# Ammonium Sulfate Leaching of NaOH-Treated Monazite

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## Abstract

Rare earth elements (REEs) can be extracted from monazite under aggressive decomposition and leaching conditions. Much of the waste rocks are removed prior to the extraction process to minimize the costs and waste generation, which is difficult with coal byproducts. The possibility of extracting REEs from low-grade monazite concentrates under relatively mild conditions has been explored to simulate the extraction of REEs from coal byproducts.

It has been found that monazite can be decomposed in 10 to 50% NaOH solutions at 80 ºC, with the resulting hydrous oxide being subjected to the ammonium sulfate leaching at pH 4. The ζ-potential measurements conducted in the presence of the lixiviant suggest that the $NH_4^+$ ions displace the hydrated $Ln^{3+}$ ions from the surface of $Ln(OH)_3(s)$ by an ion-exchange mechanism, which may be driven by the large differences in the hydration enthalpies between the charged species involved. This approach may be advantageous over acid leaching, including the regeneration of spent lixiviant, lower chemical consumption, and leaching at higher pH.

**Keywords**: Rare earth elements, NaOH pretreatment, monazite leaching, ammonium sulfate, ion-exchange leaching, enthalpy of hydration

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## 1. INTRODUCTION

Rare earth elements (REEs) occur in more than 160 discrete minerals. Of these, only three rare earth minerals (REMs), *i.e.*, bastnaesite ($LnCO_3F$), monazite ($LnPO_4$), and xenotime ($YPO_4$) have been commercially exploited. The ore grades are 6 and 8.9% at the Bayan Obo and Mountain Pass mines (Krishnamurthy and Gupta, 2015). The mined ores are upgraded to 30-92% REO by flotation prior to chemical leaching (Qi, 2018) to reduce the volume of the materials treated by acid and/or base at high temperatures to extract REEs into solution.

The grades of the ion-adsorption clays (IACs) mined in the five provinces in south China are in the range of 0.05-0.3% REO. Despite the low grades, these provinces have been supplying >80% of the world's demand for heavy rare earth elements (HREEs) since the mid-1990s (Yang *et. al*., 2013). The lanthanide ($Ln^{3+}$) ions are present on the surfaces of clay minerals (kaolinite and halloysite) as adsorbed species, they can be readily extracted into solution by the ion-exchange mechanism,

$$\text{Clay-Ln}^{3+} + 3\text{NH}_4^+ \rightarrow \text{Clay-3NH}_4^+ + \text{Ln}^{3+} \qquad [1]$$

in which $NH_4^+$ ions are shown to displace the $Ln^{3+}$ ions. The displacement mechanism has been explained by the large differences in the hydration enthalpies of the $Ln^{3+}$ and $NH_4^+$ ions (Moldoveanu and Papangelakis, 2012).

Being a salt of hard acids ($Ln^{3+}$) and hard base ($PO_4^{3-}$), monazite is extremely stable thermodynamically. In this regard, it is not surprising that a harder base, *e.g*., $OH^-$ ions, must be used to convert $LnPO_4$ to form acid-soluble $Ln(OH)_3(s)$. Due to the relatively small difference in basicity between the $PO_4^{3-}$ ($pK_b = 1.7$) and $OH^-$ ($pK_b = 0$) ions, monazite decomposition requires high concentrations (60-75%) of NaOH solutions and temperatures (120-150 $^oC$) (Kim *et al*., 2012). Caustic decomposition is selective but incurs high reagent costs. As a means to reduce the cost and minimize wastewater generation, the process is implemented on monazite concentrates assaying 55-65% REO (Qi, 2018). Also, the spent NaOH solution is recycled. Another way to defray the cost is to produce $Na_3PO_4$ as a salable byproduct. Still another way to minimize the reagent cost is to carry out caustic decomposition in a ball mill (Lazo *et al*., 2020; Abdel-Rehim *et al*., 2002; Kim *et al*., 2009). Nevertheless, caustic decomposition is aggressive enough to dissolve gangue minerals, creating significant wastewater that needs to be treated. Acid cracking, on the other hand, can be used to decompose low-grade concentrates by virtue of lower reagent costs. It can also handle large particle sizes as the acid can readily penetrate the mineral matrix. However, acid leaching is not selective and has the disadvantage of operating under corrosive environments.

At Bayan Obo, mixed bastnaesite-monazite concentrates are decomposed by roasting in a rotary kiln at >300 $^oC$ in the presence of $H_2SO_4$ to produce $Ln_2(SO_4)_3$ that can be readily leached in water (Cen *et al*., 2021). However, the sulfate salts are not highly soluble in water and their solubilities decrease with temperature. Therefore, the water leaching is carried out at ambient temperatures using large amounts of water usually 7-10 times the weight of the concentrate. A small part (~10%) of the Bayan Obo concentrate is, however, decomposed by NaOH at 140-200 $^oC$, followed by HCl leaching at pH 1-1.5 (Zhu *et al*., 2015).

Monazite concentrates contain usually 50-60% REO and 4-12% $ThO_2$ and 0.3-0.5% U. The radioactive elements and other impurities must be removed from the leach liquor prior to solvent extraction. Lapidus and Doyle (2015) explored the possibility of selectively leaching the actinides from monazite using ammonium oxalate to find that complete recovery of both metals was limited by passivation of the mineral as rare-earth phosphates or oxalates. Lazo *et al.* (2017) showed that $Ln^{3+}$ ions reprecipitate as oxalate ($Ln_2(ox)_3$) while the $PO_4^{3-}$ ions are released into the solution. The authors found also that the precipitate can be dissolved in the presence of 0.1 M ethylenediaminetetraacetic acid (EDTA) at pH 10 and 25 °C. Thus, oxalate can be used to decompose monazite in acidic pH. It is not as powerful as NaOH in releasing $PO_4^{3-}$ ions but without co-extracting a large proportion of impurities into the solution (Lazo *et al.*, 2018).

Due to the extreme stability of monazite, the conditions for its alkali decomposition process have remained essentially the same for the past 40 years with minor variations (Krishnamurthy and Gupta, 2015). Monazite concentrates pulverized typically to <10 μm are treated in high concentrations of NaOH solutions at 150 °C to convert them to $Ln(OH)_3(s)$ before acid leaching. Amer et al. (2018) showed recently that ammonium sulfate ($(NH_4)_2SO_4$) rather than an acid can be used as a lixiviant for the extraction of the $Ln^{3+}$ ions from the hydroxide. It has been shown that the ammonium salt can selectively extract $Ln^{3+}$ ions but not Th or U, which appears to be a significant advantage over acid leaching.

Coal is a significant source of REEs. Bryan *et al.* (2015) analyzed the coal quality database and determined that the REEs in coal favor partitioning to clay materials and only small amounts are fixed by ion-exchange processes into the organic phase. The REE contents accumulated on kaolinite are 5-10 times greater than those of coal as a whole. Estimates of inferred REE resources contained in coal kaolinite are 10.9 million metric tonnes at a cutoff grade of 500 ppm. REEs are also present in resistive detrital sands such as monazite, xenotime, zircon, and rutile. It is, therefore, necessary to develop processes that can be used to extract REEs from stable minerals such as monazite to make coal byproducts as a non-conventional source.

The objective of the present work has been to develop a sustainable method of extracting REEs from the coal byproducts, which include monazite and clay materials. Since the particle sizes of the rare earth minerals (REMs) in coal are small (<15 μm) and the concentrations are low, it is difficult to produce high-grade concentrates by flotation for volume reduction. Under these circumstances, it is critically important to develop methods of extracting REEs under relatively mild conditions to minimize energy consumption and wastewater generation. The approaches taken to meet these requirements were to decompose monazite concentrates at relatively low NaOH concentrations at temperatures below 100 °C and to subsequently dissolve the hydrous oxides using $(NH_4)_2SO_4$ as a lixiviant at pH 4. The test results have been analyzed to better understand the mechanisms involved in ammonium sulfate leaching. Encouraging results have also been obtained with the extraction of REEs from the clay materials isolated from coal as will be reported in future communication.

## 2. EXPERIMENTAL

### 2.1. Sample and reagents

A Ce-type monazite sample assaying 24.3% total REE (TREE) and 5-8 cm in size was obtained from Khyber Mineral Co., Westmont, IL. The as-received sample was wet-ground in a ball mill to 80% passing ($d_{80}$) 14.6 μm, and the mill product was floated twice in a 4-L Denver laboratory flotation cell using potassium octyl hydroxamate as the collector. A froth product assaying 48.9 %TREE was obtained, which was equivalent to ~75% pure monazite. Table 1 shows

Table 1. Elemental composition of the monazite sample before and after flotation

| Element | Grade before flotation(wt.%) | Grade after flotation(wt.%) |
|---|---|---|
| Ce | 10.26 | 18.80 |
| Nd | 5.80 | 12.68 |
| La | 2.47 | 5.18 |
| Sm | 2.01 | 4.68 |
| Pr | 1.37 | 3.06 |
| Gd | 1.04 | 2.38 |
| Y | 0.86 | 1.49 |
| Other REEs | 0.39 | 0.66 |
| Th | 3.15 | 7.68 |
| U | 0.11 | 0.22 |
| P | 4.81 | 9.57 |

the elemental composition of the monazite sample before and after flotation.

