

Rare Earth Extraction from Clayey Waste Materials by Alkali Pretreatment

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ABSTRACT

The increasing demand for rare earth elements (REEs) and the depletion of conventional rare earth deposits have enabled secondary REE resources to be promising feedstocks for REEs. Studies have been conducted in developing technologies that can physically preconcentrate and/or chemically extract REEs from low-REE-grade clayey waste materials (e.g., coal-based clays). However, the low REE grades and poor leachability of REE-bearing species still make the recovery of REEs from coal-based clays challenging. The primary objective of this study is to develop leaching technologies that can extract REEs from clayey waste materials under mild conditions (<100 °C).

In the first part of this work, a novel leaching process consisting of NaOH pretreatment followed by ammonium sulfate leaching has been proposed to recover REEs from monazite, which served as a proxy for the rare earth phosphates identified in coal-based clays. In this process, monazite can be decomposed at 80 °C. The following ammonium sulfate leaching was conducted under less aggressive conditions (i.e., pH 4 and room temperature) to recover REEs. After releasing RE^{3+} ions from $\text{RE}(\text{OH})_3(\text{s})$ by acid, the role of ammonium sulfate in the leaching process may be explained by an ion exchange mechanism. Sulfate ions also benefit the leaching process by complexing with RE^{3+} ions.

The influences of temperature and particle size on the leaching kinetics of REEs from the NaOH-treated monazite by ammonium sulfate were also investigated based on the shrinking core model. It was found that the leaching process is controlled by a chemical reaction with an activation energy of 61.28 kJ/mol. Besides ammonium sulfate, ammonium formate is a promising lixiviant for NaOH-treated monazite. However, other carboxylate ligands tested were inefficient at room temperature, mainly due to the slow dissolution kinetics of $\text{RE}(\text{OH})_3(\text{s})$ resulting from the passivation of the binuclear surface complexes.

Subsequently, the feasibility of decomposing rare earth phosphates by NaOH in the presence of ethylenediaminetetraacetic acid (EDTA) was explored by constructing the stability diagrams for La-, Nd-, and $\text{Y-PO}_4\text{-H}_2\text{O}$ systems, respectively. The simulation results were validated using three coal-based clay samples. The leaching results of both HCl and ammonium sulfate indicated that the pretreatment conducted by combining EDTA with dilute NaOH solutions (5-10%) could significantly enhance the REE leachability of the clay samples, with the light REEs (LREEs) being preferentially extracted compared to heavy REEs (HREEs). Under optimal conditions, the co-extraction of Al and Si can be significantly reduced.

Besides liberated phosphate mineral particles, X-Ray photoelectron spectroscopy (XPS) analyses conducted on the synthetic ion adsorption clay samples revealed that phosphate could also passivate the REEs adsorbing on the surface of clay minerals in the form of “clay-RE- PO_4 ”. This finding may partially explain the poor ion exchangeability of REEs in coal-based clays. After subjecting to the proposed NaOH pretreatment technique, the passivated REEs on the surface of clay can be effectively removed.

Lastly, the possibility of preconcentrating REEs from a kaolinite flotation reject material was explored by froth flotation and the hydrophobic-hydrophilic separation (HHS). A final concentrate assaying 10,765 ppm of REEs and 71% of recovery was obtained by the HHS process, which was superior to flotation in dealing with ultrafine particles. The microscopic characterization of the concentrate revealed that rare earth phosphates were the major REE-bearing species. The leaching results showed that the proposed NaOH pretreatment followed by ammonium sulfate leaching was also an effective method to recover REEs from the upgraded clayey waste material under mild conditions (<100 °C).

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GENERAL AUDIENCE ABSTRACT

Rare earth elements (REEs) play a significant role in industrial production. Currently, much effort has been made to recover REEs from clays isolated from mining wastes such as coal byproducts. However, the concentrations of REEs in those clayey waste materials are too low, and they are not amenable to leaching even using strong acids. The developed extraction techniques usually need to be carried out at elevated temperatures (e.g., $>100\text{ }^{\circ}\text{C}$) and consume substantial amounts of chemicals, which are not cost-effective and environmentally friendly. Given the issues, this study proposed a novel leaching technology that can recover REEs from clayey waste materials under mild conditions ($<100\text{ }^{\circ}\text{C}$). Firstly, to simulate the recovery of REEs from coal-based clay materials, a monazite sample was pretreated with caustic soda (i.e., NaOH) at $80\text{ }^{\circ}\text{C}$ for 24 h to convert the difficult-to-dissolve REEs (i.e., rare earth phosphate) into readily soluble forms (rare earth hydroxide), after which they were dissolved in 0.5 M ammonium sulfate solution at pH 4 and room temperature. A conceptual model was developed to explain the leaching mechanism of ammonium sulfate, which was found to be an ion exchange process. The proposed leaching process was also used to extract REEs from clay materials isolated from coal-based clay samples. A chelating ligand named ethylenediaminetetraacetic acid (i.e., EDTA) was added to the dilute NaOH solutions to reduce the alkali consumption during NaOH pretreatment. It was found that the presence of EDTA can improve the performance of NaOH pretreatment. Additionally, the content of REEs in a kaolinite waste material was physically upgraded to 10,765 ppm with $\sim 72\%$ recovery using a novel separation technique called hydrophobic-hydrophilic separation (HHS). The NaOH pretreatment and ammonium sulfate leaching process can also effectively recover REEs from the concentrate. The proposed leaching technology in this study can extract REEs from other low-grade clayey waste materials under mild conditions, which helps reduce wastewater generation and energy consumption. Furthermore, it will relieve the supply risk of REEs in the future.

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Table of Contents

Chapter 1 Introduction.....	1
1.1 Background	1
1.2 Literature Review	2
1.2.1 Rare Earth Elements and Their Demands	2
1.2.2 Leaching Technologies of REEs from Bastnaesite and Monazite	5
1.2.3 Ion Adsorption Clays	10
1.2.4 REEs in Coal.....	13
1.3 Research Objectives and Dissertation Outline	18
1.3.1 Research Objectives	18
1.3.2 Dissertation Outline	18
Reference	19
Chapter 2 Ammonium Sulfate Leaching of NaOH-Treated Monazite	25
Abstract.....	25
2.1 Introduction.....	25
2.2 Experimental	26
2.2.1 Sample and Reagents	27
2.2.2 Methods and Procedure.....	27
2.3 Results	29
2.3.1 Ammonium Sulfate Leaching	29
2.4 Discussion.....	37
2.5 Summary and Conclusion	41
2.6 Acknowledgment.....	42
Reference	42
Chapter 3 Leaching Kinetics of Alkali-treated Monazite by Ammonium Sulfate and the Leaching Performance of Carboxylate Ligands	45
Abstract.....	45
3.1 Introduction.....	45
3.2 Experimental	46
3.2.1 Samples and Reagents.....	46
3.2.2 Methods.....	47
3.3 Results and discussion	47
3.3.1 Leaching Kinetics of Ammonium Sulfate.....	48
3.3.2 Leaching Performance of Carboxylate Ligands.....	51
3.3.3 Passivation Effect of Organic Ligands on the Dissolution of $\text{La}(\text{OH})_3(\text{s})$	54
3.4 Conclusion	59
Reference	60
Chapter 4 Rare Earth Recovery from Coal-based Clays after NaOH Pretreatment with Ethylenediaminetetraacetic Acid.....	63

Abstract.....	63
4.1 Introduction.....	63
4.2 Experimental	64
4.2.1 Samples and Chemicals	64
4.2.2 NaOH Pretreatment.....	65
4.2.3 Leaching Tests	65
4.2.4 Sample Characterization	66
4.3 Results and Discussion.....	66
4.3.1 Thermodynamic Simulation.....	66
4.3.2 REE Recovery.....	69
4.3.3 Leaching Characteristics of Impure Elements (Al, Si, and P)	80
4.4 Summary and Conclusions.....	86
Reference	86
Chapter 5 Influences of Phosphate on the Ion Exchangeability of Rare Earth Elements Adsorbed on Clay Surfaces.....	89
Abstract.....	89
5.1 Introduction.....	89
5.2 Experimental	91
5.2.1 Materials and Reagents	91
5.2.2 Synthesis of REE and/or Phosphate-doped IACs	91
5.2.3 Leaching Tests	92
5.2.4 Sample Characterization	93
5.3 Results and Discussion.....	94
5.3.1 Leaching Behavior of Apatite Samples.....	94
5.3.2 Effect of Phosphate Content on the Ion-exchange Leaching Efficiency.....	95
5.3.3 REE Speciation of the Synthesized Kaolinite Samples	98
5.3.4 Activation of the P-passivated IACs	101
5.4 Summary and Conclusions.....	105
Reference	106
Chapter 6 Rare Earth Element Extraction from a Kaolinite Mining Waste after Physical Preconcentration.....	108
Abstract.....	108
6.1 Introduction.....	108
6.2 Experimental	110
6.2.1 Sample Preparation and Reagents.....	110
6.2.2 Physical Beneficiation.....	110
6.2.3 Sample Characterization	111
6.2.4 Alkali Pretreatment and Chemical Leaching	112
6.3 Results and Discussion.....	113

6.3.1 Physical Beneficiation.....	113
6.3.2 Sample Characterization of the Upgraded Concentrate	114
6.3.3 Chemical Leaching	120
6.3.4 Proposed Processing Circuit	129
6.4 Summary and Conclusions.....	129
Reference	130
Appendix A Summary of the SEM Characterization Results of the Flotation Concentrate	133
Chapter 7 Conclusions, Original Contributions, and Recommendations	141
7.1 Conclusions.....	141
7.2 Original Contributions	142
7.3 Recommendations	142

List of Figures

Figure 1.1 Proposed conceptual flowsheet for the REE extraction from clayey materials refuse.	2
Figure 1.2 Application of REEs (Peiravi et al., 2021).	3
Figure 1.3 Rare earth criticality assessment conducted by European Commission (Blengini et al., 2020)..	4
Figure 1.4 Rare earth demand prediction: Totals and individual REE market share (Alonso et al., 2012)..	4
Figure 1.5 A schematic diagram for the processing of bastnaesite (Cen et al., 2021).	5
Figure 1.6 A typical process flowsheet of sulfuric acid baking of monazite (Demol et al., 2019).	8
Figure 1.7 Plot of the correlation of TREE (excluding >300 ppm REE) and Al in US coals (Byran et al., 2015).	14
Figure 2.1 Results of the ammonium sulfate leaching tests conducted on a monazite sample ($d_{80} = 14.61 \mu\text{m}$) at 0.5 M $(\text{NH}_4)_2\text{SO}_4$, 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.	29
Figure 2.2 XRD spectra of i) untreated monazite of $d_{80}=14.61 \mu\text{m}$, 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).	30
Figure 2.3 Ce 3d XPS spectra of i) untreated monazite of $d_{80}=14.61 \mu\text{m}$; ii) NaOH-pretreated monazite at 30% NaOH and 80°C for 24 h; iii) leach residue.	31
Figure 2.4 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 $(\text{NH}_4)_2\text{SO}_4$ leaching at pH 4 and 25 °C for 2 h.	32
Figure 2.5 Comparison between extracting REEs from the NaOH pretreated monazite ($d_{80} = 14.61 \mu\text{m}$) at 80 °C for 24 h, followed by $(\text{NH}_4)_2\text{SO}_4$ 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).	33
Figure 2.6 The total and individual REE recoveries of a monazite sample pretreated in a 50% NaOH solution at 80 °C and $d_{80} = 14.61 \mu\text{m}$). The pretreated samples were leached in a 0.5 M $(\text{NH}_4)_2\text{SO}_4$ solution at pH 4 at different temperatures.	34
Figure 2.7 Total REE recovery leached by various sulfate-based lixiviants at pH 4 after 30% NaOH pretreatment at 80 °C for 24 h, $d_{80} = 14.61 \mu\text{m}$	35
Figure 2.8 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, $d_{80} = 14.61 \mu\text{m}$	36
Figure 2.9 Effect of different anions of ammonium salts on REE extraction from the monazite particles pretreated in a 30% NaOH solution at 80°C; with $d_{80} = 14.61 \mu\text{m}$	37
Figure 2.10. The solubility diagram $\text{La}(\text{OH})_3(\text{s})$ in water at 25 °C.	39
Figure 2.11 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, $d_{80} = 14.61 \mu\text{m}$	40
Figure 2.12 Proposed mechanism for the ion-exchange leaching of the NaOH-treated monazite using $(\text{NH}_4)_2\text{SO}_4$, as lixiviant. Red spheres represent hydrated water molecules.	41

Figure 3.1 Plot of (a) $1-(1-x)^{1/3}$ vs. time and (b) Arrhenius plot of leaching kinetics of NaOH-treated monazite by $(\text{NH}_4)_2\text{SO}_4$ as a function of temperature.	49
Figure 3.2 Plot of (a) $1-(1-x)^{1/3}$ vs. time (a) and (b) Arrhenius plot of leaching kinetics of NaOH-treated monazite by $(\text{NH}_4)_2\text{SO}_4$ as a function of particle size.	50
Figure 3.3 Stability diagrams of La in the La-H ₂ O system in the presence of (a) ammonium acetate, (b) ammonium acetate, (c) ammonium citrate, and (d) EDTA, respectively, condition: $[\text{La}^{3+}] = 0.01 \text{ M}$	52
Figure 3.4 Leaching results of a monazite sample by different carboxylate-based lixivants at pH 4 and room temperature. The samples were pretreated in a 30% NaOH solution at 80 °C for 24 h, $d_{80} = 14.61 \mu\text{m}$. Note: the concentrations of sulfate, formate, acetate, and citrate were 0.5 M, while EDTA and DTPA were 0.1 M. The leaching result of AS was used as a reference.	53
Figure 3.5 Leaching results of a monazite sample by 0.1 M DTPA as a function of pH at room temperature. The sample was pretreated in a 30% NaOH solution at 80 °C for 24 h, $d_{80} = 14.61 \mu\text{m}$	53
Figure 3.6 Leaching behavior of TREE from $\text{La}(\text{OH})_3(\text{s})$ by 0.5 M ammonium acetate at pH 4 and different temperatures.	54
Figure 3.7 Plot of (a) $1-3(1-x)^{2/3}+2(1-x)$ vs. time and (b) Arrhenius plot of leaching kinetics of $\text{La}(\text{OH})_3(\text{s})$ by 0.5 M ammonium acetate at pH 4 and different temperatures.	55
Figure 3.8 Leaching behavior of TREE from $\text{La}(\text{OH})_3(\text{s})$ by 0.1 M EDTA at pH 4 and different temperatures.	56
Figure 3.9 Plot of (a) $1-3(1-x)^{2/3} + 2(1-x)$ vs. time and (b) Arrhenius plot of leaching kinetics of $\text{La}(\text{OH})_3(\text{s})$ by 0.1 M EDTA at pH 4 and different temperatures.	57
Figure 3.10 FTIR results of 0.5 M ammonium citrate solution and $\text{La}(\text{OH})_3(\text{s})$ before and after leaching, respectively. “ $\text{La}(\text{OH})_3$ ” and “ $\text{La}(\text{OH})_3+\text{Cit}$ ” refer to the spectra of $\text{La}(\text{OH})_3$ before and after ammonium citrate leaching, respectively. “Cit. sol.” and “Cit. leachate” represent the spectra of ammonium citrate solution before and after leaching, respectively.	58
Figure 3.11 FTIR analysis of $\text{La}(\text{OH})_3(\text{s})$ leached by various lixivants. (After mixing $\text{La}(\text{OH})_3(\text{s})$ with organic ligands, the stretching band of $-\text{COO}^-$ at $1662\text{--}1620 \text{ cm}^{-1}$ in the leaching liquor shifted to 1578 cm^{-1} in the leaching residues, suggesting the coordination of La^{3+} with $-\text{COO}^-$).	59
Figure 4.1 Fraction diagrams of La in the systems of (a) $\text{La-PO}_4\text{-H}_2\text{O}$ and (b) and $\text{La-PO}_4\text{-EDTA-H}_2\text{O}$ at 25 °C, conditions: $[\text{La}^{3+}] = [\text{PO}_4^{3-}] = 10^{-5} \text{ M}$, $[\text{EDTA}] = 0.1 \text{ M}$	67
Figure 4.2 Species diagrams of (a) La, (b) Nd (b), and (c) Y in the system of $\text{REE-PO}_4\text{-EDTA-H}_2\text{O}$, conditions: $[\text{La}^{3+}] = [\text{Nd}^{3+}] = [\text{Y}^{3+}] = [\text{PO}_4^{3-}] = 10^{-5} \text{ M}$	68
Figure 4.3 Species diagrams of (a) La, (b) Nd, and (c) Y in the systems of $\text{REE}^{3+}\text{-PO}_4\text{-EDTA-Al-H}_2\text{O}$, conditions: $[\text{REE}^{3+}] = [\text{PO}_4^{3-}] = 10^{-5} \text{ M}$, $[\text{Al}^{3+}] = 0.1 \text{ M}$	69
Figure 4.4 Fraction diagram of 0.1 M EDTA as a function of pH at 25 °C.	70
Figure 4.5 Effect of pH on the leaching efficiency of (a) 0.5 M AS and (b) 1 M HCl on the LR sample, pretreatment conditions: 10% NaOH with 0.1 M EDTA, 60 °C, 24 h; leaching conditions: room temperature, 1h. (Note: “AS” in (a) refers to ammonium sulfate, the same below.)	71
Figure 4.6 TREE and individual REE recoveries of ammonium sulfate leaching from three different coal-derived clays after NaOH pretreatment with 0.1 M EDTA. (Pretreatment conditions: 10% NaOH with 0.1 M EDTA, 60 °C, 24 h, leaching conditions: 0.5 M AS, room temperature, 1h,	

pH 3.).....	72
Figure 4.7 Partitions of REEs into the NaOH solutions during the pretreatment of the LR sample by NaOH pretreatment with 0.1 M EDTA at 80 °C for 24 h.....	73
Figure 4.8 TREE recovery of AS at pH 3 and 1 M HCl from the LR sample after NaOH pretreatment by NaOH with and without 0.1 M EDTA at 40 (a) and 80 °C (b).....	74
Figure 4.9 Leaching curves of TREE recovery of the AS and HCl leaching from the LR sample after NaOH pretreatment without and with 0.1 M EDTA at 40 °C.	75
Figure 4.10 Leaching curves of TREE recovery of the AS and HCl leaching from the LR sample after NaOH pretreatment without and with 0.1 M EDTA at 80 °C.....	76
Figure 4.11 Individual REE recovery of (a) AS leaching after NaOH pretreatment without EDTA, (b) AS and (c) HCl leaching after NaOH pretreatment with EDTA from the LR sample at 40 °C. “1st” and “2nd” refer to the REEs partitioned into used NaOH and leaching solution, respectively.....	78
Figure 4.12 Individual REE recovery of a) AS leaching after NaOH pretreatment without EDTA, b) AS and c) HCl leaching after NaOH pretreatment with EDTA from the LR sample at 80 °C. “1st” and “2nd” refer to the REEs partitioned into NaOH and leaching solutions, respectively.....	79
Figure 4.13 SEM images and EDS spectra of two HREE-bearing mineral particles and their corresponding EDS spectra identified in the 1 M leaching residue of the LR sample after NaOH pretreatment.....	80
Figure 4.14 Leaching behaviors of (a) TREE and (b) P in the NaOH solutions during the NaOH pretreatment with 0.1 M EDTA of the LR sample at 80 °C for 24 h.....	81
Figure 4.15 Correlation of TREE versus P recovery in the AS leaching of the LR sample after NaOH pretreatment under various conditions. (Pretreatment conditions: 2, 5, and 10% NaOH with and without 0.1 M EDTA, 40-80 °C 24 h, leaching conditions: 0.5 M AS, room temperature, 1h, pH 3.).....	82
Figure 4.16 Correlations of (a) TREE versus Al recovery, (b) TREE versus Si recovery, and (c) Si versus Al recovery in the leaching of the LR samples. (Pretreatment conditions: 2, 5, and 10% NaOH with and without 0.1 M EDTA, 40-80 °C, 24 h, leaching conditions: 0.5 M AS, room temperature, 1h, pH 3.).....	83
Figure 4.17 XRD patterns of non-treated LR sample and NaOH-treated LR samples by 10% NaOH with 0.1 M EDTA for 24 h at different temperatures. (C: calcite; K: kaolinite; M: muscovite/illite; S: sodalite; Q: quartz; R: rutile.).....	84
Figure 4.18 The mass ratio of TREE/(Al+Si+Fe) in the different leaching tests conducted on the LR sample after NaOH pretreatment with and without EDTA by 0.5 M AS at pH 3 and 1 M HCl, (a): 40 °C; (b): 80 °C.....	85
Figure 5.1 Leaching characteristics of TREE, P, and Ca from (a) hydroxyapatite and (b) fluorapatite by 0.1 M HCl at room temperature for 1 h.....	94
Figure 5.2 TREE and phosphate contents in the synthesized kaolinite samples as a function of the molar ratio of (La+Nd+Dy)/P. (Note: phosphate content was calculated in H ₂ PO ₄ ⁻).....	95
Figure 5.3 TREE recovery (a) and individual REE recovery (b) in the leaching of the synthesized kaolinite samples by 0.5 M ammonium sulfate at pH 4 and room temperature for 1 h.	96
Figure 5.4 Stability diagrams for La in the systems of (a) La ³⁺ -H ₂ O and (b) La ³⁺ -PO ₄ ³⁻ -H ₂ O system (b) at	

25 °C, condition: $[La^{3+}] = [PO_4^{3-}] = 10^{-5}$ M.....	97
Figure 5.5 XRD patterns of (a) the blank kaolinite and artificial kaolinite samples with the molar ratio of (La+Nd+Dy)/P being (b) 0.94; (c) 0.84; (d) 0.76; (e) 0.70.	98
Figure 5.6 XPS spectra of $La3d_{5/2}$ and $P2p$ of the feed and artificial kaolinite samples.	99
Figure 5.7 Proposed mechanism for the phosphate-passivated REEs in the synthesized IACs phosphate and the involved leaching process.....	101
Figure 5.8 Stability diagrams of La in La- PO_4 -EDTA- H_2O system with varying phosphate concentrations at 25 °C. $[La^{3+}] = 10^{-5}$ M, $[PO_4^{3-}] = 10^{-5}$ M (a); $[PO_4^{3-}] = 5 \times 10^{-5}$ M (b); $[PO_4^{3-}] = 10^{-4}$ M (c).102	102
Figure 5.9 Effect of temperature on the REE recovery of the EDTA leaching from the REE-P-kaolinite sample with (La+Nd+Dy)/P = 0.70, conditions: 0.1 M EDTA, pH 10, 1 h. “AS” refers to ammonium sulfate.	103
Figure 5.10 Ammonium sulfate leaching of REEs from the REE-P-kaolinite sample with (La+Nd +Dy)/P = 0.70 after NaOH pretreatment in the absence (a) and presence (b) of 0.1 M EDTA. Pretreatment: 2-10% NaOH, 60 °C, 1 h. Leaching: 0.5 M ammonium sulfate, pH 4, room temperature.	104
Figure 6.1 Flowsheet for the flotation and HHS tests performed on the kaolinite flotation reject material (Note: “Conc.” refers to concentrate).....	111
Figure 6.2 Recovery versus grade curves of the flotation and the HHS tests performed on the kaolinite flotation reject material for REE preconcentration.	113
Figure 6.3 XRD spectra of a) the kaolinite flotation reject feed, b) flotation concentrate, and c) flotation tailing. Note: A: anatase; Z: zircon; R: rutile; K: kaolinite.	115
Figure 6.4 SEM images of P1 (a) and P22 (b) and their corresponding EDS spectra a_1 and b_1	116
Figure 6.5 Statistical analysis of the elemental compositions of the LREE-enriched particles identified from the flotation concentrate by SEM-EDS.	117
Figure 6.6 TEM image (a), EDS spectrum (b), and diffraction pattern (c) of a crandallite group mineral particle identified in the flotation concentrate.....	118
Figure 6.7 SEM images of two HREE-enriched particles and their EDS spectra of the selected areas. (a): xenotime; (b): zircon. (a1) and (b1) are the corresponding EDS spectra of the selected areas in (a) and (b), respectively.....	118
Figure 6.8 SEM images of two REE-enriched particles co-existed with other minerals. (a): a REM particle (a_2) associated with clay (a_1); (b): a REM particle (b_2) intergrew with TiO_2 (b_1).	119
Figure 6.9 Effect of NaOH concentration on the TREE recovery of ammonium sulfate and 1 M HCl leaching from the flotation concentrate ($d_{80} = 15.0$ μm after NaOH pretreatment conducted at 80 °C for 1 h. The leaching tests were all conducted at room temperature.	121
Figure 6.10 Effect of NaOH concentration on the individual REE recovery of ammonium sulfate (a) and 1 M HCl leaching (b) from the flotation concentrate ($d_{80} = 15.0$ μm after NaOH pretreatment conducted at 80 °C for 1 h. The leaching tests were all conducted at room temperature.	122
Figure 6.11 SEM image (a) and EDS spectrum (b) of a xenotime particle found in the leaching residue of 1 M HCl after 50% NaOH pretreatment at 80 °C for 1 h.	123
Figure 6.12 Effect of particle size on the TREE recovery of ammonium sulfate after NaOH pretreatment conducted at 80 °C for 1 h. The leaching tests were all conducted at room temperature.	123

Figure 6.13 Effect of pretreatment time on the TREE recovery (a) and individual REE recovery (b) of 0.5 M ammonium sulfate, pH 3, room temperature. Pretreatment: 50% NaOH, 80 °C, 1-24 h; leaching conditions: 0.5 M ammonium sulfate, pH 3, and room temperature.....	124
Figure 6.14 Partitions of TREE, Sc, and major impure elements (Al, Si, P, Ca, Fe, and Ti) in the used NaOH solutions of the leaching tests shown in Figure 6.9.....	125
Figure 6.15 SED images and the EDS spectra of REMs found in the flotation concentrate after NaOH pretreatment (80 °C, 1 h). (a): xenotime; (b): probably monazite associated with $\text{TiO}_2(\text{s})$, and their corresponding EDS spectra (a_1) and (b_1), respectively.....	126
Figure 6.16 The Mass ratios of the amount of REEs over the total amounts of the contaminants (Mg, Ca, Al, Si, and Fe) in the leachates of the NaOH-treated samples shown in Figure 6.9 as a function of NaOH concentration.	127
Figure 6.17 Partitions of Ti in the leachates as a function of NaOH concentration in the leachates of the tests shown in Figure 6.9.	127
Figure 6.18 XRD spectra of a) flotation concentrate; b) 10% NaOH-treated; c) 30% NaOH-treated; d) 50% NaOH-treated; e) 30% NaOH-treated + AS leached; f) 30% NaOH-treated + 1 M HCl leached; g) 50% NaOH-treated + 1 M HCl leached flotation concentrate. Note: A: anatase; Z: zircon; R: rutile.	128
Figure 6.19 Proposed conceptual flowsheet for the processing of kaolinite flotation concentrate for the production of different products.	129

List of Tables

Table 1.1 Summary of the representative lixiviants developed for IACs.	11
Table 1.2 Representative leaching techniques for rare earth extraction from coal and coal refuse before combustion.....	16
Table 2.1 Elemental composition of the monazite sample before and after flotation.....	27
Table 2.2 Thermodynamic data used for the solubility diagram for $\text{La}(\text{OH})_3(\text{s})$	38
Table 3.1 Kinetic parameters for the ammonium sulfate leaching of REEs from the NaOH-treated monazite as a function of leaching temperature.	48
Table 3.2 Kinetic parameters for the ammonium sulfate leaching of REEs from the NaOH-treated monazite as a function of particle size.	50
Table 3.3 The pKa and Log K values (La-ligand) of the organic acids used in this study.	51
Table 3.4 Kinetic parameters of $\text{La}(\text{OH})_3(\text{s})$ by 0.5 M ammonium acetate leaching at different temperatures.....	54
Table 3.5 Kinetic parameters of $\text{La}(\text{OH})_3(\text{s})$ leached by 0.1 M EDTA at different temperatures.	55
Table 4.1 Ash content (%), d_{80} (μm), and the contents of P and individual REE (in ppm, dry whole basis) of the samples used for rare earth extraction (Note: d_{80} refers to 80% of particles passing a specific size).	65
Table 5.1 REE concentrations in the feed, NaOH-cleaned, and synthesized kaolinite samples (in ppm). .	92
Table 5.2 $\text{La}_{3\text{d}_{5/2}}$ characteristic values for REE and/or phosphate-doped kaolinite samples at pH 4 and several standard La compounds.....	100
Table 5.3 Partition of REE recovery in the NaOH solution and the leachate of ammonium sulfate in the leaching of the REE-P-kaolinite sample (REE/P = 0.70). Pretreatment: 2-10% NaOH, 60 °C, 1 h. leaching: 0.5 M ammonium sulfate (AS), pH 4, room temperature.	105
Table 6.1 Major element concentrations of the feed and flotation products (in wt.%).	110
Table 6.2 TREE and individual REE concentrations in the feed and flotation products (in ppm).	112
Table 6.3 Material balances for the flotation and HHS tests.	114
Table A1 Summary of the EDS spectra for the REE-bearing particles.	138

Chapter 1 Introduction

1.1 Background

Rare earth elements (REEs) have wide applications in the production of advanced products and devices in high-tech fields (e.g., clean energy and wind turbines) due to their unique physical and chemical properties (Yin et al., 2022). Over the past decades, their indispensable and irreplaceable roles have caused an increasingly growing consumption of REEs globally. Meanwhile, the imbalanced distribution in geography and the gradual exhaustion of the traditional REE deposits (such as bastnaesite, monazite, and ion adsorption clays) have fueled the urgency to find alternative REE resources (Peiravi et al., 2021). In the US, the domestic production of REEs is limited, and the processing of final REE products relies on other countries (Bagdonas et al., 2022). Accordingly, many governments and research institutes have initiated several investigations to find alternative REE sources (such as electronic waste, clayey waste materials, and industrial byproducts) and develop cost-effective extraction techniques to maintain a reliable and sustainable REE supply chain during the past decade (Schmid et al., 2019; Opare et al., 2021; Gaustad et al., 2021). For instance, the European Union recognized the importance of REE recycling from electronic waste and electronic equipment (Peelman et al., 2016). The US Department of Energy (DOE) launched a \$140 million program to design and construct REE and critical mineral refineries using unconventional resources in 2022 (DOE, 2022).

Of the alternative REE sources, clayey waste materials such as coal-derived clay and kaolinite mining waste with low REE grades are considered promising REE feedstocks. For instance, although the average total REE (TREE) contents in lignite and bituminous coals worldwide are only 69 and 72 ppm, respectively, the vast volume of coal mined each year worldwide (at a 5-billion-ton level) contains a significant amount of REEs (Yang, 2019; Zhang et al., 2020). Therefore, it enables the recovery of REEs from coal-related materials to be attractive. The research and development of suitable extraction techniques require an in-depth insight into the modes of occurrence of REEs in coal-based clays. Except for certain fractions of ion-adsorbed REEs, Finkelman et al. (2018) found that rare earth phosphate minerals (e.g., monazite and xenotime) in micro-dispersed particles are the dominant occurrences of REEs in the bituminous coals through sequential extraction, with 70% of light REEs (LREEs) and 50% of heavy REEs (HREEs) associating with those phosphate minerals.

Both physical beneficiation and chemical leaching have been used to upgrade or extract REEs from coal-derived clays such as fine coal refuse. With the exception of froth flotation, it was found that most conventional physical separation techniques (e.g., gravity and magnetic separation) normally gave poor recoveries and enrichment ratios even after ultra-fine grinding (Zhang et al., 2020; Eterigho-Ikelegbe et al., 2021; Lin et al., 2017). This is mainly attributed to the low TREE content (around 300 ppm) and the ultrafine grain size ($<10\ \mu\text{m}$) of the rare earth minerals (REMs) in coal-derived clays. However, the hydrophobic-hydrophilic separation (HHS) process, a novel separation technique to deal with ultrafine particles, showed a more promising potential to concentrate REE-bearing species from coal-derived clays (Gupta et al., 2016). A HHS final concentrate assayed 17,428 ppm of TREE on an ash basis was obtained with a feed assaying of only ~ 350 ppm of REEs. However, the application of the HHS process on an industrial scale is still constrained by the costs of ultra-fine grinding and the low recovery.

Accordingly, intensive studies have focused on recovering REEs from coal-based clays by chemical leaching, which is followed by other hydrometallurgical processes (e.g., solvent extraction) to produce final REE products. Due to the poor leachability of REEs in coal-based clays, thermal or alkali pretreatment is normally required to convert the REE-bearing species into readily leachable forms (e.g., rare earth oxide and hydroxide) prior to chemical leaching (e.g., acid and ion exchange leaching). Although satisfactory leaching recoveries can be achieved by the currently proposed leaching techniques (Zhang et al., 2020; Eterigho-Ikelegbe et al., 2021), issues such as high chemical consumption, massive dissolution

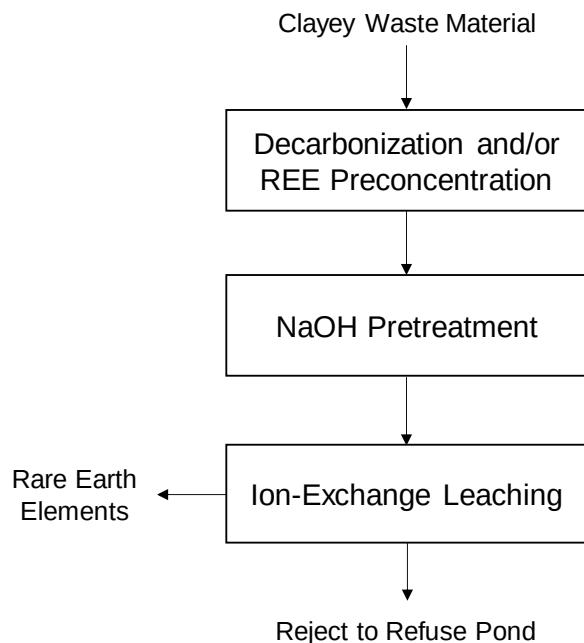


Figure 1.1 Proposed conceptual flowsheet for the REE extraction from clayey materials refuse.

of gangue minerals, poor selectivity of REEs over impure elements, and the resulting the poor economic viability still need to be addressed.

In this research, a conceptual flowsheet is proposed to recover REEs from clayey waste materials such as coal-derived clay and kaolinite mining waste. As shown in Figure 1.1, the clayey waste material is initially subjected to the decarbonization and/or REE preconcentration step. It has been found that approximately one-third of the material in thickener underflow is recoverable coal. The decarbonization step is to recover clean coal as a byproduct by the HHS process. On the other hand, the majority of the REEs in coal-derived clays were found to mainly associate with inorganic materials (e.g., clays) (Yang, 2019). The decarbonization step can also benefit the leaching step by reducing the sample volume subjected to it. However, it should be noted that the decarbonization step is not necessary for non-coal-derived clays. Physical preconcentration may be conducted to upgrade the REE-bearing species in all the clayey materials for volume reduction.

In the extraction step, NaOH pretreatment is performed to transfer the difficult-to-leach REEs in clayey waste materials into readily leachable forms. Ion-exchange leaching conducted under weakly acidic conditions has been successfully applied to recover REEs from ion adsorption clays (IACs) in South China. This simple and effective extraction technique enables the recovery of REEs from the IACs with only 0.03-0.3 wt.% in rare earth oxide (REO) to be economically feasible. Accordingly, the clayey waste materials after NaOH pretreatment are subjected to ammonium sulfate leaching to recover REEs in this study.

1.2 Literature Review

1.2.1 Rare Earth Elements and Their Demands

As defined by the IUPAC, the term “rare earth elements” refers to a group of elements consisting of 15 lanthanide elements (from La to Lu), scandium (Sc), and yttrium (Y) (Peelman et al., 2016). These 17 elements are categorized as a group since they normally occur in the same mineral deposits and show similar chemical properties caused by lanthanide contraction (Sadri et al., 2017). Although different

classifications of REEs have been created according to their differences in atomic numbers, supply risk, solubility, etc., REEs are commonly divided into light REEs (LREEs) and heavy REEs (HREEs) according to their atomic numbers (Peiravi et al., 2021). LREEs contain La, Ce, Pr, Nd, Sm, and Sc, while Eu, Gd, Tb, Dy, Ho, Er, Tm, Lu, and Y belong to HREEs.

Figure 1.2 shows the consumer end products of REEs in various industries, as summarized by Peiravi et al. (2021). As shown, REEs are widely used in high-tech industries such as magnets, catalysts, electronics, glass, ceramics, and metal alloys (Krishnamurthy and Gupta, 2015; Sadri et al., 2017). For instance, Dy and Nd play critical roles in wind energy and electric mobility fields (Patricia et al., 2020). The criticality assessment performed by the European Commission (Blengini et al., 2020) shows that LREEs and HREEs are at the highest level of supply risk relative to other raw materials. Given the critical roles of REEs in the manufacturing economy, they are considered strategic materials by many countries. The global demand for REEs has been increasingly climbing over the past decade. As predicted by Alonso et al. (2012) (see Figure 1.4), the REE demand will be around 380,000 metric tons in 2035, which is approximately 80% more than the annual production of REEs in 2019 (210,000 metric tons) (Vaughan et al., 2021). At the same time, the fractional REE demand predicted that Ce, La, Nd, and Y are the ones that will continue to see increased consumption compared to the rest of the REEs.

The global REE reserves (in REO) have been estimated to be around 120 million metric tons, of which China, Vietnam, and Brazil account for 36.7%, 18.3%, and 17.5%, respectively, according to the United States Geology Survey report (USGS, 2022). The remaining 27.5% is shared by other countries. It indicates that REE resources are not evenly distributed (Cen et al., 2021). Although REE ore deposits have been discovered in around 34 countries, the mining and exploration of rare earth resources on a large scale have taken place only in some countries (Sadri et al., 2017). South Africa, Brazil, and India were the primary countries with rare earth industries in the 1950s. Subsequently, the US became the most dominant supplier of REEs from the 1960s to 1980s due to the significant exploitation of the Mountain Pass. After that, China had gradually become the largest provider of REEs since the 1990s (Jha et al., 2016). Although several export restrictions have been imposed by the Chinese government, the REO production in China was still around 60.0% of the world's annual production in 2021, which was followed by the US (15.4%) and Burma (7.8%), respectively (USGS, 2022).

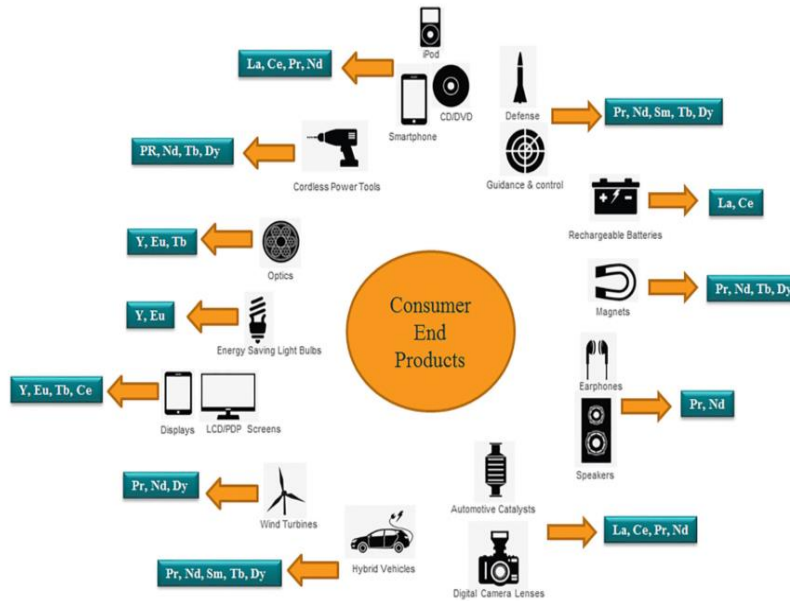
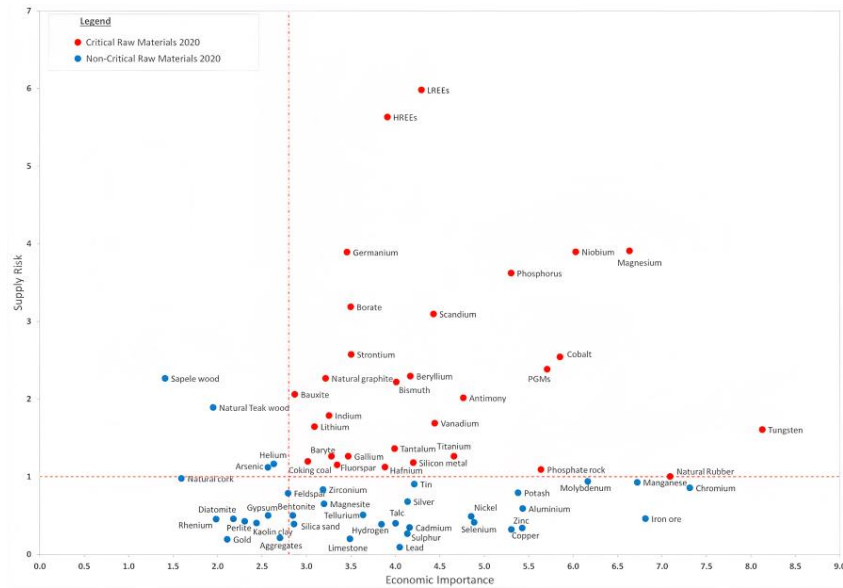


Figure 1.2 Application of REEs (Peiravi et al., 2021).



