



Orijinal Araştırma / Original Research

EXTRACTION OF LANTHANUM AND CERIUM FROM A BASTNASITE ORE BY DIRECT ACIDIC LEACHING

DİREKT ASİT LİÇİ İLE BASTNAZİT CEVHERİNDEN LANTANYUM VE SERYUM KAZANIMI

Sait Kursunoglu^{a,*}, Soner Top^{a,**}, Shokrullah Hussaini^{b,***}, Hasan Serkan Gokcen^{b,****}, Mahmut Altiner^{c,*****}, Safak Ozsarac^{d,*****}, Muammer Kaya^{b,*****}

^a Abdullah Gul University, Engineering Faculty, Materials Science and Nanotechnology Engineering Department, Kayseri, TURKEY

^b Eskisehir Osmangazi University, Faculty of Engineering and Architecture, Mining Engineering Department, Eskisehir, TURKEY

^c Cukurova University, Engineering Faculty, Mining Engineering Department, Adana, TURKEY

^d Batman University, Faculty of Engineering and Architecture, Geological Engineering Department, Batman, TURKEY

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Anahtar Sözcükler:

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Bastnazit cevheri.

ABSTRACT

The extraction of lanthanum (La) and cerium (Ce) from a bastnasite ore by direct acidic leaching was investigated. The effects of acid concentration and leaching temperature on the extraction of La and Ce from the ore were tested. Using nitric (HNO₃), more than 85% of the La and Ce were simultaneously extracted into leach solution whereas the La and Ce dissolutions were determined as less than 85% by using sulfuric acid (H₂SO₄). The La dissolution exceeded 90% by using hydrochloric acid (HCl); however, the Ce dissolution remained below 85% under the following conditions: solid-to-liquid ratio of 20% (w/v), the acid concentration of 20%, leaching temperature of 25 °C and leaching time of 1 h. The result revealed that HNO₃ could be used as a solvent for the maximum simultaneous extraction of the La and Ce from the bastnasite ore. The leaching temperature had no crucial effect on the dissolution of La and Ce when HNO₃ or HCl solutions were preferred as a solvating agent. However, the leaching temperature had a slight positive effect on the dissolutions of La and Ce when H₂SO₄ was used as a solvent.

ÖZ

Direkt asit liçi ile bir bastnazit cevherinden lantanyum (La) ve seryum (Ce) ekstraksiyonu araştırılmıştır. Bastnazit cevherinden La ve Ce ekstraksiyonuna asit konsantrasyonu ve liç sıcaklığının etkileri test edilmiştir. Nitrik asit (HNO₃) kullanarak La ve Ce'un %85'ten fazlası liç çözültisine alınmıştır ancak çözünme değerleri sülfürik asit (H₂SO₄) kullanıldığında %85'ten az olarak belirlenmiştir. La çözünümü hidroklorik asit (HCl) kullanımıyla %90'ı geçmiştir fakat Ce çözünümü %20 (g/L) katı-sıvı oranı, %20 asit konsantrasyonu, 25 °C liç sıcaklığı ve 1 saat liç süresi şartları altında %85'in altında kalmıştır. Sonuçlar bastnazit cevherinden eş zamanlı olarak maksimum La ve Ce çözünümüne ulaşılabilmek için çözücü olarak HNO₃ kullanılabilirliğini ortaya koymuştur. Çözücü olarak HNO₃ ve HCl tercih edildiğinde liç sıcaklığının La ve Ce çözünümüne önemli bir etki yapmadığı belirlenmiştir. Fakat çözücü olarak H₂SO₄ kullanılmasıyla liç sıcaklığının La ve Ce çözünmeleri üzerine hafif bir pozitif etkisi saptanmıştır.

* Sorumlu yazar / Corresponding author: sait.kursunoglu@agu.edu.tr • <https://orcid.org/0000-0002-1680-5482>

** soner.top@agu.edu.tr • <https://orcid.org/0000-0003-3486-4184>

*** shok1390@gmail.com • <https://orcid.org/0000-0003-0287-0061>

**** hgokcen@ogu.edu.tr • <https://orcid.org/0000-0001-5093-6769>

***** maltiner@cu.edu.tr • <https://orcid.org/0000-0002-7428-5999>

***** safak.ozsarac@batman.edu.tr • <https://orcid.org/0000-0002-8319-9275>

***** mkaya@ogu.edu.tr • <https://orcid.org/0000-0001-5260-2589>

INTRODUCTION

The unique properties of rare earth make their usage inevitable for the high technological fields. Rare earth elements (REEs) are mainly used in the production of ceramics, automobile catalytic converters, fluid shredder catalysts, glass additives and polishing, metallurgical alloys, neodymium magnets, lasers, and rechargeable battery alloys (Jha et al., 2016; Swain and Mishra, 2019; Huang et al., 2019).