The monazite concentrate obtained by flotation was dried in an oven and used for a series of leaching experiments. Representative splits from the flotation product were ground to $d_{80}$ = 8.25 and 4.95 μm in a planetary ball mill for 1 and 2 h, respectively, for leaching tests. The monazite samples were analyzed by ICP-MS after digesting them at 1,000 °C in lithium metaborate and $Na_2CO_3$ as described by Larijani *et al*., (2016).

Reagent grade NaOH and HCl from Fisher Scientific were used for leaching experiments, while all other regents were of analytical grades. Deionized water with a resistivity of 18.2 MΩ·cm at 298.15 K was used in all solution preparation and leaching tests.

## 2.2. Methods and procedure

### *2.2.1. NaOH pretreatment*

Monazite is a salt of hard acids and a hard base. Therefore, it takes a harder base, *e.g*., $OH^-$ ions, to disengage the $PO_4^{3-}$ ions from the lanthanide ($Ln^{3+}$) ions and decompose the mineral as follows,

$$LnPO_4(s) + 3NaOH \rightarrow Ln(OH)_3(s) + 3Na^{3+} + PO_4^{3-} \qquad [2]$$

to form $Ln(OH)_3(s)$, which is acid-soluble. In the present work, a monazite sample ground to a desired particle size was pretreated in a NaOH solution before subjecting it to $(NH_4)_2SO_4$ leaching at pH 4.0. That $pK_b$ = 1.7 and 0 for $PO_4^{3-}$ and $OH^-$ ions, respectively, warrants the NaOH pretreatment step.

In each experiment, a 0.5 g monazite sample was mixed with a 20 mL NaOH solution in a 50 mL alkali-resistant polytetrafluoroethylene (PTFE) beaker and heated on a hot plate at temperatures in the range of 60-80 ºC for 24 h, while the mixture was being agitated at 600 rpm by means of a Teflon-coated magnetic stir bar. The NaOH concentrations were varied in the range of 10-50% w/v. The temperature of the sample suspension was monitored within ±1 °C by means of a temperature probe placed in the sample suspension. The beaker was covered with paraffin film to keep the evaporative loss of water to less than 1 mL. The pretreated slurry was then subjected to solid-liquid separation by centrifugation at 5,000 rpm for 10 min. The residual NaOH was removed by re-pulping the residue with deionized water, followed by centrifugation. This water washing step was repeated three times.

### *2.2.2. Leaching tests*

The monazite samples pretreated with NaOH and water-washed were subjected to a series of leaching experiments at room temperature using various lixiviants. In each test, a 0.5 g sample was mixed with 40 mL of a lixiviant solution in a 50 mL polypropylene beaker. The slurry was then agitated magnetically for 2 h to provide adequate mixing. During leaching, aliquots of HCl and NaOH solutions both of 0.5 M were added to maintain the pH at 4.0±0.1. For the leaching experiments conducted at different temperatures, a Soxhlet extraction apparatus was used to minimize solvent loss.

Samples of the slurry were taken intermittently and analyzed for REE content to monitor the kinetics of leaching. After a given reaction time, 0.4 mL of the slurry was taken from the beaker by means of a 1 mL disposable syringe and was centrifuged at 3,000 rpm for 5 min for solid-liquid separation. The volume of the leach liquor taken at different time intervals was measured by means of a 1 mL graduated cylinder, with each solution being diluted 2,000 times with a mixed $HNO_3$ (2.5%) and HCl (0.5%) solution for ICP-MS analysis. The recovery ($R$) of an REE species was determined using the following relationship,

$$R = 100 \times \frac{C_l V}{C_f M} \qquad [3]$$

in which $C_l$ and $V$ are the REE concentration and volume of the leach liquor, respectively; and $C_f$ and $M$ are the REE concentration and weight of the sample, respectively. Each test was repeated at least twice with the results averaged.

### *2.2.3. ζ-potential measurements*

Zeta-potential measurements were conducted on the monazite samples treated under different chemical conditions using the Malvern Zeta spectrometer (Model Zs90). The measurements were conducted on the NaOH-pretreated sample dispersed in pure water and in a 0.5 M $(NH_4)_2SO_4$ solution at pH 4.0. The objective of the measurement was to derive information on the changes in ionic composition at the solid/liquid interface, which may shed light on the role of the lixiviant in leaching the NaOH-treated monazite. The measurements were conducted at least three times at a given reagent condition, with the results averaged.

### *2.2.4. Powder X-ray diffraction studies*

The monazite samples pretreated with NaOH and subsequently leached with $(NH_4)_2SO_4$ as a lixiviant were subjected to X-ray diffraction analysis using the Rigaku MiniFlex 600 XRD analyzer equipped with Cu-Kα radiation (λ = 1.54 Å). The spectra were recorded over a 2$\theta$ range from 10-80° with a step size of 0.04° and a dwell time of two seconds.

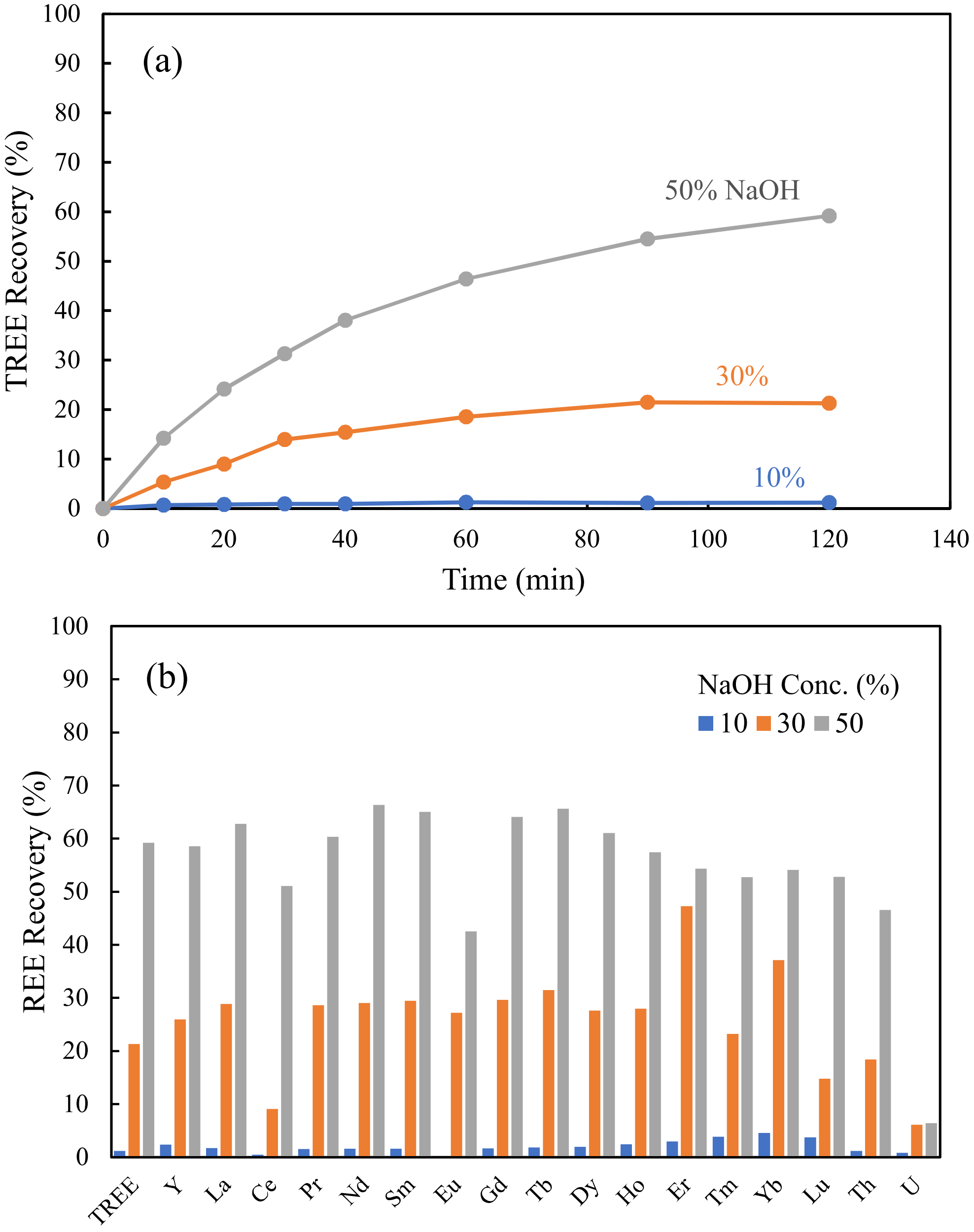

Figure 1. Results of the ammonium sulfate leaching tests conducted on a monazite sample ($d_{80}$ = 14.61 µm) at 0.5 M $(NH_4)_2SO_4$, pH 4, and ambient temperature after the NaOH pretreatment step in 10, 30, and 50% solutions at 80 °C for 24 h; a) total REE recoveries, b) element-by-element recoveries.