The abundances of REEs in the earth's crust are relatively higher than some valuable elements such as platinum group metals (Cotton, 2013). However, their occurrences in nature are not in elemental states or individual REE compounds (Cen et al., 2021). The REE ore deposits explored so far are mixtures of nearly all REEs (Alonso et al., 2012). This property renders the mining of individual REEs economically unviable. REEs commonly occur in the forms of rocks, including basalt, granite, gneiss, shale, and silicate (Cen et al., 2021). To date, over 250 REMs have been identified in the world. However, only a few of them can be physically upgraded to REE concentrates (Krishnamurthy and Gupta, 2015). Bastnaesite, monazite, and xenotime are the primary REE resources that have been processed at commercial scales. Other than those three REMs, IACs, known as weathered crust elution-deposited rare earth ores, have also been commercially exploited as an important source for HREEs, which are at higher supply risks compared to LREEs. Around 95% of the total REE reserves are contributed by those four mentioned resources (Gupta, 2021). Other than the traditional REE resources, secondary REE resources such as coal and coal refuse have received intensive attention in the past decade, aiming to strengthen the security of REE supply chains.

1.2.2 Leaching Technologies of REEs from Bastnaesite and Monazite

The chemical leaching technologies for REEs from bastnaesite and monazite are reviewed respectively in the following sections. Since monazite and xenotime are rare earth phosphate minerals, the hydrometallurgical processing of xenotime is essentially similar to those of monazite. Therefore, the leaching processes for xenotime were not reviewed in this study.

1.2.2.1 Bastnaesite Leaching

Bastnaesite ((Ce, La)(CO₃)F) is a primary REM since it has the largest proven reserve compared to its counterparts, and around 70% of the world's REEs are extracted from this mineral (Chi et al., 2004). Besides the dominant components such as Ce, La, Pr, and Nd, bastnaesite normally contains 0.2-0.3 wt.% Th and 8-10 wt.% F as suggested by its formula (Wang et al., 2017; Suli et al., 2017). The two largest bastnaesite mines discovered in the world are the Bayan Obo mine, Inner Mongolia, China and the Mountain Pass, California, US, respectively. Figure 1.5 shows the conceptual flowsheet used to process bastnaesite constructed by Cen et al. (2021). After various physical separations, the bastnaesite ores are physically preconcentrated to bastnaesite concentrates, which are then subjected to a hydrometallurgical processing step before it becomes final REE products.

Many metallurgical processes have been developed for the processing of bastnaesite in the past decades (Krishnamurthy and Gupta, 2015; Cen et al., 2021). In the 1960s, the Molycorp process was proposed to extract REEs from bastnaesite concentrates assaying ~60% of REO. The concentrate is firstly roasted in an air atmosphere at 620 °C to release CO₂ (Eq. 1.1). Meanwhile, Ce(III) is oxidized into Ce(IV), i.e., CeO₂, which is not readily leachable by acids at room temperature. Subsequently, the roasted product is subjected to 30% HCl leaching, which is aimed at dissolving the REEs but CeO₂ (Eq. 1.2). In the next step, as suggested by Eq. 1.3, the insoluble rare earth fluorides are converted to RE(OH)₃ by NaOH. Later, the resulting REE hydroxides are leached by HCl.



The Mountain Pass mine resumed production in 2018. Currently, there is no on-site hydrometallurgical processing of the bastnaesite concentrate since it is exported to China for further

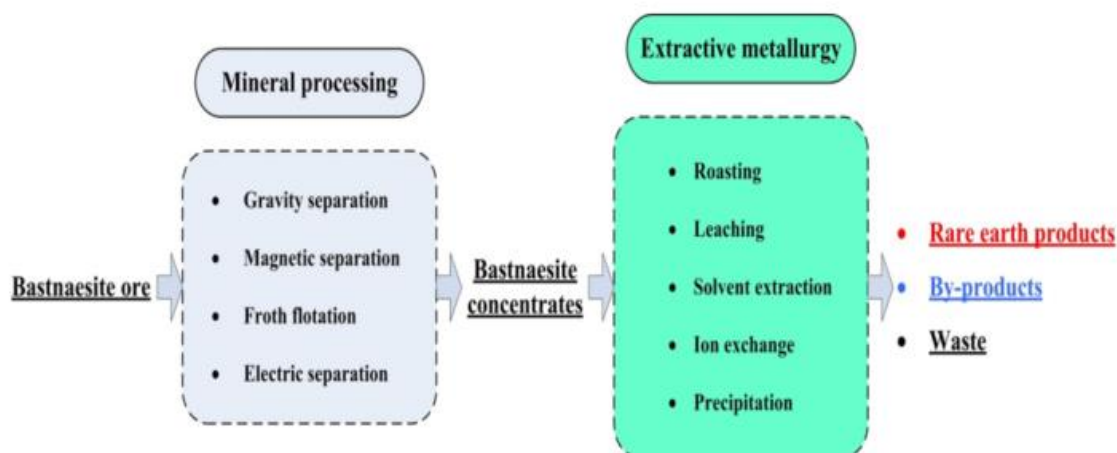


Figure 1.5 A schematic diagram for the processing of bastnaesite (Cen et al., 2021).

processing (McNulty et al., 2022). The process used before in the Mountain Pass mine was as follows (Sadri et al., 2017): 1) the flotation concentrate was initially leached by 10 wt.% HCl at pH 1 to remove calcite, after which the REE grade of the bastnaesite concentrate was further improved to 68-72 wt.% in REO; 2) a roasting process, performed at 620 °C for 3 h, was employed to decompose the fluorocarbonate and facilitate the formation of REO, such as the oxidation of Ce(III) to Ce(IV); 3) 30 wt.% HCl solution was used to leach the roasting product, leaving CeO₂ and ThO₂ as insoluble residues; 4) the REEs in the leaching liquor were precipitated as REE insoluble double sulfate salts by adding Na₂SO₄ after impurity removal using Na₂CO₃.

As one of the significant REE resources in China, bastnaesite is a major contributor to the annual REE production. Currently, the major processing technologies of bastnaesite include sulfuric acid roasting and NaOH decomposition process, which are applied in Bayan Obo, China (Cen et al., 2021). It is worth noting that the bastnaesite ores processed in Bayan Obo are mixed rare earth concentrate, i.e., a combination between bastnaesite and monazite. In the sulfuric acid roasting process, bastnaesite and monazite are both decomposed into rare earth sulfates by concentrated sulfuric acid at >300 °C, with CO₂ and HF being formed simultaneously (Eq. 1.4). The decomposed products are leached by water, then followed by impurity removal and solvent extraction, respectively (Wang et al., 2017). The NaOH decomposition process starts from the conversion of bastnaesite ore to rare earth hydroxide (Eq. 1.5), and the resulting hydroxide is then subjected to HCl leaching to recover the REEs (Krishnamurthy and Gupta., 2015).



Other representative processing methods for bastnaesite include HNO₃ digestion-solvent extraction, chlorination process, and Na₂CO₃ decomposition-HCl leaching, etc. (Krishnamurthy and Gupta, 2015). Although the current industry processes are effective, substantial efforts have been made to develop cleaner processes that can reduce the intensive energy and chemical consumption and mitigate the environmental concerns resulting from the conventional processes. A process consisting of roasting bastnaesite concentrate with ammonium chloride followed by hot water leaching was proposed by Chi et al. (2004). At elevated temperatures, ammonium chloride is transformed to NH₃ and HCl in the gas phase (Eq. 1.6). Then, HCl reacts with RE₂O₃, resulting from the decarbonization of bastnaesite (Eq. 1.7), forming water-soluble RECl₃ (Chi et al., 2004; Cen et al., 2021) (Eq. 1.8). However, one problem associated with this process is the formation of insoluble species, i.e., RE₂F₆, which leads to the loss (approximately one third) of REEs into the leaching residue (Chi et al., 2004). To avoid the loss of REEs, bastnaesite is roasted with MgO before chlorination roasting since MgO can deactivate the fluorine by converting it to MgF₂ (Eq. 1.9) (Chi et al., 2004). Subsequently, hot water leaching is performed to dissolve the RECl₃.



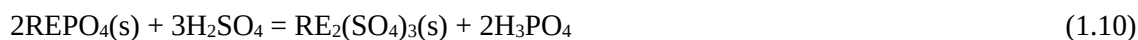
Another environmentally friendly processing method was proposed by Wang et al. (2013). Prior to H₂SO₄ leaching, bastnaesite is initially subjected to an oxidation roasting step, which can convert Ce and Th into Ce(IV) and Th(IV), respectively. After that, solvent extraction using HEHEHP (2-ethylhexyl phosphonic acid mono-2-ethylhexyl) is conducted to isolate REE(III) from the rest of the components (e.g., Ce(IV), Th(IV), and F(I)) by leaving most of REE(III) in the raffinate and the latter ones in the organic phase (Wang et al., 2013). Additionally, an additive that can fix fluorine such as Ca(OH)₂ was also used in the roasting of bastnaesite, and it can convert fluorine into CaF₂ (Cen et al., 2021). The above cleaner processing methods can potentially render the processing of bastnaesite under less aggressive conditions

and produce fewer amounts of waste products.

1.2.2.2 Monazite Leaching

The strategy of processing monazite is to either directly leach the concentrate ores or convert them to readily leachable forms by concentrated reagents since it is a thermally and chemically stable mineral (Lazo et al., 2017). Concentrated reagents (e.g., 98% H₂SO₄ or 50% NaOH) and elevated temperatures are typically required to decompose monazite. Regarding the hydrometallurgical processing of physically beneficiated monazite ores, recent research progresses and commercialized techniques have been reported in several review papers. Jha et al. (2016) and Demol et al. (2019) reviewed the acid baking process of rare earth concentrate ores, while Kumari et al. (2015) provided a review of the physical beneficiation and acid leaching of monazite. Likewise, alkali cracking of monazite has been thoroughly reviewed by Sadri et al. (2017) and Kumari et al. (2019). A general review of the processing methods of rare earth ore concentrates was provided by Zhang et al. (2013). Among the reported technologies, alkaline cracking (applied in the Indian Rare Earths Ltd. plant) and acid baking (applied in the Bayan Obo deposit in China and the Mt. Weld Deposit in Australia) are two important commercialized processes, with the former one being preferentially used (Demol et al., 2019). Given that several review papers have been provided by previous researchers, only the representative processing methods and newly developed processes were summarized in this section to avoid duplication.

Acid baking method Decomposition of monazite by mineral acids (e.g., HCl, HNO₃, and H₂SO₄) has been thoroughly described by Kumari et al. (2015) and Demol et al. (2019). Among the acid baking methods, sulfuric acid baking is the one that has been commercialized since it can dissolve REEs and remove impure elements. After the digestion of monazite in acids, the REEs in the pregnant leaching solutions are precipitated by oxalic acid at specific pH values and then followed by calcination and solvent extraction steps.



In a typical sulfuric acid baking process, a monazite concentrate is mixed with concentrated sulfuric acid (93 to 98 wt. %) and baked at elevated temperatures (Sadri et al., 2017; Demol et al., 2019). During the acid baking stage, rare earth phosphates are converted to rare earth sulfates. Subsequently, water leaching is performed to solubilize the sulfates. Leaching solutions containing rare earth sulfate can be obtained after filtration or thickening. The involved chemical reactions for the digestion of monazite by H₂SO₄ are listed in (Eqs. 1.10 and 1.11). A typical flowsheet of sulfuric acid baking of monazite is shown in Figure 1.6. With the acid baking method, over 80% TREE recovery can be achieved (Demol et al., 2019). However, one significant problem associated with the sulfuric acid baking process is the loss of phosphate ion, an important component of monazite (Kumari et al., 2015). Another issue is that the final REE products produced by the acid baking method normally do not have high purities since many impurities in monazite concentrate ores are co-extracted (Galvin et al., 2018). In addition, the presence of radioactive elements (i.e., Th and U) in the leaching residue negatively impacts the environment. Because of the drawbacks, alkali cracking tends to be more prevalent in industrial practice relative to the acid baking process (Galvin et al., 2018).

Alkali pretreatment Alkali treatment, also known as caustic cracking, is another effective path to remove phosphorus (i.e., dephosphorization) from monazite in industry. The application of alkali treatment to monazite processing was proposed by Rhône-Poulenc (Krumholz, 1957). Typically, alkali treatment is performed by ~60% NaOH at ~160 °C for 1-4 h, with a solid/liquid ratio of ~1:1 (Galvin et al., 2018; Lazo, 2019; Gupta, 2021). The involved chemical reactions are shown in (Eqs. 1.12 and 1.13). After alkali pretreatment, the resulting rare earth hydroxide cake is subjected to water leaching for the removal of trisodium phosphate, which is a byproduct that can be used as fertilizer. Subsequently, the rare earth

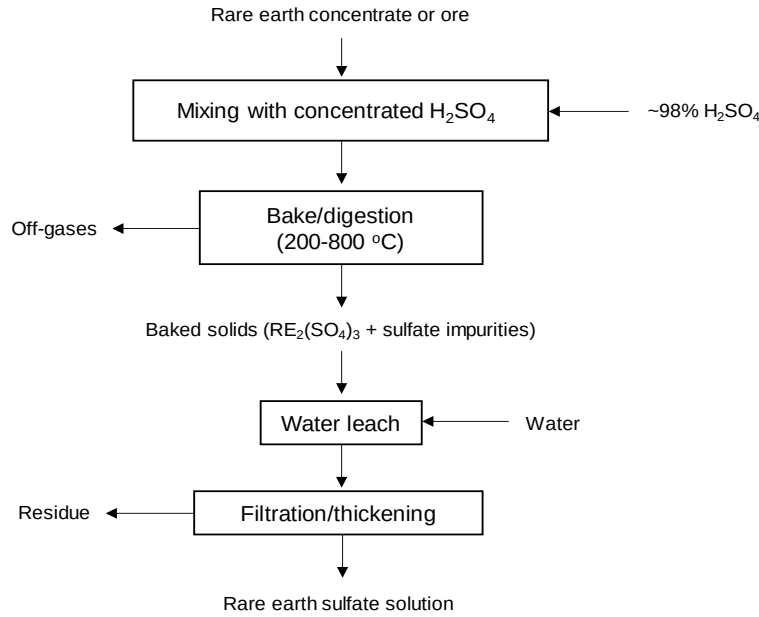
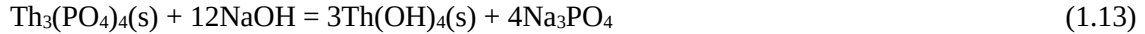


Figure 1.6 A typical process flowsheet of sulfuric acid baking of monazite (Demol et al., 2019).

hydroxide is dissolved in acids such as H_2SO_4 , HCl , and HNO_3 .



Other additives have also been tested by researchers, attempting to develop effective reagents for the decomposition of monazite concentrate ores. To separate REEs from Th, Merritt (1990) roasted monazite with sodium carbonate (Na_2CO_3) in a reducing and sulfurizing environment at 900°C , after which rare earth phosphate was converted to a mixing product consisting of rare earth oxysulfide and thorium-rich oxide, etc. The results showed that, except for Y, over 80% of the target REEs were recovered. Alkali treatment of a mixed mineral concentrate ore (a mixture of bastnaesite and monazite) and monazite with CaO-NaCl-CaCl_2 was studied by Xue et al. (2007) and Sun et al. (2007), respectively. With a series of pretreatment tests being conducted at $700\text{--}750^\circ\text{C}$ for 1 h, 90.8% decomposition of the mixed mineral concentrate can be obtained, while the decomposition rate of the monazite sample was only 79%. This finding suggested that more aggressive conditions are required to further enhance the decomposition of monazite. Moreover, potassium hydroxide (KOH) was selected as a baking reagent for the removal of phosphorus from monazite (Galvin et al., 2018). Compared to NaOH, KOH can achieve not only comparable performance on dephosphorization but also recover tri-potassium phosphate as a more economically promising byproduct (Kumari et al., 2019). Additionally, charred coal was also utilized for the dephosphorization of monazite due to the reducibility of carbon (Xing et al., 2010). It was found that a 98% dephosphorization rate was obtained after roasting monazite with charred coal at 1400°C for 2 h.

The advantages of alkali pretreatment were summarized by Lazo (2019) as follows: 1) phosphorus can be separated from rare earth hydroxide after alkali pretreatment, and the removed phosphorus is a marketable byproduct (e.g., fertilizer); 2) The alkaline solutions can be reused after purification. However, some difficult-to-dissolve rare earth compounds (e.g., CeO_2), which need more aggressive conditions for complete extraction, can be formed during the alkali treatment stage.

Alternative techniques for monazite processing In industrial practice, concentrated reagents and

elevated temperatures are still widely used to decompose monazite concentrates. The generation of large volumes of wastewater materials and radioactive waste materials has caused serious concerns over environmental protection. These issues have prompted the development of cleaner processing flowsheets with environment-friendly reagents.

(1) Novel processing methods

Other than conventional alkali baking performed at elevated temperatures, the alkali decomposition of monazite with grinding has been examined. Zhang et al. (1994) decomposed monazite by mechanically grinding with the addition of some chemical additives such as CaO and CaCl₂ in a ball mill at room temperature. The optimal treatment conditions determined were as follows: grinding the sample for 12 h with a charge ratio of 15:1 under an argon atmosphere. After grinding, around 95% of REEs from the decomposed monazite can be dissolved by 6 M HCl leaching. Another mechanochemical treatment of an Egyptian monazite concentrate was conducted in a ball mill autoclave (Abdel-Rehim, 2002). After grinding the sample at 150-170 °C for 1-2.5 h in 50% NaOH solution, a complete recovery (99.8%) of REEs can be achieved by 10% HCl solution. Such high leaching efficiency was mainly attributed to the grinding action. It can effectively remove the product layer and lead the newly generated surfaces of monazite to be more accessible to NaOH solution.

Other than performing the alkaline roasting pretreatment by conventional heating methods (e.g., muffle furnace), the decomposition of mixed rare earth concentrate mined in Bayan Obo using a self-designed microwave heating system was explored by Huang et al. (2019). After the sample was treated by 45% NaOH at 450 °C for 40 min, 88.73% of the decomposition ratio of the concentrate can be achieved. Compared to traditional heating methods, microwave heating requires a lower decomposition temperature as the author summarized.

(2) Novel lixiviants designed for monazite leaching

Several investigations have been performed to develop reagents that can replace concentrated acids and bases used in monazite processing. Given their unique complexing ability, organic ligands have been used to enhance the decomposition of rare earth minerals (monazite, apatite, etc.). Lazo et al. (2017a) studied the dissolution behaviors of different minerals (e.g., silicates and phosphates) by a series of organic acids. The authors pointed out that reagents like citric acid, oxalic acid, and ethylenediaminetetraacetic acid (EDTA) exhibited promising potential to solubilize REE-bearing minerals. Another finding reported by the authors is that the performance of organic acid on the leaching of the minerals was highly dependent on pH, which can affect the protonation/deprotonation of chelating ligands, surface charge of minerals, stability of soluble species, etc.

Goynes et al. (2010) systematically examined the dissolution of monazite and apatite in the presence of two types of organic acids: aliphatic and aromatic organic acids with low molecular weights. The influences of the type of organic acids, concentration, and the content of the dissolved O₂ in the leaching systems on the release of REY from those two minerals were systematically examined. It was discovered that the decomposition of both monazite and apatite was enhanced by oxalate, citrate, and phthalate, although the amounts of dissolved REY were still at very low levels (<10 g/kg). Furthermore, it was concluded that the dissolution characteristics of those two minerals were more likely to be governed by the crystal structure of each mineral and the dissolution behaviors were difficult to be predicted only by the stability constants of REE-ligand complexes.

Lazo et al. (2017b) investigated the dissolution behaviors of monazite in the presence of several organic acids (gluconic, maleic, tartaric, citric, oxalic, and mantellic acid) at acidic pH values (e.g., 1.3, 2, and 5 respectively). The results showed that oxalic acid could enhance the leachability of monazite to the greatest extent among the ligands tested. Different from other acids, oxalic acid can convert rare earth phosphate to rare earth oxalate as a solid, which was illustrated by thermodynamic prediction. The authors

also concluded that the limited performance of oxalic acid leaching was more likely to be explained by the consumption of oxalate rather than the passivation mechanism, as reported by Lapidus (2015a). In the second paper of this series, EDTA leaching at pH 10 was employed to dissolve the solid rare earth oxalate generated in the oxalic acid pretreatment step, with higher fractions of Nd (>60%), Ce (>40%), and La (>40%) being extracted (Lazo et al., 2018). Ammonium sulfate leaching of monazite after alkaline pretreatment was proposed by Amer et al. (2018), and the results showed that 94.6% of the REEs could be extracted by 300 g/L ammonium sulfate at 120 °C for 2 h. Although these advancements are still on lab scales, those new lixiviants provide new pathways about how to replace conventional concentrated reagents for monazite leaching and alleviate the resulting environmental concerns.

Selective recovery of Th and/or U from monazite In monazite, the concentrations of Th and U normally range from 5-10% (in ThO₂) and 0.2-0.4% (in U₃O₈), respectively, depending on the origin of the monazite (Amer et al., 2019). Separating these two radioactive elements from leachates is of great importance in mitigating the resulting radioactive pollution. An effective method that can selectively isolate U from REEs and Th in a NaOH-treated monazite sample was proposed by Amer et al. (2019). 98% of U can be selectively recovered from the hydrous oxide cake by urea (150 g/L, 5 h, room temperature, and S/L ratio = 4). Subsequently, the removal of Th from REEs is achieved by dissolving the residue in a mixed solution consisting of Na₂CO₃ and NaHCO₃. Another new lixiviant proposed for the separation of U from an alkali-cracked monazite concentrate is diethylenetriaminepentaacetic acid (DTPA) (Gado et al., 2019). Nearly all the REEs and Th can be dissolved using 20% DTPA at 100 °C for 8 h, leaving U in the residue for further purification. Essentially, the selective recovery of U or Th from the hydroxide cake of monazite depends on the differences in the solubilities of the metal-ligand complexes of those three metals. For example, the U-DTPA complexes are insoluble, which is opposite those of Th and REEs. Lapidus et al. (2015a) examined the potential of selectively dissolving Th and U from monazite using ammonium oxalate at varying pH and temperatures. However, the authors found that a complete recovery of those two metals was difficult due to the formation of a passivation layer resulting from the precipitation of rare earth phosphates or oxalates. In the second paper of this series (Lapidus et al., 2015b), several approaches, such as using EDTA, adding other metal ions (Fe³⁺ and Al³⁺), and ultrasonic treatment, were used to inhibit the formation of the passivation layer. However, those methods were inefficient in selectively isolating Th and U. Only after NaOH pretreatment, the leaching performance can significantly be improved.

1.2.3 Ion Adsorption Clays

As mentioned in Section 1.2.1, ion adsorption clays, commercially exploited in South China, are an important source of HREEs, even though their REE contents of them are merely 0.03-0.3 wt.% (Papangelakis and Moldoveanu, 2014). Globally, over 80% of HREEs are supplied by IACs. They were first discovered in Jiangxi Province, China in 1969. Besides South China, similar IAC deposits have also been found in Brazil, Madagascar, Thailand, etc. (Nie et al., 2020; Moldoveanu and Papangelakis, 2021). Foley et al. (2015) investigated the associations of REEs in the granite-derived regolith collected from the southeastern US, which had notable similarities with the IACs mined in South China.

Geologically, it is widely acknowledged that IACs were derived from the weathering of granitic and igneous rocks that are enriched with REEs. This process can lead to the formation of aluminosilicate minerals such as kaolinite (Bao and Zhao, 2008; Moldoveanu and Papangelakis, 2012). REEs in IACs are found to adsorb on the negatively charged surface of clay minerals (i.e., kaolinite, montmorillonite, and illite) in the form of ions via weak electrostatic force. Borst et al. (2020) studied the adsorption mechanisms of IACs using X-ray absorption spectroscopy. The results revealed that REEs adsorb on the surface of clays as outer-sphere complexes, and each REE³⁺ ion coordinates with 8 or 9 hydrated water molecules. Despite the low grades of REEs, the exploitation of IACs is still economically attractive because of its several advantages over other conventional REMs: 1) low investment and costs in mining and processing; 2) low radioactivity; 3) enrichment of middle and heavy REEs (Xiao et al., 2017; Papangelakis et al., 2012). These advantages enable IACs to be a critical source for HREEs.

Table 1.1 Summary of the representative lixivants developed for IACs.

Lixivants	Leaching methods/conditions	Leaching efficiency of TREE	Reference
Sulfates and chlorides with different cations: Cs^+ , Na^+ , NH_4^+ , Li^+	Batch leaching, 0.5 M; S/L=1:2, 60 min, 25 °C	Performance: $\text{Cs}^+ > \text{NH}_4^+ > \text{Na}^+ > \text{Li}^+$, Cs and NH_4 -salts can achieve 80-90% of leaching efficiency	Moldoveanu and Papangelakis, 2012
Sulfates and chlorides of Al^{3+} , Mg^{2+} , and NH_4^+	Column leaching, varied the ratio of $\text{Al}_2(\text{SO}_4)_3$ and $(\text{NH}_4)_2\text{SO}_4$, S/L=1:1	Performance: $\text{Al}^{3+} > \text{NH}_4^+ > \text{Mg}^{2+}$; 108.2% of leaching efficiency was obtained when the volume ratio of $\text{Al}_2(\text{SO}_4)_3/(\text{NH}_4)_2\text{SO}_4$ was 0.2:0.8	Yang et al., 2019
0.2 M MgSO_4	Batch leaching, S/L=1:5, 25 °C	>95% of leaching efficiency	Xiao et al., 2015
0.2 M FeSO_4	Soak leaching for screening tests of lixivants. Column leaching studied the effect of FeSO_4 (at pH =2, 298 K)	FeSO_4 outperformed than other lixivants, TREE leaching efficiency was 102%, and Ce partition in the leachate was 5.31%	Xiao et al., 2016
MgSO_4 , FeSO_4 , and ascorbic acid	Column leaching, 0.2 M MgSO_4 combined with FeSO_4 and ascorbic acid, pH=2	85.85% of leaching efficiency and 5.33% of Ce partition were achieved by combining 0.2 M MgSO_4 with 0.5 g/L ascorbic acid	Xiao et al., 2017
0.3 M NH_4Cl in conjunction with acetic, malonic, citric, tartaric, succinic, and malic acid	Batch leaching, S/L=1:10, pH 3-6, 2 h, 25 °C	Even in the low dosages (in mM level), organic acids benefited the leaching process (RE extraction increased from 9.66 to ~10.80 mmol/Kg)	Wang et al., 2017

Note: S/L: the ratio of the mass of solid over the volume of liquid; Batch leaching: leaching tests performed in containers with agitation.

Table 1.1 Summary of the representative lixivants developed for IACs (continued).

Lixivants	Leaching method/conditions	Leaching efficiency of TREE	Reference
Formates of NH_4^+ , K^+ , and Na^+	Column leaching, S/L=1:2, pH= 5.5-6.0, room temperature	87% of leaching efficiency was achieved by 1 wt.% ammonium formate	Chen et al., 2020
Combination of ammonium acetate and ammonium citrate	Column leaching, S/L=1:2, pH= 4, various temperatures	85.4% of leaching efficiency was obtained when the molar ratio of ammonium acetate and ammonium citrate was 7:3 and at 313 K	Chai et al., 2020
$(\text{NH}_4)_2\text{SO}_4$ combined with EDTA	Batch leaching, solid concentration: 50 g/L,	By 0.2% $(\text{NH}_4)_2\text{SO}_4$ and 0.005 M EDTA, 93.5% of La were extracted	Tang et al., 2018
Various chelating agents (EDDS, NTA- Na_3 , etc.) added to $(\text{NH}_4)_2\text{SO}_4$ and NaCl	Batch leaching, S/L=1:2, 30 min, wide initial pH ranges (2.3-8.5 for $(\text{NH}_4)_2\text{SO}_4$ system and 1.8-9.2 for NaCl systems), ambient temperature	Moderate improvements (6-10%) of leaching efficiency were found in the $(\text{NH}_4)_2\text{SO}_4$ systems, the recovery can be improved by 10-20% with the addition of EDDS and NTA in NaCl systems	Moldoveanu and Papangelakis, 2021
Addition of sodium dodecyl sulfate (SDS) into $(\text{NH}_4)_2\text{SO}_4$	Column leaching, S/L=1:1, solution pH=5.5, room temperature	The addition of 0.04% (mass fraction) SDS in $(\text{NH}_4)_2\text{SO}_4$ solution led to 5% more REEs being recovered and 25% less consumption of $(\text{NH}_4)_2\text{SO}_4$	Zhang et al., 2021

Note: S/L represents the ratio of the mass of solid over the volume of liquid; Batch leaching: leaching tests performed in containers with agitation.

REEs in IACs can be easily extracted by inorganic salt solutions such as NaCl and $(\text{NH}_4)_2\text{SO}_4$ via an ion exchange mechanism (Jun et al., 2010; Moldoveanu and Papangelakis, 2012). A detailed overview of the leaching technologies developed for IACs was provided by Papangelakis and Moldoveanu (2014). According to this study, three generations of leaching techniques have been developed for IACs by Chinese scientists and engineers. Initially, NaCl was developed as a lixiviant for IACs in batch leaching. NaCl was indeed an effective lixiviant. However, the final REE product had low purities (<92% TREO contents). Later, ammonium sulfate, which can be used in a lower concentration (0.3 M), was proposed for the batch and heap leaching of IACs in the early 1980s. Ammonium sulfate leaching can obtain final REE products with high purities (>92% REO). Additionally, in order to minimize the environmental concerns such as vegetation deterioration and soil damage associated with the mining and processing of IACs, the in-situ leaching by ammonium sulfate was proposed as the third-generation leaching technique, which is currently applied in South China.

The leaching mechanism of IACs by ammonium sulfate is explained by an ion exchange leaching mechanism, and the involved chemical equation is usually expressed as follows (see Eq. 14) (Moldoveanu and Papangelakis, 2012):



in which one mole of Ln^{3+} ion can be displaced by three moles of NH_4^+ ions. Although ammonium sulfate is an effective lixiviant for IACs, the issues such as high lixiviant dosage and nitrogen pollution of water bodies still need to be addressed (Yang et al., 2013; Xiao et al., 2017; Yang et al., 2019). On the other hand, even though ion-exchangeable REEs are found to be the dominant occurrence of REEs in IACs, REEs in other difficult-to-leach modes, such as Fe-Mn colloids and mineral forms, have also been recognized in IACs (Chi et al., 2005). In such cases, only using ammonium sulfate is not able to completely recover those hard-to-leach REEs (Xiao et al., 2015). As such, efforts have been made to develop alternative lixiviants for the leaching of IACs. On the other hand, investigations have also been conducted to reduce the dosage of ammonium sulfate by adding different additives (Moldoveanu and Papangelakis, 2021). The representative lixiviants, including inorganic salts and chelating agents, proposed for IACs by previous literature are summarized in Table 1.1. Generally, those proposed lixiviants for IACs can be classified into the following types: 1) inorganic salts that can substitute ammonium sulfate; 2) chemicals that have reducing and/or chelating effect, which can enhance the leachability of REEs in colloidal phase; and 3) chelating agents that can be used either as additives to ammonium sulfate or alone. Additionally, several additives were used as impurity inhibitors, permeability promoters, and swelling inhibitors to minimize the co-extraction of impure elements (e.g., Al, Fe, etc.), thereby mitigating the resulting environmental issues (Nie et al., 2020). Therefore, the applications of the alternative lixiviants not only have the potential to improve the leaching efficiency but also alleviate the environmental pressures caused by ammonium salts and other contaminants.

1.2.4 REEs in Coal

1.2.4.1 Abundances and Occurrences of REEs in Coal

Coal and coal byproducts (e.g., coal, coal refuse, coal ash, acid mine drainage) contain large amounts of REEs (Zhang et al., 2020). It was estimated that the total amount of REEs in coal is 50 million metric tons, which accounts for 50% of the conventional rare earth reserves (Zhang et al., 2015). On a global scale, the average contents of total REY in coal and coal ash materials are only 68.5 and 404 ppm, respectively (Lin et al., 2017). However, several coal deposits with relatively higher REE concentrations have been identified in several locations. For instance, the REE contents in the Far East coal deposits and the Fire Clay coal bed were found to range from 300-1000 ppm and 522-4198 ppm, respectively (Seredin, 1996; Hower et al., 1999). Based on the data reported by the USGS, the coal samples with >700 ppm of

TREE (in an ash basis) are uniformly distributed in most of the coal basins in the US, while the TREE contents of the samples collected from northern and central Appalachian and the Black Warrior basin were over 1,000 ppm (Palmer et al., 2015; Zhang et al., 2015). Therefore, coal and coal-derived materials have been identified as promising alternative REE sources.

REEs in coal are primarily associated with inorganic and organic matter. Regarding the organically bound REEs, they are mainly found in low-rank and low-ash coals, which have been reported by several studies (Seredin and Dai et al., 2012; Finkelman et al., 2018). It was observed that the ash content and TREE content were inversely correlated in a batch of REE-enriched lignite samples, and the REEs tended to be enriched in light-specific gravity fractions (Laudal et al., 2018). According to Seredin et al. (1999), around 50% of the TREEs were associated with humic substance in two Russian coals, and more amounts of middle REEs were found to be concentrated in the humic fraction. Compared to LREEs, HREEs tend to have a stronger affinity for the organic matter in coals (Zhang et al., 2015). Moreover, as a fuel for power generation plants, organically bound REEs in clean coal products will finally report to the ash products after coal combustion. Although the partition of REEs associated with the organic and inorganic matter is dependent on coal rank and coalfield, several studies have shown that only minor fractions of REEs bound to organic matter are found in most coal samples tested (Eskenazv, 1987; Bike et al., 1991; Zheng et al., 2007).

The mode of occurrence of REEs in inorganic matter has also been commonly identified. Bike et al. (1991) investigated the elemental sites and mineralogy of REEs in bituminous coals from the Sydney Basin. The results showed that clays are the primary host for those elements. At the same time, several secondary REE minerals, such as phosphates, were observed by scanning electron microscopy (SEM) analysis in the study. By performing a series of particle size, density, and magnetic separation tests, Lin et al. (2017) concluded that the majority of REEs in coal ash, coal-derived clay, and shale samples have associations with the major elements such as Al and Si. It was also found by Bryan et al. (2015) that the TREE content is positively correlated to the Al content in eastern US coals as shown in Figure 1.7. Inorganically associated REEs are mainly in the following forms: 1) syngenetic clastic and pyroclastic minerals; 2) diagenetic and epigenetic minerals of authigenic origin (Seredin and Dai et al., 2012). Zhang

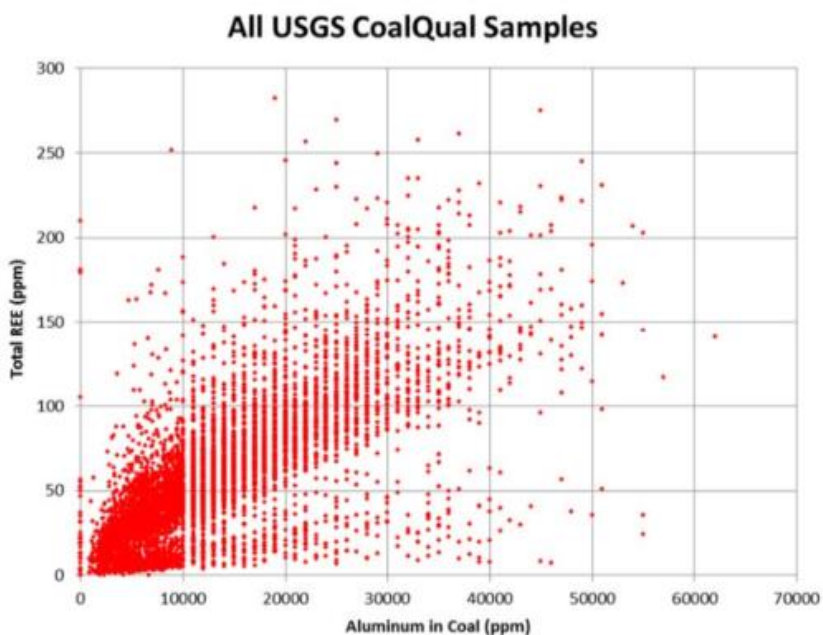


Figure 1.7 Plot of the correlation of TREE (excluding >300 ppm REE) and Al in US coals (Bryan et al., 2015).

et al. (2015) summarized that accessory minerals (e.g., monazite and xenotime), resistant minerals (e.g., monazite, xenotime, and zircon), and clay minerals (kaolinite, illite) are the dominant REE-bearing minerals in coal.

Dai et al. (2012) further classified REEs in coal into five forms: water-soluble, ion-exchangeable carbonate, organic, and aluminum silicate form, respectively. The fraction of each form can be determined by sequential extraction (Tessier et al., 1979). Of the five occurrences, REEs in ion-exchange, carbonate, and metal oxide forms are considered readily leachable forms, while the other two forms are normally difficult-to-extract under mild conditions (<100 °C). The higher the fraction of the readily leachable REEs, the lower the costs required in the extraction step of REEs. However, Zhang et al. (2019a) found that less than 2% of the REEs were in ion-exchange and carbonate forms in the samples collected from Fire Clay, West Kentucky No. 13, and Illinois No. 6 coal seams. Moreover, by sequentially leaching the coal samples with various chemicals, Finkelman et al. (2018) systematically quantified the occurrences of 42 elements in 20 bituminous and subbituminous coal samples. The results indicated that over 90% of LREEs and 70% of HREEs were associated with phosphates and clays in high-rank coal. Therefore, only minor fractions of REEs were found in easy-to-leach form based on the coal and coal byproduct samples tested so far.

As mentioned in Section 1.2.3, REEs in the IACs mined in South China are normally associated with kaolinite. In coal-derived clays, the associations of REEs with kaolinite have also been found. Zhang et al. (2018) studied the association characteristics of REEs in Fire Clay seam coal middlings by sequentially performing several stages of grinding and flotation tests, and it was found that REEs in the sample tended to associate with kaolinite, possibly dispersed in aluminosilicates as REMs and/or adsorbed on the surface of clays. It is worth noting that coal-based clays with higher fractions of ion-adsorbed REEs were only reported by Rozelle et al. (2016). The authors used three lixiviants (i.e., ammonium sulfate, ionic liquid, and a deep eutectic) to extract REEs from two US coal samples collected from the Upper Kittanning Bed, with over 69% TREE recovery being achieved. The leaching mechanism of ammonium sulfate was attributed to an ion exchange process by the authors. However, except for those two samples, the fractions of ion-exchangeable REEs in other coal and coal byproducts were normally very low.