Lanthanides are erbium (Er), cerium (Ce), ytterbium (Yb), dysprosium (Dy), gadolinium (Gd), praseodymium (Pr), holmium (Ho), lanthanum (La), europium (Eu), promethium (Pm), neodymium (Nd), samarium (Sm), scandium (Sc), lutetium (Lu), terbium (Tb), thulium (Tm), and yttrium (Y) elements, whose atomic numbers are in the range of 57-71 in the periodic table (Chen, 2011). Lanthanides exist as carbonate, oxide, phosphate, and silicates in rock form. REEs are classified as light rare earth (LREE) and heavy rare earth (HREE) minerals (Zhang et al., 2018). The atomic numbers of LREEs are in the range of 57-64. HREEs have atomic numbers between 65-71. The difference is because LREEs have a non-pair 4f electron layer. The HREEs have a double electron in the 4f layer. Although scandium (Sc) is the lightest element that differs from its status as a metal, it has a transitive property and is neither in the heavy nor light category. Yttrium (Y) is another transitive metal, chemically similar to lanthanides.

Although approximate 250 minerals are containing REEs, most of the world's rare earth reserves include bastnasite ($\text{La}(\text{CO}_3)\text{F}$) and monazite ($(\text{Ce},\text{La},\text{Nd},\text{Th})\text{PO}_4$) minerals (Gupta and Krishnamurthy, 2005; Demol et al., 2018). Xenotime ($\text{Y}(\text{PO}_4)$) is the other important REE mineral resource (Chelgani et al., 2015).

Alkali digestion and sulfuric acid baking processes followed by water leaching are used for REE beneficiation from high and low-grade monazite ores, respectively (Lucas et al., 2014). Water leaching after sulfuric acid baking is also applied to the bastnasite and xenotime minerals to extract the REEs (Demol et al., 2019). Under the influence of several chemicals, physical and biological processes, rare earth elements, which are separated from the primary rock and adsorbed to clay minerals, form weathered

crust elution-deposited rare earth ores. Column leaching with ammonium sulfate and ammonium formate was successfully applied for the recovery of REEs from these ores (Feng et al., 2018; Zhou et al., 2019). Coal fly ashes and bottom ashes as secondary resources, which are a by-product of coal-burning thermal power plants, can be utilized for the extraction of REEs. REEs were successfully obtained by direct leaching or alkali fusion-leaching methods from these combustion products (Peiravi et al., 2017; Tang et al., 2019; Tuan et al., 2019). The recovery of REEs from waste materials, such as scraps, cathode ray tubes, magnets, and glasses are of increasing importance (Yin et al., 2018; Jowitt et al., 2018; Liu et al., 2019).

The main objective is to investigate the extraction of La and Ce from a bastnasite ore using inorganic acids through a direct acidic leaching process under the atmospheric conditions. By applying the direct acidic leaching method, physical mineral processing techniques such as attrition scrubbing, screening, and desliming by a cyclone were eliminated.

1. MATERIALS AND METHODS

The bastnasite ore used in this study was taken from the Beylikahir deposit in Turkey. The ore was firstly crushed in a laboratory jaw crusher and then ground in a laboratory ball mill. The ground ore was subjected to particle size analysis by using Mastersizer 2000 (Malvern). The chemical composition of the ground ore was determined by X-Ray Fluorescence (XRF) (Zetium, PANalytical) while the mineralogical composition was identified using a Bruker Discover D8 (XRD) instrument with Cu K α 1 (wavelength 1.54060 Å) radiation source and calibrated with a silicon standard for alignment of the $2\theta = 5^\circ\text{--}75^\circ$ radiation generated at 40 mA and 40 kV. The mineral phases were identified using Diffrac Suite EVA software equipped with the current ICDD PDF-2/Minerals database. To confirm the XRD data, the ore sample was examined by field emission scanning electron microscopy (FE-SEM) coupled with energy-dispersive X-ray spectroscopy (EDX) (Zeiss GeminiSEM 300).

A 150-mL Pyrex beaker, which was placed on a digital temperature controlled hot plate equipped with a magnetic stirrer, was used in the leaching

experiments. One hundred milliliters of lixiviant and 20 g of ore were added to the beaker and then heated to the desired temperature. After the leaching test was finished, the leach slurry was filtered under vacuum through a Buchner funnel fitted with Whatman 1 filter paper, and the filtered residue was washed several times with pure water. The leach residue was dried in an oven at 105 °C for 24 h and subsequently subjected to XRF analysis (Minipal 4, PANalytical). Metals dissolutions were calculated by the following equation (Equation 1):

$$D(\%) = \frac{C_f - C_r}{C_f} * 100 \quad (1)$$

where, C_i is the initial La and Ce concentrations in the feed (%), C_r the final La, and Ce concentrations in the residue (%).

In the leaching tests, analytical grades of hydrochloric acid, nitric acid, and sulfuric acid were used. In all leaching tests, the solid-to-liquid ratio, stirring speed, and leaching time were kept constant at 1:5 (w/v), 300 rpm, and 1h, respectively.