### 2.2.5. *X-ray photoelectron spectroscopy analysis*

The sample preparation method employed for XPS analysis was the same as used for the

XRD analyses. A PHI VersaProbe III scanning XPS microscope with a monochromatic Al K-α X-ray source (1486.6 eV) was used to collect XPS spectra over a 200 μm×200 μm area. The adventitious carbon peak at 284.8 eV was used for binding energy correction.

## 3. RESULTS

### 3.1. Ammonium sulfate leaching

### *3.1.1. NaOH Pretreatment*

A series of rare earth extraction tests were conducted by first treating the monazite sample in a NaOH solution and subsequently extracting the $Ln^{3+}$ ions into the solution from the sample using $(NH_4)_2SO_4$ as a lixiviant. The pretreatment steps were carried out in 10, 30, and 50% w/v NaOH solutions at 80 °C for 24 h, while the leaching steps were carried out at room temperature in 0.5 M $(NH_4)_2SO_4$ solution at pH 4.0. The sample suspensions were agitated by means of a magnetic stirring bar for 2 h. The results presented in Figure 1a show that as the NaOH concentration was increased from 30 to 50%, the recoveries increased from 21 to 60%. Although not shown in Figure 1, the recoveries obtained after the pretreatments at 60 °C were ~40% maximum.

Thus, monazite decomposition and ammonium sulfate leaching are favored at higher NaOH concentrations and higher temperatures. These results agree with the work of Panda *et al.* (2014), who reported the large activation energy of $E_a$ = 58.04 kJ/mol. These investigators pretreated Korean monazite at 150-180 °C in a 50% NaOH solution and dissolved the products in 6 M HCl solutions. The authors showed also that up to 99.99% of the phosphorus can be removed

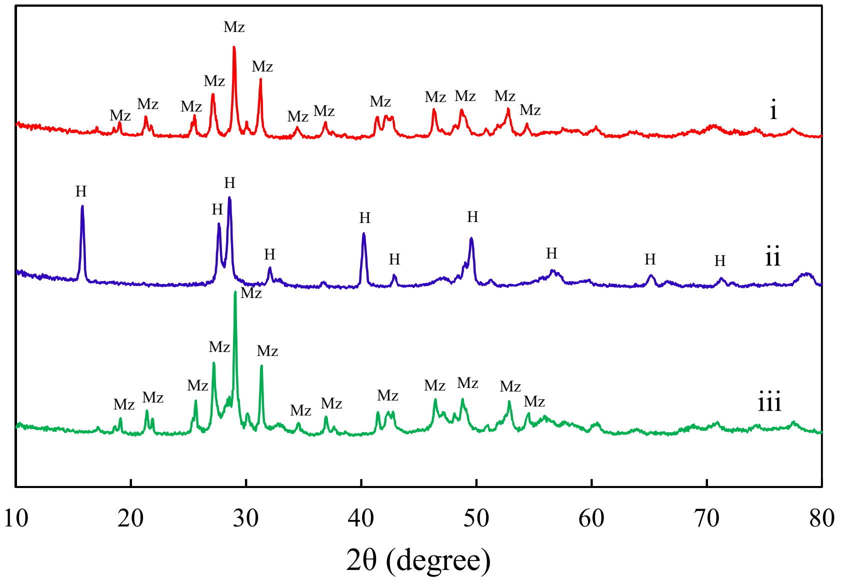

Figure 2. XRD spectra of i) untreated monazite of $d_{80}$=14.61 μm, ii) monazite pretreated in a 30% NaOH solution at 80 °C for 24 h, and iii) of leach residue. The second spectrum shows hydroxide formation, which disappears after the ammonium sulfate leaching. The third spectrum shows the reappearance of the monazite substrate after the leaching (Mz: monazite; H: rare earth hydroxide).

from monazite after the NaOH pretreatment steps conducted at 170 ºC for 2-4 h. This finding is consistent with the monazite decomposition mechanism represented by Reaction [2].

Figure 1b shows the element-by-element REE recoveries obtained at 80 ºC. Despite the relatively mild operating conditions employed, the recoveries of the key elements were reasonably high: 66.3% Nd, 62.8% La, 61.0% Dy, 65.0% Sm, and 60.3% Pr. The Ce and Eu recoveries were lower as shown. The low Ce recoveries may be attributed to the oxidation of Ce(III) to Ce(IV) during the NaOH pretreatment step as will be shown later in conjunction with the XPS spectra. On the other hand, the low Eu recoveries may be attributed to the formation of the insoluble $EuSO_4$ during the $(NH_4)_2SO_4$ leaching step.

The standard half-cell potentials given below

$$Ce^{4+} + e = Ce^{3+} \qquad E_0 = 1.62\ V \qquad [4]$$

$$Eu^{3+} + e = Eu^{2+} \qquad E_0 = -0.378\ V \qquad [5]$$

may provide an explanation for the experimental results obtained in the present work. Although the thermodynamic data show that the $Ce^{3+}$ ions are more difficult to be oxidized than the $Eu^{3+}$ ions, they can be readily oxidized to $Ce^{4+}$ ions and form $CeO_2$ at pH > 9.5 at potentials slightly above 0 V SHE (Kim and Osseo-Asare, 2012). The low solubility of $CeO_2$ may account for the low extraction efficiencies of cerium observed in the present work. The $Eu^{3+}$ ions, on the other hand, are much more unstable than the $Ce^{3+}$ ions. Therefore, they can be readily reduced to $Eu^{2+}$ ions and form insoluble $EuSO_4(s)$ when $(NH_4)_2SO_4$ is used as a lixiviant, which explains the low extraction efficiencies observed in the present work. It is possible that the $Ce^{3+}$ to $Ce^{4+}$ oxidation causes the $Eu^{3+}$ ions to be reduced to $Eu^{2+}$ ions during the NaOH pretreatment step.

Figure 2 shows the XRD spectra of the monazite sample before and after the NaOH pretreatment. Also shown is the spectrum of the residue left after the $(NH_4)_2SO_4$ leaching. The results show that monazite had been converted to rare earth hydroxide ($Ln(OH)_3$) after the NaOH pretreatment step. Note also that after the leaching, most of the hydroxides formed on the monazite surface were removed, leaving the unreacted monazite as the residue.

Figure 3 shows the XPS spectra of a monazite sample before and after the NaOH pretreatment and the $(NH_4)_2SO_4$ leaching steps. As shown, the oxidation state of Ce changes from Ce(III) to Ce(IV) as clearly indicated by the satellite peaks at 916.3 eV and 882 eV. It has been reported that $CeO_2$ or $Ce(OH)_4$ are sparingly soluble in weakly acidic solutions and hence dissolve only under aggressive conditions (Kumari *et al.*, 2019; Li *et al.*, 2017).

### *3.1.2. Particle Size*

Monazite decomposition in a NaOH solution is a heterogeneous interaction occurring at the solid/liquid interface. The reaction occurs initially on the monazite surface to form a layer of $La(OH)_3(s)$. At a steady-state, the reaction rate may be controlled by the rate of diffusion of the $OH^-$ ions through the product layer. Qi (2018) showed that monazite decomposition in NaOH solutions can be modeled using the Valency's equation (Habashi, 1969),

$$1-\tfrac{2}{3}R-\left(1-R\right)^{2/3}=\frac{2MDC}{\alpha\rho r_0^2}t \qquad [6]$$

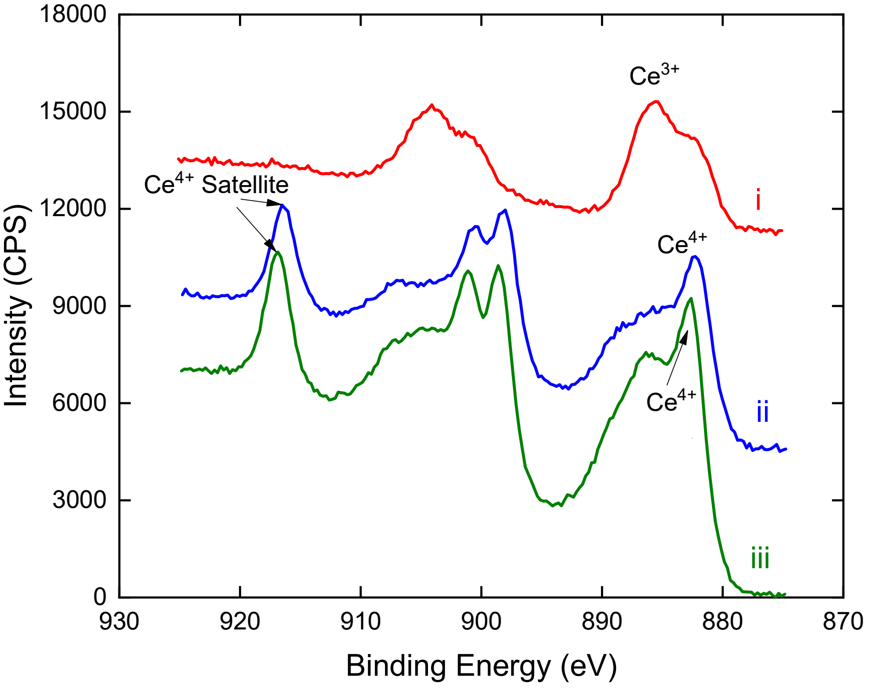

Figure 3. Ce 3d XPS spectra of i) untreated monazite of $d_{80}$=14.61 μm; ii) NaOH-pretreated monazite at 30% NaOH and 80°C for 24 h; iii) leach residue.