In coal preparation plants, most of the REEs associated with inorganic matter in the run-of-mine coals report to coal refuse materials and fly/bottom ash (Luttrell et al., 2019). Compared to coal byproducts before combustion, REEs in the ash products are mainly associated with silicates and aluminosilicates since the majority of REEs are fused into an amorphous aluminosilicate glass matrix, which usually requires roasting by strong alkalis or acids at high temperatures to destroy the resulting structures for REE extraction (Lin et al., 2018; King et al., 2018; Mahandra et al., 2021). Consequently, REE recovery from coal ash products was not considered in this study given their poor leachability. Therefore, the recent progress on coal ash leaching is not covered in this study.

1.2.4.2 REE Extraction from Coal-derived Materials by Physical Preconcentration

Physical preconcentration of REEs from coal and coal-derived materials can reduce the volume of material subjected to the following chemical leaching step. The research progress involved has been systematically reviewed by Zhang et al. (2020) and Eterigho-Ikelegbe et al. (2021). Separation methods such as gravity, magnetic, and froth flotation were employed by Honaker et al. (2014) to upgrade REMs from coal refuse materials. The highest enrichment ratio achieved was only 1.2 via riffle table and multi-gravity separator, indicating a poor separation efficiency by gravity separation. However, improved separation performances were obtained via froth flotation by the authors. An enrichment ratio of 10.9 was obtained by performing column flotation with multi-stages using oleate as a collector, whereas the corresponding recovery of the concentrate was only <5%. Meanwhile, when single- or multi-stage conventional flotation was performed, lower enrichment ratios and recoveries were obtained. The authors also performed the beneficiation by wet high-intensity magnetic separation. After a three-stage separation, the final concentrate assay was 7,000 ppm of REEs on a whole basis, which was improved by 14 times compared to the feed. However, the recovery was still <5%.

Table 1.2 Representative leaching techniques for rare earth extraction from coal and coal refuse before combustion.

Sample source	Pretreatment	Leaching conditions	Leaching results	Reference
Fire Clay middling from Eastern Kentucky	None	1 M H ₂ SO ₄ , 10g/L, D ₈₀ = 8.7 um, 75 °C, 2 h	75% TREE recovery, less HREEs were extracted	Yang et al., 2020
Two samples with high ash content from the Upper Kittanning Bed	None	1 M (NH ₄) ₂ SO ₄ , mass ratio:1:2, room temperature, 1 h	90% of TREE recovery was achieved	Rozelle et al., 2016
Underclay rock samples from Central Appalachian coal seams	None	0.1 M Citrate + 0.5 M NaCl, 1, 10% solid concentration, pH=3.5	The recoveries of La, Ce, Nd, Eu, and Dy in 02 and 03 sample were larger than 30%	Montross et al., 2020
Different density fractions of West Kentucky No. 13 and Fire Clay	Oxidation pretreatment by low-temperature plasma (LTP) as a function of time (4, 8, 16, 32 h)	NaOH-treated samples were leached sequentially by deionized water, 0.1 M ammonium sulfate, 1.2 M H ₂ SO ₄ , 1% solid concentration, 75 °C, 5 h	LTP oxidation pretreatment enhanced the leachability of 1.60 SG float fraction but didn't have minor impact on the REE leaching of 2.20 SG sink fraction	Gupta, 2021
Middling and coarse refuse samples from Pocahontas No. 3 seam	Calcination at 600 °C for 2 h, no additives	1.2 M HCl, 1% solid concentration, 75 °C, 5 h	After calcination, around 80-90% LREEs and 40-60% HREEs were extracted respectively	Zhang et al., 2019b
Fine refuse from West Kentucky # 13	NaOH pretreatment by 8 M NaOH, S/L = 1/10., 2 h, 75 °C	Treated sample leached by 1.2 M H ₂ SO ₄ at 75 °C with a 1% solid concentration for 5 h	After NaOH pretreatment, the TREE recovery increased from 22 to 75%, noticeable improvements were found for LREEs	Yang et al., 2019
Flotation tailings from East Kootenay coalfield	20% solid concentration, 5-30 wt. % NaOH, 130-190 °C, for 30-120 min	Treated samples were leached by 7.5 wt. % HCl at 50 °C for 30 min	After treated by 30 wt.% NaOH at 190 °C for 30 min, the LREE and HREE recovery values were 97 and 76% respectively	Kuppusamy et al., 2019

Additionally, Zhang et al. (2017) successfully preconcentrated REMs from a thickener underflow sample (i.e., Fire Clay coal) by conventional flotation and a laboratory flotation column using fatty acid as a collector, and the corresponding REE assays of the concentrates after multi-stage flotation were 2,300 and 4,700 ppm, respectively. Moreover, poor separation performances were obtained through other separation techniques, such as electrostatic separation and X-ray transmission sensor-based sorting, according to Eterigho-Ikelegbe et al. (2021). However, it is worth noting that some promising results were also obtained by the HHS process. This novel technique renders hydrophobic particles agglomerated in the presence of hydrocarbon oils (e.g., heptane), after which those hydrophobic particles can be separated by phase separation. One of the advantages of the HHS process is its outstanding performance in handling ultrafine particles. Through this process, a final concentrate assaying 17,428 ppm of REEs (on an ash basis) was achieved from a thickener underflow product (Gupta et al., 2016). Although ultrafine grinding was applied, the HHS process exhibited more promising potential in the enrichment of REEs from low-grade materials relative to other traditional beneficiation methods.

Given the above review, except for flotation and magnetic beneficiation methods, most of the physical separation techniques are not able to effectively preconcentrate REEs from coal refuse materials due to REEs in finely dispersed mineral particles. Substantial energy is normally required to have good liberation of REMs by grinding, rendering physical beneficiation less cost-effective.

1.2.4.3 REE Extraction from Coal-derived Materials by Chemical Leaching

Considering the poor performances of physical beneficiation, chemical leaching has been considered a more promising approach to extracting REEs from coal-derived materials. Peiravi et al. (2021) summarized the methods used to extract REEs from non-conventional sources (e.g., coal-based materials, iron ore tailings, etc.). However, that paper focuses more on reviewing chemical extraction techniques for the REE recovery from coal fly ash. Moreover, the recent progress of rare earth extraction from coal and coal byproducts via chemical leaching methods has been systematically reviewed by Zhang et al. (2020) and Eterigho-Ikelegbe et al. (2021). The leaching methods developed include direct acid or salt leaching and acid leaching after alkaline or calcination pretreatment. The representative leaching technologies are summarized in Table 1.2.

As indicated by Zhang et al. (2020), the performances of direct salt and acid leaching were sample-dependent. For low-rank coals such as Fort Union lignite coals, decent TREE recoveries (70-90%) can be achieved even by dilute acids (e.g., 0.5 M H_2SO_4) at 40 °C with varying contact times (1 to 48 h) (Laudal et al., 2019), which is mainly due to that REEs associated with organic matter are amenable to acid leaching. However, relatively low extraction recoveries were obtained when direct acid leaching (e.g., 1 M HNO_3 at 75 °C) was performed on several coal-derived clay samples such as thickener underflow and middlings after decarbonization (Honaker et al., 2017).

Alkali and calcination pretreatment techniques are applied to enhance the leachability of REEs in coal and coal refuse. As shown in Table 1.2, both pretreatment methods could significantly improve TREE recovery compared to direct leaching. However, compared to LREEs, relatively inferior enhancement in the leachability of HREEs was normally noticed for both pretreatment methods due to the occurrence of HREEs in hard-to-leachable forms. The involved mechanisms of those two pretreatment methods were also summarized by Zhang et al. (2020). The roles of thermal pretreatment are as follows: 1) liberation of REMs after the dehydration of clay minerals; 2) transformation of organically associated REEs into their REE oxide forms; and 3) conversion of REE-bearing minerals such as rare earth phosphate minerals into their readily leachable forms such as rare earth oxide. Although the combustible organic matter associated with coal refuse can reduce the energy input to roasters, calcinating the coal refuse samples with only hundreds of ppm of REEs at around 600 °C for a few hours (e.g., 2 h) is still an energy-consuming pretreatment

process, which is economically prohibited in commercial applications.

Alkali pretreatment benefits the REE leaching process by converting the resistant REMs into more leachable forms. For instance, monazite can be decomposed into its hydroxide form. On the other hand, REMs encapsulated by the dominant minerals (e.g., clays) can be liberated after the decomposition of clays during the alkali pretreatment (Zhang et al., 2020). Compared to calcination pretreatment, alkali pretreatment can be performed at $<100\text{ }^{\circ}\text{C}$. Although high alkali concentrations are normally required, one advantage is that those base solutions can be recycled after purification, a technique that has been applied in the caustic cracking of monazite in the industry, thereby reducing the related chemical costs. It should be noted that alkali pretreatment may cause the dissolution of gangue minerals, leading to the co-extraction of substantial amounts of contaminants into the leachates. Fortunately, this issue can be mitigated by optimizing the pretreatment conditions and finding other efficient lixiviants that can replace acids. Accordingly, this research used alkali pretreatment to enhance the leachability of REEs in coal refuse and other clayey waste materials.

1.3 Research Objectives and Dissertation Outline

1.3.1 Research Objectives

The principal goal of this work is to develop leaching technologies that can extract REEs from clayey waste materials, including coal-based clays and kaolinite mining waste. Monazite was used as a proxy for the rare earth phosphates in those materials. The data obtained from this work will provide fundamental information for industrial process development and design. The specific objectives of the dissertation are as follows:

1. Investigate the feasibility of using alkali pretreatment followed by ammonium sulfate leaching to extract REEs from monazite under mild conditions ($<100\text{ }^{\circ}\text{C}$), and evaluate the influences of experimental variables (e.g., NaOH concentration, temperature, and particle size) on the leaching efficiency.
2. Explain the leaching mechanism of ammonium sulfate during the leaching process of NaOH-treated monazite and determine the corresponding leaching kinetics type.
3. Select effective lixiviants from carboxylate chelating ligands for REE extraction from alkali-treated monazite and explain the involved leaching mechanisms.
4. Assess the possibility of using ammonium sulfate leaching to extract REEs from coal-based clay samples after alkali pretreatment with dilute NaOH concentrations. Also, examine the influences of NaOH pretreatment and the following leaching step on the dissolution of gangue minerals by solution chemical composition analyses and material characterization techniques.
5. Evaluate the effect of phosphate on the ion exchangeability of REEs in IACs by synthesizing a series of artificial IACs with varying amounts of apatite-derived phosphate being doped.
6. Explore the possibility of upgrading REEs from a kaolinite flotation reject material by flotation and the HHS process. Study the leaching characteristics of REEs and the major impure elements of the flotation concentrate by ammonium sulfate and HCl after alkali pretreatment.

1.3.2 Dissertation Outline

The dissertation consists of seven chapters. Chapter 1 introduces the research background and objectives of this study. A detailed literature review, including (a) the applications and commercial resources of REEs, (b) the leaching technologies proposed for commercialized REMs, and (c) the extraction techniques of extracting REEs from coal-derived materials, is also provided. Chapter 2 reports the

experiment results of REE extraction from NaOH-treated monazite by ammonium sulfate under mild conditions. The effects of NaOH concentration, particle size, and temperature on the leaching recovery were examined. The leaching mechanism of ammonium sulfate was also investigated in chapter 2. Chapter 3 delineates the leaching kinetics study of NaOH-treated monazite by ammonium sulfate based on the experimental data reported in chapter 2. On the other hand, it also gives the results of lixiviant screening tests conducted on the NaOH-treated monazite sample. Chapter 4 describes the application of the extraction process (i.e., NaOH pretreatment followed by ammonium sulfate leaching) to coal-derived clays. To reduce the alkali consumption, a new NaOH pretreatment technique with the addition of EDTA has also been explored in chapter 4. Chapter 5 explored the possibility that a certain fraction of REEs may adsorb on the surface of clay but in a phosphate-passivated form by synthesizing a series of phosphate-passivated rare earth ion adsorption clays. In chapter 6, the preconcentration of REEs from a kaolinite flotation reject by the HHS process and flotation was investigated. The flotation concentrate was subjected to ammonium sulfate and HCl leaching tests after NaOH pretreatment. Chapter 7 summarizes the conclusions, original contributions, and recommendations of this dissertation.

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Chapter 2 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 (<100 °C) 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 °C, 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 $\text{Ln}(\text{OH})_3(\text{s})$ 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.

2.1 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, and they can be readily extracted into solution by the ion-exchange mechanism,



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 $\text{Ln}(\text{OH})_3(\text{s})$. Due to the relatively small difference in basicity between the PO_4^{3-} ($\text{pK}_b = 1.7$) and OH^- ($\text{pK}_b = 0$) ions, monazite decomposition requires high concentrations (60-75%) of NaOH solutions and temperatures (120-150 °C) (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 (Abdel-Rehim et al., 2002; Kim et al., 2009; Lazo et al., 2020). 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-monzazite concentrates are decomposed by roasting in a rotary kiln at $>300\text{ }^{\circ}\text{C}$ in the presence of H_2SO_4 to produce $\text{Ln}_2(\text{SO}_4)_3$ 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 ($\sim 10\%$) of the Bayan Obo concentrate is, however, decomposed by NaOH at $140\text{--}200\text{ }^{\circ}\text{C}$, followed by HCl leaching at pH 1-1.5 (Zhu et al., 2015).

Monazite concentrates usually contain 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 ($\text{Ln}_2(\text{ox})_3$) while the PO_4^{3-} ions are released into the solution. The authors also found that the precipitate can be dissolved in the presence of 0.1 M ethylenediaminetetraacetic acid (EDTA) at pH 10 and $25\text{ }^{\circ}\text{C}$. 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 $<10\text{ }\mu\text{m}$ are treated in high concentrations of NaOH solutions at $150\text{ }^{\circ}\text{C}$ to convert them to $\text{Ln}(\text{OH})_3(\text{s})$ before acid leaching. Amer et al. (2018) showed recently that ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) 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 ($<15\text{ }\mu\text{m}$) 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 $100\text{ }^{\circ}\text{C}$ and to subsequently dissolve the hydrous oxides using $(\text{NH}_4)_2\text{SO}_4$ 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.

2.2 Experimental

2.2.1 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 2.1 shows 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 reagents were of analytical grades. Deionized water with a resistivity of 18.2 $\text{M}\Omega\cdot\text{cm}$ at 298.15 K was used in all solution preparation and leaching tests.

2.2.2 Methods and Procedure

2.2.2.1 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,



to form $\text{Ln}(\text{OH})_3(\text{s})$, 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 $(\text{NH}_4)_2\text{SO}_4$ leaching at pH 4.0. That $\text{pK}_b = 1.7$ 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

Table 2.1 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

alkali-resistant polytetrafluoroethylene (PTFE) beaker and heated on a hot plate at temperatures in the range of 60-80 °C 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.

2.2.2.2 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 HNO₃ (2.5%) and HCl (0.5%) solution for ICP-MS analysis. The recovery (*R*) of an REE species was determined using the following relationship,

$$R = 100 \times \frac{C_l V}{C_f M} \quad (2.3)$$

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.

2.2.2.3 Zeta-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 (NH₄)₂SO₄ 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.

2.2.2.4 Powder X-ray Diffraction Studies

The monazite samples pretreated with NaOH and subsequently leached with (NH₄)₂SO₄ as a lixiviant were subjected to X-ray diffraction analysis using the Rigaku MiniFlex 600 XRD analyzer equipped with Cu-K α radiation ($\lambda = 1.54$ Å). The spectra were recorded over a 2θ range from 10-80° with a step size of 0.04° and a dwell time of two seconds.

2.2.2.5 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 $\mu\text{m} \times 200 \mu\text{m}$ area. The adventitious carbon peak at

284.8 eV was used for binding energy correction.

2.3 Results

2.3.1 Ammonium Sulfate Leaching

2.3.1.1 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 $(\text{NH}_4)_2\text{SO}_4$

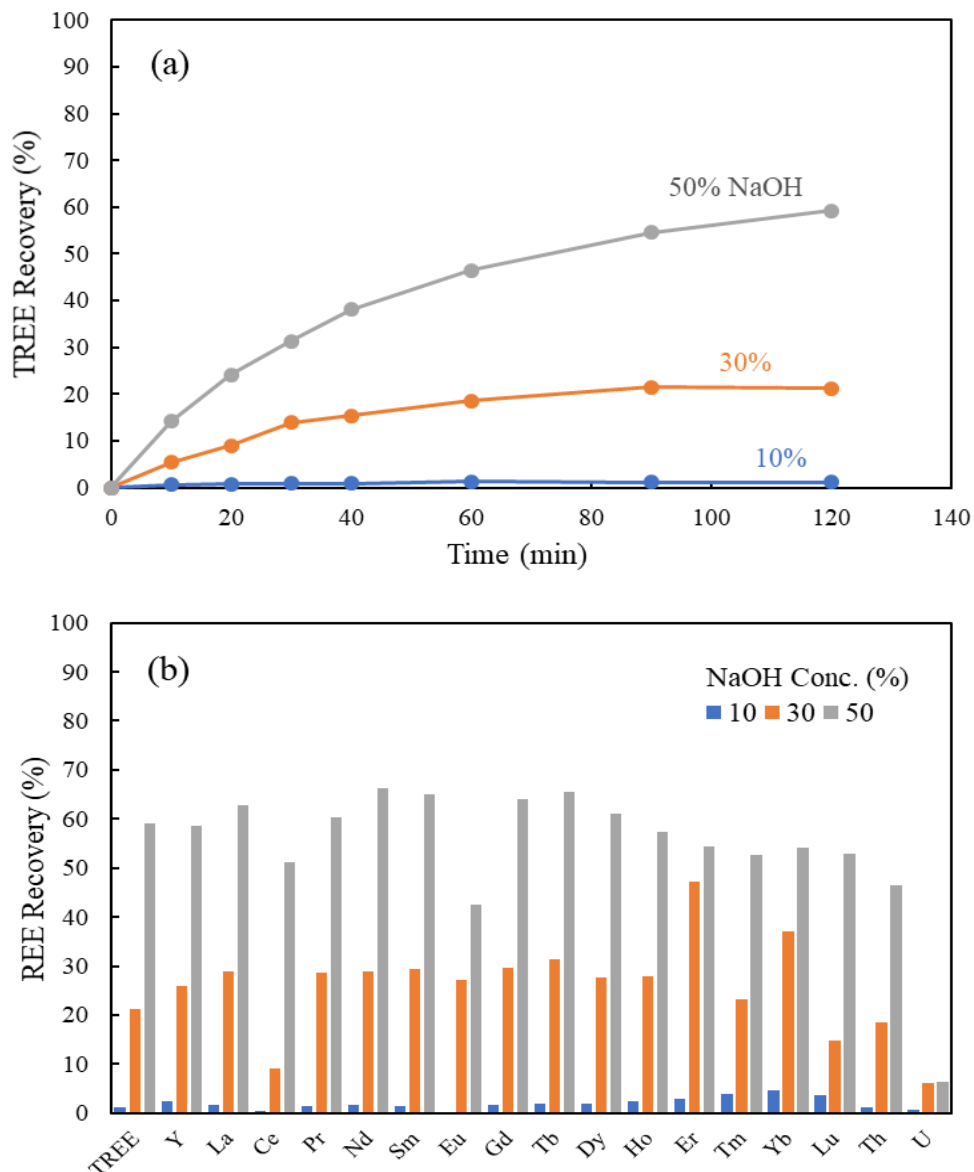


Figure 2.1 Results of the ammonium sulfate leaching tests conducted on a monazite sample ($d_{80} = 14.61 \mu\text{m}$) at 0.5 M $(\text{NH}_4)_2\text{SO}_4$, pH 4, and ambient temperature after the NaOH pretreatment step in 10, 30, and 50% solutions at 80 °C for 24 h; a) total REE recoveries, b) element-by-element recoveries.

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 (NH₄)₂SO₄ 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 2.1a show that as the NaOH concentration was increased from 30 to 50%, the recoveries increased from 21 to 60%. Although not shown in Figure 2.1, 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 also showed that up to 99.99% of the phosphorus can be removed from monazite after the NaOH pretreatment steps conducted at 170 °C for 2-4 h. This finding is consistent with the monazite decomposition mechanism represented by Reaction (2.2).

Figure 2.1b shows the element-by-element REE recoveries obtained at 80 °C. 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 EuSO₄ during the (NH₄)₂SO₄ leaching step.

The standard half-cell potentials given below

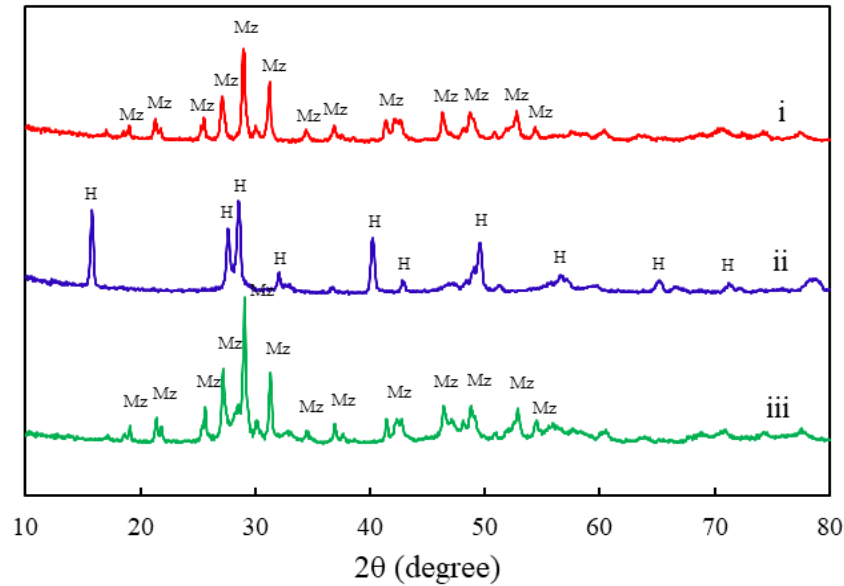


Figure 2.2 XRD spectra of i) untreated monazite of $d_{80}=14.61$ μm, ii) monazite pretreated in a 30% NaOH solution at 80 °C for 24 h, and iii) of leach residue. The second spectrum shows hydroxide formation, which disappears after the ammonium sulfate leaching. The third spectrum shows the reappearance of the monazite substrate after the leaching (Mz: monazite; H: rare earth hydroxide).

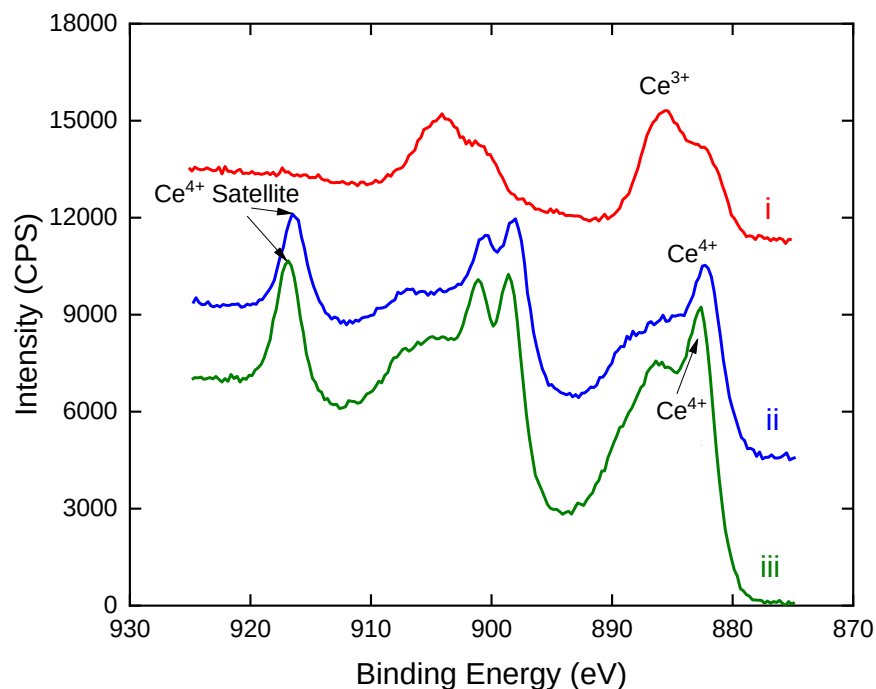


Figure 2.3 Ce 3d XPS spectra of i) untreated monazite of $d_{80}=14.61 \mu\text{m}$; ii) NaOH-pretreated monazite at 30% NaOH and 80°C for 24 h; iii) leach residue.

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^{2+} ions, they can be readily oxidized to Ce^{4+} ions and form CeO_2 at $\text{pH} > 9.5$ 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 $\text{EuSO}_4(\text{s})$ when $(\text{NH}_4)_2\text{SO}_4$ 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 2.2 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 $(\text{NH}_4)_2\text{SO}_4$ leaching. The results show that monazite had been converted to rare earth hydroxide $\text{Ln}(\text{OH})_3$ 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 2.3 shows the XPS spectra of a monazite sample before and after the NaOH pretreatment and the $(\text{NH}_4)_2\text{SO}_4$ 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 $\text{Ce}(\text{OH})_4$ are sparingly soluble in weakly acidic solutions and hence dissolve only under aggressive conditions (Li et al., 2017; Kumari et al., 2019).

2.3.1.2 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 $\text{La}(\text{OH})_3(\text{s})$. 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),

$$1 - \frac{2}{3} R - (1 - R)^{2/3} = \frac{2MDC}{\alpha \rho r_0^2} t \quad (2.6)$$

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 ρ the molecular weight and density of the mineral, D and C the diffusion coefficient and OH^- concentration, respectively, α the stoichiometry factor, and ρ is the particle density. Eq. (2.6) 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

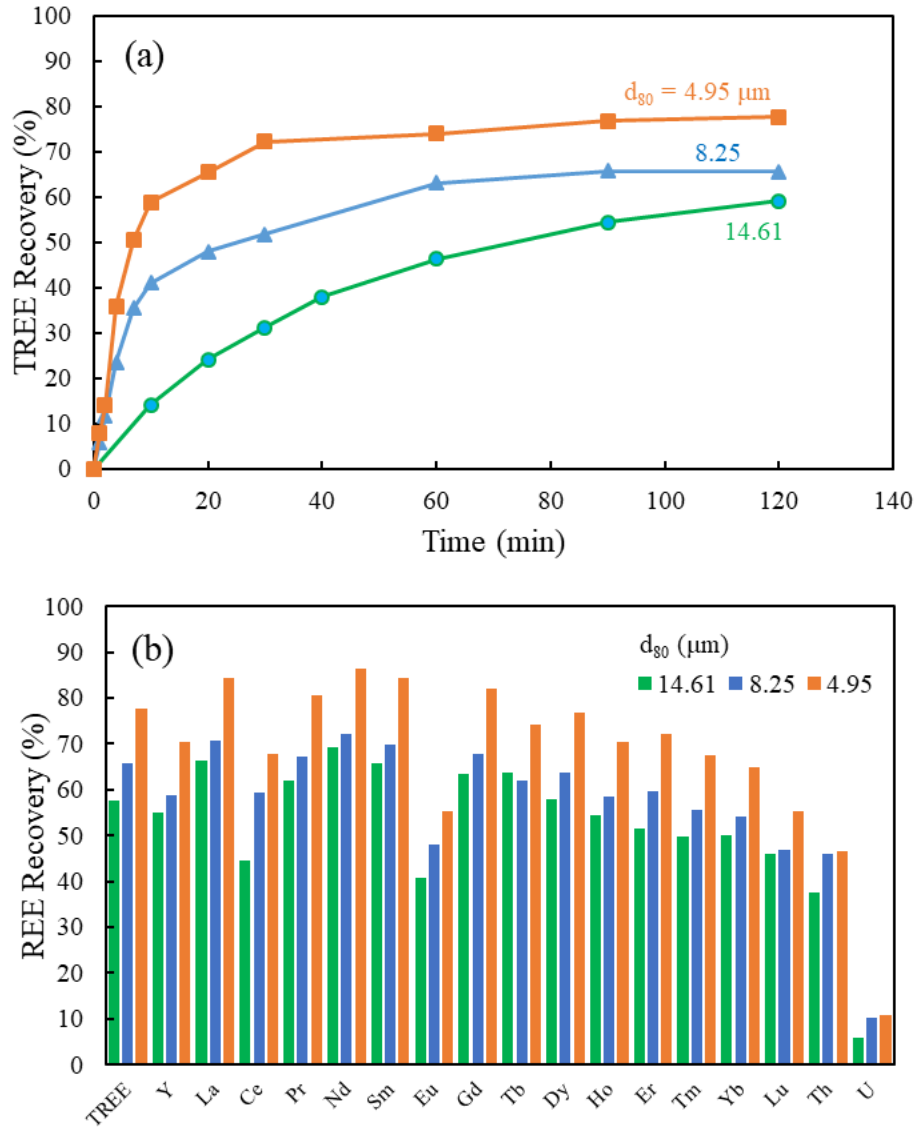


Figure 2.4 Effect of particle size on a) TREE recoveries, and b) individual REE recoveries. Monazite particles were pretreated in a 50% NaOH solution at 80°C for 24 h, followed by $(\text{NH}_4)_2\text{SO}_4$ leaching at pH 4 and 25 °C for 2 h.

to less than 45 μm , often below 10 μm (Krishnamurthy and Gupta, 2015).

Figure 2.4a 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. (2.6). 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 $(\text{NH}_4)_2\text{SO}_4$ leaching at 0.5 M at pH 4 and 25 °C for 2 h. As shown in Figure 2.4b, the recoveries of the three major elements of monazite, i.e., La, Pr, and Nd, were close to 85% at $d_{80} = 4.95 \mu\text{m}$.

In the present work, the OH^- ions displaced the PO_4^{3-} ions from the monazite structure and formed $\text{Ln}(\text{OH})_3(\text{s})$ on the mineral surface, which in turn was leached by using $(\text{NH}_4)_2\text{SO}_4$ as a lixiviant. In the conventional caustic soda leaching process, the $\text{Ln}(\text{OH})_3(\text{s})$ 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

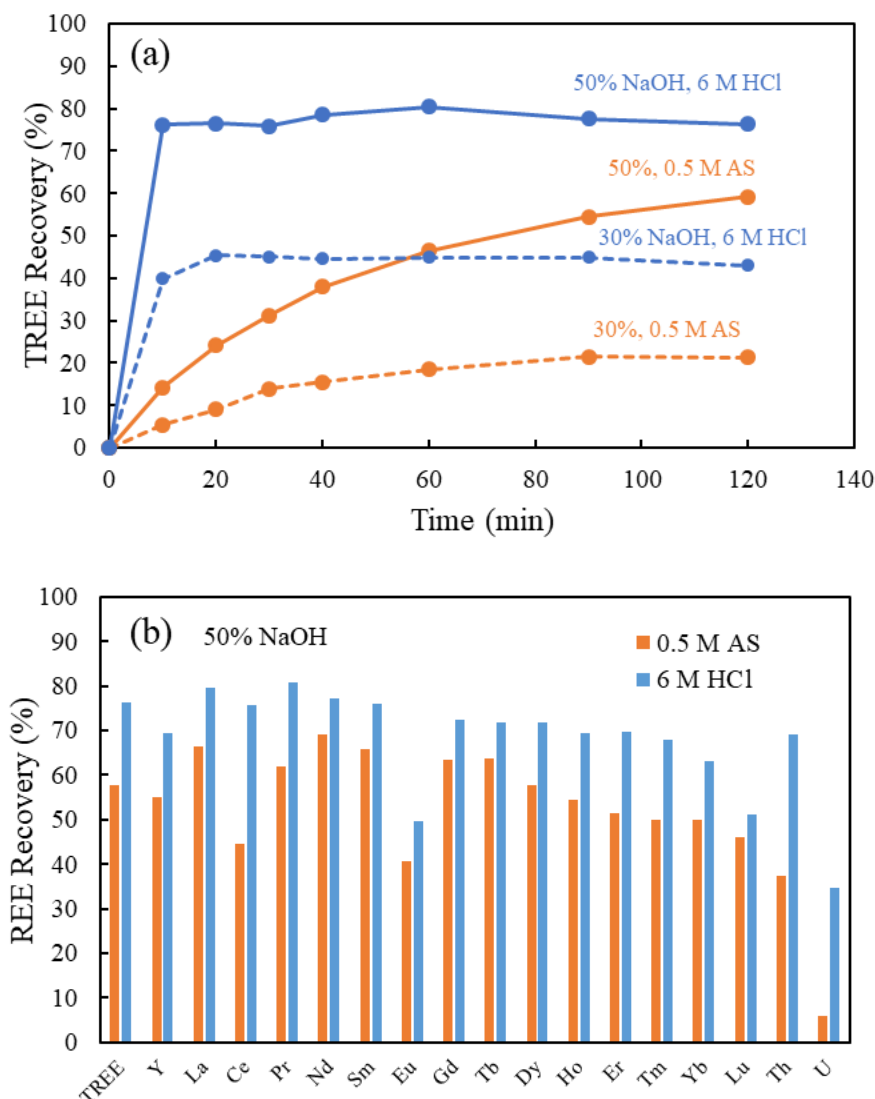


Figure 2.5 Comparison between extracting REEs from the NaOH pretreated monazite ($d_{80} = 14.61 \mu\text{m}$) at 80 °C for 24 h, followed by $(\text{NH}_4)_2\text{SO}_4$ leaching at pH 4 and 25°C and by acid leaching in a 6 M HCl solution; (a) TREE recoveries; (b) corresponding individual REE recoveries. “AS” denotes ammonium sulfate (the same below).

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 lixivants, i.e., $(\text{NH}_4)_2\text{SO}_4$ and HCl, are compared in Figure 2.5a. As shown, the kinetics of $(\text{NH}_4)_2\text{SO}_4$ leaching was slower than that of the HCl leaching. On the other hand, the ammonium sulfate leaching released substantially less U into solution, which may be a distinct advantage of using $(\text{NH}_4)_2\text{SO}_4$ rather than HCl as a lixiviant. Amer et al. (2018) showed that $(\text{NH}_4)_2\text{SO}_4$ and NH_4Cl are more selective against $\text{Fe}_2(\text{SO}_4)_3$ 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 2.5a 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 lixivants for

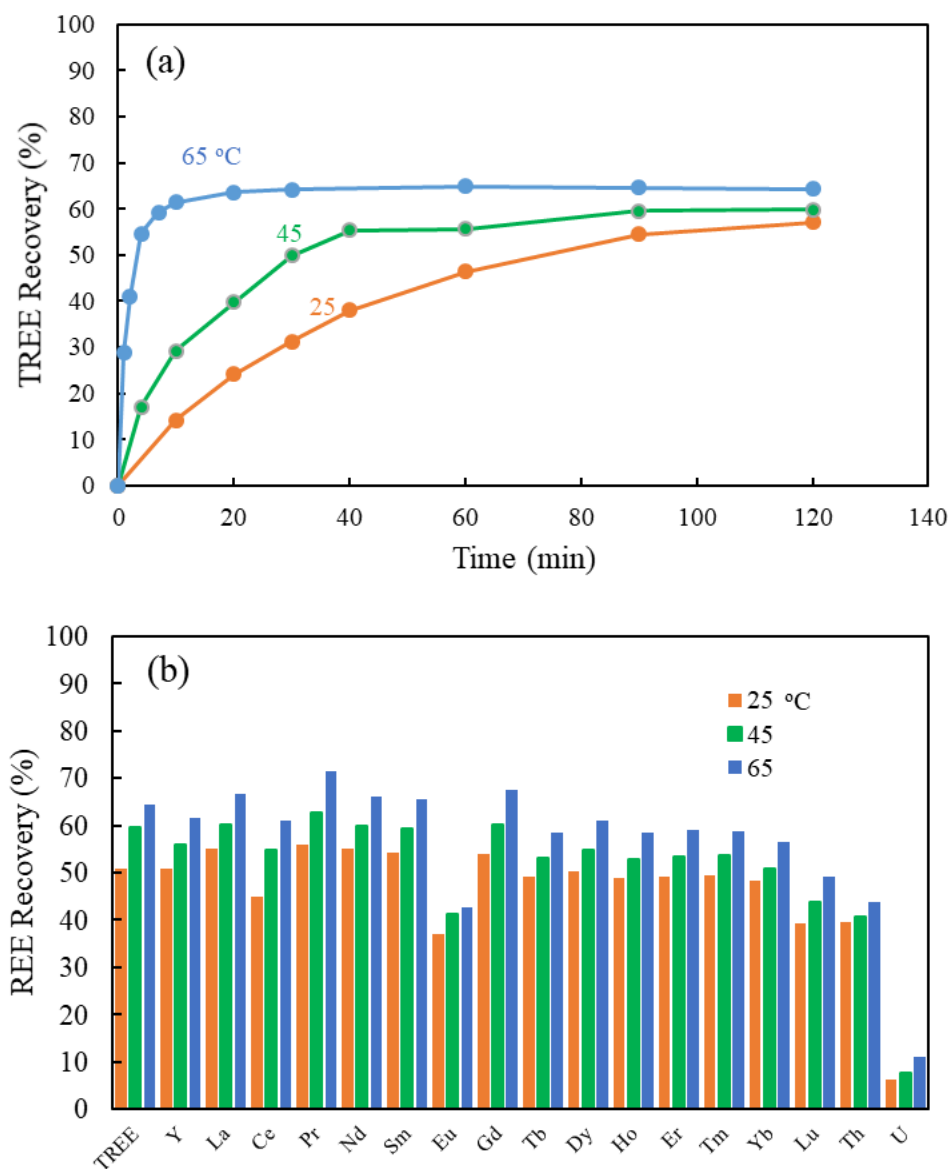


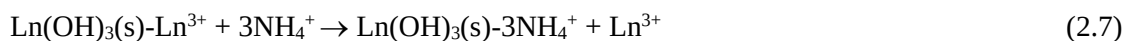
Figure 2.6 The total and individual REE recoveries of a monazite sample pretreated in a 50% NaOH solution at 80 °C and $d_{80} = 14.61 \mu\text{m}$). The pretreated samples were leached in a 0.5 M $(\text{NH}_4)_2\text{SO}_4$ solution at pH 4 at different temperatures.

the $\text{Ln}(\text{OH})_3(\text{s})$ leaching determines the kinetics. Much of the excess NaOH can be readily recycled, however.

The results presented in Figure 2.6a show that the kinetics of the $(\text{NH}_4)_2\text{SO}_4$ leaching was 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 2.5a). Even the ultimate TREE recoveries improved at the higher ammonium sulfate leaching temperature as shown in Figures 2.6a 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 $(\text{NH}_4)_2\text{SO}_4$ as lixiviant is lower than obtained at 6 M HCl concentration (Figure 2.5), 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 $(\text{NH}_4)_2\text{SO}_4$ solution.

2.3.1.3 Effect of Different Cations

The results presented in the foregoing sections showed that $(\text{NH}_4)_2\text{SO}_4$ can be used as a lixiviant for $\text{Ln}(\text{OH})_3(\text{s})$ 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 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 $\text{Ln}(\text{OH})_3(\text{s})$ surface as follows,



which is akin to the ion-exchange mechanism described by Eq. (2.1) 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 leaching experiments have been conducted, the NaOH -treated monazite is positively charged with its $\zeta = 40$ mV as shown in Figure 2.11. Since Ln^{3+} ions

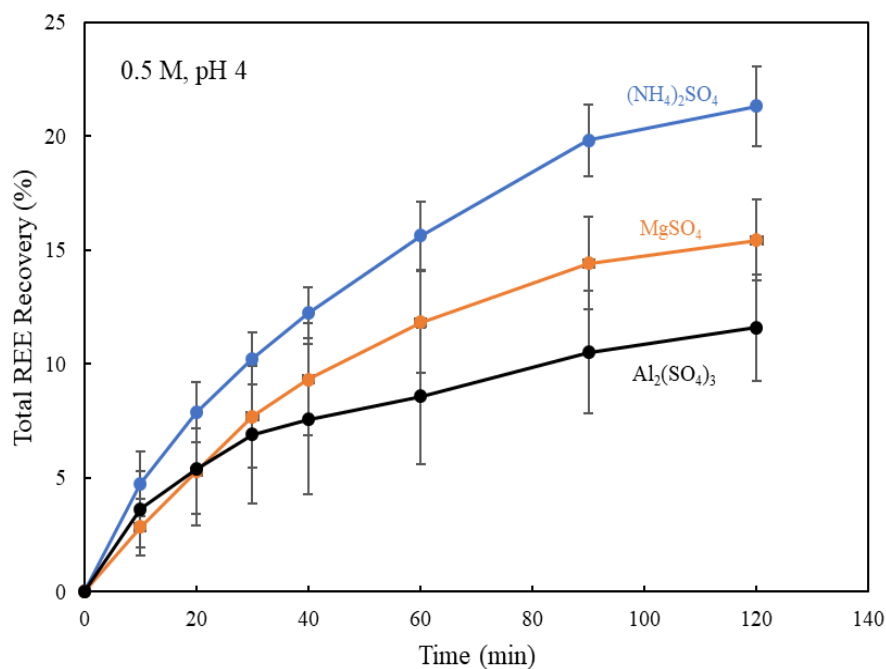


Figure 2.7 Total REE recovery leached by various sulfate-based lixiviants at pH 4 after 30% NaOH pretreatment at 80 °C for 24 h, $d_{80} = 14.61 \mu\text{m}$.