2. RESULTS AND DISCUSSION

2.1. Material Characterization

Figure 1 shows the particle size distribution of the ground ore. The results showed that 80% of the sample is smaller than 124 µm. Table 1 shows the elemental compositions of the rare earth ore by XRF and ICP analyses. The XRD pattern is given in (Figure 2) shows that the major peaks were from fluorite (card no: 04-0864) and barite (card no: 24-1035). The minor peaks were also determined as Ce-bastnasite (card no: 11-0340) and La-bastnasite (card no: 41-0595). According to Yorukoglu et al., (2003), the main host mineral in the pre-concentrated ore was determined as bastnasite, mica, fluorite, and barite. Kul et al., (2008) reported that fluor spar (CaF_2), barite (BaSO_4), and bastnasite (LnFCO_3) were the main minerals in the pre-concentrated ore. Kursun et al. (2018) reported that fluorite (CaF_2) and barite ($(\text{Ba}, \text{Pb}) \text{SO}_4$) were the main mineral phases and bastnasite could not be detected in the ore sample. A representative ore SEM-EDX mapping result is given in Figure 3. The presence of La, and Ce in the sample confirms that the XRD

analysis is in good agreement with the findings of previous researchers (Yorukoglu et al., 2003; Kul et al., 2008; Kursun et al., 2018).

Table 1. Elemental composition of the rare earth ore

Main Elements	Weight (%)	Rare Earths	
		Elements	(mg/kg)
Ba	31.8	La	7248
Ca	26.8	Ce	11912
F	17.7		
Fe	5.6		
Si	4.0		
S	3.6		
Al	2.0		
Mn	1.4		