in which $R\ (= 1 - W/W_0)$ is the fraction of the mineral reacted with $W_0$ being the weight of the monazite particle of radius $r_0$ at time $t = 0$ and W the weight at time $t$, $M$ and $\rho$ the molecular weight and density of the mineral, $D$ and $C$ the diffusion coefficient and $OH^-$ concentration, respectively, $\alpha$ the stoichiometry factor, and $\rho$ is the particle density. Eq. [6] shows that the rate at which monazite decomposition is approximately proportional to the NaOH concentration and is inversely proportional to the square of particle size, *i.e.*, $r_0^2$. From this equation, one can understand why the industry grinds monazite concentrates to less than 45 μm, often below 10 μm (Krishnamurthy and Gupta, 2015).

Figure 4a shows the effect of particle size studied in the present work. As shown, both the kinetics and ultimate REE recoveries increased substantially with decreasing particle size as suggested by Eq. [6]. The kinetics tests were conducted with monazite samples with $d_{80}$ = 14.61, 8.25, and 4.95 μm after pretreatments in 50% NaOH solutions at 80 °C for 24 h, followed by the $(NH_4)_2SO_4$ leaching at 0.5 M at pH 4 and 25 °C for 2 h. As shown in Figure 4b, the recoveries of the three major elements of monazite, *i.e.*, La, Pr, and Nd, were close to 85% at $d_{80}$ = 4.95 μm.

In the present work, the $OH^-$ ions displaced the $PO_4^{3-}$ ions from the monazite structure and formed $Ln(OH)_3(s)$ on the mineral surface, which in turn was leached by using $(NH_4)_2SO_4$ as a lixiviant. In the conventional caustic soda leaching process, the $Ln(OH)_3(s)$ is dissolved in HCl solutions at pH ~3 (Gupta and Krishnaswami, 2015; Qi, 2018) and/or at pH 1-1.5 (Zhu *et al.*, 2015) In the present work, we used a 6 M HCl solution to ensure the complete dissolution of the hydroxides formed after the pretreatments in 30 and 50% NaOH solutions. The results obtained using the two different lixiviants, *i.e.*, $(NH_4)_2SO_4$ and HCl, are compared in Figure 5a. As shown, the kinetics of $(NH_4)_2SO_4$ leaching was slower than that of the HCl leaching. On the other hand,

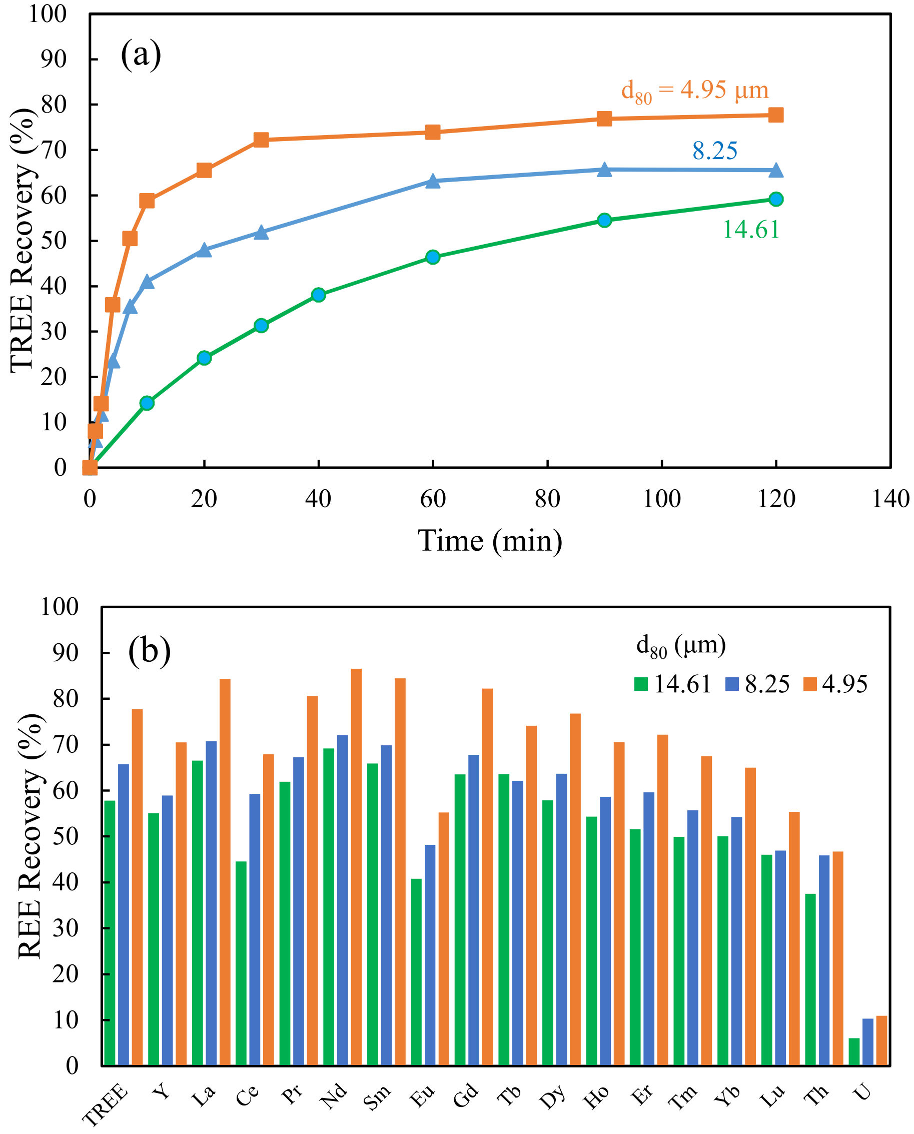

Figure 5. Effect of particle size on a) TREE recoveries, and b) individual REE recoveries. Monazite particles were pretreated in a 50% NaOH solution at 80°C for 24 h, followed by $(NH_4)_2SO_4$ leaching at pH 4 and 25 °C for 2 h.

the ammonium sulfate leaching released substantially less U into solution, which may be a distinct advantage of using $(NH_4)_2SO_4$ rather than HCl as a lixiviant. Amer *et al.* (2018) showed that $(NH_4)_2SO_4$ and $NH_4Cl$ are more selective against $Fe_2(SO_4)_3$ and $FeCl_3$, which may be related to the high electrochemical potential created by the $Fe^{3+}$ ions. According to Krupka and Serne (2002), $UO_2$ becomes soluble at higher potentials in the presence of carbonate ions. The results presented in Figures 5a and -b show that the REE recoveries were higher at the higher NaOH concentration. These results clearly indicate that REE recovery depends critically on the NaOH concentrations, while the type of lixiviants for the $Ln(OH)_3(s)$ leaching determines the kinetics. Much of the excess NaOH can be readily recycled, however.

The results presented in Figure 6a show that the kinetics of the $(NH_4)_2SO_4$ leaching was