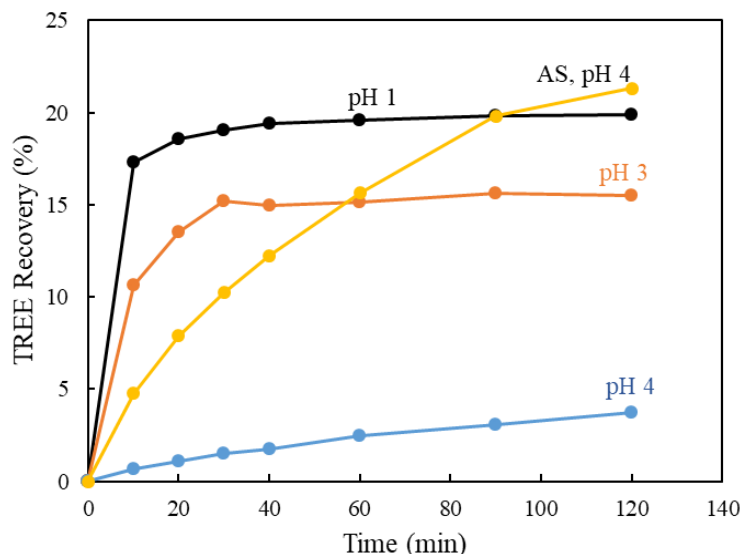


Figure 2.8 REE recovery of monazite leached in HCl solutions of different pH. The samples were pretreated in a 30% NaOH solution at 80 °C for 24 h, $d_{80} = 14.61 \mu\text{m}$.

are the most predominant charge 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 (2.1) due to the large differences in the hydration enthalpies (Moldoveanu and Papangelakis, 2012). To explore the possibility that Reaction (2.7) may also be controlled by the hydration enthalpies of ionic species involved, a series of leaching experiments were conducted on a NaOH-treated monazite sample using $(\text{NH}_4)_2(\text{SO}_4)$, MgSO_4 , and $\text{Al}_2(\text{SO}_4)_3$ as lixiviants at pH 4. All experiments were conducted using 0.5 M solutions at pH 4, $d_{80} = 14.61 \mu\text{m}$, 2 h leaching time, and at ambient temperatures. The results presented in Figure 2.7 show that the NH_4^+ ions with $\Delta H_{\text{hyd}}^0 = -307 \text{ kJ mole}^{-1}$ gave the highest REE recoveries, followed by Mg^{2+} ions with $\Delta H_{\text{hyd}}^0 = 1,921 \text{ kJ mole}^{-1}$, and Al^{3+} ions with $\Delta H_{\text{hyd}}^0 = -4,665 \text{ kJ mole}^{-1}$ (Smith, 1977). The error bars for the tests conducted with $(\text{NH}_4)_2\text{SO}_4$ and MgSO_4 were reasonable with <3% standard error at a 95% confidence interval, while the tests conducted with $\text{Al}_2(\text{SO}_4)_3$ were larger due to the possible precipitation of $\text{Al}(\text{OH})_3$.

The results presented in Figure 2.7 suggest 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 Xiao et al., 2016; (Ran et al., 2017).

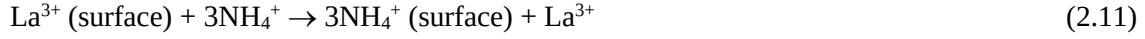
For comparison, Figure 2.8 shows the results obtained using HCl as the sole lixiviant for $\text{Ln}(\text{OH})_3(\text{s})$ at different pH values. As expected, leaching efficiencies increased with decreasing pH. Note here that the REE recovery obtained in a 0.5 M $(\text{NH}_4)_2\text{SO}_4$ solution at pH 4, was higher than the recoveries obtained using HCl at pH 1, 3, and 4, demonstrating the benefits of using $(\text{NH}_4)_2\text{SO}_4$ as a lixiviant.

2.3.1.4 Effect of Different Anions

Figure 2.9 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 (Haas et al., 1995; Smith et al., 2004),



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



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, $(\text{NH}_4)_2\text{SO}_4$ gave the best results, justifying its use as the optimal lixiviant for $\text{Ln}(\text{OH})_3(\text{s})$. This finding is similar to the thermodynamic consideration that the stability of ThO_2 diminishes considerably in the presence of sulfate ions (Kim et al., 2012).

2.4 Discussion

Monazite decomposition requires an aggressive treatment either in concentrated H_2SO_4 at 200-220 °C or in 60-70% NaOH solutions at 140-180 °C (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 $\text{Ln}(\text{OH})_3$ at 10-30% NaOH concentrations. However, the reaction rates were too slow to be of practical use at the

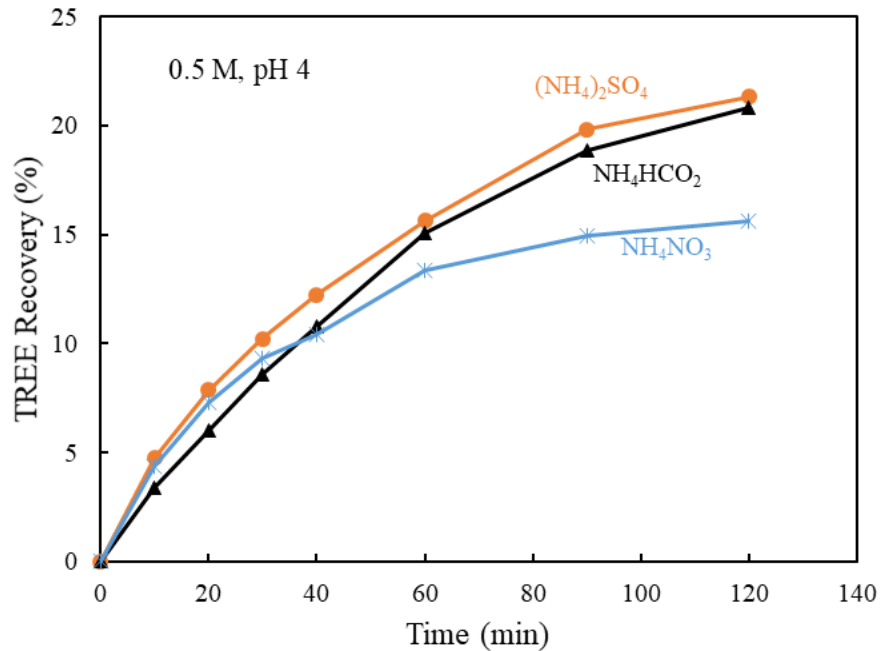


Figure 2.9 Effect of different anions of ammonium salts on REE extraction from the monazite particles pretreated in a 30% NaOH solution at 80°C; with $d_{80} = 14.61 \mu\text{m}$.

temperature range investigated. It appears that a 50% NaOH may be the minimum required at 80 °C, 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 ($\text{Na}_3\text{PO}_4 \cdot 10\text{H}_2\text{O}$) at 60 °C (Habashi, 2012). Another approach to improving the kinetics was to decrease the particle size. At $d_{80} = 4.95 \mu\text{m}$, we obtained a 77.7% REE recovery, with an 86.5% Nd recovery at 80 °C.

The results presented herein showed that $(\text{NH}_4)_2\text{SO}_4$ can be used as a lixiviant for leaching the $\text{Ln}(\text{OH})_3(\text{s})$ formed as a result of monazite decomposition via NaOH pretreatment. However, its kinetics was slower than observed with 6 M HCl solutions at 25 °C as shown in Figures 2.5a and -b. At higher temperatures, however, the kinetics of the ammonium sulfate leaching was much faster as shown in Figures 2.6a and -b. It should be noted also that the $(\text{NH}_4)_2\text{SO}_4$ leaching at pH 4 was comparable to the HCl leaching at pH 1.0 as shown in Figure 2.8, which may be an important advantage of using $(\text{NH}_4)_2\text{SO}_4$ 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 ($\Delta H_{\text{hyd}}^0 = -1,091 \text{ kJ mole}^{-1}$) than that ($\Delta H_{\text{hyd}}^0 = -307 \text{ kJ mole}^{-1}$) of the NH_4^+ ions (Smith, 1977). Therefore, the latter can more readily displace the Ln^{3+} ions from the $\text{Ln}(\text{OH})_3(\text{s})$ surface in accordance to Eq. (2.7). Another advantage of using ammonium sulfate rather than acid as lixiviant may be that the extraction of U should be less. Using $(\text{NH}_4)_2\text{SO}_4$ 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 $\text{AlO}_4(\text{OH})_2$ 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 (2.1). On the edge surfaces of kaolinite, however, Ln^{3+} ions adsorb as partially-hydrated ions on the $\text{Al}(\text{OH})_2^-$ and $\text{Si}(\text{OH})_2^-$ 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: $\Delta H_{\text{hyd}}^0 = -307$ and

Table 2.2 Thermodynamic data used for the solubility diagram for $\text{La}(\text{OH})_3(\text{s})$.

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

(Data sources: Shkolnikov et al., 2009; Hass et al., 1995; Lee et al., 1992)

-3,296 kJ mole⁻¹, respectively. Furthermore, the hydration numbers are 4 and 8-9 for the NH₄⁺ and Ln³⁺ 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 such as Ln³⁺ ions with $-\Delta H_{\text{hyd}}^0 > 3,000$ kJ mole⁻¹ retain at least part of the hydration water and thus form weaker bonds with the surface. The Ln³⁺ 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 2.10 shows the solubility diagram for La(OH)₃(s) constructed using the thermodynamic data presented in Table 2.2. As shown, the La³⁺ ion concentration increases with decreasing pH, which should favor the ion-exchange leaching in accordance to Reaction (2.7). In the present work, the (NH₄)₂SO₄ leaching has been conducted mostly at pH 4 where La³⁺ ions are the most predominant La-bearing species. At pH < 3, La₂(OH)₂⁴⁺ 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., La³⁺, La(OH)₂⁺, La(OH)₄⁻, shown in Figure 2.10, 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 2.10 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 La₂O₃, as predicted using an electrostatic model for the adsorption of H⁺ and OH⁻ ions (Yoon et al., 1979).

Figure 2.11 shows a set of ζ -potential measurements conducted on the monazite sample pretreated

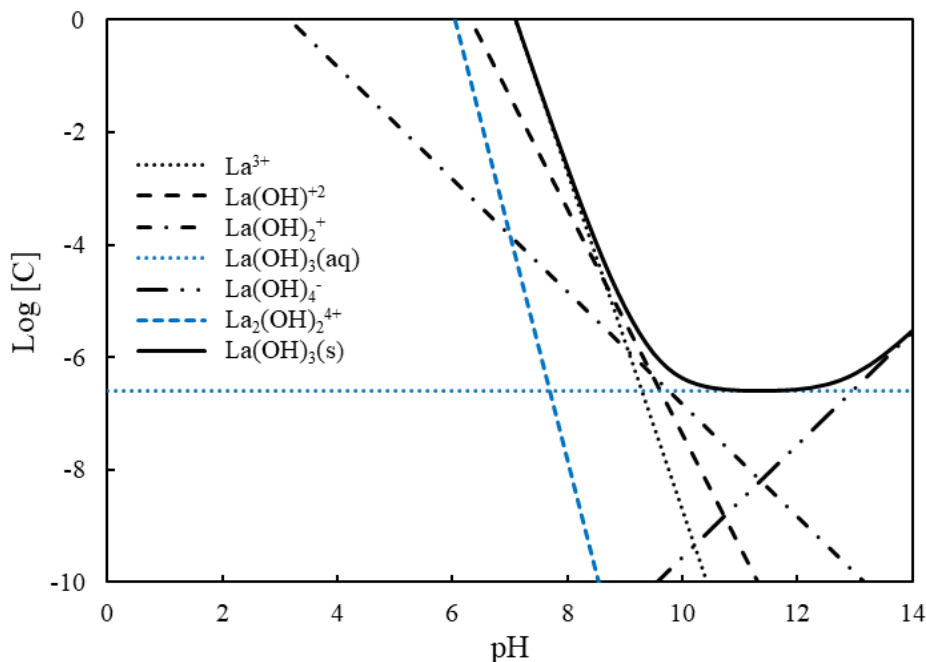


Figure 2.10. The solubility diagram La(OH)₃(s) in water at 25 °C.

with NaOH and subsequently with $(\text{NH}_4)_2\text{SO}_4$. At pH 4, the ζ -potential of the monazite sample was +40.6 mV due to the adsorption of the Ln^{3+} ions on the $\text{Ln}(\text{OH})_3(\text{s})$ surface. When the NaOH-treated monazite was placed in an $(\text{NH}_4)_2\text{SO}_4$ 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 (2.7).

Based on the ζ -potential data presented in Figure 2.11, a conceptual model for the ion-exchange leaching mechanism may be proposed as depicted in Figure 2.12. At pH 4.0, the $\text{Ln}(\text{OH})_3(\text{s})$ formed as a result of the NaOH pretreatment is positively charged due to the readsorption of the Ln^{3+} ions derived from the $\text{Ln}(\text{OH})_3(\text{s})$. As the $(\text{NH}_4)_2\text{SO}_4$ 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. (2.8). 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 (energy barrier) 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 $-\Delta H_{\text{hyd}}^0 = 307 \text{ kJ mole}^{-1}$ can readily shed their hydration sheaths and form a strong electrostatic bond to the surface, and thereby displacing the Ln^{3+} ions from the surface. The latter ions are weakly attached to the surface as they are strongly hydrated with $-\Delta H_{\text{hyd}}^0 = 3,296 \text{ kJ mole}^{-1}$.

Reactions (2.1) and (2.7) represent the ion-exchange leaching mechanisms for IACs and $\text{Ln}(\text{OH})_3(\text{s})$, 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., $(\text{NH}_4)_2\text{SO}_4$, for the extraction of Ln^{3+} ions from $\text{Ln}(\text{OH})_3(\text{s})$, which is an important aspect of process economics.

Borst et al (2020) conducted synchrotron X-ray absorption studies on the IAC samples from Madagascar and found that Y and Nd are adsorbed as easily leachable 8- to 9-coordinated outer-sphere

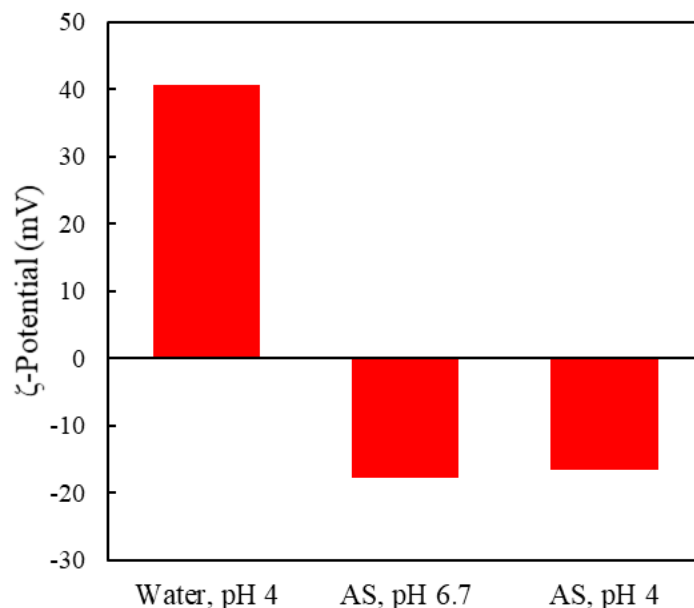


Figure 2.11 The zeta potentials of NaOH-treated monazite in different media. The samples were pretreated in a 30% NaOH solution at 80 °C for 24 h, $d_{80} = 14.61 \text{ }\mu\text{m}$.

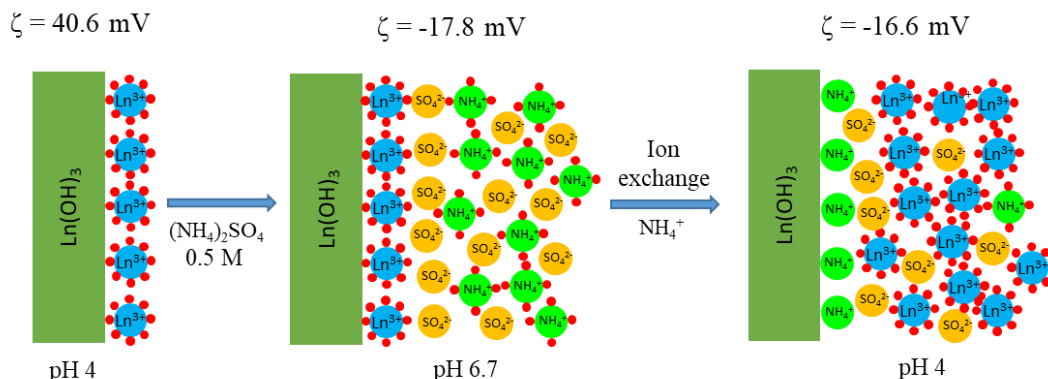


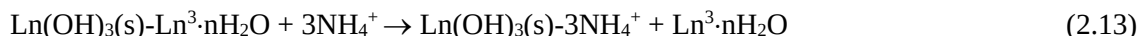
Figure 2.12 Proposed mechanism for the ion-exchange leaching of the NaOH-treated monazite using $(\text{NH}_4)_2\text{SO}_4$, as lixiviant. Red spheres represent hydrated water molecules.

complexes on kaolinite. This finding suggests that the hydration of REEs is a prerequisite to the ion-exchange leaching by the NH_4^+ ions from the solution. In this regard, the following reaction



may be regarded as the activation step necessary for the ion-exchange leaching of $\text{Ln}(\text{OH})_3(\text{s})$. In accordance with Borst et al. (2020), “n” in Reaction (2.12) may be in the range of 8-9. As discussed above, the monovalent NH_4^+ ions cannot displace the trivalent Ln^{3+} ions unless the lanthanide ions in the hydroxide solid are hydrated via Reaction 2.12.

In this regard, Reaction 2.7 may be rewritten as



in which the Ln^{3+} ions hydrated via Reaction 2.12 are displaced by the bare NH_4^+ ions. This mechanism is supported by the large difference in hydration enthalpies, i.e., -3,296 vs. -305 kJ mole⁻¹, for the tri- and mono-valent ions, respectively.

Reaction 2.12 suggests that the H^+ rather than NH_4^+ ions may be the true lixiviant for $\text{Ln}(\text{OH})_3(\text{s})$. Indeed, rare earth hydroxides obtained from caustic leaching are being leached by H_2SO_4 at pH 1-1.5 at the Bayan Obo mine (Zhu et al., 2015). However, using $(\text{NH}_4)_2\text{SO}_4$ as lixiviant makes it possible to leach the same material at pH 3-5, which makes the process developed in the present work sustainable.

There may be another advantage of using $(\text{NH}_4)_2\text{SO}_4$ rather than HCl as a lixiviant. Amer et al. (2018) showed that the $(\text{NH}_4)_2\text{SO}_4$ leaching of alkali-treated monazite produced leach liquors with nondetectable amounts of U and Th. The experimental data presented in Figures 2.4 and 2.5 show 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). The lower degree of U extraction in the ammonium sulfate leaching process may be attributed to the mild leaching condition in the present work.

2.5 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 °C 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 °C 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. Additionally, sulfate ion benefits the leaching process by forming complexes with lanthanide ions.

2.6 Acknowledgment

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Chapter 3 Leaching Kinetics of Alkali-treated Monazite by Ammonium Sulfate and the Leaching Performance of Carboxylate Ligands

Abstract

Our previous paper (Liu et al., 2022) showed that the leaching efficiency of rare earth elements (REEs) from alkali-treated monazite with ammonium sulfate could be significantly affected by particle size and temperature. This study evaluated the experimental data from a kinetic aspect according to the shrinking core model. Other than ammonium sulfate, the possibility of using carboxylate ligands (acetate, citrate, EDTA, and DTPA) as lixiviants for alkali-treated monazite has also been explored. Pure lanthanum hydroxide ((La(OH)₃(s)) served as a substitution for NaOH-treated monazite and was employed to explain the poor leaching performance of carboxylate ligands.

The kinetics analysis showed that the leaching rate of ammonium sulfate is a chemical reaction-controlled process, and the determined activation energy (E_a) was 61.28 kJ/mol. The established empirical equation for the leaching of NaOH-treated monazite by ammonium sulfate is $1 - (1 - x)^{\frac{1}{3}} = 4.79 \cdot r_0^{-2} e^{-\frac{61280}{RT}}$. Except for formate, other tested carboxylate ligands were inefficient to recover REEs from NaOH-treated monazite at room temperature, which is opposite to the thermodynamic prediction. The overall recoveries of ammonium acetate and EDTA leaching of La(OH)₃(s) were significantly improved as the temperature increased to 70-80 °C. The involved kinetics analysis showed that the leaching process was inner-diffusion controlled with large E_a values. As suggested by the Fourier transform infrared spectroscopy (FTIR) analysis, binuclear surface complexes were likely to be formed and significantly constrained the dissolution kinetics of REEs from La(OH)₃(s), leading to poor leaching recovery at room temperature.

3.1 Introduction

The global demand for rare earth elements (REEs), especially for heavy REEs (HREEs), has been increasing as they are widely used in high-tech industries (e.g., clean energy) due to their unique chemical and physical properties (Dutta et al., 2016). According to the United States Geological Survey report (USGS, 2022), the world mine production of rare earth oxide (REO) increased from 210,000 to 280,000 metric tons from 2019 to 2021 (Vaughan et al., 2021). Alonso et al. (2012) predicted that the world's annual REE demand will be around 380,000 metric tons in 2035. Of the four commercialized rare earth sources (i.e., monazite, bastnaesite, xenotime, and ion adsorption clays (IACs)), monazite (REPO₄) mainly contains light REEs (LREEs), and its orthophosphate lattice is extremely stable thermodynamically. Therefore, typical hydrometallurgical processes employed to recover REEs from this mineral include acid baking followed by water leaching and caustic cracking before acid leaching (Kim and Osseo-Asare; 2012 Kumari et al., 2015). Those approaches require concentrated reagents (e.g., 95 % H₂SO₄ or 70% NaOH) and high temperatures, which lead to the massive generation of toxic wastes, creating serious concerns over environmental sustainability (Maes et al., 2017; Ilyas et al., 2021). It is, therefore, necessary to develop methods of extracting REEs from monazite under less aggressive conditions.

It has been shown that ion-exchange leaching with ammonium sulfate (AS) as a lixiviant is effective to extract REEs from the IACs mined in South China (Jun et al., 2010). In IACs, REEs are adsorbed on the negatively charged surfaces of clay minerals via weak electrostatic forces. Therefore, they can be readily desorbed by an ion-exchange mechanism rather than the strong chemical forces required to break the chemical bonds between the RE³⁺ and PO₄³⁻ ions in monazite crystal lattices. Furthermore, ion-exchange leaching is fast, requiring activation energies (E_a) as low as 9.24 kJ/mol (Jun et al., 2010), while the caustic leaching of monazite is slow due to the high activation energy of E_a (=58.04 kJ/mol) (Panda et al., 2014).

Amer et al. (2018) used AS as a lixiviant to extract REEs from alkali-treated monazite (i.e., the

hydroxide cake of monazite). The result showed that 94.6% of the REEs could be recovered under optimal conditions. Liu et al. (2022) also found that AS can be used as a lixiviant for leaching REEs from the hydroxide cake of monazite at pH 4 and room temperature. The authors found that the extraction mechanism is one of ion exchange leaching that can be explained by the large differences in the hydration enthalpies (ΔH_{hyd}^o) between the NH_4^+ (-307 kJ/mol) and Ln^{3+} (e.g., La^{3+} : -3,296 kJ/mol) ions. Moreover, the authors reported that temperature and particle size were two important factors that determine the leaching kinetics and REE recoveries. However, the involved experimental data have not been quantitatively interpreted from a leaching kinetics aspect.

It is widely acknowledged that leaching kinetics is important for the design and optimization of extractive processes (Ray et al., 2018). Of the various kinetic models established for the non-catalytic solid-liquid leaching process, the shrinking core model is commonly used for the leaching systems consisting of non-porous particles and a reagent (Want et al., 2017). The model assumes that the size of a solid particle gradually shrinks as the leaching process proceeds. However, few kinetics studies have been conducted on monazite leaching. Panda et al. (2014) examined the kinetics of phosphorus dissolution from monazite during the NaOH pretreatment stage (50% w/v NaOH, 170 °C for 4 h) as a function of leaching temperature. The results showed that the reaction is a chemical reaction-controlled process, and the calculated activation energy was 58.04 kJ/mol. For the subsequent acid leaching step, which is normally conducted at elevated temperatures (e.g., 80 °C), the reaction rates are usually too rapid to be measured (Panda et al., 2014; Kumari et al., 2015).

On the other hand, ammonium formate was another effective leaching agent that achieved leaching efficiency comparable to AS in our previous study (Liu et al., 2022). The presence of formate can benefit the leaching performance by forming stable complexes with REEs. However, the stability constant (i.e., Log K) between La^{3+} ion and formate is merely 1.74, which is lower than other chelating ligands such as aminopolycarboxylic acids (APCAs), which contain several carboxylate groups connected to one or more nitrogen atoms (Mackey et al., 1962; Goynes et al., 2010). Due to their unique metal binding property, one of the applications of APCAs is to remove metals (e.g., Co, Ni, Cu, Zn, and Cd) from contaminated water by forming water-soluble complexes (Sillanpää, 1997; Repo et al., 2013). Several researchers showed that organic ligands (mainly low molecular weight organic acids) are promising reagents for the decomposition of monazite (Goynes et al., 2010; Lapidus et al., 2015a, 2015b; Lazo et al., 2017). Gado et al. (2019) selectively recovered 99% of REEs and 98% of thorium (Th) from the hydrous oxide cake of Rosetta monazite by diethylenetriaminepentaacetic acid (DTPA), leaving uranium (U) as a solid in the leaching residue. The strong complexing ability of APCAs may suggest that they can be potential lixiviants for the hydroxide cake of monazite. However, literature is somewhat limited regarding the usage of carboxylate ligands as lixiviants for the hydroxide cake of monazite.

As a continuation of our earlier study, the first aim of this research is to examine the effects of leaching temperature and particle size on the leaching kinetics of REEs from NaOH-treated monazite by AS based on the shrinking core model. On the other hand, the leaching performances of a series of carboxylates were evaluated as potential lixiviants for NaOH-treated monazite. The involved leaching mechanisms were investigated by kinetics analysis and chemical characterization of the leaching residues.

3.2 Experimental

3.2.1 Samples and Reagents

The monazite sample used for the extraction tests in this study was the same monazite concentrate (TREE content: 48.9% and particle size (d_{80}) = 14.6 μm) as the one utilized in our previous study (Liu et al., 2022). The procedures for sample preparation and elemental composition have also been reported in detail in that paper. Reagent grade sodium hydroxide (NaOH), lanthanum hydroxide ($\text{La}(\text{OH})_3$), ammonium formate (NH_4HCO_2), ammonium acetate ($\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$), ammonium citrate ($\text{C}_6\text{H}_{17}\text{N}_3\text{O}_7$), ethylenediamine-

tetraacetic acid disodium salt (Na₂EDTA), and DTPA were purchased from Fisher Scientific. Nitric acid (HNO₃) and hydrochloride acid (HCl) were of trace metal grade for the preparation of ICP-MS diluting solution. Deionized (DI) water was utilized in all solutions and leaching tests.

3.2.2 Methods

3.2.2.1 NaOH pretreatment and Leaching Tests

To keep consistent with our previous study (Liu et al., 2022), the benchmark conditions set for NaOH pretreatment tests were: 30% NaOH, 80 °C, and 24 h, although the efficiency of alkali pretreatment by 30% NaOH solution is inferior to the one obtained by 50%. The leaching result of AS from the 30% NaOH-treated sample was also used for comparison purposes in this study. In a given pretreatment experiment, a known amount (0.5 g) of monazite sample was added into a 30% NaOH solution in a polytetrafluoroethylene (PTFE) beaker with a solid/liquid ratio of 25 g/L. The mixture was heated on a hotplate stirrer with a temperature probe for temperature control (± 1 °C). Paraffin film was employed to seal each beaker to avoid liquid loss caused by evaporation. After agitating the mixture at 600 rpm for 24 h, the solid and NaOH solution were separated by means of centrifuge (5,000 rpm for 10 min). Later, the residue was thoroughly washed with DI water for the removal of residual NaOH before being subjected to the leaching step.

The NaOH-treated NaOH samples were leached by various carboxylate ligands at 25 °C for 2 h. Due to the low solubilities of EDTA and DTPA, their concentrations were set as 0.1 M. Except for those two, the concentrations of other lixivants were all 0.5 M. Unless otherwise specified, the pH for each leaching reagent were all set at 4.0 ± 0.05 . Before mixing with the sample, the pH of each lixiviant was initially adjusted to the target leaching pH. In each leaching test, 0.5 g of the NaOH-treated sample was added into 40 mL of each lixiviant in a 50 mL disposable polypropylene beaker. 0.5 M HCl and NaOH were added for pH adjustment. 0.3 mL of representative slurry samples were withdrawn at different time intervals from the beaker using a 1 mL disposable syringe to monitor the leaching kinetics. The liquid sample was filtered immediately by means of a 0.22 μ m pore size syringe filter provided by Cobetter Filtration Equipment Corp. The elemental composition of each filtrate was determined by ICP-MS after diluting 2,000 times with a mixed acid solution (2.5% HNO₃ and 0.5% HCl). The leaching recovery (R) was calculated using Eq. (3.1),

$$R = 100 \times \frac{C_l V}{C_f M} \quad (3.1)$$

in which C_l and V refer to 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, as described in Liu et al. (2022).

La(OH)₃ was also utilized as an ideal model for the NaOH-treated monazite and leached by 0.5 M ammonium acetate and 0.1 M EDTA, respectively, at different temperatures, which were conducted on a Soxhlet extraction apparatus. Other experimental procedures were the same as the one used for the leaching test of NaOH-treated monazite.

3.2.2.2 Fourier-transform infrared spectroscopy (FTIR) analysis

To gain insights into the leaching mechanisms of the carboxylate ligands, FTIR analysis (Varian 670 FTIR spectrometer) was performed to characterize the chemical changes in La(OH)₃(s) and its various leaching residues. Prior to the FTIR tests, the leaching residues were thoroughly washed with DI water to remove physically adsorbed lixivants and were dried in an oven at 60 °C. A few milligrams of solid and liquid samples were directly placed on the sample plate of the instrument over the optic window. The spectra were recorded from 700 to 4,000 cm⁻¹ with a spectral resolution of 0.07 cm⁻¹.

3.3 Results and discussion

3.3.1 Leaching Kinetics of Ammonium Sulfate

3.3.1.1 Effect of Leaching Temperature on the Leaching Kinetics

The effects of leaching temperature on the TREE recovery have been studied in our previous study (Liu et al., 2022). In this section, the kinetic type and involved activation energy were determined based on those experimental data. Essentially, the leaching process of NaOH-treated monazite by AS can be considered a non-catalytic heterogeneous solid-liquid reaction. As a classical model, the shrinking core model has been commonly applied in fluid-solid reactions such as the leaching of metals from minerals (Gbor and Jia, 2004; Long et al., 2020). According to this model, if the NaOH-treated monazite ore particles can be considered hard spheres, the leaching process could be described by one of the standard equations of shrinking-core models (Jun et al., 2010). Furthermore, this model assumes that the leaching process is dependent either on the diffusion of reactants through an ash layer, or through the solution boundary, or through a solid product layer, or on the surface chemical reaction rate (Li et al., 2010). The standard rate equations of shrinking core models are shown as follows (Jun et al., 2010):

Chemical reaction controls:

$$1 - (1 - x)^{\frac{1}{3}} = k_1 t \quad (3.2)$$

Outer diffusion controls:

$$1 - (1 - x)^{\frac{1}{3}} = k_2 t \quad (3.3)$$

Inner diffusion controls:

$$1 - \frac{2}{3}x - (1 - x)^{\frac{2}{3}} = k_3 t \quad (3.4)$$

Mixed controls:

$$1 - (1 - x)^{\frac{1}{3}} = k_4 \frac{C_0 M}{r_0 \rho} \quad (3.5)$$

where x is the fraction of REEs being leached (% recovery), k_1 , k_2 , k_3 , and k_4 are the chemical constants (i.e., apparent rate constant); t and C_0 are the real leaching time (min) and initial concentration of the lixiviant used, respectively; r_0 and ρ are the initial radius and the molar density of the ore sample particle, respectively; M is the mass of the sample particle.

$$k_1 = A e^{-\frac{E_a}{RT}} \quad (3.6)$$

After leaching by ammonium sulfate conducted at various temperatures, it was found that the plot of $1 - (1 - x)^{\frac{1}{3}}$ vs. t at each temperature (see Figure 3.1a) is a straight line. And they had larger regression coefficients (i.e., R^2) compared to other models. The related kinetic parameters are summarized in Table

Table 3.1 Kinetic parameters for the ammonium sulfate leaching of REEs from the NaOH-treated monazite as a function of leaching temperature.

T/°C	k	b	R ²
25	0.0036	0.008	0.9863
45	0.0064	0.0241	0.9515
65	0.0551	0.0285	0.9255

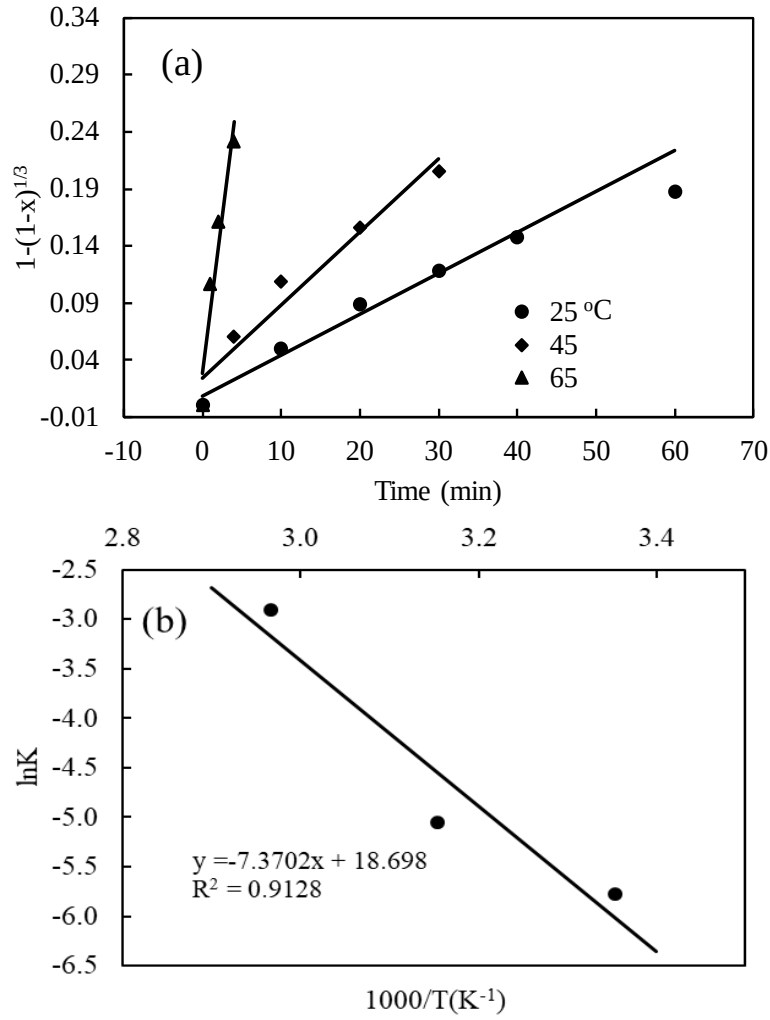


Figure 3.1 Plot of (a) $1-(1-x)^{1/3}$ vs. time and (b) Arrhenius plot of leaching kinetics of NaOH-treated monazite by $(NH_4)_2SO_4$ as a function of temperature.

3.1. It suggested that either chemical reaction or outer diffusion control model, i.e., $1 - (1 - x)^{\frac{1}{3}} = kt$, fits the experimental data best. To further specify the kinetics type, the activation energy (E_a) was determined using the Arrhenius equation (see Eq. (3.6)). When $E_a > 42$ kJ/mol, the reaction is a chemical-controlled process. It belongs to a mixing-controlled reaction, i.e., a combination of chemical and diffusion processes, if the determined E_a is between 20-34 kJ/mol (Jun et al., 2010). According to the Arrhenius plot of $\ln k$ vs. $1/T$ (Figure 3.1b), the calculated E_a was 61.28 kJ/mol. It reveals that the leaching rate of REEs from the NaOH-treated monazite by AS can be classified as a chemical reaction-controlled process.

3.3.1.2 Effect of Particle Size on the Leaching Kinetics

The experimental data related to the effect of particle size on TREE recovery have also been reported in our previous study (Liu et al., 2022). The expanded Arrhenius equation by incorporating the radius of the ore particle was employed to investigate the influences of particle size on the leaching kinetics (Jun et al., 2010) as shown in Eq. (3.7):

$$k_1 = A' r_0^n e^{-\frac{E_a}{RT}} \quad (3.7)$$

Table 3.2 Kinetic parameters for the ammonium sulfate leaching of REEs from the NaOH-treated monazite as a function of particle size.