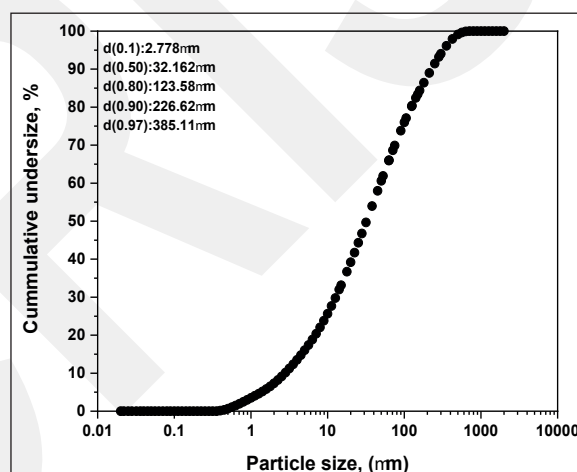


Figure 1. The particle size distribution of the ground ore

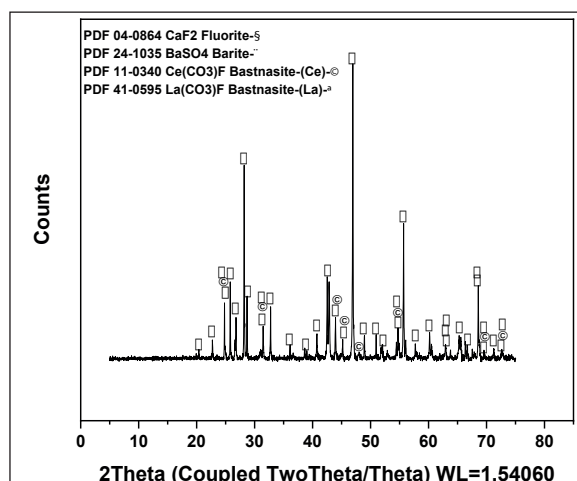


Figure 2. X-ray diffraction pattern of the bastnasite ore

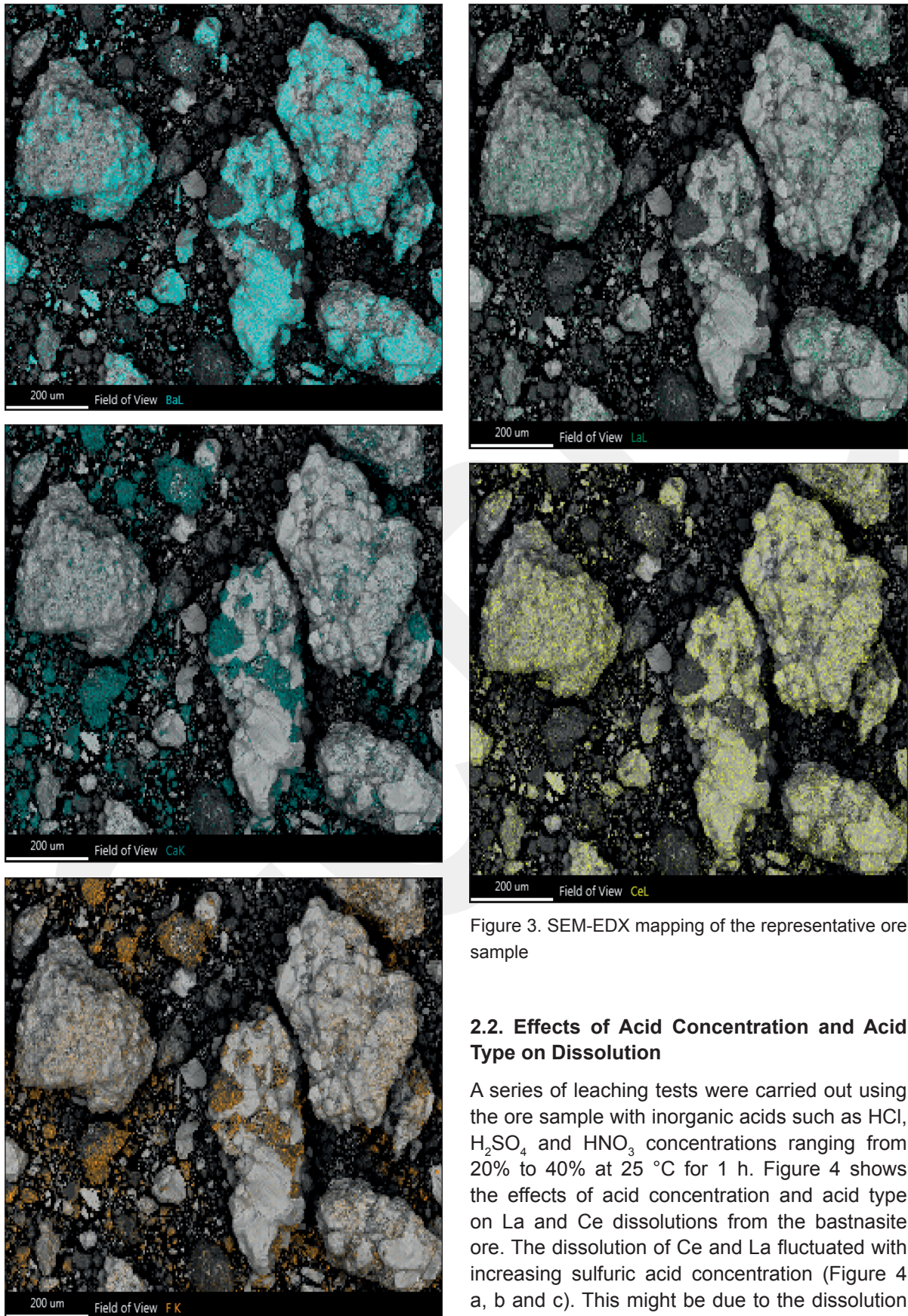


Figure 3. SEM-EDX mapping of the representative ore sample

2.2. Effects of Acid Concentration and Acid Type on Dissolution

A series of leaching tests were carried out using the ore sample with inorganic acids such as HCl, H₂SO₄ and HNO₃ concentrations ranging from 20% to 40% at 25 °C for 1 h. Figure 4 shows the effects of acid concentration and acid type on La and Ce dissolutions from the bastnasite ore. The dissolution of Ce and La fluctuated with increasing sulfuric acid concentration (Figure 4 a, b and c). This might be due to the dissolution

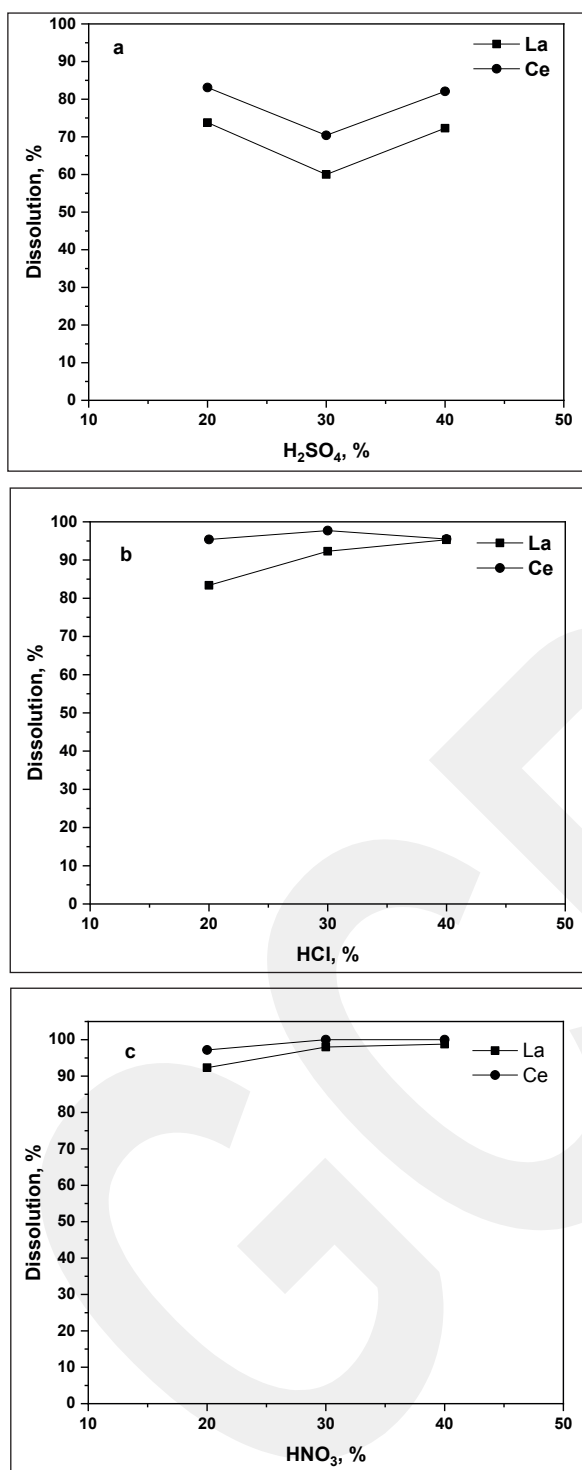
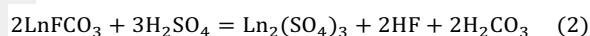