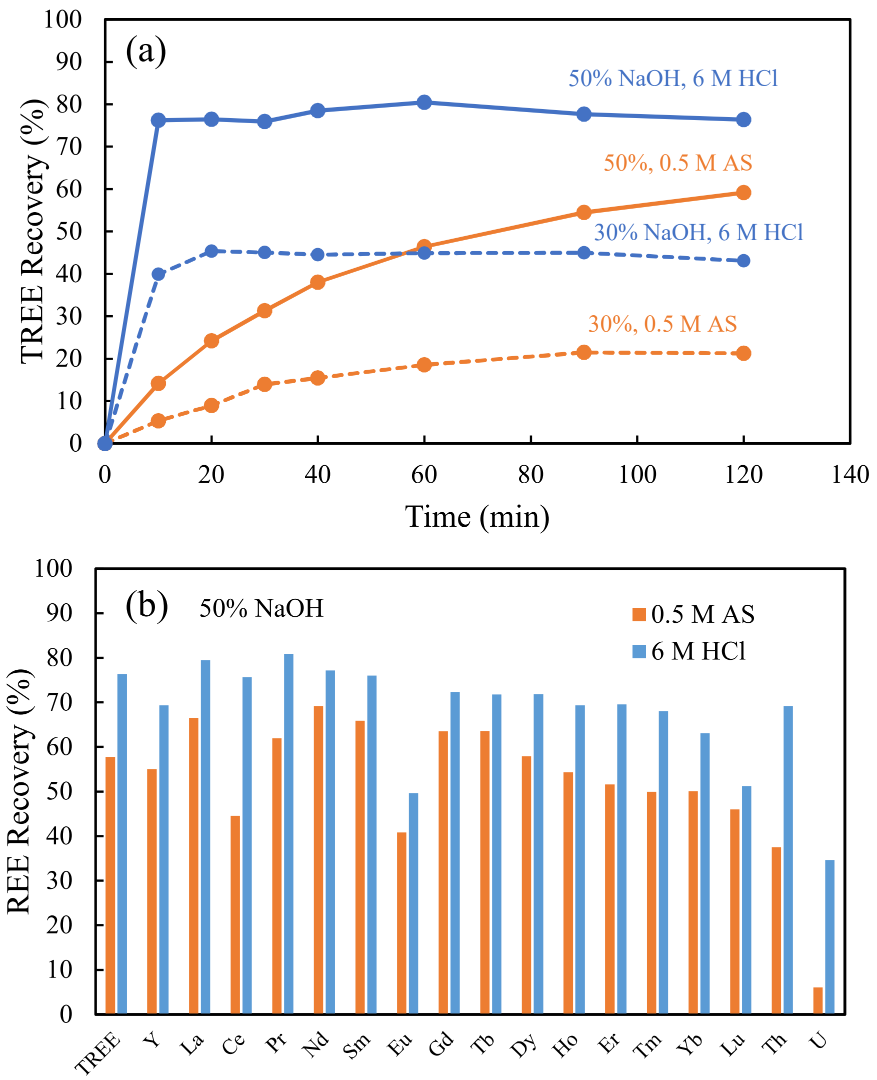

Figure 6. Comparison between extracting REEs from the NaOH pretreated monazite ($d_{80} = 14.61\ \mu m$) at 80 °C for 24 h, followed by $(NH_4)_2SO_4$ leaching at pH 4 and 25°C and by acid leaching in a 6 M HCl solution; (a) TREE recoveries; (b) corresponding individual REE recoveries. “AS” denotes ammonium sulfate (the same below).

greatly improved by increasing the temperature. At 65 °C, the kinetics was as fast as obtained using a 6 M HCl solution at 25 °C (see Figure 5a). Even the ultimate TREE recoveries improved at the higher ammonium sulfate leaching temperature as shown in Figures 6a and -b. These improvements were made without significantly increasing the release of U into the leach liquor. Note here that the TREE recovery obtained using $(NH_4)_2SO_4$ as lixiviant is lower than obtained at 6 M HCl concentration (Figure 5), which may be attributed to the likelihood that Ce can be more readily leached in a 6 M HCl solution than in a 0.5 M $(NH_4)_2SO_4$ solution.

### *3.1.3. Effect of Different Cations*

The results presented in the foregoing sections showed that $(NH_4)_2SO_4$ can be used as a lixiviant for $Ln(OH)_3(s)$ as shown also by Amer *et al.* (2017). Ammonia ($NH_3$) that forms complexes with some of the common transition metals, *e.g.*, Cu, Ni, Co, Zn, *etc.*, are used as an

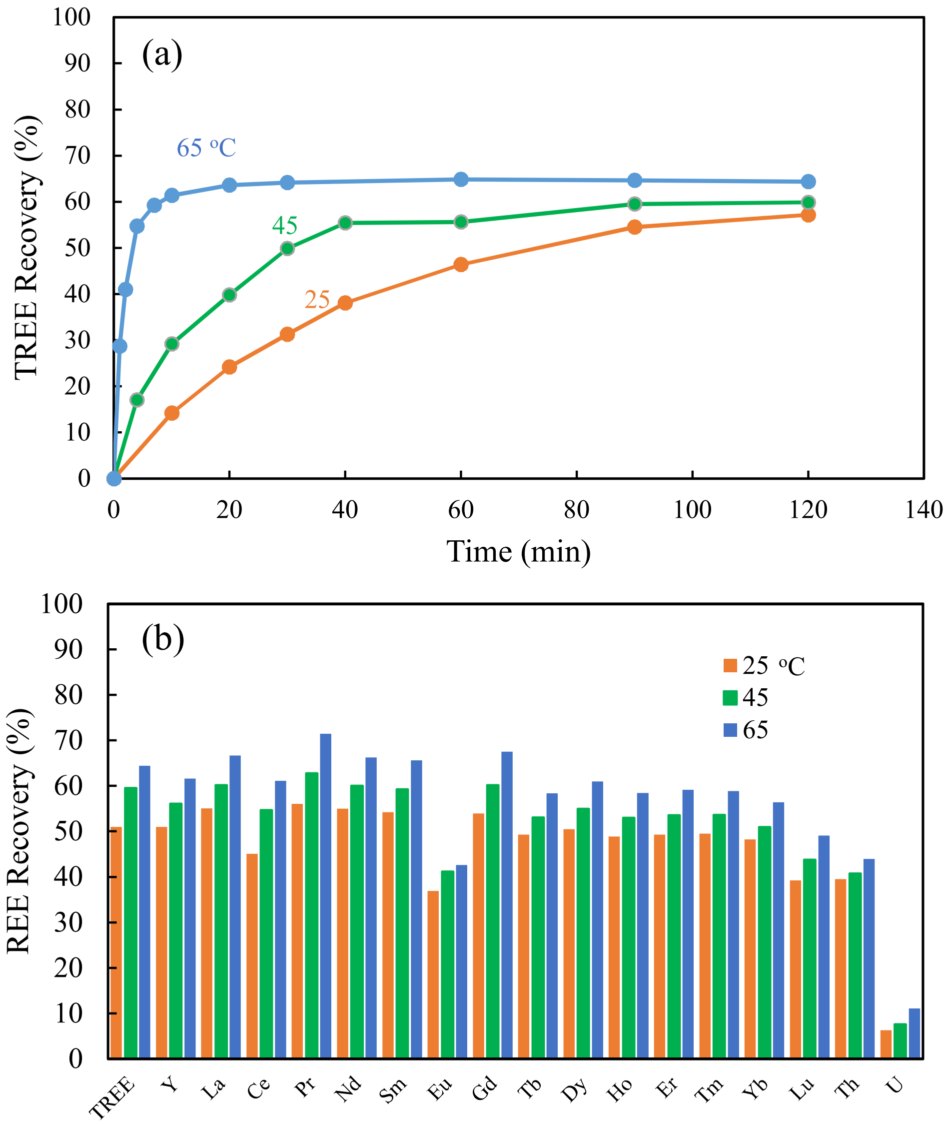

Figure 7. The total and individual REE recoveries of a monazite sample pretreated in a 50% NaOH solution at 80 °C and $d_{80} = 14.61$ µm). The pretreated samples were leached in a 0.5 M $(NH_4)_2SO_4$ solution at pH 4 at different temperatures.

efficient lixiviant for their oxides (Meng and Han, 1996). It appears, however, that $Ln^{3+}$ ions do not form stable complexes with ammonia. Therefore, it would be reasonable to explore the possibility of $NH_4^+$ ions displacing the $Ln^{3+}$ ions adsorbed on the $Ln(OH)_3(s)$ surface as follows,

$$Ln(OH)_3(s)\text{-}Ln^{3+} + 3NH_4^+ \rightarrow Ln(OH)_3(s)\text{-}3NH_4^+ + Ln^{3+} \qquad [7]$$

which is akin to the ion-exchange mechanism described by Eq. [1] for leaching IACs. When an oxide or hydroxide is placed in an aqueous medium, it acquires surface charges which vary with pH. Parks and de Bruyn (1962) found that the point of zero charge (p.z.c.) of the solid is usually equal to the iso-electric point (i.e.p.) of the solution, which led them to suggest that the surface charging mechanism is an integral part of solubilization. At pH ~4, where the ammonium sulfate