$d_{80}/\mu\text{m}$	k	b	R^2
14.61	0.0036	0.0162	0.9695
8.25	0.0167	0.0162	0.976
4.22	0.0314	0.0065	0.9899

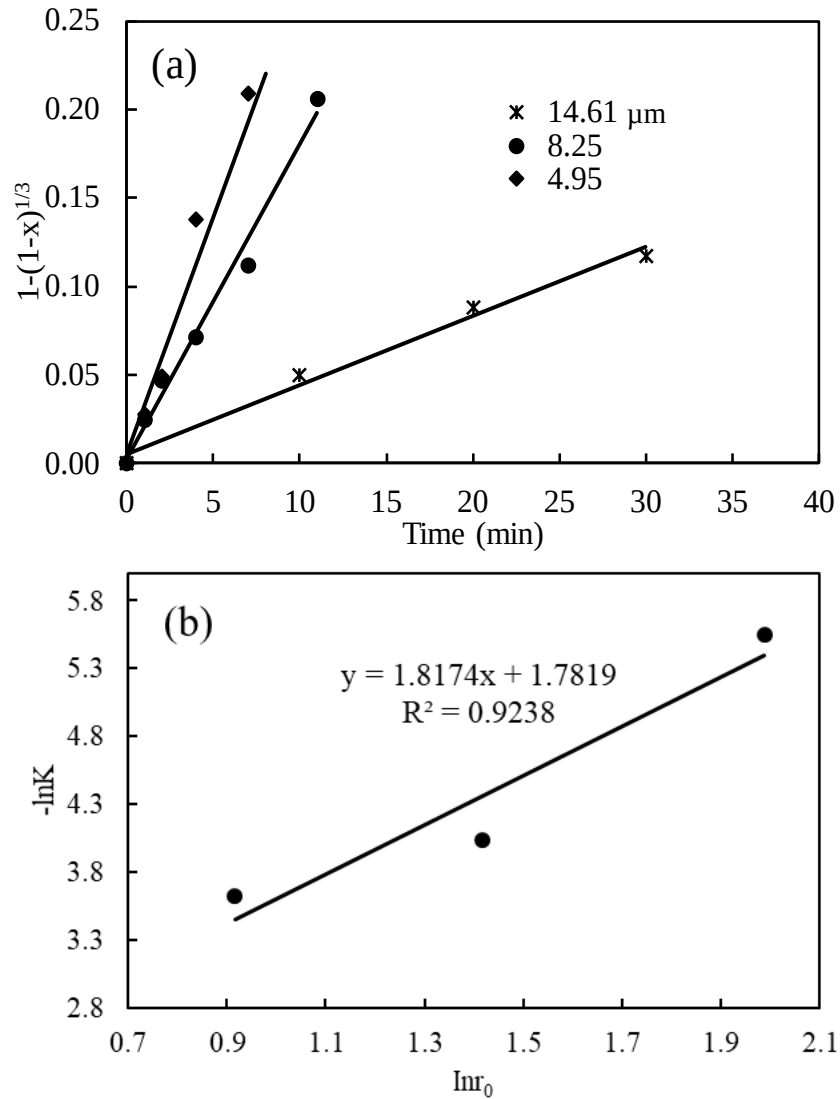


Figure 3.2 Plot of (a) $1-(1-x)^{1/3}$ vs. time (a) and (b) Arrhenius plot of leaching kinetics of NaOH-treated monazite by $(\text{NH}_4)_2\text{SO}_4$ as a function of particle size.

where r_0 is the radius of particle size and n is the order of the particle size.

$$\ln k_1 = n \cdot \ln r_0 + \ln A' - \frac{E_a}{RT} \quad (3.8)$$

The k_1 value of each size fraction was calculated from the linear relationship of $1 - (1 - x)^{\frac{1}{3}}$ vs. t (see Figure 3.2a). The corresponding kinetic parameters are summarized in Table 3.2. After taking a natural logarithm on both sides of Eq. (3.7), a linear correlation can be found (see Eq. 3.8) between $\ln k$ and $\ln r_0$, with n and $\ln A' - \frac{E_a}{RT}$ being the slope and intercept, respectively. Based on this, a plot of $\ln k$ and $\ln r_0$ can be constructed, as shown in Figure 3.2b. The determined n and A' are -2.0335 ($n \approx 2$) and 4.79, respectively. Therefore, Eq. (3.7) can be rewritten as follows:

$$k_1 = 4.79 \cdot r_0^{-2} e^{-\frac{61280}{RT}} \quad (3.9)$$

After combining Eqs. 3.9 and 3.2 together, the empirical equation of the leaching kinetics can be expressed as:

$$1 - (1 - x)^{\frac{1}{3}} = 4.79 \cdot r_0^{-2} e^{-\frac{61280}{RT}} \quad (3.10)$$

This equation can be used to quantitatively describe the effects of particle size and temperature on the leaching kinetics of REEs from the hydroxide cake of monazite by AS.

3.3.2 Leaching Performance of Carboxylate Ligands

3.3.2.1 Carboxylate Ligands

Several ammonium-based organic ligands with different numbers of carboxylate groups (from 1 to 3), EDTA, and DTPA were used as lixiviants in this section. The pKa and Log K (La-ligand) values of the organic ligands are shown in Table 3.3. The screening tests were carried out on the monazite samples that had been treated with 30% NaOH at 80 °C for 24 h. Other experimental conditions, such as temperature, solid concentration, and agitation speed, remained the same as the cases reported in our previous study (Liu et al., 2022), and the leaching results of AS and ammonium formate were shown for comparison purposes. Considering the low solubilities (<0.5 g/L) of DTPA and EDTA in water at 25 °C, their concentrations were 0.1 M for the leaching tests.

Before the leaching tests, stability diagrams for the La-ligand-H₂O systems were constructed by the Medusa software and its Hydra database (Puigdomenech et al., 2013) to provide a thermodynamic basis for the leaching of RE(OH)₃(s) by those organic ligands. Figure 3.3 shows the stability diagrams of La in

Table 3.3 The pKa and Log K values (La-ligand) of the organic acids used in this study.

Organic acids	pKa	Chemical reaction and the corresponding Log K	
Formic acid	3.75	$\text{La}^{3+} + \text{HCOO}^- = \text{La}(\text{HCOO})^{2+}$	1.74
Acetic acid	4.75	$\text{La}^{3+} + \text{CH}_3\text{HCOO}^- = \text{La}(\text{CH}_3\text{HCOO})^{2+}$	2.55
Citric acid	3.14, 5.77, 6.4	$\text{La}^{3+} + \text{Cit}^{3-} = \text{LaCit}$	9.18
EDTA	0.0, 1.5, 2.0, 2.69	$\text{La}^{3+} + \text{EDTA}^{4-} = \text{LaEDTA}^-$	17.93
DTPA	1.68, 2.1, 2.6, 4.15, 8.2, 9.9	$\text{La}^{3+} + \text{DTPA}^{5-} = \text{LaDTPA}^{2-}$	19.48

Note: “Cit” refers to citric acid. Data source: Smith and Martell, 1989; Wang et al., 2017; Banerjee et al., 2021; Raaflaub, 1956; Martin and Zalupski, 2010.

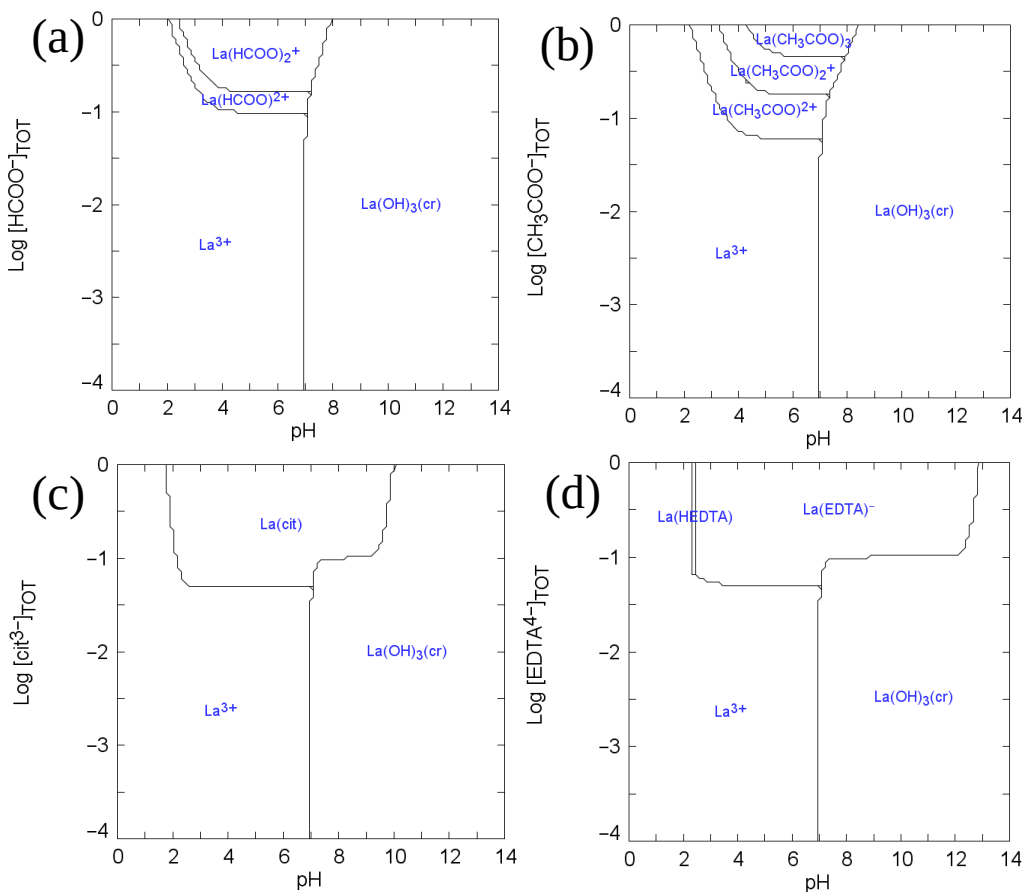


Figure 3.3 Stability diagrams of La in the La-H₂O system in the presence of (a) ammonium acetate, (b) ammonium acetate, (c) ammonium citrate, and (d) EDTA, respectively, condition: [La³⁺] = 0.01 M.

the presence of formate, acetate, citrate, and EDTA, respectively. The concentration of La³⁺ ion was estimated from the molar concentration of 0.5 g of the monazite sample dispersed in 40 mL lixiviant. The stability diagram of each ligand shows that the dissolution of La(OH)₃(s) is thermodynamically favored at acidic and neutral pH. From formate to EDTA, the region of La-ligand complexes gradually expands, which is consistent with the increasing trend of the Log K value from formate to DTPA (see Table 3.3). In the presence of EDTA, La forms soluble La-EDTA complexes (i.e., La-EDTA⁻) over a wide pH range (i.e., from pH 2.0 to 12.0) even when the concentration is only 0.01 M. The region of La-EDTA complexes is significantly larger than the one in the case of acetate. At 0.01 M, the window of La-acetate only ranges from pH 5.0 to 7.5. This comparison is consistent with the order of complexing ability (i.e., EDTA > acetate), as shown in Table 3.3.

Figure 3.4 shows the leaching results of the NaOH-treated monazite sample by different carboxylate-based lixiviants at pH 4. It shows that, except for formate, only less than 2.0% of REEs were extracted by acetate, citrate, EDTA, and DTPA. The poor leaching recoveries were opposite to the thermodynamic prediction. If the leaching process was only dependent on the complexing ability, the chelating ligands with larger stability constants should have resulted in higher leaching efficiencies. As such, there might be other reasons that were responsible for the poor leaching efficiency of the organic ligands.

3.3.2.2 Effect of pH on the Leaching Efficiency of DTPA

It is widely acknowledged that the speciation of organic ligands in solution is pH-dependent due to

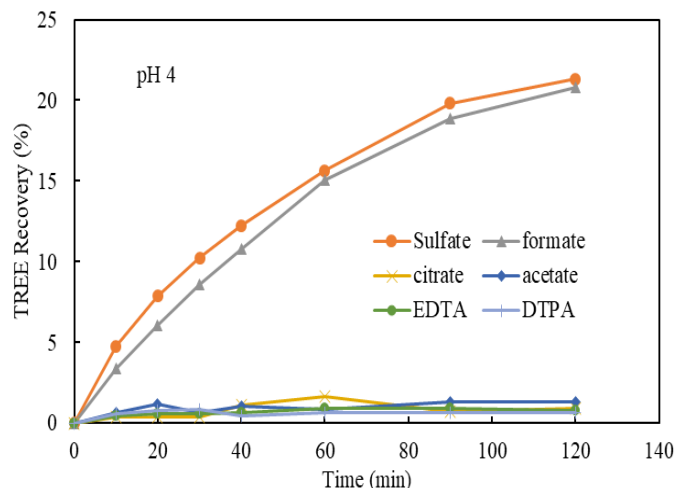


Figure 3.4 Leaching results of a monazite sample by different carboxylate-based lixivants at pH 4 and room temperature. The samples were pretreated in a 30% NaOH solution at 80 °C for 24 h, $d_{80} = 14.61 \mu\text{m}$. Note: the concentrations of sulfate, formate, acetate, and citrate were 0.5 M, while EDTA and DTPA were 0.1 M. The leaching result of AS was used as a reference.

the degree of protonation. The deprotonated ligands would be more available since the dissociation of a chelating agent increases with pH (Moldoveanu and Papangelakis, 2021). Accordingly, leaching pH might be one possible reason for the poor leaching recoveries achieved by those organic ligands.

In this part, the effect of pH on the leaching efficiency of NaOH-treated monazite by 0.1 M DTPA was investigated (see Figure 3.5). However, the TREE recovery was still poor (<2%) at each pH. It suggested that the availability of the dissociated ligands did not affect the leaching process. In one industry practice, the dissolution of NaOH-treated monazite can be completed by HCl at around pH 3, indicating that $\text{RE}(\text{OH})_3(\text{s})$ can be dissolved at that pH (Qi, 2018). However, even at pH 2, the TREE recovery obtained in this study was only 0.8% in the presence of DTPA. Moreover, according to our previous study (Liu et al., 2022), even the recovery of HCl leaching of the NaOH-treated monazite at pH 4 was also higher than the DTPA leaching conducted at pH 4 in this study (4.0% versus 0.8%). These observations indicated that

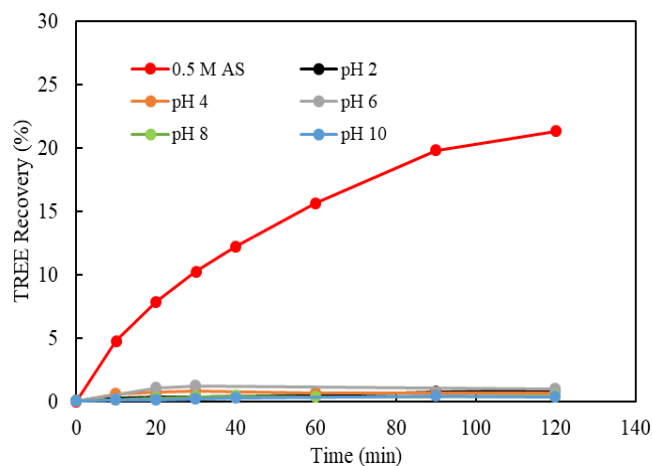


Figure 3.5 Leaching results of a monazite sample by 0.1 M DTPA as a function of pH at room temperature. The sample was pretreated in a 30% NaOH solution at 80 °C for 24 h, $d_{80} = 14.61 \mu\text{m}$.

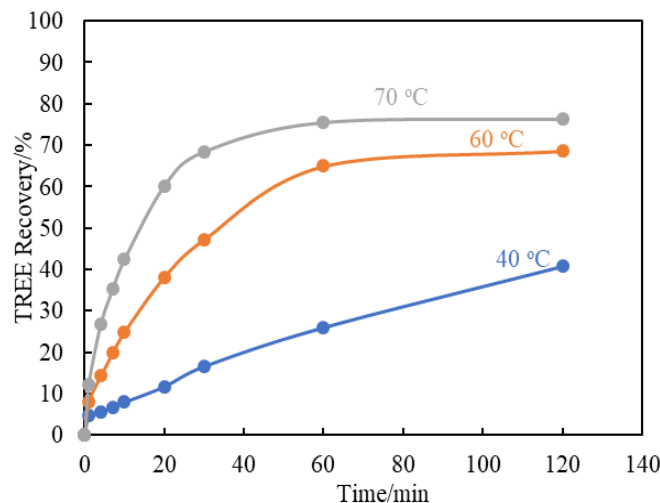


Figure 3.6 Leaching behavior of TREE from $\text{La(OH)}_3(\text{s})$ by 0.5 M ammonium acetate at pH 4 and different temperatures.

the presence of DTPA in the leaching system imposed a negative impact on the leaching efficiency. The H^+ ions added for pH adjustment may be consumed by the protonation of organic ligands due to their buffering effect rather than the dissolution of $\text{RE(OH)}_3(\text{s})$.

3.3.3 Passivation Effect of Organic Ligands on the Dissolution of $\text{La(OH)}_3(\text{s})$

3.3.3.1 Leaching Kinetics Studies of Ammonium Acetate and EDTA

As mentioned in Section 3.1, Gado et al. (2019) selectively extracted Th and REEs from the hydroxide cake of monazite using DTPA as a lixiviant. The optimal conditions for the DTPA leaching were: 20% DTPA, 100 °C, 8 h, and S/L = 1:30, under which the recoveries of REEs and Th were 99 and 98%, respectively. Accordingly, the motivation of this section is to examine the effect of temperature on the leaching behavior of REEs from $\text{La(OH)}_3(\text{s})$ by the carboxylate ligands. $\text{La(OH)}_3(\text{s})$ was used as a substitution for NaOH-treated monazite. Ammonium acetate (0.5 M) and EDTA (0.1 M) were used as lixiviants for the dissolution of $\text{La(OH)}_3(\text{s})$ at various leaching temperatures. The involved leaching kinetics were also analyzed based on the shrinking core model to enhance the understanding of the involved leaching mechanism.

As presented in Figure 3.6, the leaching kinetics of TREE from $\text{La(OH)}_3(\text{s})$ by ammonium acetate was significantly affected by temperature. The leaching equilibrium was achieved within 60 min at 70 °C. At 40 °C, the final TREE recovery was only 40.7%. It was improved to 76.3% at 70 °C. It should be noted that different amounts of 0.5 M HCl were consumed at each temperature during the leaching process (i.e., 3.6, 4.8, and 5.2 mL for 40, 60, and 70 °C, respectively) to maintain the pH stable at 4.0. Figures 3.7a and -b were used to determine the corresponding kinetics type and activation energy, respectively. The kinetic parameters of ammonium acetate leaching are summarized in Table 3.4. It was found that the leaching rate

Table 3.4 Kinetic parameters of $\text{La(OH)}_3(\text{s})$ by 0.5 M ammonium acetate leaching at different temperatures.

T/°C	k	b	R ²
40	0.0006	-0.0031	0.9768
60	0.0035	-0.0068	0.9955
70	0.0083	-0.0038	0.9962

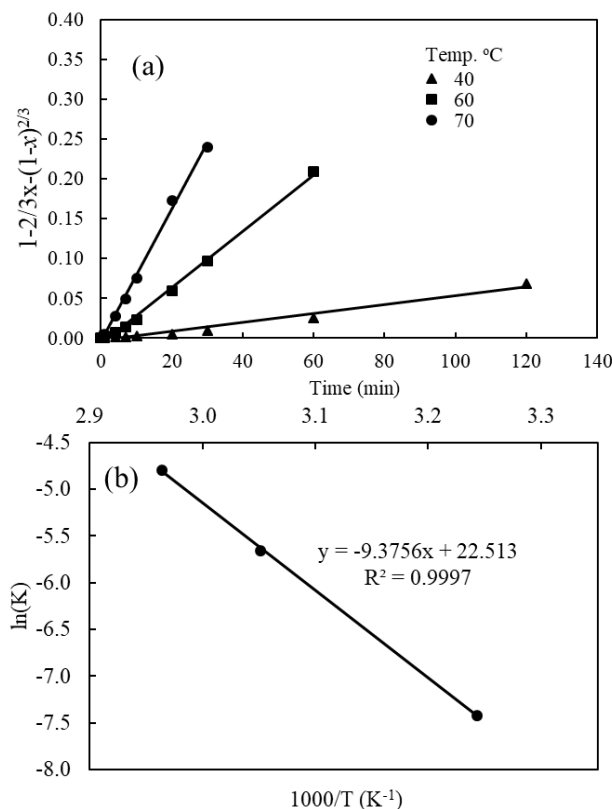


Figure 3.7 Plot of (a) $1-3(1-x)^{2/3}+2(1-x)$ vs. time and (b) Arrhenius plot of leaching kinetics of $\text{La}(\text{OH})_3(\text{s})$ by 0.5 M ammonium acetate at pH 4 and different temperatures.

of ammonium acetate is an inner diffusion-controlled reaction. It indicates that the rate-limiting step of ammonium acetate leaching was the transportation of the reactants or the products through an interface (Groot et al., 2013), suggesting that a passivation layer may be formed on the surface of $\text{La}(\text{OH})_3(\text{s})$. The large activation energy (77.95 kJ/mol) determined from the Arrhenius equation suggested that a high energy barrier needs to be overcome before the dissolution of REEs from $\text{La}(\text{OH})_3(\text{s})$ in the presence of ammonium acetate.

Figure 3.8 shows the effect of temperature on the leaching process of $\text{La}(\text{OH})_3(\text{s})$ by 0.1 M EDTA at pH 4. It can be seen that a slower leaching rate and lower TREE recovery were obtained by EDTA compared to the ones obtained by ammonium acetate. Even at 80 °C, the TREE recovery by EDTA was only 60.8%, which was comparable to the one achieved by ammonium acetate at 60 °C. This comparison indicated that chelating ligands with more complex sites further deteriorated the leaching performance. The plots used to determine the kinetic model and activation energy are shown in Figures 3.9a and -b, respectively. Table 3.5 shows the related kinetic parameters used to determine the kinetic type. Based on these results, the leaching kinetics of $\text{La}(\text{OH})_3(\text{s})$ by EDTA is also an inner diffusion-controlled reaction.

Table 3.5 Kinetic parameters of $\text{La}(\text{OH})_3(\text{s})$ leached by 0.1 M EDTA at different temperatures.

T/°C	k	b	R ²
60	0.0002	-0.0008	0.9847
70	0.0007	-0.0045	0.9788
80	0.0016	-0.0056	0.9904

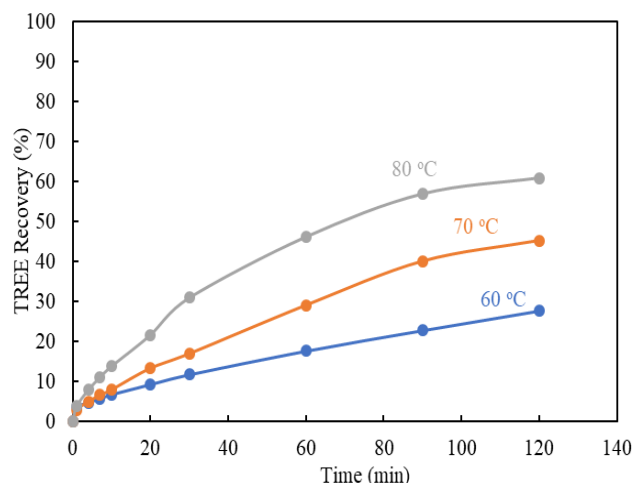


Figure 3.8 Leaching behavior of TREE from $\text{La}(\text{OH})_3(\text{s})$ by 0.1 M EDTA at pH 4 and different temperatures.

The corresponding E_a value (101.87 kJ/mol) was larger than those of ammonium acetate. It suggests that higher activation energy is required to remove La from $\text{La}(\text{OH})_3(\text{s})$ in the presence of EDTA compared to that in the case of ammonium acetate. In terms of leaching efficiency, the carboxylate-based ligands with multiple binding sites (except for formate) are not effective lixivants for the leaching of REEs from the hydroxide cake of monazite at room temperature.

3.3.3.2 FTIR Analysis

The leaching kinetics study showed that both leaching rates of REEs from $\text{La}(\text{OH})_3(\text{s})$ using ammonium acetate and EDTA as lixivants are limited by the diffusion of reactants or products through an interface. Essentially, the leaching process of NaOH-treated monazite by organic ligands can be simplified as the dissolution of $\text{La}(\text{OH})_3(\text{s})$ in the presence of various organic ligands. Several studies have been reported on the influences of organic ligands on the dissolution of oxide minerals. Bondietti et al. (1993) investigated the effects of several organic and inorganic ligands on the dissolution of Fe(III) (hydr)oxides. It revealed that the formation of mononuclear surface complexes could enhance iron hydroxide dissolution, while it was inhibited if binuclear surface complexes were generated. This is explained by the fact that the removal of two metal ions each time from the surface with binuclear complexes consumes more energy. The adsorption of EDTA and the EDTA-metal complexes (metals: Ca, Zn, Ni, et al.) on goethite was investigated by Nowack et al. (1996). In the system consisting of EDTA and goethite, the adsorption of EDTA at the low pH values (pH < 6.5) was in the manner of binuclear complexes, while the mononuclear type was found at the high pH values (pH 6.5-8.5). Because of this, the dissolution of goethite gradually increased with pH and maximized at pH 8. Moreover, the authors found that the EDTA complexes of LaEDTA can strongly adsorb on the surface of goethite over a wide pH range (pH 5.2-8.0). Chin et al. (1991) examined the dissolution behaviors of Al from kaolinite in the presence of protons, low molecular weight organic ligands, soil humic acid, etc. It was found that the soil humic acid and organic matter derived from stream water did not enhance the dissolution process under the conditions explored. The proposed surface coordination model showed that the formation of binuclear surface complexes could block the dissolution process, as shown in Eq. (3.11),



in which “M” and “B” refer to Al and the organic ligands, respectively. This study indicated that the kinetics of the surface-controlled dissolution reactions were very slow. Similar findings have also been reported by Eick et al. (1999).

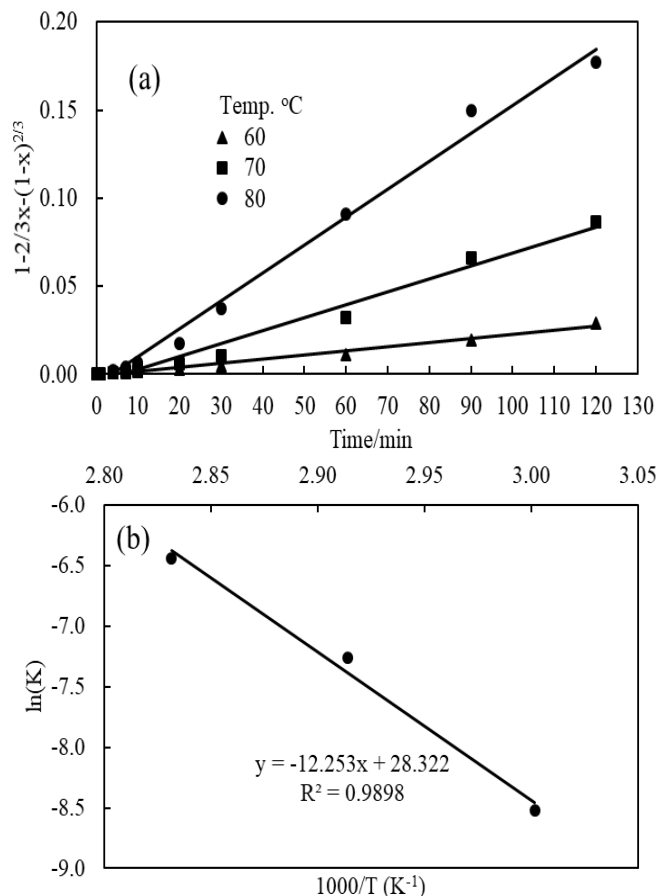


Figure 3.9 Plot of (a) $1 - \frac{2}{3}x - (1-x)^{2/3}$ vs. time and (b) Arrhenius plot of leaching kinetics of $\text{La}(\text{OH})_3(\text{s})$ by 0.1 M EDTA at pH 4 and different temperatures.

According to the above studies, the formation of binuclear surface complexes on the NaOH-treated monazite may also be responsible for the poor leaching recoveries of the carboxylate ligands used in this study. Regarding the tested ligands, especially citrate, EDTA, and DTPA, which have multiple complex sites, they are more complicated than formate in terms of molecular structure. The REE-ligand complexes with large sizes formed on the surface of $\text{RE}(\text{OH})_3(\text{s})$ may inhibit the interaction between the ligands and REEs within the crystal lattice (Lapidus et al., 2015b). To support the hypothesis, FTIR was used to characterize the surface variations of the $\text{RE}(\text{OH})_3(\text{s})$ before and after leaching. To avoid the interference of impure elements contained in the monazite sample, pure $\text{La}(\text{OH})_3(\text{s})$ was used as a substitution for NaOH-treated monazite for the FTIR analysis. Initially, the ammonium citrate solution and $\text{La}(\text{OH})_3(\text{s})$ before and after leaching were analyzed by FTIR, respectively. As is shown in Figure 3.10, similar FTIR spectra were observed for the ammonium citrate solution before and after leaching. The $\text{O}=\text{C}=\text{O}$ stretching at peak 2255 cm^{-1} was assigned to CO_2 , probably introduced from the air during agitation (Vanderah et al., 2012). The peak at 3303 cm^{-1} was attributed to the N-H stretching of ammonium ions, and the existence of the carboxylate group was confirmed by the peak at 1639 cm^{-1} . In the leaching residue, the peak at 1639 cm^{-1} shifted toward lower wave numbers (1578 cm^{-1}) compared to the ammonium citrate solutions (Sun et al., 2014). This change was due to the chemical bonds formed between the carboxylate group ($-\text{COO}^-$) and $\text{La}(\text{III})$, which was not observed in the spectrum of $\text{La}(\text{OH})_3(\text{s})$ feed sample. This comparison suggested that the interaction between citrate and $\text{La}(\text{OH})_3(\text{s})$ was an inner-sphere coordination (probably binuclear surface complexes) formed on the surfaces of $\text{La}(\text{OH})_3(\text{s})$. However, it is difficult to determine the specific type of complexes due to the resolution of FTIR.

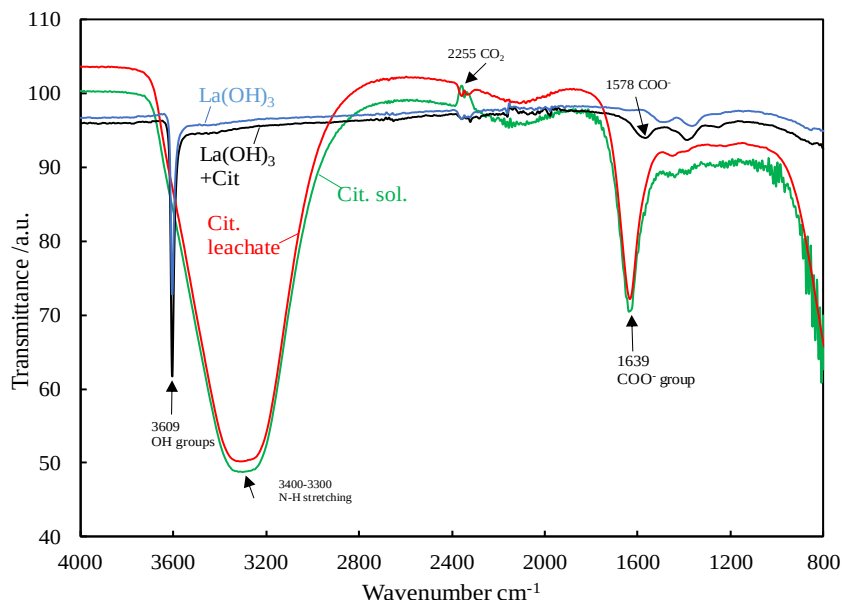


Figure 3.10 FTIR results of 0.5 M ammonium citrate solution and $\text{La}(\text{OH})_3(\text{s})$ before and after leaching, respectively. “ $\text{La}(\text{OH})_3$ ” and “ $\text{La}(\text{OH})_3 + \text{Cit}$ ” refer to the spectra of $\text{La}(\text{OH})_3$ before and after ammonium citrate leaching, respectively. “Cit. sol.” and “Cit. leachate” represent the spectra of ammonium citrate solution before and after leaching, respectively.

Figure 3.11 shows the partial FTIR spectra of the leaching residues of $\text{La}(\text{OH})_3(\text{s})$ by other carboxylate ligands tested and AS. It can be seen that the peak at 1578 cm^{-1} was observed for the samples leached by the carboxylate-based lixivants, while it was not observed in $\text{La}(\text{OH})_3(\text{s})$ feed sample and the one leached by AS. These observations indicated the adsorption of $-\text{COO}^-$ on the surface of $\text{La}(\text{OH})_3(\text{s})$ as surface complexes after being leached by the organic ligands. The peak at 1578 cm^{-1} was also noticed in the residues leached by formate and acetate. It suggested that the adsorption of $-\text{COO}^-$ on the surface of $\text{La}(\text{OH})_3(\text{s})$ also occurred in the formate leaching, although formate and acetate achieved largely different leaching recoveries. Both formate and acetate have one carboxylate group. The uniqueness of acetate is that it has a $-\text{CH}_3$ group. However, this difference should not affect the types of surface complexes of formate and acetate formed on $\text{La}(\text{OH})_3(\text{s})$. Under such cases, the contrasting leaching efficiencies between formate and acetate may be explained by their differences in pK_a values, which are 3.75 and 4.75 for formic acid and acetic acid, respectively (see Table 3.3). As indicated by the pK_a values, formate is a weaker base. As such, the complexes between formate and La were less stable compared to those of acetate and La. Therefore, the inhibiting effect of surface complexes on the dissolution of $\text{La}(\text{OH})_3(\text{s})$ was less significant in the case of formate compared to that of acetate.

The FTIR analysis along with the kinetics studies indicated that the poor leaching efficiency of the carboxylate ligands was due to the formation of surface complexes, which significantly reduced the rate of the dissolution of REEs from $\text{La}(\text{OH})_3(\text{s})$. Among those complexes, the binuclear surface complexes may be the dominant species and cover the surface sites of $\text{La}(\text{OH})_3(\text{s})$, which reduced the dissolution rate of $\text{La}(\text{OH})_3(\text{s})$. On the other hand, it should be noted that the protonation of the carboxylate ligands, which behaved like a buffer, also consumed most ($>50\%$) of the acid added during the pH adjustment step. Under such cases, less fraction of acid was consumed by the dissolution of $\text{La}(\text{OH})_3(\text{s})$. In addition, it can be seen that the poor leaching results of the ligands (except for formate) were inconsistent with the simulated results shown in Figure 3.3. This may be explained by the fact that the dissolution kinetics of REEs from $\text{La}(\text{OH})_3(\text{s})$ in the presence of the carboxylate ligands was too slow to match the predicted results.

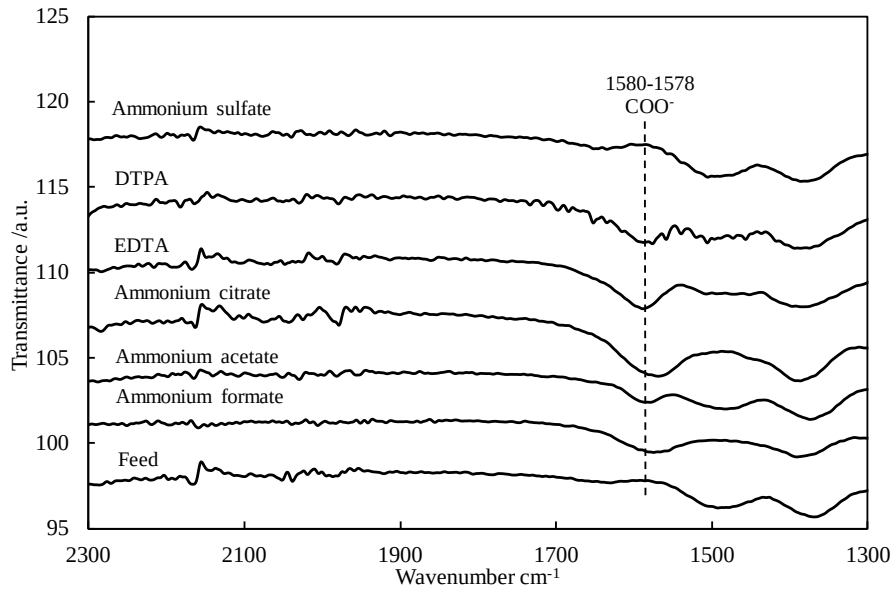


Figure 3.11 FTIR analysis of $\text{La}(\text{OH})_3(\text{s})$ leached by various lixivants. (After mixing $\text{La}(\text{OH})_3(\text{s})$ with organic ligands, the stretching band of $-\text{COO}^-$ at $1662\text{--}1620\text{ cm}^{-1}$ in the leaching liquor shifted to 1578 cm^{-1} in the leaching residues, suggesting the coordination of La^{3+} with $-\text{COO}^-$).

The findings from this study show that the dissolution of $\text{La}(\text{OH})_3(\text{s})$ in the presence of the carboxylate ligands is largely different from the acid leaching. Without the presence of organic ligands, the surface hydrolysis reactions of $\text{La}(\text{OH})_3(\text{s})$ in acid can be described as follows (Fang et al., 2017):



The large stability constant suggests that Eq. (3.12) is the dominant reaction during the dissolution of $\text{La}(\text{OH})_3(\text{s})$ by acids, which is why acid leaching of the hydroxide cake of monazite normally gives satisfied leaching recovery (>90%). However, in the presence of organic acids (e.g., citrate and EDTA), the dissolution of $\text{La}(\text{OH})_3(\text{s})$ becomes a surface-controlled dissolution process, which has a much slower kinetics compared to acid leaching. Organic ligands can adsorb on the surface of $\text{La}(\text{OH})_3(\text{s})$ and form varying surface complexes. The surface complexation of $\text{La}(\text{OH})_3(\text{s})$ and EDTA can be described by the following reactions:



in which “L” represents EDTA. A small fraction of REEs is released through Eq. (3.14), while Eqs. (3.15) and (3.16) indicate the generation of difficult-to-dissolve binuclear surface complexes, which reduces the dissolution kinetics of REEs from rare earth hydroxide.

3.4 Conclusion

In this study, the leaching kinetics of NaOH-treated monazite by ammonium sulfate was assessed

based on the experimental data obtained in our previous study. The possibility of using carboxylate ligands as lixiviants for NaOH-treated monazite has also been examined. It was found that the ammonium sulfate leaching of NaOH-treated monazite is a chemical reaction-controlled process with an activation energy of 61.28 kJ/mol. After incorporating the particle size, the established empirical equation for the ammonium sulfate leaching of NaOH-treated monazite is $1 - (1 - x)^{\frac{1}{3}} = 4.79 \cdot r_0^{-2} e^{-\frac{61280}{RT}}$. The lixiviant screening tests found that, except for ammonium formate, the carboxylate ligands with stronger complexing ability were ineffective lixiviants for NaOH-treated monazite at room temperature. Leaching tests conducted on pure La(OH)₃(s) by acetate and EDTA showed that significant improvements in recovery can be obtained at elevated temperatures. The corresponding kinetics studies found that both leaching rates were inner diffusion-controlled, and the activation energies in the cases of ammonium acetate and EDTA were 77.95 and 101.87 kJ/mol, respectively. The kinetic type along with the FTIR analysis indicated that the poor leaching recoveries were mainly attributed to the slow leaching rate caused by a passivation layer (possibly binuclear surface complexes). Another reason is the consumption of acid by the protonation of the organic ligands during the pH adjustment stage. Compared to acetate, the unique performance of formate may be explained by its weaker basicity, leading to the formation of less stable surface complexes.

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Chapter 4 Rare Earth Recovery from Coal-based Clays after NaOH Pretreatment with Ethylenediaminetetraacetic Acid

Abstract

Rare earth element (REE) extraction from coal and coal byproducts is challenging mainly due to the low REE grades and the poor leachability. Alkali treatment followed by acid leaching has been successfully utilized to extract REEs from monazite under aggressive conditions. In this study, stability diagrams of La-, Nd-, and Y-PO₄-H₂O systems were created to explore the thermodynamic feasibility of extracting REEs from coal-based clays after NaOH pretreatment with and without the presence of ethylenediaminetetraacetic acid disodium (Na₂EDTA). The pretreated samples were subjected to 0.5 M ammonium sulfate leaching at pH 3 and 1 M HCl leaching, respectively. The effects of NaOH concentration (2-10%) and temperature (40-80 °C) on the leaching efficiency were examined.

The stability diagrams indicate that the addition of 0.1 M EDTA significantly favors the decomposition of rare earth phosphate by forming REE-EDTA complexes, which was consistent with the experimental results. However, opposite to the prediction, NaOH pretreatment had a limited impact on the leachability of heavy REEs (HREEs, e.g., Y) due to the existence of refractory HREE-bearing minerals (e.g., xenotime and zircon). Over 60% of Ce, Nd, Pr, and Sm can be extracted by ammonium sulfate at pH 3 after being treated with 10% NaOH at 40 °C for 24 h, under which only limited fractions of Al (5.3%) and Si (2.8%) were dissolved. Higher extraction efficiency can be obtained at higher pretreatment temperatures (60 and 80 °C) but accompanied by the elevated decomposition of the gangue minerals. The comparable leaching levels of ammonium sulfate and 1 M HCl suggested that the former is a promising lixiviant, which can selectively recover REEs via an ion-exchange leaching mechanism.

4.1 Introduction

Many countries have considered rare earth elements (REEs) critical raw materials in recent years since they are widely applied in high-tech fields (e.g., clean energy and the production of advanced magnets and catalysts). Due to the imbalanced distribution of conventional rare earth resources (e.g., monazite and bastnaesite) and the supply risk, coal and coal byproducts (e.g., coal ash, acid mine drainage, and fine coal refuse, etc.) have been taken as an alternative feedstock for REEs (Yang et al., 2020; Zhang et al., 2020; Gaustad et al., 2021). The benefits of using coal-based materials mainly include 1) the elimination of mining costs; 2) lower concentrations of radioactive elements than traditional rare earth ore deposits; and 3) higher concentrations of more critical REEs, as summarized by Zhang et al. (2020).