Figure 4. Effects of acid concentration and acid type on dissolution at 25°C for 1 h (a- leaching with H₂SO₄, b- leaching with HCl, c- leaching with HNO₃)

of other rare earth metals and/or impurities such as iron, manganese, magnesium, and calcium which are the acid consuming mineral phases

in the bastnasite ore. 73.8% La and 83.1% Ce dissolutions were achieved by using 20% of sulfuric acid concentration at 25 °C within 1h of leaching time. In the case of HCl, La and Ce dissolutions slightly increased with increasing acid concentration (Figure 4b). 83.4% La and 95.4% Ce were taken into the leach solution using 20% of hydrochloric acid concentration at 25 °C within 1h. It was determined that La and Ce dissolved together from the ore. In the HNO₃ solution, La and Ce dissolutions showed a similar dissolution trend with (Figure 4c). 92.3% La and 97.2% Ce simultaneously dissolved by using 20% of nitric acid at 25 °C within 1 h. HNO₃ was determined as the most suitable inorganic acids for the simultaneous dissolution of La and Ce from the bastnasite ore. The effect of acid concentration on dissolution efficiencies of Th, Nd, Ce, and La was investigated by Kursun et al., (2018). The researcher found that the optimum results were achieved at 60°C using 3.42 mol/L HNO₃, solid-to-liquid ratio of 35%, 120 min leaching time. Under these optimum conditions, 94% Th, 82% Ce, 77% Nd, and 70% La dissolved. After the leaching process, these rare earth metals could be selectively extracted from the pregnant leach solution (PLS) which are remained relatively mildly acidic conditions to prevent alkaline consumption. Thus, 20% of acid concentration was selected as optimum for further studies. Direct leaching of bastnasite ore with sulphuric acid is possible via the following chemical reaction (Equation 2).



2.3. Effects of Leaching Temperature on Dissolution

The leaching tests were carried out using 20% H₂SO₄, HNO₃ and HCl at various temperatures ranging from 40-80 °C using the bastnasite ore for 1 h. Figure 5 shows the effect of temperature on La and Ce dissolutions over the studied temperature range.

An increase in operating temperature had a slightly positive effect on the dissolutions of La, and Ce. It is seen that high dissolution rates of La and Ce can be achieved at high temperatures under atmospheric conditions. 79.8% La and 91.3% Ce were taken into the leach solution at 80 °C using sulphuric acid (Figure 5 a, b and c).

In the case of HCl leaching, La and Ce dissolutions remained relatively constant until 60 °C and then La dissolution slightly increased with increasing leaching temperature up to 80 °C (Figure 5b). It was revealed that La and Ce could be extracted from the bastnasite ore at 40 °C. 89.6% La and 97.8% Ce were extracted from the ore at 40 °C.