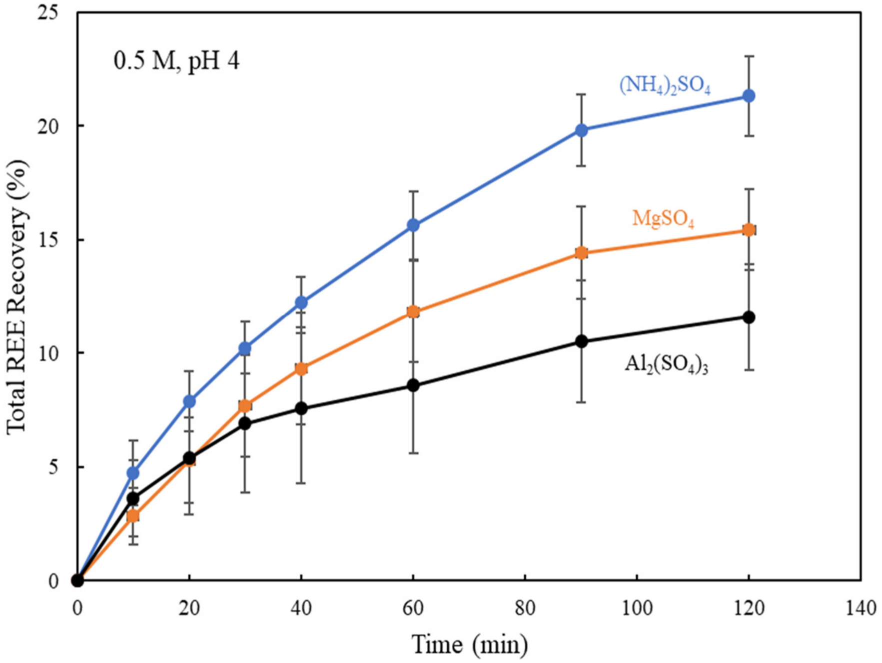

Figure 8. Total REE recovery leached by various sulfate-based lixiviants at pH 4 after 30% NaOH pretreatment at 80 °C for 24 h, $d_{80}$ = 14.61 µm.

leaching experiments have been conducted, the NaOH-treated monazite is positively charged with its $\zeta$ = 40 mV as shown in Figure 11. Since $Ln^{3+}$ ions are the most predominant charges species in this pH range, it may be reasonable to view that the $Ln^{3+}$ ions are present as adsorbed species.

As has already been noted, the $Ln^{3+}$ ions adsorbed on clay are displaced by the $NH_4^+$ ions as shown in Reaction [1] due to the large differences in the hydration enthalpies (Moldoveanu and Papangelakis, 2012). To explore the possibility that Reaction [7] may also be controlled by the hydration enthalpies of ionic species involved, a series of leaching experiments were conducted on an NaOH-treated monazite sample using $(NH_4)_2(SO_4)$, $MgSO_4$, and $Al_2(SO_4)_3$ as lixiviants at pH 4. All experiments were conducted using 0.5 M solutions at pH 4, $d_{80}$ = 14.61 µm, 2 h leaching time, and at ambient temperatures. The results presented in Figure 7 show that the $NH_4^+$ ions with $\Delta H_{hyd}^{o}$ = -307 kJ mole$^{-1}$ gave the highest REE recoveries, followed by $Mg^{2+}$ ions with $\Delta H_{hyd}^{o}$ = 1,921 kJ mole$^{-1}$, and $Al^{3+}$ ions with $\Delta H_{hyd}^{o}$ = -4,665 kJ mole$^{-1}$ (Smith, 1977). The error bars for the tests conducted with $(NH_4)_2SO_4$ and $MgSO_4$ were reasonable with < 3% standard error at a 95% confidence interval, while the tests conducted with $Al_2(SO_4)_3$ were larger due to the possible precipitation of $Al(OH)_3$.

The results presented in Figure 7 suggests that the cationic species, from which hydration water can be more readily stripped off may serve as better lixiviants. A bare cationic species should have a stronger electrostatic attraction to the negatively charged surface sites and hence can displace the $Ln^{3+}$ ions by an ion-exchange mechanism. It has been shown clearly that in the ion-exchange leaching of clays, $NH_4^+$ ions are better lixiviants than the $Mg^{2+}$ and $Al^{3+}$ ions (Ran *et al.*, 2017; Xiao et al., 2016).

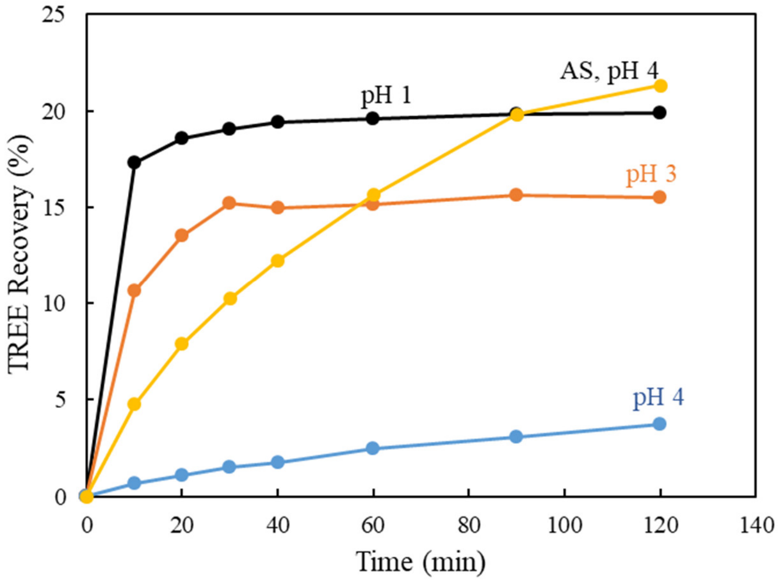

Figure 9. REE recovery of monazite leached in HCl solutions of different pH. The samples were pretreated in a 30% NaOH solution at 80 °C for 24 h, $d_{80}$ = 14.61 µm.

For comparison, Figure 8 shows the results obtained using HCl as the sole lixiviant for $Ln(OH)_3(s)$ at different pH values. As expected, leaching efficiencies increased with decreasing pH. Note here that the REE recovery obtained in a 0.5 M $(NH_4)_2SO_4$ solution at pH 4, was higher than the recoveries obtained using HCl at pH 1, 3 and 4, demonstrating the benefits of using $(NH_4)_2SO_4$ as a lixiviant.

### *3.1.4. Effect of Different Anions*

Figure 9 shows the results of using ammonium salts of different anions, *i.e.*, $SO_4^-$, $HCO_2^-$ and $NO_3^-$, as lixiviants. As can be seen, the sulfate performed the best, followed by formate, and nitrate, which was in the same order of the stability constants of the following reactions (Smith *et al.*, 2004; Haas *et al.*, 1995),

$$La^{3+} + SO_4^{2-} \rightarrow LaSO_4^- \qquad 10^{3.64} \qquad [8]$$

$$La^{3+} + HCOO^- \rightarrow La(HCOO)^{2+} \qquad 10^{1.74} \qquad [9]$$

$$La^{3+} + NO_3^- \rightarrow LaNO_3^{2+} \qquad 10^{0.58} \qquad [10]$$

The higher the stability constant, the lower the $La^{3+}$ ion concentrations in solution, which will shift the following ion-exchange reaction

$$La^{3+} \text{ (surface)} + 3NH_4^+ \rightarrow 3NH_4^+ \text{ (surface)} + La^{3+} \qquad [11]$$

to the right and, thereby, increase the extraction efficiency. The $Ln^{3+}$ ions other than the $La^{3+}$ shown above as an example should behave likewise. The results obtained using the three different ammonium salts of three different anions, $(NH_4)_2SO_4$ gave the best results, justifying its use as the optimal lixiviant for $Ln(OH)_3(s)$. This finding is similar to the thermodynamic consideration that

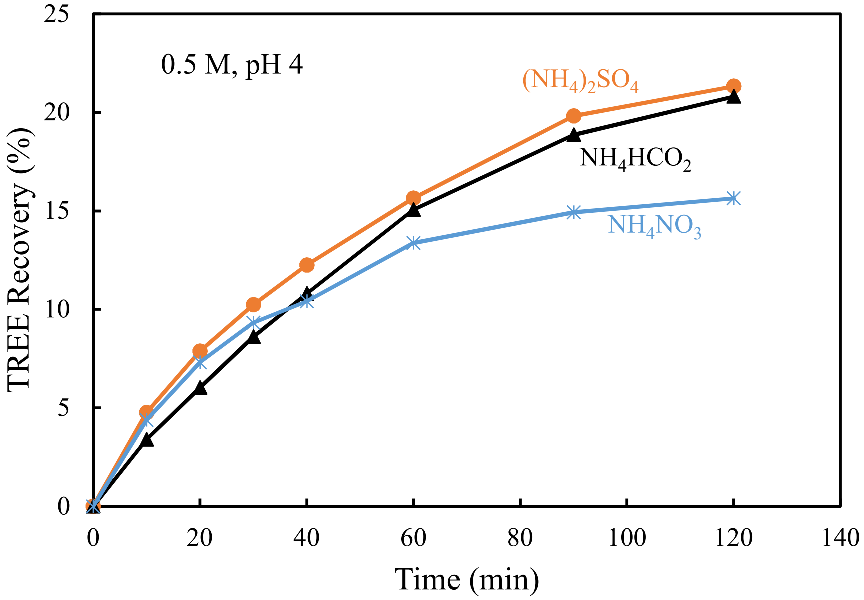

Figure 10. Effect of different anions of ammonium salts on REE extraction from the monazite particles pretreated in a 30% NaOH solution at 80°C; with $d_{80}$ = 14.61 µm.

the stability of $ThO_2$ diminishes considerably in the presence of sulfate ions (Kim *et al*., 2012).