However, extraction of REEs from coal-derived materials in the US is difficult for various reasons. The most significant challenge is the low-contained values due to their low head grades, which limit viable options. The rare earth minerals (REMs) found in coal refuse are smaller than 10 µm in size (Rozelle et al., 2016), making it difficult to recover them by flotation, a standard separation method used in the mineral processing industry. Another problem is that REEs in coal-derived clays are not in easy-extractable forms. It has been reported that the modes of occurrences of REEs in coal-based materials include mineral phases (e.g., carbonates and phosphate minerals), ion adsorbed, and organically bound forms (Hower et al., 1999; Seredin and Dai, 2012; Zhang et al., 2020). Among them, rare earth phosphates (e.g., monazite and xenotime), which are thermodynamically stable, were found to be the dominant REE occurrence in several coal refuse materials (Yang et al., 2021; Ji et al., 2022). Due to the poor separation performance of physical separation methods, hydrometallurgical leaching of REEs from these materials has been identified as a more promising approach. Prior to a chemical leaching step, those resistant phosphate minerals normally need to be thermally or chemically pretreated, which can transform them into more readily leachable forms (e.g., rare earth oxides or hydroxides).

Of the developed pretreatment methods, alkali pretreatment is commonly used to solubilize rare earth phosphates in coal-derived samples since it has been successfully used for the decomposition of monazite concentrate on an industrial scale (Krishnamurthy and Gupta, 2015). Yang et al. (2020) reported that the total REE (TREE) recovery increased from 22% to 75% in a fine coal refuse sample leached by 1.2 M sulfuric acid after being pretreated by 8 M NaOH at 75 °C for 2 h. Kuppusamy et al. (2019) conducted NaOH pretreatment with 30% NaOH at 190 °C for 30 min to recover clean coal and REEs from fine coal refuse samples. After the pretreatment, the recoveries of light REE (LREE) and heavy REE (HREE) were 97% and 76%, respectively. Additionally, by performing NaOH pretreatment using 6 M NaOH at 120 °C for 2 h, Yang et al. (2021) found that >60% of TREE recoveries can be achieved by acid leaching from three overburden materials. Although satisfactory recoveries can be achieved in those studies, the NaOH concentrations used were still too high for the coal refuse with low TREE contents. On the other hand, the substantial dissolution of clay minerals caused by NaOH pretreatment enables the downstream processes (e.g., selective precipitation and solvent extraction) to be complicated and less cost-effective. As such, the necessity to perform the pretreatment using dilute NaOH solutions was felt.

By virtue of their complexing ability, organic ligands (e.g., carboxylates with low molecule weight) have been used to recover REEs in recent years. Several carboxylic acids were utilized to maximize the leaching efficiency of REEs from an ion-adsorption clay sample (Wang et al., 2017). Of the reagents tested, the authors found that citric acid was the most efficient ligand to benefit the leaching process due to its stronger complexing ability. Montross et al. (2020) extracted REEs from central Appalachian coal seam underclays by citrate anions. It was concluded that the major advantage of this chelating ligand is that it can selectively extract REEs without bringing considerable amounts of impure elements into the leachates. To develop cost-efficient and environmentally friendly leaching reagents, Moldoveanu and Papangelakis (2021) used different chelating agents to recover REEs from ion-adsorption clay ores collected from Africa. The dosage of ammonium sulfate can be reduced when chelating ligands (e.g., nitrilotriacetic acid-trisodium form (NTA- Na_3) and N, N'-ethylenediaminedisuccinic acid (EDDS)) were utilized as additives, which led to 10-20% improvements in TREE recovery. The authors also revealed that chelating ability, toxicity, biodegradability, and economic viability are four criteria to assess the performance of a given chelating ligand. In addition, different carboxylic acids were applied to leach REEs from a coal ash material (Banerjee et al., 2021). At pH 1.6-2.3, 5% tartaric acid was able to extract 65% of LREEs but only 19% of HREEs at 90 °C. The authors also revealed that the appreciable selectivity of REEs over impure elements enables the organic acids to be potential alternatives for mineral acids for leaching. According to the above studies, chelating ligands are beneficial to REE leaching. However, relatively little is known about the enhancement of chelating ligands in decomposing rare earth phosphate minerals in coal-derived clays during NaOH pretreatment.

In this study, the impacts of alkali pretreatment on the leachability of REEs in coal-derived clays have been investigated. To reduce NaOH consumption, ethylenediaminetetraacetic acid (EDTA) was used as an additive to enhance the pretreatment efficiency. A series of thermodynamic predictions was also conducted to understand the role of EDTA during the pretreatment step. Our previous study has found that ammonium sulfate leaching at pH 4 is an effective method to recover REEs from NaOH-treated monazite. (Liu et al., 2022). The benefit of using ammonium sulfate as a lixiviant is that it can reduce acid consumption relative to the conventional acid leaching process. Therefore, ammonium sulfate leaching was also used to extract REEs from the NaOH-treated clay samples in this study. Additionally, the effects of experimental variables, such as NaOH concentration and pretreatment temperature, on the leaching efficiency were systematically examined to determine an optimal condition, under which the maximum extraction efficiency can be obtained without significantly dissolving the gangue minerals.

4.2 Experimental

4.2.1 Samples and Chemicals

Three US coal-based clays, including a thickener underflow (LR) from WV, a spiral middling (MM) from MD, and an underclay (UC) sample from central PA, were collected for extraction tests. The as-received UC sample with a high ash content (91.2%) was initially crushed from ~5 to 0.5 cm by a jaw crusher and then further ground to 5 μm by a ball mill. As two fine coal refuse samples from coal preparation plants, the hydrophobic-hydrophilic separation (HHS) process was conducted on the as-received LR and MM samples to remove the clean coal (i.e., decarbonization), according to the procedure described by Gupta et al. (2016). This step also helps reduce the sample volume subjected to the chemical leaching step. The decarbonized clay samples (i.e., LR and MM) and the ground UC samples served as feed materials for rare earth extraction after drying in an oven at 60 °C. The TREE content in the clay samples was determined by ICP-MS after being fused at 1000 °C with the addition of lithium metaborate as a flux (Larijani et al., 2016). The ash content, particle size, and elemental composition of those three samples are shown in Table 4.1. The amounts of Al and Si in the LR sample were 12.48% and 24.72%, respectively. Sodium hydroxide (NaOH), ethylenediaminetetraacetic acid disodium salt (Na_2EDTA), and ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) were in reagent grade. The acids (i.e., HCl and HNO_3) used for preparing ICP-MS diluting solution were of trace metal grade. Those chemicals were all purchased from Fisher Scientific. Deionized water (DI) was utilized in all solution preparation and leaching tests.

4.2.2 NaOH Pretreatment

A series of NaOH pretreatment tests with and without the addition of 0.1 M EDTA was performed on the clay samples. Effects of experimental variables such as NaOH concentration (2, 5, and 10% w/v) and temperature (40, 60, and 80 °C) on the leaching performance of the LR sample were systematically explored. In each experiment, a 0.5 g clay sample and 20 mL of NaOH solution were mixed in a 50 mL polytetrafluoroethylene (PTFE) beaker. The beaker was heated on a magnetic hotplate stirrer at desired temperatures for 24 h. The leaching slurry was stirred at 600 rpm via a Teflon-coated magnetic stir bar. The temperature of the sample suspension was controlled within $\pm 1^\circ\text{C}$ by means of a temperature probe placed in the sample suspension. For the NaOH pretreatment with EDTA, when the NaOH solution was preheated to the desired temperature, a known amount of EDTA solid was immediately added to the PTFE beaker, creating NaOH solutions with 0.1 M EDTA. The beaker was sealed with paraffin film to keep the evaporative water loss to less than 0.5 mL. The pretreated slurry was then subjected to solid-liquid separation by centrifugation at 5,000 rpm for 10 min. The supernatant (i.e., the used NaOH solution) was collected and saved for composition analysis via ICP-MS. The residue was subjected to leaching tests after washing three times with deionized water to remove residual NaOH.

4.2.3 Leaching Tests

The pretreated-clay samples were subjected to a series of leaching experiments at room temperature using 0.5 M ammonium sulfate or 1 M HCl. In each test, 0.5 g of the sample and 40 mL lixiviant solution

Table 4.1 Ash content (%), d_{80} (μm), and the contents of P and individual REE (in ppm, dry whole basis) of the samples used for rare earth extraction (Note: d_{80} refers to 80% of particles passing a specific size).

Sample	Ash	P	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd
LR	90.4	1619.3	26.8	42.4	83.2	150.9	15.2	60.0	11.6	2.4	10.1
MM	86.6	1976.2	12.5	35.9	43.7	96.0	10.9	43.3	8.8	2.0	8.2
UC	91.2	529.5	34.2	38.8	69.5	151.2	15.9	60.4	12.2	2.2	10.4
Sample	Tb	Dy	Ho	Er	Tm	Yb	Lu	Th	U	TREE	d_{80}
LR	1.6	8.8	1.7	4.9	0.0	4.7	0.0	20.2	5.1	424.3	9.0
MM	1.1	7.0	1.4	3.6	0.5	3.3	0.5	11.3	3.4	278.5	4.8
UC	1.5	8.9	1.6	4.7	0.7	4.6	0.7	72.7	9.2	416.8	5.0

was mixed in a 50 mL polypropylene beaker. The slurry was magnetically agitated for 1 h. Except for investigating the effect of pH on the leaching efficiency, the pH of ammonium sulfate leaching was maintained at $\text{pH } 3.0 \pm 0.05$ by adding aliquots of HCl and NaOH solutions both of 0.5 M. Slurry samples of 0.3 mL were collected by means of a 1 mL disposable syringe at 1, 4, 7, 10, 20, 30, and 60 min since the start of each leaching test to examine the leaching kinetics. The slurry samples were filtered immediately using syringe filters (0.22 μm pore size) supplied by Cobetter Filtration Equipment Corp. Subsequently, the elemental concentration of each filtrate was measured by ICP-MS after diluting 100 times with a mixed HNO_3 (2.5%) and HCl (0.5%) solution. Leaching recovery (R) was determined using the following relationship,

$$R = 100 \times \frac{C_l V}{C_f M} \quad (4.1)$$

where C_l and V represent 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. The same procedure was used for the HCl leaching at different pH values.

4.2.4 Sample Characterization

The mineralogical compositions of the LR leaching feed and four NaOH-treated LR samples at varying temperatures (25, 40, 60, and 80 °C) were characterized by X-ray diffraction (XRD) using Bruker D8 Advance Twin diffractometer along with a copper X-ray source. The XRD spectra were recorded over a 2θ range from 5-70° with a step size of 0.02°. The XRD spectra were analyzed by MDI Jade 6 software. The REE mineralogy of a HCl leaching residue (pretreatment conditions: 10% NaOH, 80 °C, and 24 h) was characterized by scanning electron microscopy (JSM-IT500HR SEM) equipped with an energy dispersive X-ray spectrometer (EDS detector by Oxford Instruments).

4.3 Results and Discussion

4.3.1 Thermodynamic Simulation

Before performing NaOH pretreatment and leaching experiments, thermodynamic simulation was carried out to understand the possible roles of EDTA in enhancing the performance of NaOH pretreatment by the Medusa program and its Hydra database (Puigdomenech et al., 2013). The stability constants used for the simulation work were from its database, and no new data were added to the system. La, Nd, and Y were selected as the representatives of the remaining REEs since they are the dominant REEs in the coal-based clay samples. The concentrations of those three REEs and PO_4^{3-} used for the simulation systems were all set as 10^{-5} M, which were the approximate concentrations estimated from a system with 0.5 g LR sample being dispersed into a 40 mL leaching solution.

REE- PO_4 - H_2O system is commonly employed to simulate the reaction between REPO_4 and NaOH (Yang et al., 2021). The subsequent leaching efficiency highly depends on the amount of rare earth hydroxide formed in the NaOH pretreatment stage. Initially, two fraction diagrams of La were constructed to compare the dissolution of $\text{LaPO}_4(\text{s})$ in the absence and presence of 0.1 M EDTA at 25 °C as a function of pH. As can be seen in Figure 4.1a, $\text{LaPO}_4(\text{s})$ is the predominant species over a wide pH range (2 to 13) in the La- PO_4 - H_2O system. It suggests that $\text{LaPO}_4(\text{s})$ is a thermodynamically stable mineral and can hardly be decomposed under weak acid or base conditions. When the pH is below 4, $\text{LaPO}_4(\text{s})$ starts to dissolve into La^{3+} and PO_4^{3-} ions by proton attack. Complete decomposition of the metal phosphate happens till the pH is <2. Also, $\text{LaPO}_4(\text{s})$ starts to be converted to $\text{La}(\text{OH})_3(\text{s})$ once the pH exceeds 12. The decomposition reaction of $\text{LaPO}_4(\text{s})$ is shown in Eq. (4.2).



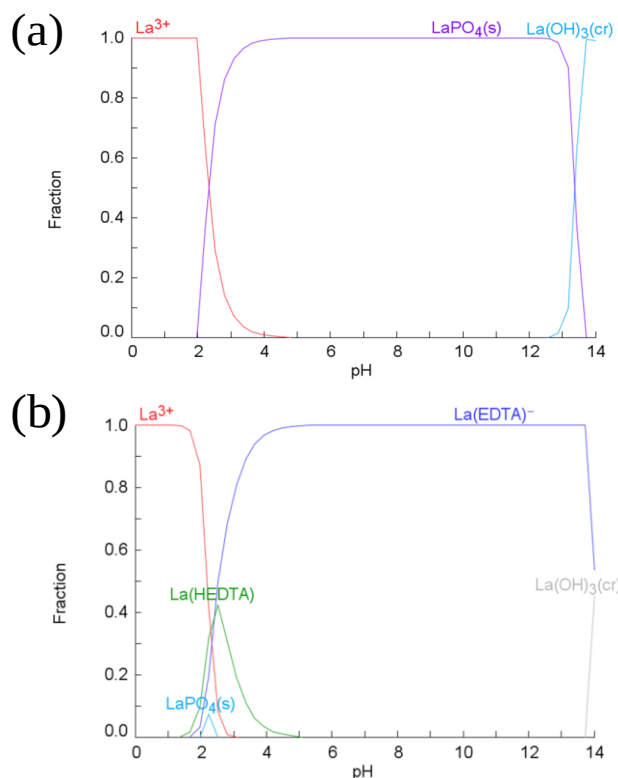


Figure 4.1 Fraction diagrams of La in the systems of (a) La-PO₄-H₂O and (b) and La-PO₄-EDTA-H₂O at 25 °C, conditions: [La³⁺] = [PO₄³⁻] = 10⁻⁵ M, [EDTA] = 0.1 M.



However, LaPO₄(s) becomes more soluble when EDTA is introduced to the La-PO₄-H₂O system. Except for a small fraction (<0.1) of LaPO₄(s) observed between pH 2.0 and 2.5, LaEDTA⁻ is thermodynamically favored and becomes the dominant species over a wide pH range (2.0-13.5) in the La-PO₄-EDTA-H₂O system. The role of EDTA in facilitating the dissolution of LaPO₄(s) may be attributed to its unique complexing ability, which enables the released La³⁺ ions to preferentially form complexes rather than reprecipitate as phosphate (see Eq. 4.3). This is equivalent to continuously removing the reaction product (i.e., La³⁺ ions) from the reaction system (see Eq. (4.2)). Therefore, the decomposition of the metal phosphate can be facilitated by moving the reaction equilibrium of Eq. (4.2) forward. It also shows that pH 13.5 is a transition point at which the disappearance of LaEDTA⁻ and the formation of La(OH)₃(s) occur. Above pH 13.5, LaEDTA⁻ is converted to La(OH)₃(s), a final product of NaOH pretreatment. This may indicate that the metal complex is not stable over pH 13.5, and thus the contribution of EDTA to the decomposition of LaPO₄(s) may be impaired at high alkali concentrations.

In addition, the stability diagrams for La-, Nd-, Y-PO₄-EDTA-H₂O systems were also created respectively to explore the speciation differences of various REEs as a function of the logarithm of the EDTA concentration and pH. As can be seen in Figure 4.2a, at lower EDTA concentrations (approximately <10^{-3.5} M), LaPO₄(s) predominates over a wide pH range (2 and 11). The minimum EDTA concentration needed for the conversion of LaPO₄(s) to LaEDTA⁻ gradually increases with pH. It is mainly due to the fact that the amount of OH⁻ ions is more available with the increase of pH, an important chemical force to facilitate the decomposition of LaPO₄(s). La(OH)₃(s) accounts for a small area as the pH is above 13.2. Similar speciation can be found in the Nd-PO₄-EDTA-H₂O system (see Figure 4.2b). The critical EDTA concentration for the conversion of NdPO₄(s) to its complexes reduces to around 10^{-4.0} M between pH 2

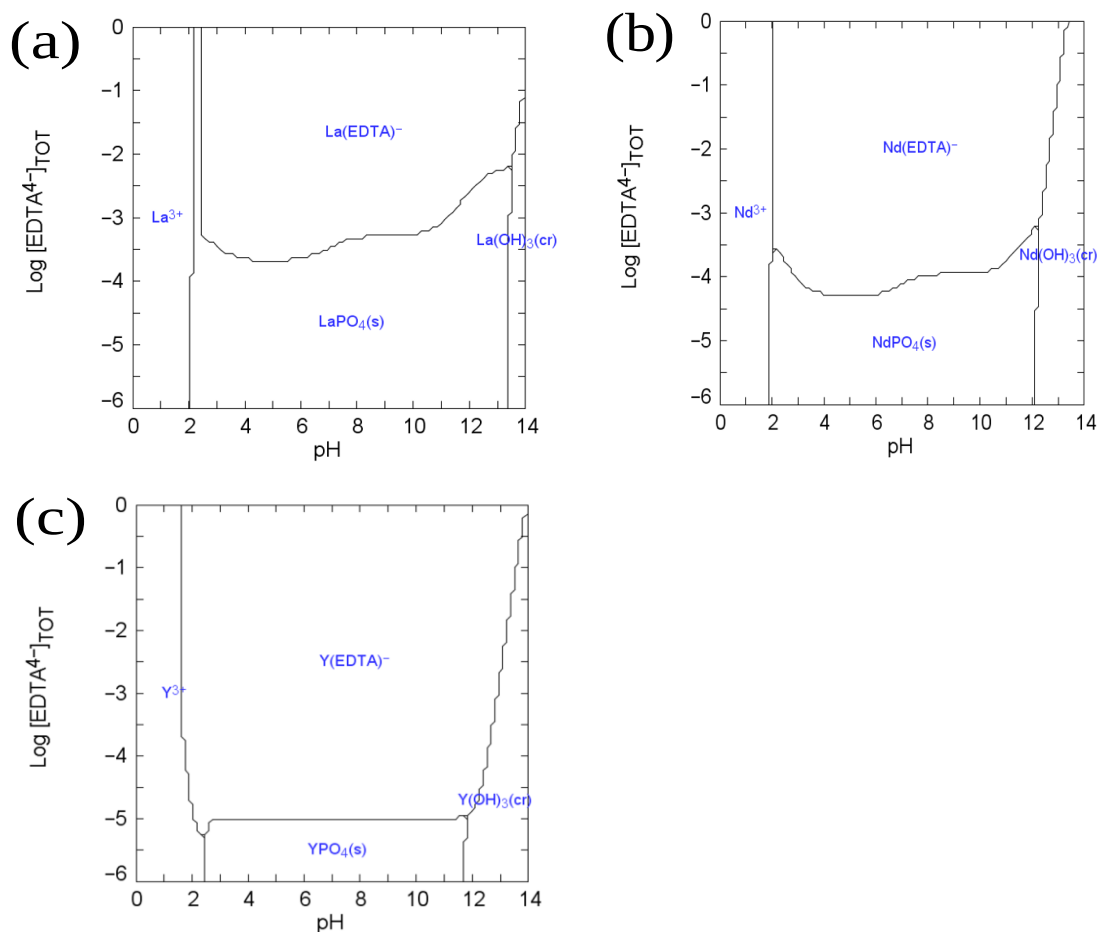


Figure 4.2 Species diagrams of (a) La, (b) Nd (b), and (c) Y in the system of REE-PO₄-EDTA-H₂O, conditions: [La³⁺] = [Nd³⁺] = [Y³⁺] = [PO₄³⁻] = 10⁻⁵ M.

and 10. Although it depends on the EDTA concentration, Nd(OH)₃(s) gradually becomes the dominant species as the pH > 12. It reveals that NdPO₄(s) is more readily soluble compared to LaPO₄(s). Regarding Y (Figure 4.2c), the minimum EDTA concentration required for the formation of YEDTA⁻ further decreases to 10⁻⁵ M between pH 2 and 12, suggesting that YPO₄(s) is more readily leachable compared to both La and Nd. According to the simulation results, it can be found that the order of the minimum EDTA concentration required for the formation of REE-EDTA complexes is in the order of La > Nd > Y, which is opposite to the order of their corresponding stability constants (i.e., Log K) of REE-EDTA, i.e., La (15.50) < Nd (16.61) < Y (18.09). This finding suggests that less amount of EDTA is required for the REE that has a stronger affinity for EDTA, i.e., the one with a larger Log K value during the decomposition of REPO₄(s).

Another worth-noting problem during the NaOH pretreatment of coal-based clays is the dissolution of gangue minerals such as clays. Significant dissolution of those minerals in the pretreatment stage introduces more contaminants (e.g., Al³⁺ and Fe³⁺) to leachates. Those impure cations can compete for EDTA with REEs and form their corresponding metal-EDTA complexes, leading to higher EDTA consumption and poor selectivity for REEs. Based on the species diagrams in Figure 4.2, 0.1 M Al³⁺ ions were added to the chemical systems to examine their impacts on the dissolution of REPO₄(s). As is shown in Figure 4.3a, with the presence of 0.1 M Al³⁺ ions, the minimum EDTA concentration required to solubilize LaPO₄(s) and NdPO₄(s) highly depends on the pH. As the pH varies from 4 to 8, elevated EDTA concentration (>0.1 M) is required to dissolve LaPO₄(s) and form LaEDTA⁻, whereas the critical concentration decreases as the further increase of pH from 8 to 12. No noticeable change is found at alkaline

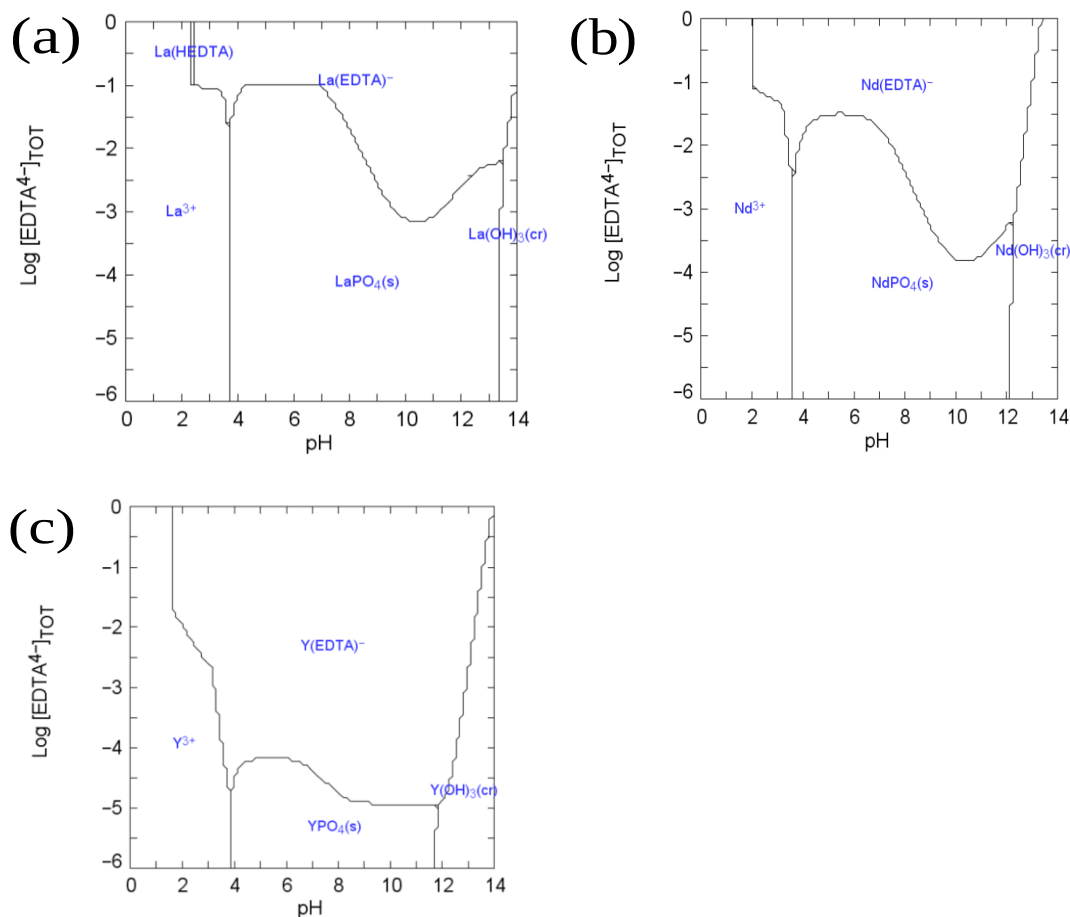


Figure 4.3 Species diagrams of (a) La, (b) Nd, and (c) Y in the systems of $\text{REE}^{3+}\text{-PO}_4\text{-EDTA-Al-H}_2\text{O}$, conditions: $[\text{REE}^{3+}] = [\text{PO}_4^{3-}] = 10^{-5} \text{ M}$, $[\text{Al}^{3+}] = 0.1 \text{ M}$.

conditions (i.e., $\text{pH} > 12$). Similar to La, the region of Nd-EDTA⁻ species also shrinks at acidic pH, and the critical EDTA concentration required increases to $10^{-1.5} \text{ M}$ between pH 3 and 7, which is 3 orders of magnitude higher than its corresponding system without adding Al^{3+} (see Figure 4.3b). Only a slight shrink of the Y-EDTA is noticed between pH 4 and 8 (Figure 4.3c). The pH-dependent influence on the speciation of each REE may be due to the fact that complete deprotonation of EDTA is achieved under more alkaline conditions relative to the cases in acidic and neutral pH, and thus the complexation between REE and EDTA is favored. This explanation is corroborated by the fraction diagram of 0.1 M EDTA at 25 °C (see Figure 4.4). It shows that the deprotonated EDTA species (i.e., HEDTA³⁻ and EDTA⁴⁻), which preferentially coordinate with REEs, predominate the system when the pH exceeds approximately 8. On the other hand, the role of NaOH in the conversion of $\text{REPO}_4(\text{s})$ to $\text{RE(OH)}_3(\text{s})$ is enhanced with the increase of pH. Although the addition of Al^{3+} ions leads to a minor variation of the speciation of the Y system, the released impure cations during NaOH pretreatment still have the potential to negatively influence the dissolution of $\text{REPO}_4(\text{s})$, especially under acidic and neutral conditions. Therefore, alkaline pH should be selected to avoid the possible interference of Al^{3+} ions on the role of EDTA during pretreatment.

4.3.2 REE Recovery

In this section, the foregoing simulation results were validated by conducting a series of NaOH pretreatment tests with and without the presence of EDTA. The preliminary extraction tests showed that the TREE recovery of the LR sample by 0.1 M EDTA was only 15% (not shown here) at pH 10 and 60 °C,

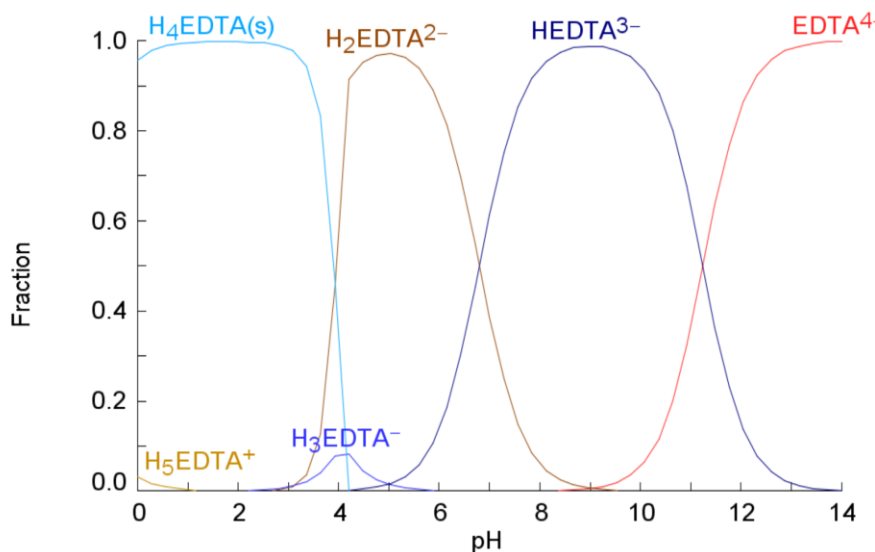


Figure 4.4 Fraction diagram of 0.1 M EDTA as a function of pH at 25 °C.

suggesting that pH 10 may not be sufficient to decompose the $\text{REPO}_4(\text{s})$. As such, to maximize the TREE recovery, the NaOH concentrations were set as 2, 5, and 10% w/v in the pretreatment tests shown later. The corresponding calculated pH values of those NaOH solutions are 13.69, 14.01, and 14.40. 0.1 M EDTA was employed to avoid the possible influences of the contaminant ions on the dissolution of $\text{REPO}_4(\text{s})$, as suggested by Figure 4.3. The treated sample was subjected to ammonium sulfate or 1 M HCl leaching. The leaching results of 1 M HCl were employed as a reference to assess the leaching performance of ammonium sulfate. The related chemical basis is that HCl can recover nearly all the readily leachable REEs due to its strong acidity.

4.3.2.1 Effect of pH on the Leaching Efficiency

In order to determine the optimal leaching pH, ammonium sulfate leaching was conducted at varying pH after the LR sample was treated by 10% NaOH with 0.1 M EDTA at 60 °C. Meanwhile, a batch of control tests by HCl was carried out at different pH, which may shed light on the leaching mechanism of ammonium sulfate. Figure 4.5a shows that pH slightly impacted the leaching recovery of ammonium sulfate. At pH 4, 43.3% of TREE recovery was achieved. When the pH decreased to 3, it increased to 56.7%. Further reducing the pH to 1 only caused slight changes in the extraction efficiency. Moldoveanu and Papangelakis (2013) examined the effect of pH on the leaching performance of two ion-adsorption clays (IACs) by ammonium sulfate. The authors found that reducing the leaching pH from 5 to 3 only slightly improved the TREE recovery. This observation was ascribed to the recovery of REEs in “surface precipitates” form (i.e., chemisorbed REEs) and the reduced REE hydrolysis. In this study, the slight influence of pH on the recovery may be explained by the fact that nearly all the readily leachable REEs generated from the NaOH pretreatment stage were removed by ammonium sulfate leaching at pH 3. The remaining REEs were in difficult-to-leach forms, which were not able to be extracted by ammonium sulfate even at pH 1. As such, it indicated that pH 3 was the optimal pH for ammonium sulfate leaching.

Figure 4.5b shows the leaching results of HCl at various pH. Compared to ammonium sulfate leaching, the TREE recovery of HCl leaching was highly pH-dependent. The recovery was only 6.5% at pH 4, while it gradually increased to 11.7% at pH 2 and 30% at pH 1, respectively. Only at pH 0, the TREE recovery was comparable to that of ammonium sulfate leaching at pH 3. The high dependence of recovery on pH may be due to the incomplete dissolution of $\text{RE}(\text{OH})_3(\text{s})$. Additionally, the released Ln^{3+} ions may reabsorb on the negatively charged surface of clays. A more acidic condition is required to desorb those REEs and remain them in the leaching solution. Consequently, the pH-dependent recovery of HCl leaching

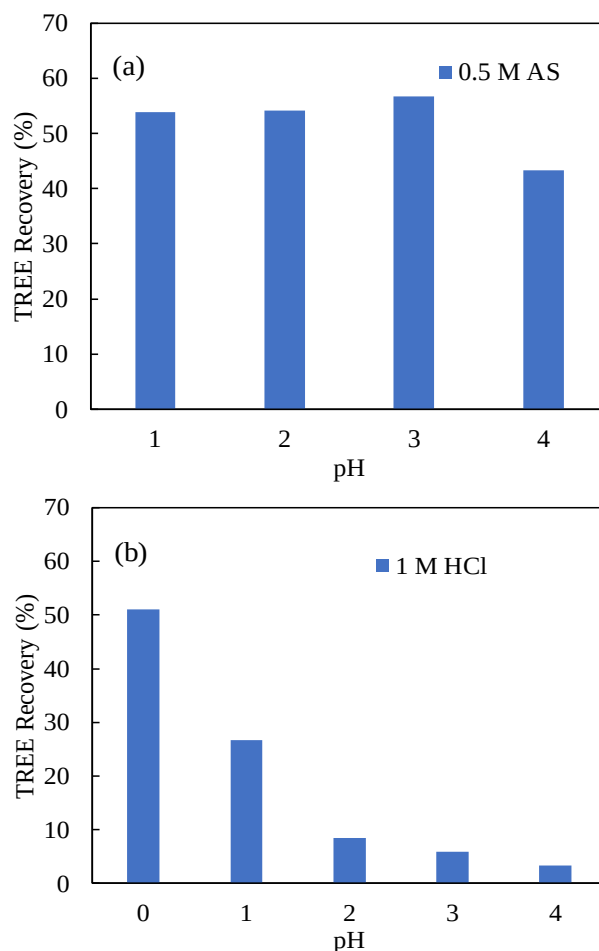


Figure 4.5 Effect of pH on the leaching efficiency of (a) 0.5 M AS and (b) 1 M HCl on the LR sample, pretreatment conditions: 10% NaOH with 0.1 M EDTA, 60 °C, 24 h; leaching conditions: room temperature, 1h. (Note: “AS” in (a) refers to ammonium sulfate, the same below.)

indicated that adding ammonium sulfate did benefit the extraction process.

With the presence of ammonium sulfate, the ion exchange between NH_4^+ and REE^{3+} ions may serve as an extra driving force to facilitate the leaching process. It has been found in our previous study that the ammonium sulfate leaching of NaOH-treated monazite at pH 4 can be explained by an ion exchange mechanism (Liu et al., 2022). It is widely acknowledged that micro-dispersed rare earth phosphates are the major REE-bearing minerals in coal-derived clays, which is similar to monazite in REE mineralogy. The major difference between them is that the REE content in monazite is much higher (approximately 3 orders of magnitude) than that in the coal-derived clay. As suggested in Section 4.3.1, REE hydroxide is the final product after alkali pretreatment at high NaOH concentrations. As such, the leaching of NaOH-treated monazite and NaOH-treated LR sample by ammonium sulfate essentially have a similar starting material, i.e., $\text{RE}(\text{OH})_3(\text{s})$. Therefore, it may be reasonable to infer that the proposed ion exchange leaching mechanism can also be used to explain the role of ammonium sulfate in the leaching of the NaOH-treated clay derived from coal. Under the acidic condition (pH 4), the first layer of REE hydroxide is converted to REE^{3+} ions and adsorbed on the outermost layer of the substrate. Subsequently, those adsorbed REE^{3+} ions can be displaced by NH_4^+ ions, driven by the differences in hydration enthalpy between them (Moldoveanu and Papangelakis et al., 2012).

4.3.2.2 Leaching Results of Different Coal-derived Clay Samples

To examine the difference in the REE leachability of various samples, another two coal-based clays (MM and UC) were also leached by ammonium sulfate and after NaOH pretreatment. As shown in Figure 4.6, ~50% of TREE recovery was obtained by ammonium sulfate from the LR sample, and the recoveries of Ce and Nd were around 67%. The highest TREE recovery (70%) was achieved from the MM sample, of which the recoveries of La, Nd, and Sm were almost 90%. However, only 40% of REEs were extracted from the UC sample, even though it has a comparable particle size to that of MM. It should be noted that the recoveries of Tm and Lu were 0 since the contents of these two REEs in the samples were too low to be detected by ICP-MS, whose detection limit is only 1 ppb. It can also be seen that the TREE recovery was positively proportional to that of Th, indicating the decomposition of rare earth phosphates. These findings suggested that the proposed leaching method can be expanded to other coal-based clay samples for REE recovery. The differences in the recovery of the different samples were mainly attributed to the varying crystallinity of the rare earth phosphates. Compared to the LR and UC samples, the MM sample may have more fraction of secondary rare earth phosphate minerals, such as crandallite group minerals and rhabdophane, which are more amenable to leaching. According to Yang et al. (2021), rare earth phosphates with high levels of crystallinity are more thermodynamically stable, which is more difficult to be decomposed by NaOH. However, the leaching process will be favored if the phosphates are poorly crystalline.

4.3.2.3 Partition Behavior of REEs into NaOH Solutions

Other than 60 °C, to examine the effects of operational variables on the leaching recovery, two batches of NaOH pretreatment tests with and without the presence of 0.1 M EDTA were performed on the LR sample at 40 and 80 °C, respectively. The treated samples were subjected to 1 M HCl and ammonium sulfate leaching at pH 3 and room temperature for 1 h. Before comparing the leaching results of ammonium sulfate and HCl, the partition behavior of REEs into NaOH solution was investigated by comparing the chemical composition of the used NaOH solution. The results revealed that negligible fractions (<0.1%) of REEs were partitioned into the NaOH solutions after pretreatment in the absence of EDTA. This finding agrees well with the observation reported by Yang et al. (2021), who also found that the REEs left in the NaOH solutions after NaOH pretreatment were non-detected by ICP-MS, which was expected since nearly all the REEs were directly converted to their hydroxides.

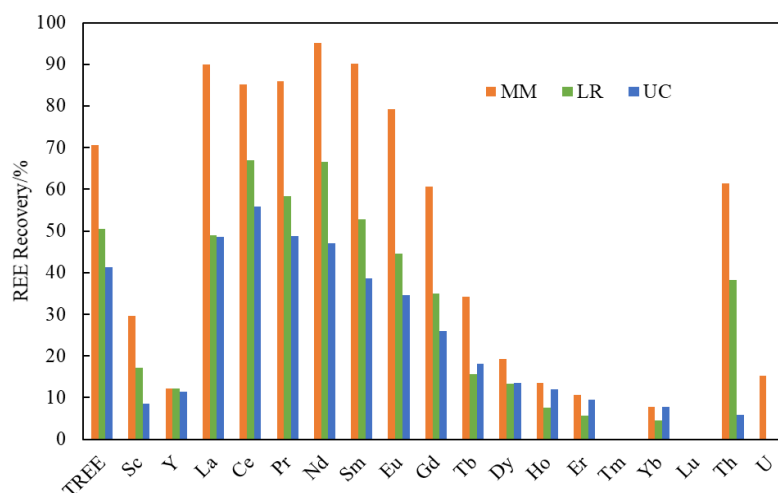


Figure 4.6 TREE and individual REE recoveries of ammonium sulfate leaching from three different coal-derived clays after NaOH pretreatment with 0.1 M EDTA. (Pretreatment conditions: 10% NaOH with 0.1 M EDTA, 60 °C, 24 h, leaching conditions: 0.5 M AS, room temperature, 1h, pH 3.)