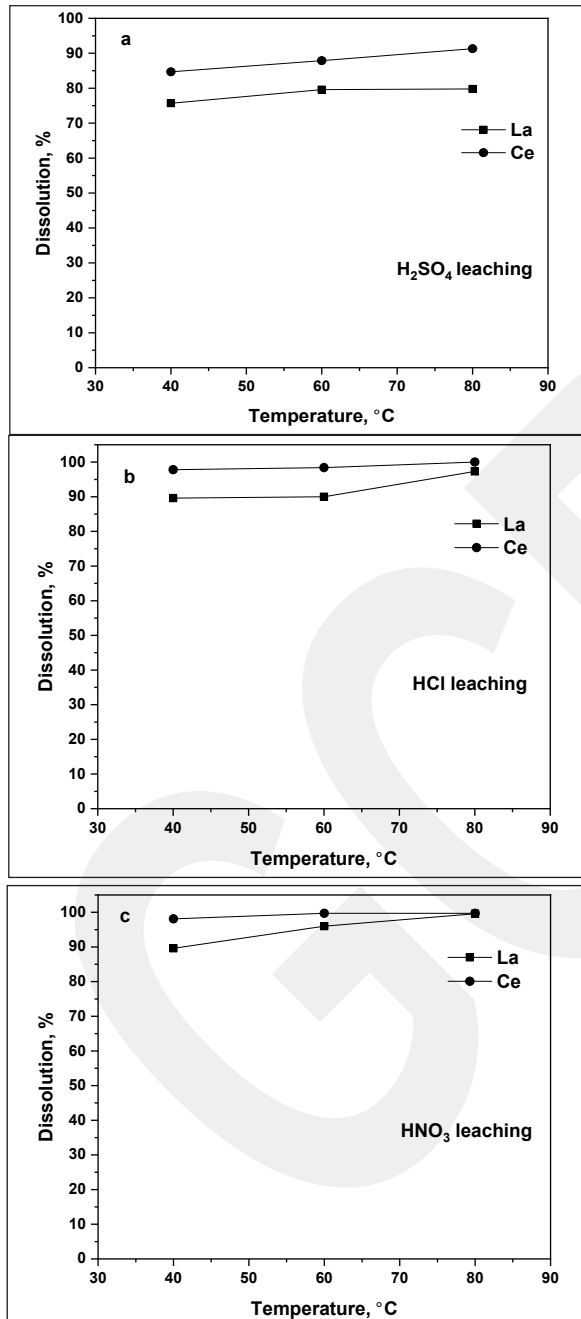
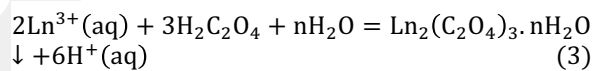


Figure 5. Effect of leaching temperature on dissolution using 20% acid for 1 h (a- leaching with 20% H₂SO₄, b- leaching with 20% HCl, c- leaching with 20% HNO₃)

La dissolution gradually increased with increasing temperature while Ce dissolution remained relatively stable when HNO₃ was used as a leaching solution (Figure 5c). 89.6% La and 98.1% Ce dissolutions were achieved at 40 °C by using a 20% HNO₃ solution under the conditions explored. Kursun et al., (2018) indicated that leaching temperature had a negligible effect on the dissolution of REEs by using sulphuric and nitric acid which is consistent with findings of current researchers' results.

2.4. Proposed Flow Sheet for the Bastnasite ore

Figure 6 shows the distribution of three species of oxalic acid at a concentration of 1 mol/L (i.e. H₂C₂O₄, HC₂O₄⁻, and C₂O₄²⁻), where the HC₂O₄⁻ and C₂O₄²⁻ ions are the predominant species in the pH range 2.5-3 and 7.0-14.0, explains why the reaction rate increases over these pH ranges. During the solution purification and REEs precipitation with oxalic acid, oxalate ionization occurs at high pH, and also times of stoichiometric oxalic acid demand (TSD) theoretically decreases. The pH of the PLS is arranged by alkaline solution and then high purity mixed rare earth oxalate was precipitated, leaving a considerable amount of impurities in barren leach solution (BLS) for further treatment. The precipitation of REEs from the solution is expressed via the following reaction (Equation 3):



Based on the experimental results obtained from the current experiments and considering a further experimental campaign, a possible flow sheet was proposed for the extraction and separation of rare earth metals from the bastnasite ore (Figure 7). The main features of this flowsheet are that one stage leaching was used to extract La and Ce from the ore. After the extraction stage, a loaded leach solution was sent to the neutralization unit to remove impurities such as Al and Fe using NaOH, CaO, CaCO₃, or MgO. The filtrate was then sent to the solvent extraction (SX) stage/precipitation followed by the thermal decomposition stage to obtain individual rare earth metals or mixed rare earth oxides.