## 4. DISCUSSION

Monazite decomposition requires an aggressive treatment either in concentrated $H_2SO_4$ at 200-220 ºC or in 60-70% NaOH solutions at 140-180 ºC (Lucas *et al*., 2014). Caustic soda is more expensive than sulfuric acid; therefore, the former is used to decompose monazite concentrates with 55-65% REO, while the latter is used to decompose lower-grade concentrates. Sulfuric acid can deeply penetrate into the mineral matrix and decompose particles of 74-149 µm, while caustic soda leaching requires the monazite concentrate to be ground to less than 45 µm, often to less than 10 µm, as mentioned in Section 3.1.2.

The results obtained in the present work showed that monazite can be decomposed to $Ln(OH)_3$ at 10-30% NaOH concentrations. However, the reaction rates were too slow to be of practical use at the temperature range investigated. It appears that a 50% NaOH may be the minimum required at 80 ºC, which may not be an insurmountable dosage rate as the unreacted NaOH can be readily recycled after removing phosphor from solution by forming trisodium phosphate ($Na_3PO_4 10 \cdot H_2O$) at 60 ºC (Habashi, 2012). Another approach to improving the kinetics was to decrease the particle size. At $d_{80}$ = 4.95 µm, we obtained a 77.7% REE recovery, with an 86.5% Nd recovery at 80 ºC.

The results presented herein showed that $(NH_4)_2SO_4$ can be used as a lixiviant for leaching the $Ln(OH)_3(s)$ formed as a result of monazite decomposition *via* NaOH pretreatment. However, its kinetics was slower than observed with 6 M HCl solutions at 25 ºC as shown in Figures 5a and -b. At higher temperatures, however, the kinetics of the ammonium sulfate leaching was much faster as shown in Figures 6a and -b. It should be noted also that the $(NH_4)_2SO_4$ leaching at pH 4 was comparable to the HCl leaching at pH 1.0 as shown in Figure 8, which may be an important advantage of using $(NH_4)_2SO_4$ as a lixiviant over the acid leaching. This advantage may be attributed to the fact that the $H^+$ ions have substantially more negative enthalpy of hydration ($\Delta H^{o}_{hyd}$ = -1,091 kJ mole$^{-1}$) than that ($\Delta H^{o}_{hyd}$ = -307 kJ mole$^{-1}$) of the $NH_4^+$ ions (Smith, 1977). Therefore, the latter can more readily displace the $Ln^{3+}$ ions from the $Ln(OH)_{3(}s)$ surface in accordance to Eq. [7]. Another advantage of using ammonium sulfate rather than acid as lixiviant may be that the extraction of U should be less. Using $(NH_4)_2SO_4$ and $NH_4Cl$ as lixiviants, Amer *et al.* (2018) detected no radioactive elements in their leach liquors. The leach liquors obtained in the present work showed, however, significant amounts of Th, which may be attributed to the sulfate ions in the system that may increase the solubility of $ThO_2$ (Kim *et al.*, 2012).

Borst *et al.* (2020) studied the adsorption of $Nd^{3+}$ and $Y^{3+}$ as proxies for the light and heavy REEs, adsorbed on kaolinite using the X-ray absorption spectroscopy (XAS), and concluded that REEs adsorb on the basal surfaces as fully-hydrated ions with 8 to 9 hydrated water molecules for both the heavy and light $Ln^{3+}$ ions, respectively. The fully-hydrated ions that are referred to as outer-sphere complexes adsorb on the basal surfaces of the $AlO_4(OH)_2$ octahedra and the $SiO_4$ tetrahedra *via* weak electrostatic interactions. Therefore, they can be readily displaced by appropriate lixiviant, *e.g.*, $NH_4^+$ ions, as shown by Reaction [1]. On the edge surfaces of kaolinite, however, $Ln^{3+}$ ions adsorb as partially-hydrated ions on the $Al\text{-}(OH)_2^-$ and $Si\text{-}(OH)_2^-$ groups and form inner-sphere complexes. According to Borst *et al.*, the inner-sphere complexes are difficult to be extracted by the ion-exchange mechanism. Thus, ion-exchange leaching can occur if the $Ln^{3+}$ ions are physically adsorbed on the basal surfaces.

Moldoveanu and Papangelakis (2012) proposed a model for the ion-exchange mechanism on the basis of the large difference in the hydration enthalpies between the $NH_4^+$ and $Ln^{3+}$ ions: $\Delta H^{o}_{hyd}$ = -307 and -3,296 kJ mole$^{-1}$, respectively. Furthermore, the hydration numbers are 4 and 8-9 for the $NH_4^+$ and $Ln^{3+}$ ions, respectively (Jia, 1987; Ikeda *et al.*, 2005). Therefore, the ammonium ions can readily shed the hydration water and be more strongly bonded to the negatively charged basal surfaces of clay. According to Miller *et al.* (1982), weakly hydrated monovalent cations can be completely dehydrated, whereas strongly hydrated trivalent cations

Table 2. Thermodynamic Data Used for the Solubility Diagram for $La(OH)_3(s)$

| Reactions | Equilibrium const. |
|---|---|
| $H_2O \rightleftharpoons H^+ + OH^-$ | $10^{-14}$ |
| $La(OH)_3(s) \rightleftharpoons La^{3+} + 3OH^-$ | $10^{-21.22}$ |
| $La(OH)^{+2} \rightleftharpoons La^{3+} + OH^-$ | $10^{-5.34}$ |
| $La(OH)_2^+ \rightleftharpoons La^{3+} + 2OH^-$ | $10^{-9.86}$ |
| $La(OH)_3(aq) \rightleftharpoons La^{3+} + 3OH^-$ | $10^{-14.09}$ |
| $La_2(OH)_2^{4+} \rightleftharpoons 2La^{3+} + 2OH^-$ | $10^{-9.59}$ |
| $La(OH)_4^- \rightleftharpoons La^{3+} + 4OH^-$ | $10^{-15.14}$ |

(Data sources: Shkolnikov et al., 2009; Hass *et al.*, 1995; Lee et al., 1992) such as $Ln^{3+}$ ions with $-\Delta H^{o}_{hyd} > 3{,}000$ kJ mole$^{-1}$ retain at least part of the hydration water and thus form weaker bonds with the surface. The $Ln^{3+}$ ions desorbed from the surface will be more fully hydrated in the bulk of the electrolyte solution, which should contribute to the driving force for the ion-exchange mechanism.

Figure 10 shows the solubility diagram for $La(OH)_3(s)$ constructed using the thermodynamic data presented in Table 2. As shown, the $La^{3+}$ ion concentration increases with decreasing pH, which should favor the ion-exchange leaching in accordance to Reaction [7]. In the present work, the $(NH_4)_2SO_4$ leaching has been conducted mostly at pH 4 where $La^{3+}$ ions are the most predominant La-bearing species. At pH < 3, $La_2(OH)_2^{4+}$ species become most predominant, which may be difficult to be removed by the ion-exchange mechanism.

Parks and de Bruyn (1962) studied the charging mechanisms of oxides and hydroxides in water and suggested that surface charge arises from the adsorption of the charged species derived from the solids. For the case of $La(OH)_3(s)$, various La-bearing species, *e.g.*, $La^{3+}$, $La(OH)_2^{+}$, $La(OH)_4^{-}$, shown in Figure 10, would readsorb on the surface and render the surface positively or negatively charged. The authors assumed that all of these species have equal adsorbability, in which case its point of zero charge (p.z.c.) should be equal to the iso-electric point (i.e.p.) of solution. The solubility diagram in Figure 10 shows that the i.e.p. occurs at pH 11.4, where the $La(OH)_2^{+}$ and $La(OH)_4^{-}$ ions are of equal concentration. Therefore, the p.z.c. of $La(OH)_3(s)$ should occur at pH 11.4 according to the theory of Parks and de Bruyn, which is known as the minimum solubility theory. The p.z.c. predicted from this theory is not far from the p,z.c. of 10.4 for $La_2O_3$. as predicted using an electrostatic model for the adsorption of $H^+$ and $OH^-$ ions (Yoon *et al.*, 1979).