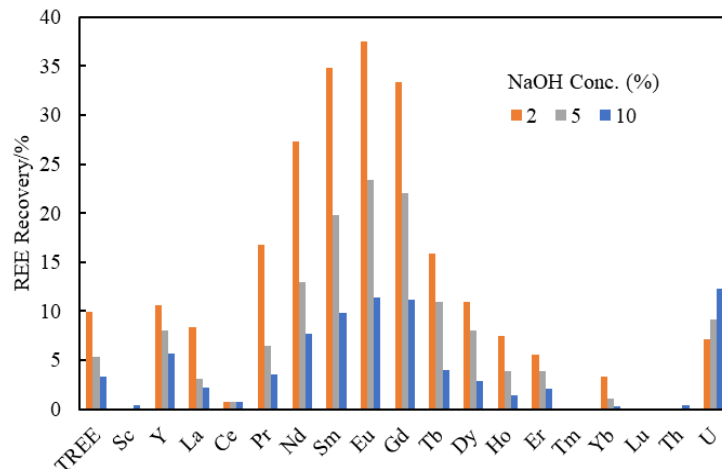


Figure 4.7 Partitions of REEs into the NaOH solutions during the pretreatment of the LR sample by NaOH pretreatment with 0.1 M EDTA at 80 °C for 24 h.

However, in the presence of EDTA, higher fractions of REEs (3 to 7%) were found to partition into the used NaOH solutions. Figure 4.7 shows the individual REE recovery in the used NaOH solutions of the pretreatment tests performed at 80 °C as an example. The elemental distribution of the REEs partitioned into the NaOH solution at 40 °C will be shown in Section 4.3.2.4. In general, the fraction of REEs partitioned into the NaOH solution decreased with the increase of NaOH concentration due to the fact that the formation of $\text{RE}(\text{OH})_3(\text{s})$ is more favored in the NaOH solution with higher concentrations. Although the TREE recoveries only ranged from 3 to 7%, the recoveries of Pr, Nd, Sm, Eu, Gd, and Tb were relatively higher than the remaining REEs in each test (see Figure 4.7). This is particularly the case for Eu, whose recoveries reached 10 to 37% depending on NaOH concentration. For the REEs located on the left- and right-hand sides of Eu, the recoveries (except Sc and Y) gradually decreased.

For the REEs that had high contents in the LR sample, it appeared that fewer fractions of them were reported to NaOH solutions. For instance, Ce, the most abundant REE (151 ppm) in the sample, had nearly no partition into the NaOH solution in each case, which suggested that almost all of this element was converted to $\text{Ce}(\text{OH})_3(\text{s})$ and $\text{CeO}_2(\text{s})$ after the pretreatment step. However, regarding Sm, which only had 11.6 ppm in the feed, its partition into the 10% NaOH solution reached 28%. This may be because the amount of Sm^{3+} ion released into the NaOH solution was too low to precipitate as $\text{Sm}(\text{OH})_3$, and thus they tended to stay as SmEDTA^- in the NaOH solution. For the HREEs located on the right side of Eu (from Gd to Yb), the decreasing trend of REE recovery was mainly due to the poor conversion efficiencies of the resistant HREE-bearing minerals (e.g., xenotime and zircon) to their readily leachable forms in the pretreatment step. This is also why limited HREEs were extracted even in the subsequent ammonium sulfate/HCl leaching step, which will be further explained later in this study. It should be noted that the fraction of REEs partitioned into NaOH solutions can be reduced by choosing an optimal NaOH concentration. Also, they may be recovered by precipitating them as hydroxides, which will be examined in our further study.

4.3.2.4 TREE Recoveries of Ammonium Sulfate and HCl Leaching

Figure 4.8 shows the leaching recoveries of ammonium sulfate and HCl from the LR sample after being treated by NaOH at 40 and 80 °C, respectively. Due to the partition of REEs into the NaOH solutions when EDTA was used in the pretreatment step, the REE recoveries shown in Figure 4.8 are the overall recoveries of REEs reported to NaOH solutions and the corresponding leaching step (i.e., in the leachates of 1 M HCl or ammonium sulfate). The partition of each element will be shown in Figures 4.11 and 4.12.

As shown in Figure 4.8a, without EDTA, relatively lower TREE recoveries were obtained by ammonium sulfate leaching compared to those treated with the addition of EDTA. After being treated with 2% NaOH only, 3.5% of the TREE recovery was achieved, while the recovery was improved to 20.3% with the presence of EDTA. More noticeable improvements in the recovery were observed in the 5% (from 5.1 to 40.7%) and 10% (from 17 to 50%) NaOH-treated samples. This comparison demonstrated that the presence of EDTA enhanced the REE leachability of the LR sample. Except for a relatively significant difference (14.5%) in the ones treated with 2% NaOH, the recoveries of 1 M HCl leaching were slightly higher than those of ammonium sulfate, suggesting that ammonium sulfate is an effective lixiviant.

The TREE recovery was improved to approximately 60% at 80 °C (see Figure 4.8b). However, compared to those at 40 °C, the enhancement of EDTA to the leaching recovery of ammonium sulfate was less significant, especially at higher NaOH concentrations (from 5 to 10%). For instance, the differences in the leaching efficiency between the samples treated with and without EDTA gradually decreased from 17% to 10% as the NaOH concentration varied from 2 to 10%. This observation was consistent with the thermodynamic prediction (see Figures 4.2 and 4.3). In the NaOH solution with high concentrations, the role of EDTA in facilitating the conversion of REPO_4 to $\text{RE}(\text{OH})_3$ is less critical. In addition, like the cases at 40 °C, the recoveries of 1 M HCl were only 2 to 5 absolute percentage points higher than those of ammonium sulfate by 5 and 10% NaOH. This comparison suggested that the leaching efficiencies of ammonium sulfate leaching were comparable to the 1 M HCl leaching at higher NaOH concentrations.

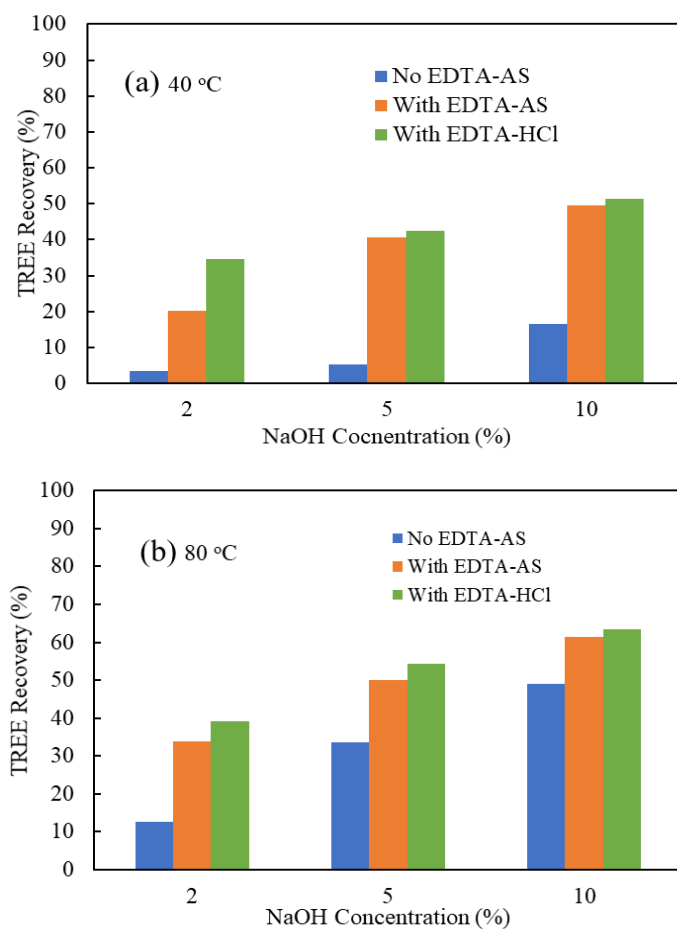


Figure 4.8 TREE recovery of AS at pH 3 and 1 M HCl from the LR sample after NaOH pretreatment by NaOH with and without 0.1 M EDTA at 40 (a) and 80 °C (b).

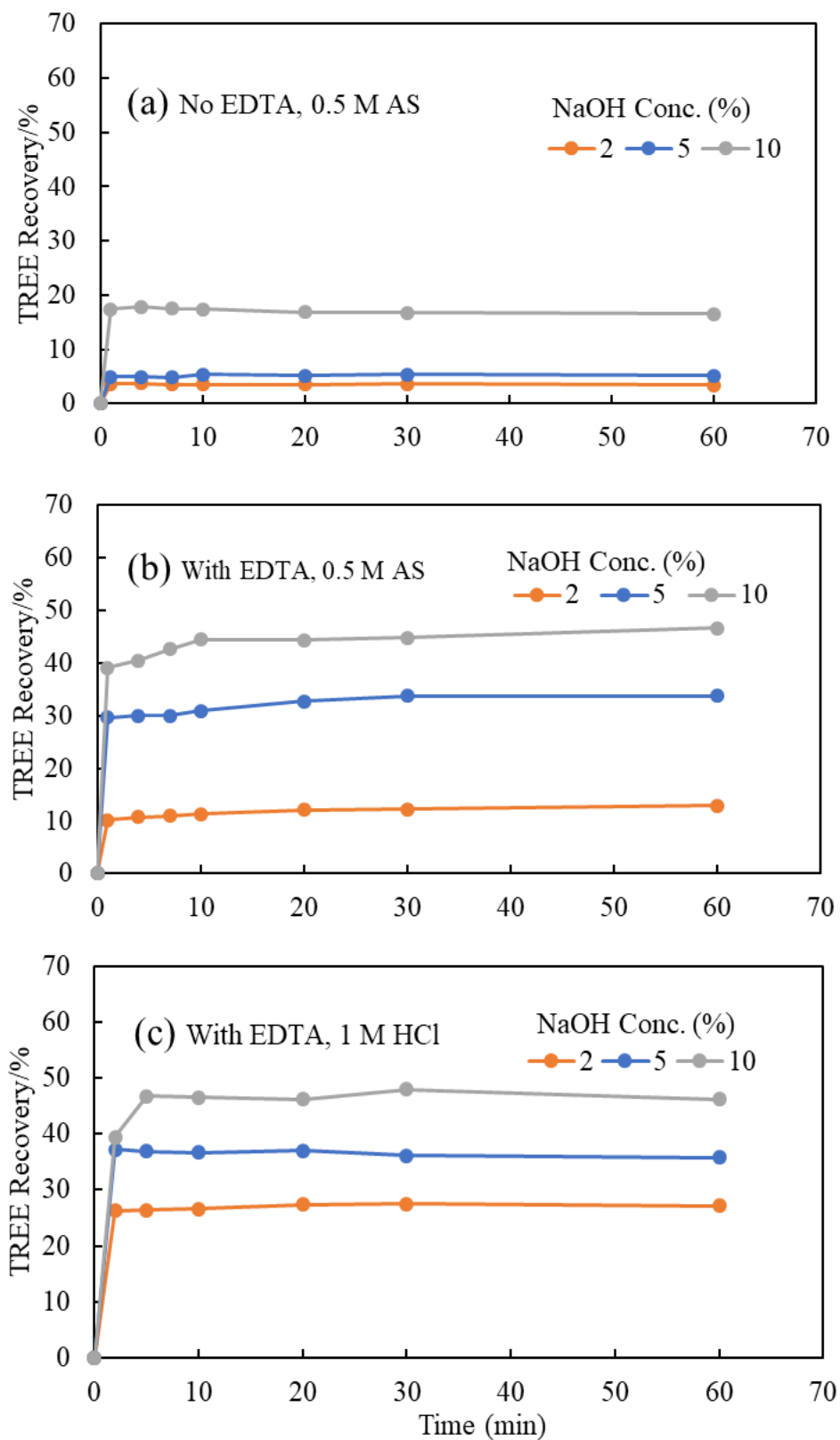


Figure 4.9 Leaching curves of TREE recovery of the AS and HCl leaching from the LR sample after NaOH pretreatment without and with 0.1 M EDTA at 40 °C.

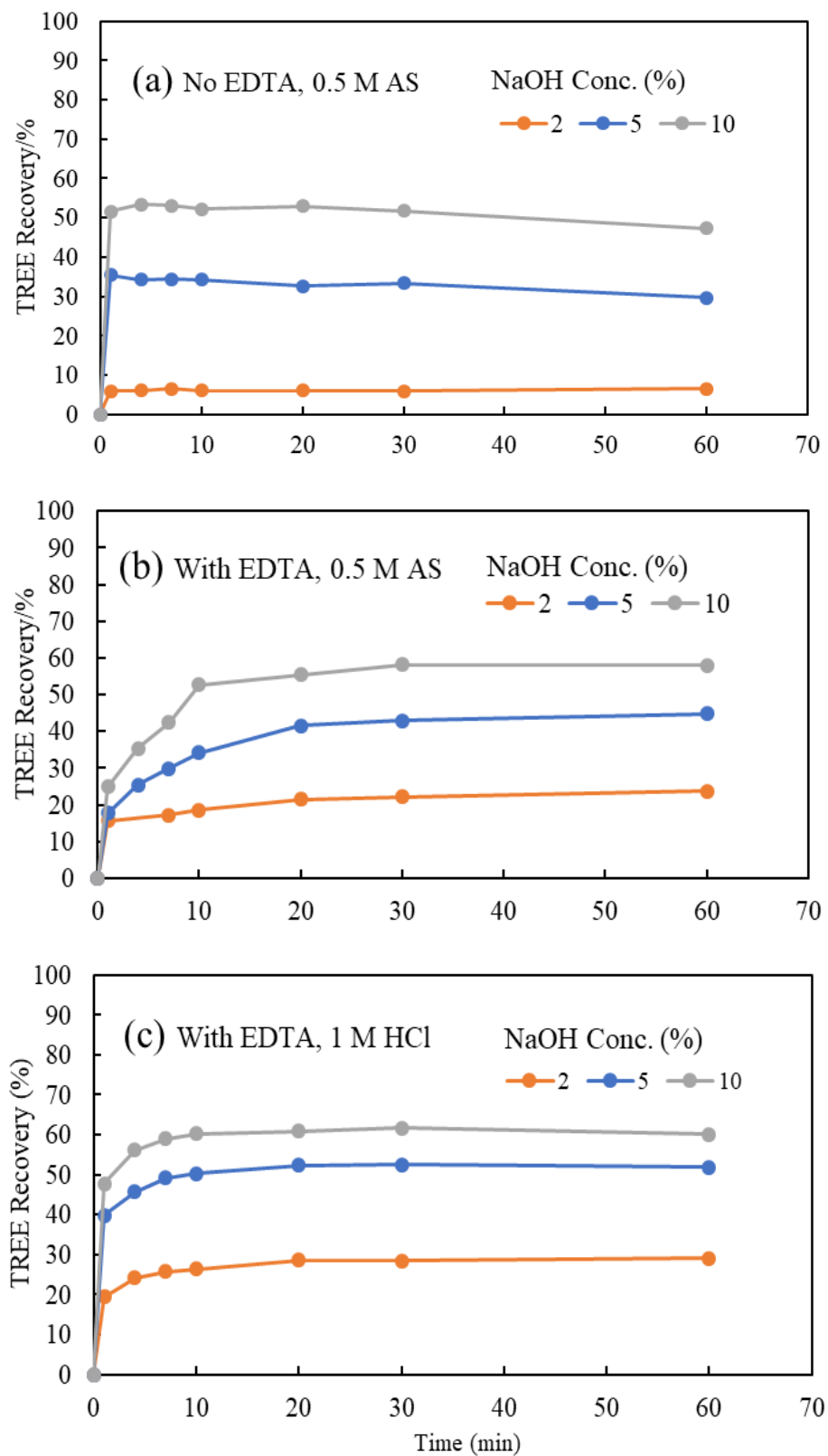


Figure 4.10 Leaching curves of TREE recovery of the AS and HCl leaching from the LR sample after NaOH pretreatment without and with 0.1 M EDTA at 80 °C.

The leaching kinetics of TREE in the leachates was also compared for the leaching tests shown in Figure 4.8. Rapid leaching rates were observed for the samples treated by NaOH without the presence of EDTA at 40 °C (see Figure 4.9) and 80 °C (see Figure 4.10). The leaching equilibrium was reached immediately from the start of the leaching process. This is mainly because only limited fractions of readily leachable REEs were produced after NaOH pretreatment, which can be removed immediately. The leaching rates of both ammonium sulfate and 1 M HCl were also similar to each other at 40 °C (Figure 4.9b and -c), while the extraction rates were relatively slower at 80 °C (Figure 4.10b and -c). It is worth noting that leaching equilibrium was reached within 10 min for all the tests. This observation is distinct from the slower leaching kinetics of NaOH-treated monazite by ammonium sulfate at room temperature (Liu et al., 2022). For instance, over 2 h was required to reach a leaching equilibrium for the monazite sample treated with 50% NaOH at 80 °C for 24 h. This was mainly attributed to the significantly higher REE grade in the monazite sample. A thicker rare earth hydroxide layer was formed after NaOH pretreatment, thereby leading to a longer contact time to dissolve it. As such, it may be concluded that fast leaching kinetics is another advantage of the proposed ammonium sulfate leaching process.

4.3.2.5 Individual REE Recovery

Individual REE distribution was also presented to investigate the leaching behavior of each REE and their differences. The recoveries of Th and U are also shown since they are constituents of some REMs (e.g., monazite and can be used to understand the involved leaching mechanism. Figure 4.11 shows the individual REE recovery of the leaching tests after the LR sample was treated at 40 °C. Without EDTA (Figure 4.11a), the REE recoveries were all less than 23%, even after being treated with 10% NaOH, suggesting limited decompositions of REE-bearing species at 40 °C. Figures 4.11b and -c show that the individual REE recoveries of ammonium sulfate leaching were comparable to those of the HCl leaching. Compared to the one without EDTA, the elemental recoveries of Ce, Pr, Nd, and Sm achieved by ammonium sulfate and HCl were improved by almost three times (over 60%) with the pretreatment conducted by 10% NaOH in the presence of EDTA. Moreover, a lower fraction of each REE was found to partition into the used NaOH solution with the increase of NaOH concentrations. Figure 4.12a shows that the REE leachability was further enhanced at 80 °C even after the pretreatment without EDTA. The REE recoveries of Ce, Pr, and Nd drastically increased from merely ~10% to 60% as the NaOH concentration varied from 2 to 10%. After adding EDTA, ammonium sulfate leaching achieved around 80% of Ce, Pr, and Nd, which were comparable (only around 5% lower) to the HCl leaching (Figure 4.12b and -c). Of those three REEs, Pr and Nd are critical elements widely applied in the clean energy sector (Yang et al., 2021). Such high recoveries of those critical REEs enabled the proposed extraction method to be a promising process.

However, it is also noticed that the impact of NaOH pretreatment on the leachability of HREEs was limited. Even by 1 M HCl leaching, the recoveries of HREEs such as Dy, Ho, Er, and Yb were less than 10%. This characteristic can be explained by the fact that LREE-bearing minerals were preferentially decomposed relatively to those of HREEs during the pretreatment stage (Zhang et al., 2019; Yang et al., 2021). The high recoveries (~80%) of Ce, Pr, and Nd indicated that most LREE-bearing REMs such as monazite and crandallite group minerals were decomposed after being subjected to the proposed extraction process. It was also found that relatively lower La recoveries were obtained relative to Nd in each test, which was consistent with the order as predicted by the simulation results shown in Figure 4.2. However, the recoveries of HREEs were opposite to the simulated results. The relatively low HREE recoveries in each test were mainly explained by the varying REE mineralogies of HREEs and LREEs. Resistant HREE-bearing minerals such as zircon and xenotime were not decomposed after leaching. Two Y-enriched particles identified by SEM from the HCl leaching residue of the 10% NaOH-treated LR sample confirmed the above hypothesis (see Figure 4.13). It can be found that those two particles were associated with zircon (Figure 4.13a) and phosphorus (Figure 4.13b, possibly xenotime), which were too refractory to be completely decomposed under the extraction conditions. According to Nawab et al. (2022), sulfuric acid baking conducted at 250 °C can substantially enhance the leachability of HREEs in coal-based clays.

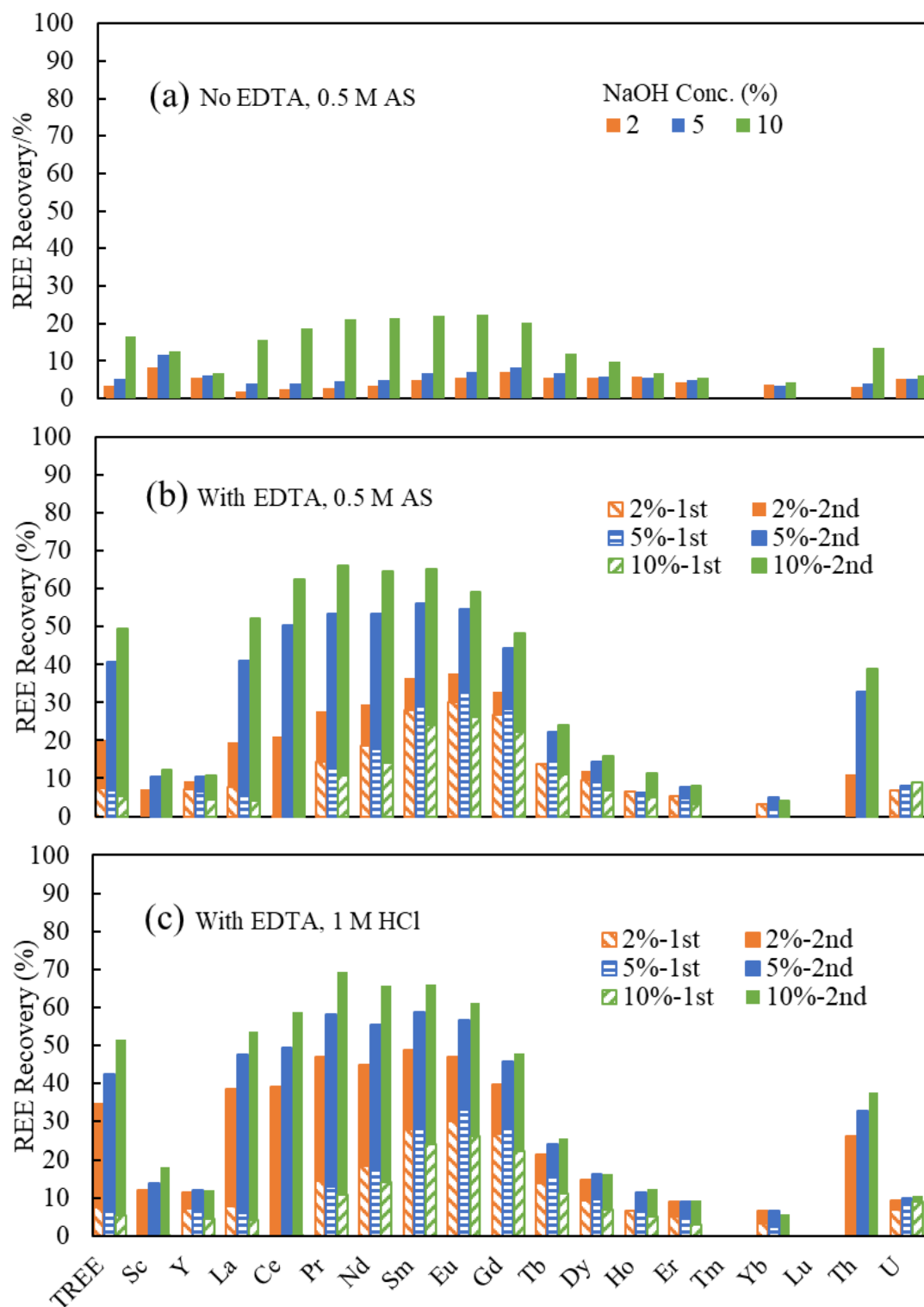


Figure 4.11 Individual REE recovery of (a) AS leaching after NaOH pretreatment without EDTA, (b) AS and (c) HCl leaching after NaOH pretreatment with EDTA from the LR sample at 40 °C. “1st” and “2nd” refer to the REEs partitioned into used NaOH and leaching solution, respectively.

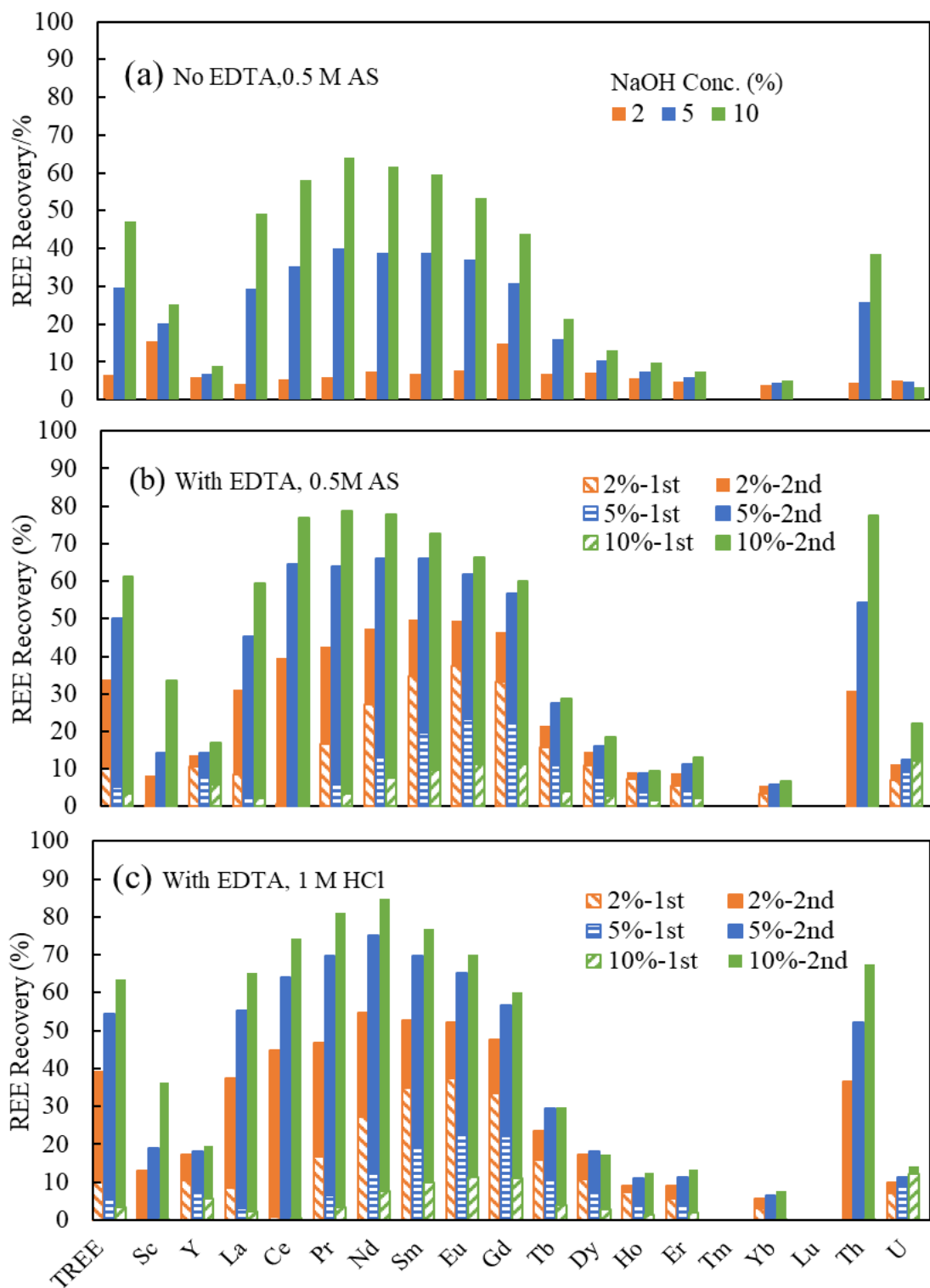


Figure 4.12 Individual REE recovery of a) AS leaching after NaOH pretreatment without EDTA, b) AS and c) HCl leaching after NaOH pretreatment with EDTA from the LR sample at 80 °C. “1st” and “2nd” refer to the REEs partitioned into NaOH and leaching solutions, respectively.

It is also noted that the recovery of Th behaved similarly to those of REEs. The higher the TREE recovery, the higher the corresponding Th recovery. It has been concluded by Hower et al. (2016) that Th is normally associated with the assemblages of detrital minerals such as zircon and REE-bearing phosphates (e.g., monazite) in coal. Accordingly, the similar leaching characteristics of Th and REEs also indirectly confirmed the presence of rare earth phosphate minerals in the LR sample. With the increase of NaOH concentration, the decompositions of rare earth phosphates were enhanced, thereby leading to higher leaching efficiencies of Th and TREE (see Figure 4.12c). The leaching behavior of U was also positively proportional to that of TREE. However, opposite to Th, nearly all the U reported to the used NaOH after being treated at 40 °C, with negligible amounts of U being found in the leaching solution. According to the Eh-pH diagrams of Th created by Kim and Osseo-Asare (2012), Th exists in its oxide form ($\text{ThO}_2(\text{s})$) in water at 25 °C at alkaline pH, which was dissolved during ammonium sulfate leaching. However, the majority of U was more likely to be in a soluble form ($\text{UO}_2(\text{OH})_4^{2-}$) at basic pH, thus reporting to the used NaOH solutions (Lapidus et al., 2015). As such, Th and U have different partition behaviors during the proposed extraction process.

4.3.3 Leaching Characteristics of Impure Elements (Al, Si, and P)

4.3.3.1 TREE versus P Recovery

It has been suggested that the major association of REEs in coal-based clays is rare earth phosphates (Yang et al., 2021). The occurrences of phosphorus in coal were found to be rare earth phosphates, apatite,

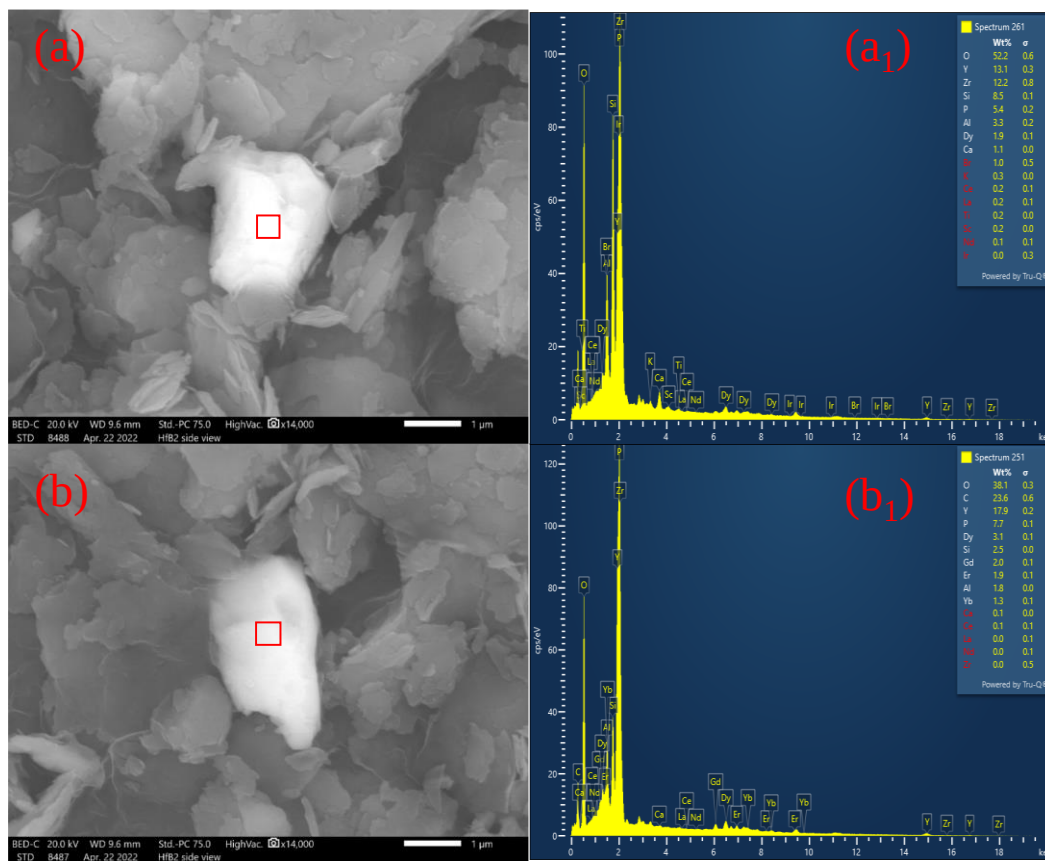


Figure 4.13 SEM images and EDS spectra of two HREE-bearing mineral particles and their corresponding EDS spectra identified in the 1 M leaching residue of the LR sample after NaOH pretreatment.

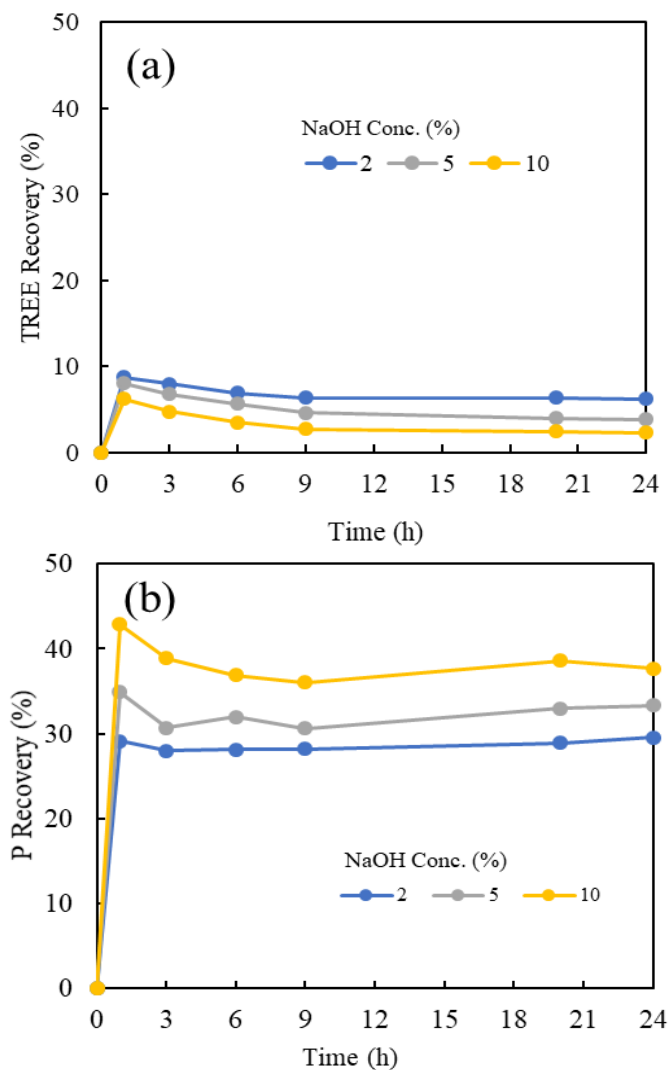


Figure 4.14 Leaching behaviors of (a) TREE and (b) P in the NaOH solutions during the NaOH pretreatment with 0.1 M EDTA of the LR sample at 80 °C for 24 h.

etc. (Finkelman et al., 2018). As such, the leaching characteristics of TREE and P in the used NaOH solutions are important to study the decomposition of rare earth phosphates since P was partitioned into the used NaOH solutions. The leaching characteristics of TREE and P in the NaOH pretreatment tests conducted at 80 °C are compared in Figure 4.14 as a function of contact time. As shown in Figure 4.14a, TREE recovery reached its maximum value in the first hour, followed by a declining trend in each test. The leaching curves of P, especially in the 5 and 10% NaOH solutions, also exhibited a similar decreasing trend in the 1-9 h and remained stable thereafter (see Figure 4.14b). The similar leaching characteristics of REE and P may be resulted from the depletion of REEs from NaOH solution by forming rare earth hydroxide and/or reprecipitating as rare earth phosphates after 1 h. The final TREE recovery gradually decreased with the increase of NaOH concentration, which was opposite to that of P. As mentioned earlier in Section 4.3.2.3, the contrasting characteristics of TREE and P can be explained by the fact that the decomposition of $\text{REPO}_4(\text{s})$ was more facilitated in the NaOH solution with higher concentrations. According to Figure 4.3, those REEs left in the NaOH solutions were more likely in the form of soluble REE-EDTA complexes, which had not been converted to the hydroxide form even after the pretreatment.

In addition, the plot of the correlation of TREE versus P recovery was also constructed. The

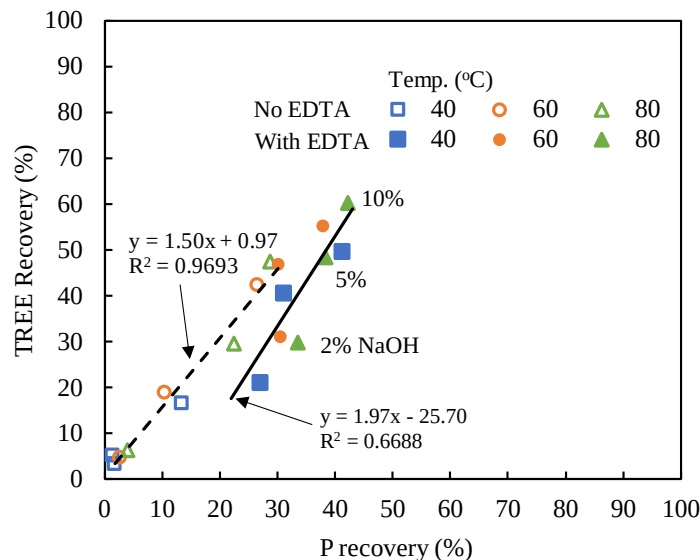


Figure 4.15 Correlation of TREE versus P recovery in the AS leaching of the LR sample after NaOH pretreatment under various conditions. (Pretreatment conditions: 2, 5, and 10% NaOH with and without 0.1 M EDTA, 40-80 °C 24 h, leaching conditions: 0.5 M AS, room temperature, 1h, pH 3.)

majority of P was detected in the used NaOH solutions, only with $\leq 5\%$ of P partitioning into the leaching solutions of ammonium sulfate. Therefore, the recoveries of TREE and P showed herein were the total recoveries reported to the used NaOH and the corresponding leaching solutions. Figure 4.15 shows the plot of TREE versus P recovery at different temperatures and NaOH concentrations in the LR sample. The data point with higher TREE recovery represents the sample pretreated with high NaOH concentration within each data set. The NaOH concentrations for the tests pretreated at 80 °C with EDTA were labeled as an example in Figure 4.15. This rule also applies to the data points shown in Figure 4.16. The results in Figure 4.15 show that TREE recovery is positively proportional to P recovery. The linear regression results showed that a steeper slope (1.97 versus 1.50) was noticed for the pretreatment conducted with EDTA, suggesting its superior enhancement of the REE leachability. It also shows that rising pretreatment temperature and NaOH concentration led to a higher dephosphorization efficiency, thereby resulting in a higher TREE recovery. On the other hand, compared to the ones pretreated without EDTA, higher P recovery was obtained from those samples pretreated with the addition of EDTA. Meanwhile, the improved dephosphorization efficiency resulted in a higher TREE recovery. This linear correlation may also confirm the previous assertion in Section 4.3.2.4 that the REEs being leached were dominantly from rare earth phosphates (e.g., monazite).