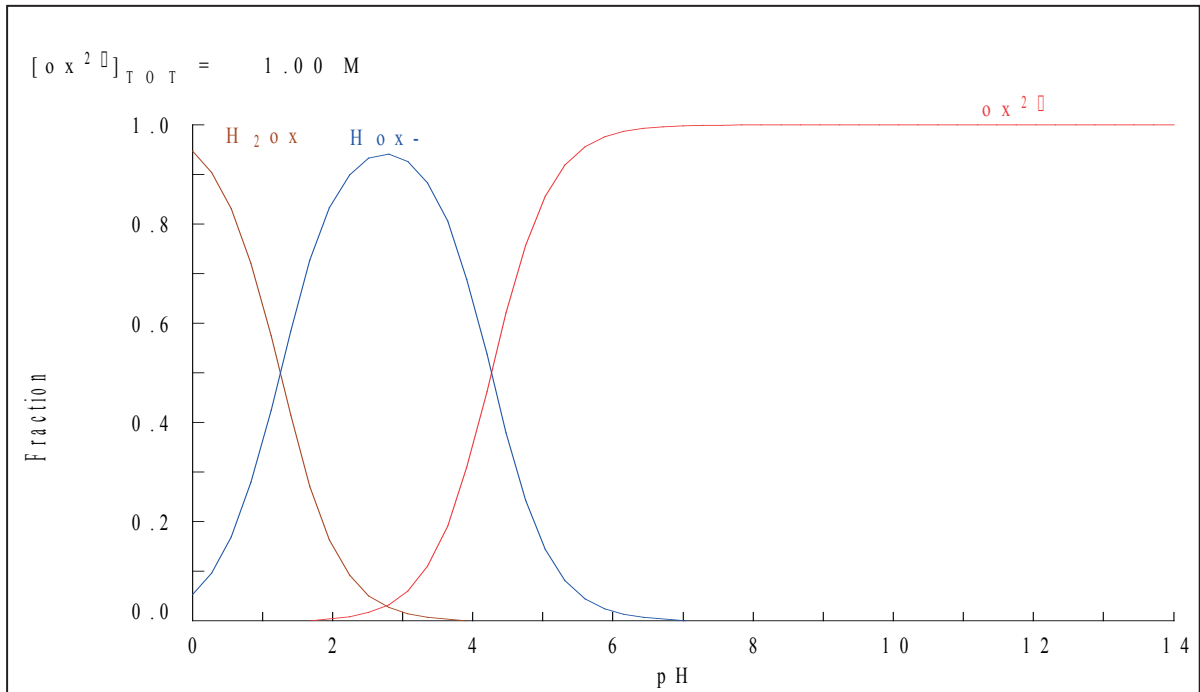


Figure 6. The distribution of three species of oxalic acid at a concentration of 1 mol/L (Software Medusa-Chemical Equilibrium Diagram)

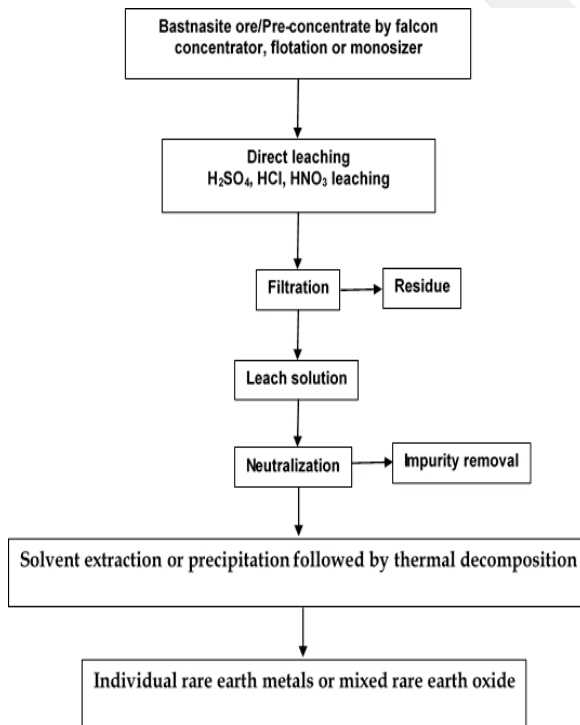


Figure 7. Possible flowsheet for the extraction and separation of rare earth metals from the bastnasite ore

CONCLUSIONS

La and Ce extractions from a bastnasite ore by using different inorganic acids were investigated. The effects of main parameters such as acid concentration and leaching temperature on dissolutions of the La and Ce were tested. It was determined that a 20% HNO₃ is enough to dissolve La and Ce from the ore. More than 85% of La and Ce extractions was achieved at 25 °C within 1h. In the H₂SO₄ solution, less than 85% La and Ce dissolved using 20% solvent at 25°C for 1 h. La dissolution was exceeded 90% by using 20% HCl at 25 °C for 1 h; however, Ce dissolution remained below 85%. The results indicated that HNO₃ could be used as a solvent for the maximum simultaneous extraction of La and Ce from the bastnasite ore. It was determined that the leaching temperature had no beneficial effect on the dissolution of La and Ce when HNO₃ or HCl was used as a solvating agent. However, H₂SO₄ had a slight positive effect on the dissolutions of La and Ce when the leaching temperature increased. By considering operation costs, the leaching temperature could be chosen as 25 °C. Based on the experimental results obtained from the experiments and considering a further campaign, a possible flow sheet was proposed

for the extraction and separation of rare earth metals from the bastnasite ore.

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REFERENCES

Chelgani, S. C., Rudolph, M., Leistner, T., Gutzmer, J., Peuker, U. A., 2015. A Review of Rare Earth Minerals Flotation: Monazite and Xenotime. *International Journal of Mining Science and Technology*, 25 (6), 877-883.

