₄, the highest REE dissolution efficiencies were obtained under the conditions of 1.5 mol/dm³. Additionally, most significant effect of temperature increase on the REE dissolution efficiencies were obtained between 30 and 40 °C, while the increase between 60

and 70 °C was negligible similar to this study. Studies conducted by Baroch (1958) on the enrichment of California bastnaesite for HNO₃ leaching showed that the maximum dissolution efficiencies of REEs reached after 2 h of leaching. It was also observed that the increase in the leaching time after this point showed no significant effect on the REEs dissolution efficiencies of REEs. However, the dissolution efficiencies obtained with H₂SO₄ were found to be higher than HNO₃ in several studies on the dissolution of different ores for H₂SO₄ and HNO₃ leaching (Meor, 2013). This can be attributed to the fact that the dissolution efficiency depends on the type of REE-containing phases (ReF₃/ReCO₃) as well as gangue minerals present (SiO₂, CaCO₃, etc.) in the ore that often affect the leaching process.

It can be concluded that the best result was obtained with HNO₃ leaching under 35% solid ratio, 3.42 mol/dm³ HNO₃, 120 min leaching time, and 60 °C pulp temperature when the dissolution rates of Th and REEs taken into consideration together. HNO₃ was more efficient than H₂SO₄ in terms of Th dissolution as the dissolution efficiency of Th reached 90% at the end of 2 h leaching time with use of 3.42 mol/dm³ HNO₃. Under these conditions, the dissolution efficiencies of Th, Ce, Nd, and La were obtained as 90.88%, 77.45%, 67.15%, and 60.22%, respectively. The relatively low leaching efficiencies of REEs can be attributed to poor dissolution capacity of bastnaesite, which has a hexagonal form in acid solutions. It was also observed that the dissolution efficiencies were improved by increasing of dissolution time, while this level of dissolution rates could not be attained with H₂SO₄ altogether.

In addition to the higher obtained dissolution efficiencies, there are several advantages of HNO₃ over H₂SO₄ for leaching of Eskisehir thorium/rare earth ores were observed. As a strong acid with a high diffusion constant, HNO₃ does not provide compounds precipitating with cations, thus it dissolves thorium more efficiently than H₂SO₄, and the acid consumption for the same efficiency was lower than H₂SO₄. Additionally, the use of HNO₃ was positively influenced the dissolution efficiency of Th as it provided no difficulty in mixing and filtration. The result of this study clearly indicated that the leaching method using common mineral acids such as H₂SO₄ and HNO₃ was a simple and applicable process which provided relatively high dissolution rates in terms of extracting some REEs and especially Th from bastnaesite containing ores.

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