Figure 11 shows a set of ζ-potential measurements conducted on the monazite sample pretreated with NaOH and subsequently with $(NH_4)_2SO_4$. At pH 4, the ζ-potential of the monazite

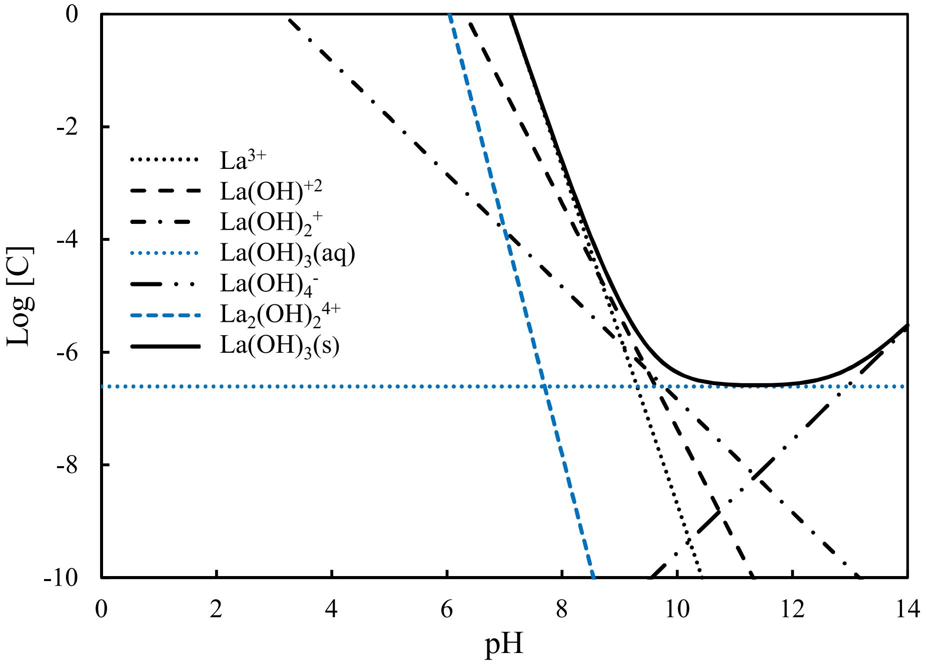

Figure 11. The solubility diagram $La(OH)_3(s)$ in water at 25 °C.

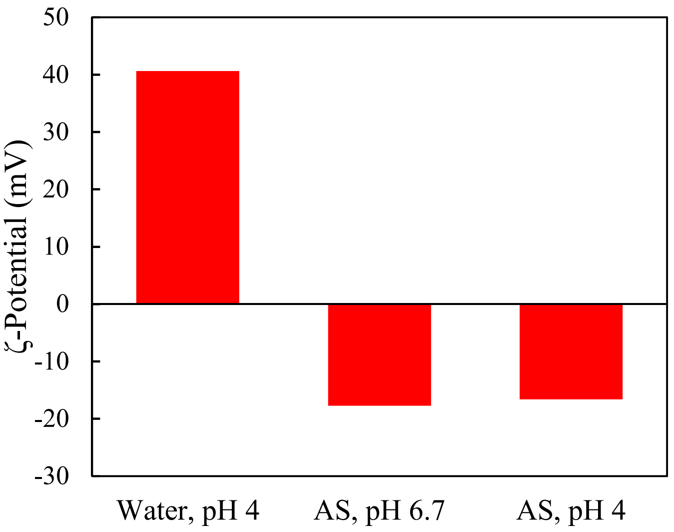

Figure 12. The zeta potentials of NaOH-treated monazite in different media. The samples were pretreated in a 30% NaOH solution at 80 °C for 24 h, $d_{80}$ = 14.61 μm.

sample was +40.6 mV due to the adsorption of the $Ln^{3+}$ ions on the $Ln(OH)_3$(s) surface. When the NaOH-treated monazite was placed in an $(NH_4)_2SO_4$ solution, the ζ-potential dropped to -17.8 mV at pH 6.7, most probably due to the adsorption of the $SO_4^{2-}$ ions to the surface. As the pH decreased to 4.0, the ζ-potential became slightly less negative possibly due to the displacement of the $Ln^{3+}$ ions by the $NH_4^+$ ion *via* the ion-exchange mechanism represented by Reaction [7].

Based on the ζ-potential data presented in Figure 11, a conceptual model for the ion-exchange leaching mechanism may be proposed as depicted in Figure 12. At pH 4.0, the $Ln(OH)_3$(s) formed as a result of the NaOH pretreatment is positively charged due to the readsorption of the $Ln^{3+}$ ions derived from the $Ln(OH)_3$(s). As the $(NH_4)_2SO_4$ lixiviant is added to the system, some of the $SO_4^{2-}$ ions adsorb to the Stern-layer, while the rest are dispersed in the diffuse layer along with the $NH_4^+$ ions as lixiviant. Sulfate ions have a strong affinity toward the $La^{3+}$ ions as shown in Eq. [8]. The $SO_4^{2-}$ ions located closer to the surface should provide a screening effect, so that the $NH_4^+$ ions can more readily approach the surface with a minimal electrostatic repulsion from the $Ln^{3+}$ ions that are already on the surface. Once on the surface, the $NH_4^+$ ions with a small hydration enthalpy of $-\Delta H_{hyd}^{o}$ = 307 kJ $mole^{-1}$ can readily shed their hydration sheaths and form a strong electrostatic bond to the surface, and thereby displace the $Ln^{3+}$ ions from the surface. The latter ions are weakly attached to the surface as they are strongly hydrated with $-\Delta H_{hyd}^{o}$= 3,296 kJ $mole^{-1}$.

Reactions [1] and [7] represent the ion-exchange leaching mechanisms for IACs and $Ln(OH)_3$(s), respectively. In the former, $NH_4^+$ ions adsorb to clay mineral surfaces and are lost to tailings. In the latter, the $NH_4^+$ ions are regenerated with continually receding solid/liquid interfaces during the entire leaching process. Therefore, there is no need to replenish the lixiviant, *i.e.*, $(NH_4)_2SO_4$, for the extraction of $Ln^{3+}$ ions from $Ln(OH)_3$(s), which is an important aspect of process economics.

There may be another advantage of using $(NH_4)_2SO_4$ rather than HCl as a lixiviant. Amer

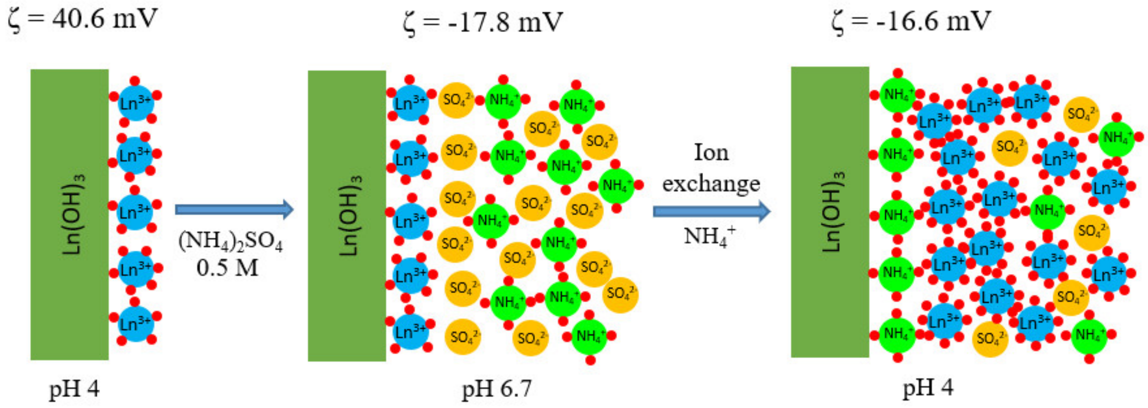

Figure 12. Proposed mechanism for the ion-exchange leaching of the NaOH-treated monazite using $(NH_4)_2SO_4$, as lixiviant. Red spheres represent hydrated water molecules.

*et al.* (2018) showed that the $(NH_4)_2SO_4$ leaching of alkali-treated monazite produced leach liquors with nondetectable amounts of U and Th. The experimental data presented in Figures 4 and 5 showed that the U concentrations are low; however, the Th concentrations were high, most probably due to the increase in the solubility of $ThO_2$ in the presence of $SO_4^{2-}$ ions (Kim *et al.*, 2012).

## 5. SUMMARY AND CONCLUSION

Extracting rare earth elements from monazite requires aggressive conditions due to its extreme stability. The possibilities of decomposing it under milder conditions have been explored. The results obtained in the present work showed that extracting rare earth elements at temperatures below 100 ºC is possible albeit at extended reaction times. It is difficult, however, to substantially decompose the mineral at NaOH concentrations below 50%, a problem that can be addressed by recycling the spent alkali as is practiced in industry.

It has been demonstrated that monazite can be decomposed at a temperature of 80 ºC or lower, producing lanthanum hydroxides that can be readily extracted using ammonium sulfate as lixiviant. Experimental data showed that ammonium sulfate may be a better lixiviant than hydrochloric acid, which may be attributed to the fact that the hydration enthalpy of the ammonium ions is less negative than that of the hydronium ions. On the other hand, the kinetics of the ammonium sulfate leaching was slower than that of the acid leaching. However, the kinetics of the former increased sharply at higher temperatures.

Based on the ζ-potential measurements conducted on the monazite samples treated with ammonium sulfate, an ion-exchange leaching mechanism has been proposed for the extraction of rare earth elements from the lanthanide hydroxides using ammonium sulfate as lixiviant. According to the model, the ammonium ions can be readily dehydrated so that they can form stronger electrostatic bonds with the surface and thereby displace the lanthanide ions that are more difficult to be dehydrated. The ion-exchange mechanism as applied to leaching lanthanide hydroxides has an important advantage of the lixiviant being regenerated. Still another advantage of the ammonium sulfate leaching at pH 4 is that uranium is left mostly in the leach residues.

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