Chen, Z., 2011. Global Rare Earth Resources and Scenarios of Future Rare Earth Industry. *Journal of Rare Earths*, 29 (1), 1-6.

Demol, J., Ho, E. Soldenhoff, K., Senanayake, G., 2019. The Sulfuric Acid Bake and Leach Route for Processing of Rare Earth Ores and Concentrates: A Review. *Hydrometallurgy*, 188, 123-139.

Demol, J., Ho, E., Senanayake, G., 2018. Sulfuric Acid Baking and Leaching of Rare Earth Elements, Thorium and Phosphate from a Monazite Concentrate: Effect of Bake Temperature from 200 to 800 °C. *Hydrometallurgy*, 179, 254-267.

Feng, J., Zhou, F., Chi, R., Liu, X., Xu, Y., Liu, Q., 2018. Effect of a Novel Compound on Leaching Process of Weathered Crust Elution-Deposited Rare Earth Ore. *Minerals Engineering*, 129, 63-70.

Gupta, C. K., Krishnamurthy, N., 2005. *Extractive Metallurgy of Rare Earths*. CRC Press, Florida.

Huang, Z., Fan, M., Tian, H., 2019. Rare Earth Elements of Fly Ash from Wyoming's Powder River Basin Coal. *Journal of Rare Earths*, 38 (2), 219-226.

Jha, M. K., Kumari, A., Panda, R., Kumar, J. R., Yoo, K., Lee, J. Y., 2016. Review on Hydrometallurgical Recovery of Rare Earth Metals. *Hydrometallurgy*, 165 (1), 2-26.

Jowitt, S. M., Werner, T. T., Weng, Z., Mudd, G. M., 2018. Recycling of the Rare Earth Elements. *Current Opinion in Green and Sustainable Chemistry*, 13, 1-7.

Kul, M., Topkaya, Y., Karakaya, I., 2008. Rare Earth Double Sulfates from Pre-Concentrated Bastnasite. *Hydrometallurgy*, 90, 129-135.

Kursun, I., Tombal, T. D., Terzi, M., 2018. Solubility of Eskisehir Thorium/Rare Earth Ores in Sulphuric and Nitric Acids. *Physicochem. Probl. Miner. Process.*, 54 (2), 476-483.

Liu, H., Li, S., Wang, B., Wang, K., Wu, R., Ekberg, C., Volinsky, A. A., 2019. Multiscale Recycling Rare Earth Elements from Real Waste Trichromatic Phosphors Containing Glass. *Journal of Cleaner Production*, 238, 117-998.

Lucas, J., Lucas, P., Le Mercier, T., Rollat, A., Davenport, W. G., 2014. *Rare Earths: Science, Technology, Production and Use*. Elsevier.

Peiravi, M., Ackah, L., Guru, R., Mohanty, M., Liu, J., Xu, B., Zhu, X., Chen, L., 2017. Chemical Extraction of Rare Earth Elements from Coal Ash. *Mining, Metallurgy & Exploration*, 34, 170-177.

Swain, N., Mishra, S., 2019. A Review on the Recovery and Separation of Rare Earths and Transition Metals from Secondary Resources. *Journal of Cleaner Production*, 220, 884-898.

Tang, M., Zhou, C., Pan, J., Zhang, N., Liu, C., Cao, S., Hu, T., Ji, W., 2019. Study on Extraction of Rare Earth Elements from Coal Fly Ash Through Alkali Fusion – Acid Leaching. *Minerals Engineering*, 136, 36-42.

Tuan, L.Q., Thenepalli, T., Chilakala, R., Vu, H. H. T., Ahn, J. W., Kim, J., 2019. Leaching Characteristics of Low Concentration Rare Earth Elements in Korean (Samcheok) CFBC Bottom Ash Samples. *Sustainability*, 11, 2562.

Yin, X., Tian, X., Wu, Y., Zhang, Q., Wang, W., Li, B., Gong, Y., Zuo, T., 2018. Recycling Rare Earth Elements from Waste Cathode Ray Tube Phosphors: Experimental Study and Mechanism Analysis. *Journal of Cleaner Production*, 205, 58-66.

Yorukoglu, A., Obut, A., Girgin, I., 2003. Effect of Thiourea on Sulphuric Acid Leaching of Bastnaesite. *Hydrometallurgy*, 68, 195-202.

Zhang, Z., Sun, N., He, Z., Chi, R., 2018. Local Concentration of Middle and Heavy Rare Earth Elements in the Col on The Weathered Crust Elution-Deposited Rare Earth Ores. *Journal of Rare Earths*, 36 (5), 552-558.

Zhou, F., Liu, Q., Feng, J., Su, J., Liu, X., Chi, R., 2019. Role of Initial Moisture Content on the Leaching Process of Weathered Crust Elution-Deposited Rare Earth Ores. *Separation and Purification Technology*, 217, 24-30.