4.3.3.2 Dissolution of Al and Si during the Leaching Process

As a coal-based clay material, aluminosilicates such as clays are the dominant minerals in the LR sample. Accordingly, the dissolution rates of Al and Si are indicators to reflect the dissolution of gangue minerals. After calcinating two coal-derived clays at 600 °C for 2 h followed by acid leaching, relatively high fractions of the dissolved Al (0 to 60%) were detected in the acid leachates (Zhang et al., 2019). Significant amounts of Al and Si dissolved in the leachates complicate the following solvent extraction step. It has been reported that the co-extraction of impurities such as Al^{3+} , Fe^{3+} , Si^{4+} , Ca^{2+} , and Mg^{2+} ions can deteriorate the performances of the extractants used in the solvent extraction step, which is mainly due to the emulsification (da Silva et al., 2018; Wang et al., 2020; Zhang et al., 2021). To minimize the negative influences of those impurities, selective removal of the contaminants by pH adjustment is normally performed prior to the solvent extraction step (Zhang et al., 2021). However, the isolation of those impure

elements causes extra operation costs, thus complicating the extraction process. Therefore, minimizing the co-extraction of impurities is critical to a proposed leaching process in terms of economic viability and waste management. In this section, the diagrams of TREE recovery versus Al and Si recovery were created

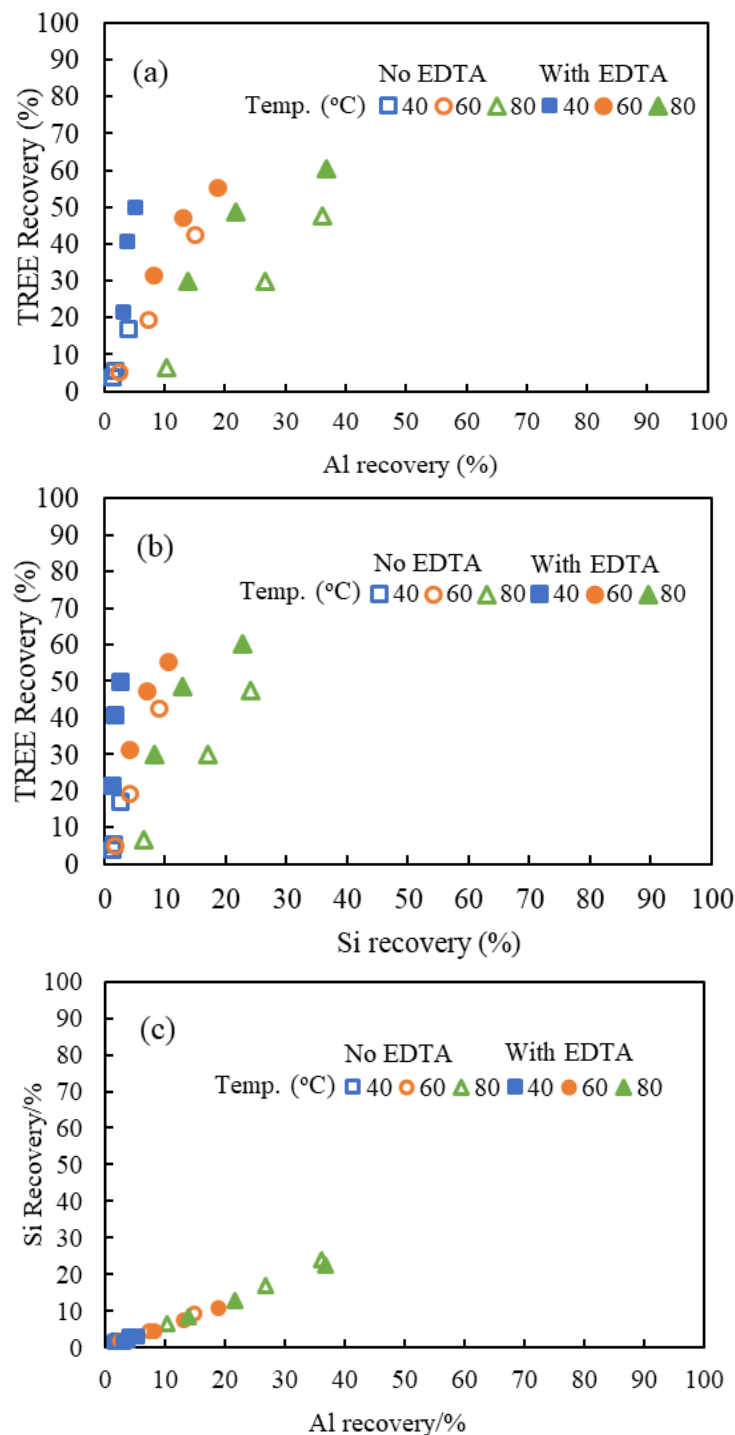


Figure 4.16 Correlations of (a) TREE versus Al recovery, (b) TREE versus Si recovery, and (c) Si versus Al recovery in the leaching of the LR samples. (Pretreatment conditions: 2, 5, and 10% NaOH with and without 0.1 M EDTA, 40-80 °C, 24 h, leaching conditions: 0.5 M AS, room temperature, 1h, pH 3.)

respectively to assist in determining an optimal condition at which relatively high TREE recovery can be obtained without significantly co-extracting contaminants into the leachates of ammonium sulfate. Again, the recoveries of REEs, Al, and Si used in the plots were the overall recoveries of REEs partitioned into NaOH solutions and the leachates ammonium sulfate.

As shown in Figure 4.16a and -b, Al and Si recovery gradually increased with the increase of NaOH concentration and pretreatment temperature. At 40 °C, the percentages of the dissolved Al and Si by the 10% NaOH with EDTA were 5.3 and 2.8%, respectively, which were at similar levels to the ones without EDTA. However, the TREE recovery of the one with EDTA (49.6%) was two times higher than that without EDTA. It demonstrated that relatively higher TREE recovery could be obtained with only around 5% dissolution of aluminosilicates. And the lower fractions of dissolved Al and Si by 2 and 5% NaOH solutions suggested limited decomposition of the gangue minerals. At 60 °C, the percentages of the dissolved Al and Si increased from 8.3 to 19.0% and from 4.4 to 10.7%, respectively as the NaOH concentration varied from 2 to 10% with EDTA. The highest TREE recovery achieved at 60 °C was 55.2%, which was only around 5% higher than the one at 40 °C. Significant decomposition of the gangue minerals was found at 80 °C, at which over 30% of Al and 20% of Si were dissolved. However, the highest TREE recovery remained at ~60%, which was comparable to the cases at 60 °C. It indicated that the elevated percentages of dissolved Al and Si did not lead to corresponding enhancements in the decomposition of REE-bearing species. However, those REE adsorbed on the surface of clays should also have been extracted along with the massive decomposition of clay minerals.

Figure 4.16c shows the plot of Al versus Si recovery. It can be seen that a linear correlation was found between them, and the recovery of Al was two times larger than the corresponding Si recoveries. This might be ascribed to the differences in the stoichiometry of Al and Si in various clay minerals. On the other hand, the dissolution of Al in other occurrences (e.g., water-soluble form, exchangeable form, and iron oxide combined Al) in the LR samples may be another reason (Chi and Jun, 2008). XRD characterizations of the LR samples after being treated with NaOH at various temperatures were performed to investigate the mineralogical variations before and after the pretreatment.

Figure 4.17 shows the XRD patterns of the LR sample after NaOH pretreatment at different

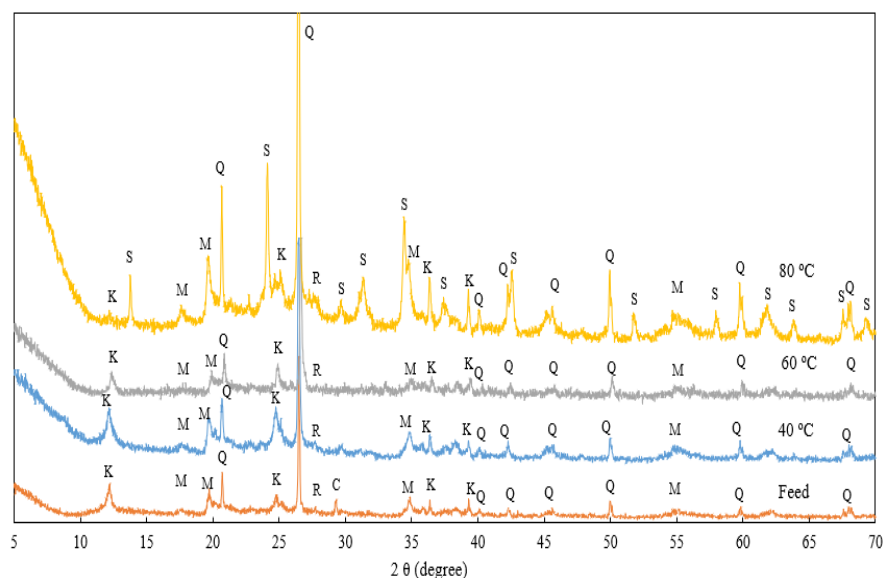


Figure 4.17 XRD patterns of non-treated LR sample and NaOH-treated LR samples by 10% NaOH with 0.1 M EDTA for 24 h at different temperatures. (C: calcite; K: kaolinite; M: muscovite/illite; S: sodalite; Q: quartz; R: rutile.)

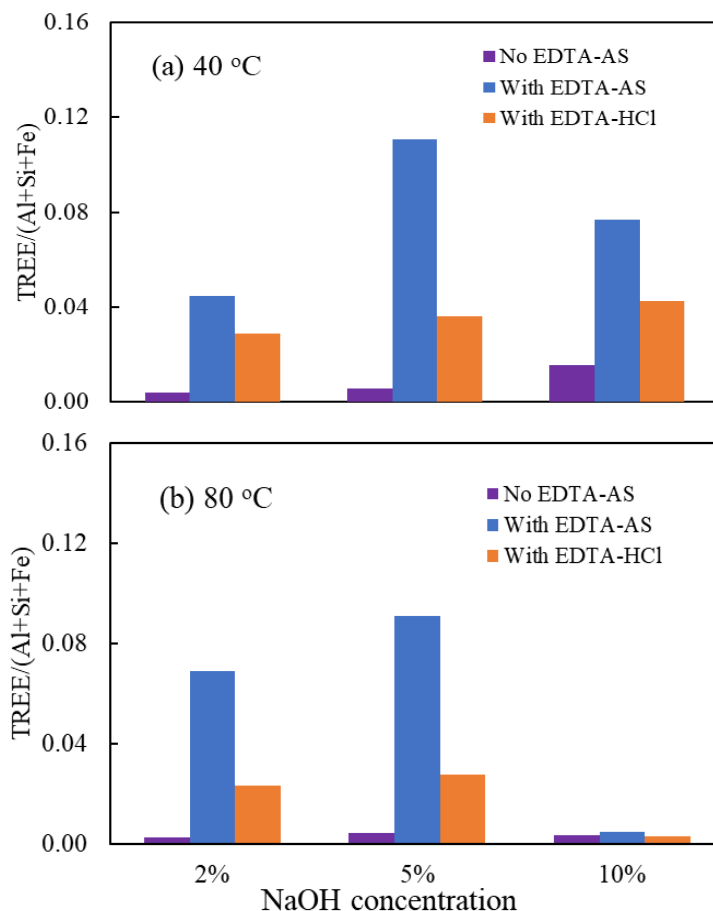


Figure 4.18 The mass ratio of TREE/(Al+Si+Fe) in the different leaching tests conducted on the LR sample after NaOH pretreatment with and without EDTA by 0.5 M AS at pH 3 and 1 M HCl, (a): 40 °C; (b): 80 °C.

temperatures. As shown, except for the disappearance of the peak of calcite, no extra noticeable difference was found in the sample treated at 40 °C relative to the feed sample. At 60 °C, the peaks of clay minerals and quartz became weaker relative to the feed sample, which was consistent with the elevated fractions of dissolved Al and Si (as suggested by Figure 4.16). However, a new mineral, i.e., sodalite ($\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{Cl}_2$), was formed in the sample after being treated at 80 °C, which was converted from kaolinite (Buhl et al., 1997; Jiang et al., 2012). On the other hand, the peak intensities of quartz ($2\theta = 20.82^\circ$, 26.62° , etc.) and muscovite ($2\theta = 17.80^\circ$) were stronger than the feed sample. This may be attributed to the enhanced decomposition of other clay minerals at 80 °C, making the quartz and muscovite relatively concentrated in the NaOH-treated sample.

According to the above analysis, it can be found that NaOH pretreatment performed at 60 and 80 °C led to significant mineralogical alteration of the feed samples, while no noticeable improvements in TREE recovery were found. The difference in the highest TREE recoveries achieved at 40 and 80 °C with EDTA was only 10%, while the discrepancy in the fractions of dissolved Al and Si was 6-10 times. Therefore, NaOH pretreatment performed by 10% NaOH with 0.1 M EDTA at 40 °C may be an optimal condition, under which relatively higher TREE recovery can be achieved without leading to significant dissolution of clay minerals.

4.3.3.3 Selectivity of the Ammonium Sulfate Leaching versus HCl Leaching

To quantitatively evaluate the selectivity of REEs over impure elements (Al, Si, and Fe), the mass ratios of TREE/(Al+Si+Fe) in the leachates of ammonium sulfate and HCl from the samples treated at 40 and 80 °C were compared in Figure 4.18. The ratio was calculated by dividing the amount of REEs extracted by the total amount of the co-extracted Al, Si, and Fe in the leachate. As shown, small ratios (<0.02) were found in the tests with the pretreatment performed at 40 °C without EDTA, mainly due to the low TREE extraction efficiency (Figure 4.18a). However, the ratios in the leachates of ammonium sulfate significantly increased to above 0.04 in the case with EDTA, and the maximum ratio (0.11) occurred in the leachate of 5% NaOH treated sample. When 1 M HCl was used as a lixiviant, the ratios decreased to <0.04, mainly resulting from the massive co-extraction of impurities by proton attack. Similar distributions were found for the tests performed at 80 °C, and all the ratios further decreased (Figure 4.18b). For instance, as the NaOH concentration increased from 5 to 10% with the addition of EDTA, the ratio in the ammonium sulfate leachates sharply reduced from 0.09 to 0.005, which was decreased by 18 times. It suggested that considerable amounts of impurities were released into the leaching solutions. As such, the extraction tests conducted at 80 °C were less selective for REEs compared to those at 40 °C. Although not shown here, the highest ratio in the ammonium sulfate leaching solutions at 60 °C with EDTA was 0.08, which was lower than those at 40 °C. The above comparisons suggested that smaller amounts of impurities were brought to the leachates by ammonium sulfate relative to 1 M HCl, indicating that the former had a better selectivity for REEs over contaminants.

4.4 Summary and Conclusions

Alkali pretreatment has been used to extract REEs from coal-derived clays under relatively aggressive conditions. The possibility of using EDTA to improve the performance of NaOH pretreatment on three coal-based clays has been explored in the present work. Stability diagrams constructed for La-, Nd-, and Y-PO₄-EDTA-H₂O systems suggest that the decomposition of rare earth phosphate can be significantly enhanced over a wide pH range (2-13) with 0.1 M EDTA.

The experimental results showed that rare earth phosphates in the clay samples could be decomposed by 2-10% NaOH at <80 °C with 0.1 M EDTA. Ammonium sulfate leaching of the NaOH-treated sample was less dependent on pH compared to HCl leaching. The optimal pH for ammonium sulfate leaching was found to be pH 3, and the involved leaching mechanism may be ion-exchange leaching. Compared to the one treated by NaOH only, adding EDTA improved the leaching efficiency by 12 to 35 absolute percentage points depending on the NaOH concentration and pretreatment temperature. The proposed method was also expanded to extract REEs from other coal-derived clay samples. The varying leaching recoveries were mainly explained by the differences in REE mineralogy and crystallinity of rare earth phosphates. It was found that LREEs were preferentially extracted than HREEs due to the varying leachability of LREE- and HREE-bearing minerals.

With a loss of ~10% TREE recovery, conducting the alkali pretreatment with EDTA at 40 °C can significantly reduce the dissolution of dominant minerals relative to the cases at 80 °C. Although HCl leaching achieved higher extraction efficiency at 80 °C, considerable amounts of impurities were co-extracted, which can negatively impact the downstream process. Ammonium sulfate leaching showed a better selectivity of REEs over the contaminants (Al, Si, and Fe) compared to 1 M HCl leaching. Therefore, ammonium sulfate has the potential to be an alternative lixiviant for HCl.

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Chapter 5 Influences of Phosphate on the Ion Exchangeability of Rare Earth Elements Adsorbed on Clay Surfaces

Abstract

Primary and secondary rare earth phosphates have been regarded as the dominant occurrence of rare earth elements (REEs) in coal-derived clays. Besides rare earth phosphate in aggregates, clay minerals such as kaolinite were also found to be host minerals for specific fractions of REEs. However, the extraction efficiencies of coal-derived clays were found to be poorer compared to those reported for the ion-adsorption clays (IACs) mined in South China. Herein, it is hypothesized that those clay-associated REEs may adsorb on the clay surfaces but be passivated by phosphate. REE (La, Nd, and Dy)- and/or phosphate-doped kaolinite samples were synthesized at pH 4 to verify this hypothesis. X-ray photoelectron spectroscopy (XPS) was utilized to determine the speciation of the REEs and phosphate doped on the synthesized clays. Additionally, based on the thermodynamic simulations, a set of direct ammonium sulfate leaching, ammonium sulfate leaching after NaOH pretreatment, and 0.1 M disodium ethylenediaminetetraacetic acid (Na_2EDTA) leaching tests were conducted to activate the passivation layer.

The results showed that the synthesized REE-P-kaolinite samples responded poorly to ion-exchange leaching due to the phosphate passivation effect. XPS characterization revealed that the REEs and phosphate might associate with clay in the form of “clay-RE- PO_4 ”. After NaOH pretreatment, the phosphate-passivated REEs can be effectively activated by converting them into a more leachable form, i.e., $\text{RE}(\text{OH})_3$. Moreover, EDTA leaching performed at alkaline pH is another pathway to improve the leaching efficiency of the passivated REEs by forming soluble complexes (RE-EDTA^-), with over 76% of the REEs being recovered. This study demonstrated that surface-deposited REPO_4 on kaolinite might be another occurrence of REEs, which impairs the ion exchangeability of REEs in coal-derived clays and IACs.

5.1 Introduction

Being a commercialized rare earth (RE) ore deposit, ion adsorption clays (IACs) mined in South China have been an important source of heavy rare earth elements (HREEs), which are of significance for social development (Borst et al., 2020). Despite the low REE grades (0.05-0.2 wt% in rare earth oxide (REO)) in IACs, they are still a critical REE resource due to their simplicity in extraction, which can offset the costs spent in mining and processing steps. The formation of IACs normally starts from the in-situ weathering of the REE-enriched minerals in granite under warm and humid conditions. Then the solubilized REE ions physically adsorb on the negatively charged surface of clay minerals such as kaolinite and halloysite (Xu et al., 2017). Other than REEs in ion-adsorbed form, IACs also contain REEs in colloidal form and weathering-resistant rare earth minerals (REMs).

During weathering, a fraction of mobile REEs can also form secondary REE-enriched minerals with varying grain sizes. Since apatite weathering is a major source of P for biological processes, sediments, and soils, Banfield et al. (1989) investigated the correlation between apatite weathering and the mobilization, fractionation, and fixation of REEs during weathering. The results showed that the light REEs (LREEs) dissolved from allanite can combine with the P released from primary apatite and form secondary phosphates, which may associate with clays and secondary Fe-Ti oxides in the forms of crystals and aggregates ($<10\text{ }\mu\text{m}$). Borst et al. (2020) compared the IACs collected from South China and Madagascar in terms of REE mineralogy and speciation using synchrotron X-ray absorption spectroscopy (XAS). The spectroscopic characterization results identified that a fraction of Y was in nanoparticulate secondary phosphates and/or heterogeneously adsorbed form in the South China clay sample. This finding was possible since secondary rare earth phosphates can dissolve again and cause the remobilization of the REEs and phosphate ions when the weathering becomes more intense (Taunton et al., 2000; Yusoff et al., 2013).

During the remobilization process, the REEs adsorbed on the surface of clays may bind with free phosphate ions and form surface-deposited REPO₄, undermining the ion exchangeability of the ion-adsorbed REEs.

Besides the typical IACs found in South China, Sanematsu et al. (2015) compared the mobility and adsorption of REEs in two groups of granites with varying weathering and phosphorous concentrations in Thailand. In the granite with high phosphorous concentrations, it was concluded that the residual monazite and secondary REPO₄ derived from apatite dissolution were responsible for the low REE mobility, i.e., having lower fractions of ion-exchangeable REEs. Those rare earth phosphates were more weathering-resistant relative to other minerals such as allanite, titanite, apatite, and REE fluorocarbonate. This explains why higher fractions of ion-exchangeable REEs are normally found in well-weathered granites with low phosphorous contents. It is widely acknowledged that apatite, a common crystalline phosphate mineral found in most igneous rocks, can be classified into geological (igneous rock) and biological (biomineralized apatite) types (Omelson et al., 2008). The latter is readily soluble and releases phosphate during the weathering of the granite. Sanematsu et al. (2015) revealed a possibility that the P released from apatite can chemically bind with and immobilize free REE ions by forming rare earth phosphates. Those immobilized REEs may be REE-bearing mineral particles and/or nanoparticulate secondary rare earth phosphates deposited on the surface of clays. This finding is consistent with the one suggested by Taunton et al. (2000), who concluded that phosphate ions could immobilize REEs during granite weathering and soil formation.

Other than conventional rare earth resources, rare earth extraction from alternative resources such as coal and coal byproducts has also been intensively investigated in the past decade. However, REE recovery from coal-derived clays is difficult due to the low REE grade, ultrafine grain size, and poor leachability of REE-bearing species. Various forms of REEs, such as organic form, accessory minerals, and resistant minerals, have been identified in coal (Zhang et al., 2018). Of them, rare earth phosphate minerals have been regarded as the dominant mode of REEs in coal (Seredin and Dai, 2012; Hower et al., 2016; Finkelman et al., 2018). For instance, it was concluded that rare earth phosphates such as monazite and crandallite group minerals are the primary REE-bearing minerals in two US coals (Ji et al., 2022). This finding has been corroborated by microscopic techniques such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

On the other hand, previous studies have reported that a certain proportion of REEs may have an association with aluminosilicate minerals (e.g., clay) in coal. By statistical analysis, Bryan et al. (2015) found that the total REE contents are positively related to Al content based on the USGS CoalQual Database, suggesting the associations of REEs with clays, especially for kaolinite. In the Permian coals collected from Huaibei Coalfield, China, Zheng et al. (2007) also concluded that REEs are likely to associate with clay minerals since REE contents are positively related to those of lithophile elements such as Si, Al, Ti, Fe, and Na. Zhang et al. (2018) investigated the association characteristic of REEs in Fire Clay seam coal middlings by sequentially performing several stages of grinding and froth flotation tests. The results also revealed that REEs tend to associate with micro-dispersed kaolinite, and they may be dispersed REMs and/or ion-adsorbed REEs. In addition to coal-based clays, Alfaro et al. (2018) studied the geochemical background of REEs in several Guba soils, and the Pearson regression results suggested that the REE contents were controlled by phosphates and aluminosilicates. These clay-associated REEs may be adsorbed on the surface of kaolinite as ions and/or deposited as secondary rare earth phosphate minerals.

The similar REE host minerals (e.g., kaolinite) between IACs and coal-based clays may reveal a possibility that coal-derived clays also contain a portion of REEs in the form of rare earth phosphate deposited on the surface of clays. Those surface-adsorbed rare earth phosphates may be partially responsible for the poor ion-exchange leaching efficiency of REEs in coal-derived clays. However, the speciation and leachability of those REEs have not been elucidated due to that their concentrations are lower than the spatial resolution of microscopical characterization techniques such as SEM-EDS (<0.1 wt.%), which renders them hard to be directly observed. Fortunately, previous studies have shown that synthesized rare earth IACs, serving as an ideal model, can be a solution. For instance, Feng et al. (2021) synthesized a set

of artificial clay samples doped with five REEs (~400 ppm for each) at various pH. The speciation of the adsorbed REEs was determined by X-ray photoelectron spectroscopy (XPS). This study confirmed the feasibility of using artificial clay samples to study the occurrence of REEs in coal-derived clays with low REE grades.

In this study, it is hypothesized that phosphate can passivate the ion-adsorbed REEs on the surface of clays, i.e., immobilizing those ion-exchangeable REEs. This hypothesis was verified by preparing a series of artificial IAC samples with varying phosphate concentrations to imitate the passivation effect that occurred in nature. XPS characterization was used to probe the speciation of the REEs and phosphate. Additionally, various leaching tests were performed to activate those phosphate-passivated REEs. Findings from this study can provide a fundamental understanding of the mode of REEs in nature.

5.2 Experimental

5.2.1 Materials and Reagents

A non-ion-exchangeable kaolinite concentrate (TREE content: 282.3 ppm; particle size: <6 μm) collected from a Georgia kaolinite company (USA) was used as an adsorbent for the synthesis of artificial clays. The fraction of the intrinsic ion-exchangeable REEs was only determined to be 3.16% by the ammonium sulfate leaching test as will be described in Section 5.2.3.1. The crude kaolinite undergoes blunging, floatation, magnetic separation, bleaching, and spray drying before it becomes a final concentrate. Hydroxyapatite powder (<5 μm) and fluorapatite (~0.1 μm) were purchased from Fisher Scientific. Other chemicals, including three rare earth chlorides (i.e., LaCl_3 , NdCl_3 , and DyCl_3), ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$), sodium hydroxide (NaOH), ethylenediaminetetraacetic acid disodium (Na_2EDTA), and sodium phosphate (Na_3PO_4) in reagent grade were also obtained from Fisher Scientific. Hydrochloric acid (HCl) and nitric acid (HNO_3) were of trace-metal grade. Deionized water was used for all the solution preparation and leaching tests.

5.2.2 Synthesis of REE and/or Phosphate-doped IACs

To mimic the formation of the P-passivated IACs, two light REEs (La and Nd) and one heavy REE (Dy) were selected to represent all the REEs. A REE stock solution containing LaCl_3 (3.10 μM), NdCl_3 (2.73 μM), and DyCl_3 (2.10 μM) was prepared for the REE doping tests (400 ppm for each REE). The leachate of hydroxyapatite by 0.1 M HCl at room temperature was used as a P stock solution to simulate the subsequent passivation effect. This is mainly because it only contained a negligible amount of REEs relative to fluorapatite, and thus it did not introduce extra REEs during the P doping. The procedure for the preparation of the HCl leachate of hydroxyapatite will be described in Section 5.2.3.3. The leachate was further diluted into three different concentrations, i.e., 8.7, 10.1, and 11.5 μM (calculated by H_2PO_4^-), to prepare the clay samples with varying passivation effects. Since the weathering of granite normally occurs under acidic pH (Xu et al., 2017), along with the fact that the pH of the coal swaps in the eastern US is in the range of 4–6 (Renton et al., 1979), the synthesis was all performed at pH 4 in this study. A stock solution of 11.5 μM Na_3PO_4 was also used as a source of P to prepare the REE-P-kaolinite sample, which can serve as a reference for the speciation determination of the artificial IACs doped with apatite-derived P. The doping of REEs and P was performed in two consecutive steps since REE^{3+} ions can precipitate with phosphate immediately and deplete the REEs from the stock solution, which affects the amount of REEs adsorbed on the surface of kaolinite.

Before synthesis, the surface of the kaolinite sample was cleaned by pretreating it at pH 12 for 1 h at room temperature. The solid/liquid ratio was maintained at 1:5. After the cleaning step, the resulting slurry was centrifuged for solid and liquid separation and washed with deionized water. Then the centrifuge residue was dried in an oven at 60 $^\circ\text{C}$ overnight. In each doping experiment, a 10 g kaolinite sample was mixed with 50 mL of the REE stock solution in a 150 mL disposable polypropylene beaker, and the resulting

slurry was stirred by means of a magnetic stirrer at room temperature in an open-air system (Feng et al., 2021). The target pH (i.e., 4) was adjusted by 0.5 M HCl and NaOH. After agitating for 1 h, the mixture was centrifuged for water removal, and the residue was washed with deionized water three times to remove the residual REEs. The REE-doped samples were then subjected to the phosphate doping step. The three apatite-derived phosphate stock solutions with varying concentrations were mixed with the REE-doped clay samples, respectively, following the same procedure used in the REE-doping step. Lastly, each residue was dried in an oven at 60 °C. The REE assays of the artificial clay samples were analyzed by ICP-MS after being fused with lithium metaborate at 1,000 °C for 15 min. The REE assays of the feed and artificial clay samples are shown in Table 5.1.

5.2.3 Leaching Tests

5.2.3.1 NaOH Pretreatment and Ammonium Sulfate Leaching

Ammonium sulfate leaching tests were conducted on the artificial kaolinite samples with and without NaOH pretreatment, respectively. Ammonium sulfate leaching without NaOH pretreatment was used to evaluate the ion exchangeability of the synthesized IACs, while NaOH pretreatment was performed to activate the phosphate-passivated REEs in the artificial kaolinite samples. The pretreatment was conducted by mixing 0.5 g of the sample with 20 mL NaOH solutions (2, 5, and 10% w/v) in a 50 mL alkali-resistant polytetrafluoroethylene (PTFE). A known amount of EDTA solid was added to create a set of NaOH solutions with 0.1 M EDTA. The beaker sealed by paraffin film was then placed on a magnetic

Table 5.1 REE concentrations in the feed, NaOH-cleaned, and synthesized kaolinite samples (in ppm).

Sample	(La+Nd+Dy)/P	TREE	P	Sc	Y	La	Ce	Pr	Nd	Sm
Feed	0.09	282.3	634.2	58.4	10.1	42.9	97.4	10.2	40.9	7.6
NaOH-cleaned	0.09	309.4	617.1	100.5	9.6	41.5	81.9	10.2	40.8	7.9
Only REE-doped	0.94	1322.8	799.8	55.1	7.0	431.6	66.1	7.6	394.6	6.9
REE-P-doped	0.84	1229.3	826.4	55.2	6.6	398.4	64.2	7.1	365.9	6.4
	0.76	1289.7	962.5	56.7	6.8	417.3	64.8	7.5	384.9	6.8
	0.70	1340.9	1088.3	56.9	7.7	432.2	72.9	8.4	400.3	7.0
Sample	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
Feed	1.5	6.6	0.9	3.7	0.5	1.1	0.1	0.5	0.0	
NaOH-cleaned	1.7	7.7	1.0	4.3	0.4	1.1	0.1	0.7	0.1	
Only REE-doped	1.5	6.7	1.6	340.9	0.4	2.1	0.1	0.6	0.1	
REE-P-doped	1.3	6.4	1.5	313	0.4	2.1	0.1	0.6	0.1	
	1.4	6.4	1.6	332.2	0.4	2.1	0.1	0.5	0.1	
	1.5	7.1	1.6	341.8	0.4	2.2	0.1	0.7	0.1	

Note: Three REEs (La, Nd, and Dy) and P were the doped elements. The ratio of (La+Nd+Dy)/P is in molar ratio.

hotplate stirrer to maintain the pretreatment temperature at 60 °C ($\pm 1^\circ\text{C}$) for 1 h. A temperature probe connected to the hotplate was used to monitor the temperature of the resulting sample suspension. After pretreatment, the treated slurry was transferred into a 50 mL centrifuge tube and centrifuged at 5,000 rpm for 10 min for solid-liquid separation. The supernatant was saved for further analysis, while the centrifuge residue was then rinsed by re-pulping it with deionized water to remove the residual NaOH.

In each ammonium sulfate leaching test, 0.5 g of the pretreated or non-pretreated artificial clay sample was mixed with 20 mL of 0.5 M ammonium sulfate solutions in a 50 mL disposable polypropylene beaker. The leaching solution was magnetically agitated for 1 h at room temperature. Aliquots of 0.5 M HCl and NaOH were added to maintain the leaching pH at 4.0 ± 0.05 during the leaching process. To examine the leaching kinetics, 0.3 mL of the liquid samples were withdrawn at different intervals by a 1 mL disposable syringe. Each liquid sample was immediately filtered by a syringe filter with a pore size of 0.22 μm . Subsequently, the filtrate was diluted 100 times with a mixed HNO_3 (2.5%) and HCl (0.5%) solution for ICP-MS analysis. The REE assays were utilized to determine the recovery (R) according to the following equation,

$$R = 100 \times \frac{C_l V}{C_f M} \quad (5.1)$$

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 average results being reported.

5.2.3.2 Direct EDTA Leaching

A batch of direct EDTA leaching tests at different temperatures (25, 40, and 60 °C) was performed on a Soxhlet extraction apparatus to activate the REEs on the synthesized kaolinite sample with the ratio of $(\text{La}+\text{Nd}+\text{Dy})/\text{P} = 0.70$. Once the EDTA solution (0.1 M, 40 mL) was preheated to the desired temperature and adjusted to the target pH (10 ± 0.1), a 1.0 g of the artificial clay sample was immediately added to the reactor. After reacting for 1 h, the slurry was collected and centrifuged. The supernatant was diluted 100 times for ICP-MS, and the REE recovery was computed by Eq. (5.1).

5.2.3.3 Acid Leaching of Apatite Samples

Two apatite samples, i.e., hydroxyapatite and fluorapatite, were leached by 0.1 M HCl at room temperature to obtain the leachate for the P-doping. In a leaching test, 0.5 g apatite solid was mixed with 40 mL of the HCl in a 50 mL disposable polypropylene beaker. The rest of the leaching procedure was the same as the ammonium sulfate leaching described in Section 5.2.3.1. The elemental compositions of the apatite samples were not determined since there is no need to calculate leaching recovery. Only the concentrations of Ca, P, and REEs in the leachates were analyzed by ICP-MS to prepare apatite-derived P stock solutions.

5.2.4 Sample Characterization

5.2.4.1 Powder X-ray Diffraction Analysis

The kaolinite samples before and after synthesis were characterized by XRD to investigate the mineralogical changes. The analyses were conducted on a Bruker D8 instrument with a Cu X-ray source. XRD patterns were acquired over a 2θ range of $5-70^\circ$ with a step time of 0.02° . MDI Jade 6 software was used to index the XRD spectra.

5.2.4.2 X-ray Photoelectron Spectra Analysis

To probe the REE speciation, the artificial clay samples doped with REEs and/or phosphate and a leaching residue were subjected to XPS analysis. A Thermo Scientific K-Alpha X-ray Photoelectron

Spectrometer (XPS) equipped with a monochromatic Al-K α X-ray source (1486.6 eV) was applied to collect a series of XPS spectra over a 400 $\mu\text{m} \times 400 \mu\text{m}$ area. The energy scale was corrected by the adventitious carbon peak at 284.8 eV.

5.3 Results and Discussion

5.3.1 Leaching Behavior of Apatite Samples

Figure 5.1 shows the leaching behaviors of the major constitutive elements (i.e., Ca, P, and TREE) of two apatite samples by 0.1 M HCl at room temperature. The molar concentration (in mM) of TREE was calculated by the atomic mass of Ce. As shown in Figure 5.1a, the concentration of TREE from the hydroxyapatite was negligible, suggesting that nearly no extra REEs will be introduced to the synthesized clay samples via the P stock solutions during the P-doping step. This helps precisely control the amount of REEs adsorbed on the synthesized clay samples. Since apatite is acid-soluble, the leaching rates of Ca and P were rapid. The final concentrations of P and Ca in the HCl leachate reached 40.0 and 8.2 mM,

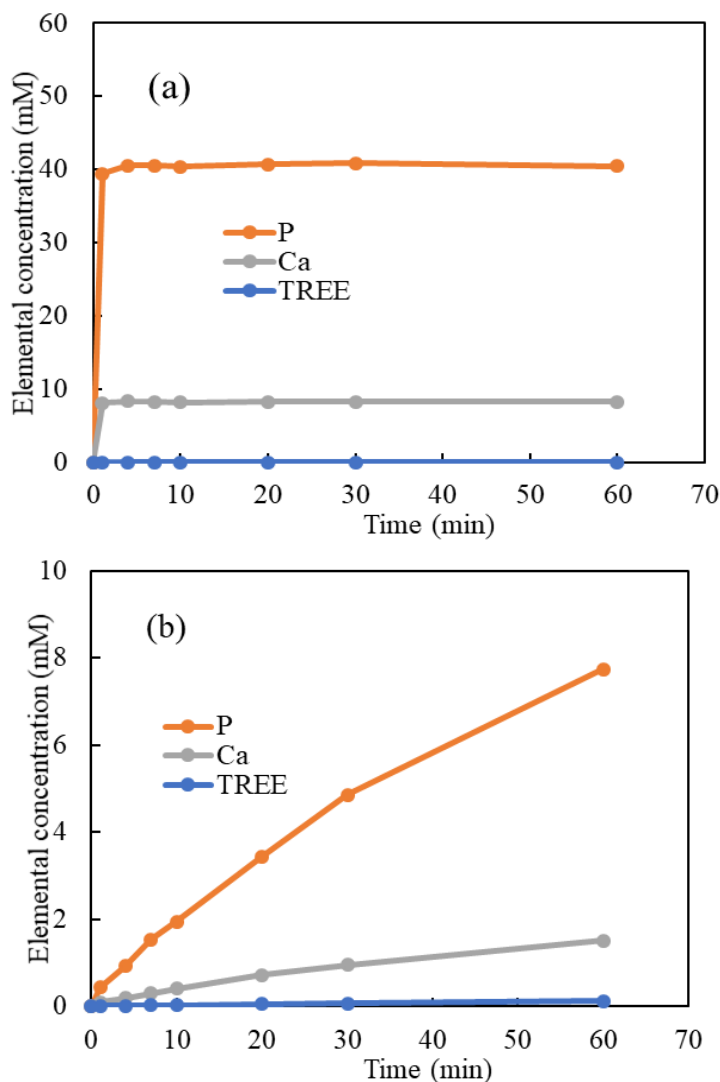


Figure 5.1 Leaching characteristics of TREE, P, and Ca from (a) hydroxyapatite and (b) fluorapatite by 0.1 M HCl at room temperature for 1 h.

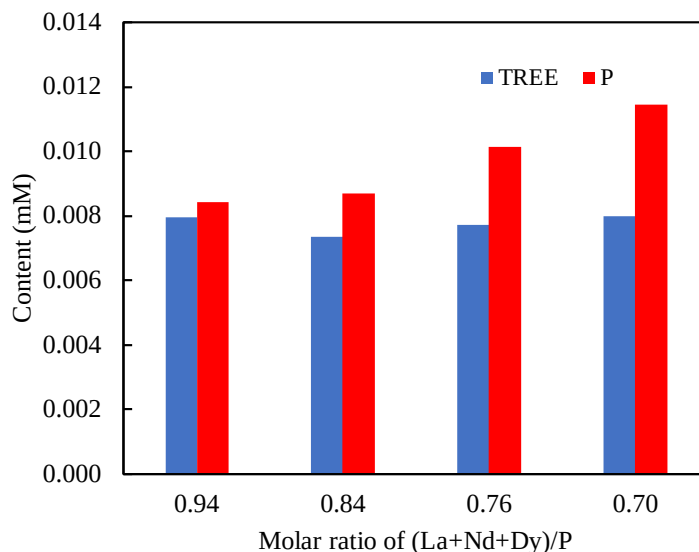


Figure 5.2 TREE and phosphate contents in the synthesized kaolinite samples as a function of the molar ratio of (La+Nd+Dy)/P. (Note: phosphate content was calculated in H_2PO_4^-)

respectively, which were higher than the highest P concentration required for synthesizing the artificial clays. However, a distinct leaching characteristic was found for the fluorapatite (Figure 5.1b). The REE concentration in the leachate was 0.12 mM, which was why hydroxyapatite was more suitable than fluorapatite to be a P-source in this study. The TREE and P contents of the synthesized samples as a function of the ratio of (La+Nd+Dy)/P are shown in Figure 5.2. The sample with the ratio of (La+Nd+Dy)/P = 0.94 was the kaolinite sample doped only by the REEs. It shows that a series of artificial IACs samples with varying P contents were prepared.

5.3.2 Effect of Phosphate Content on the Ion-exchange Leaching Efficiency

In this section, a series of ion-exchange leaching tests using ammonium sulfate as a lixiviant was conducted on the synthesized clay samples at room temperature. To avoid interference from the intrinsic ion-exchangeable REEs in the kaolinite before synthesis, the TREE recoveries and the individual REE (La, Nd, and Dy) recoveries shown in Figure 5.3a and later in this study were all calibrated by subtracting them. For the REE-kaolinite sample (i.e., the ratio = 0.94), the final TREE recovery reached 72.8%. The decreasing trend of the leaching recovery (from 85.9% to 72.8%) as a function of time may be attributed to the lanthanide hydrolysis or the reprecipitation as rare earth hydroxides (Moldoveanu and Papangelakis, 2013), which can be formed due to the elevation of localized pH of the leaching solution (Yang et al., 2020). On the other hand, phosphate ions released from the phosphate-bearing minerals in the kaolinite sample may also deplete REEs from the leachate, resulting in the formation of the decreasing trend. As also shown, the final TREE recovery gradually decreased with the increasing amount of P doped. When the ratio was reduced to 0.84, the recovery decreased to 58.8%. This value was further reduced to only 29.9% when the ratio was 0.70. Like the REE-kaolinite sample, rapid leaching rates of REEs were also observed for other tests. However, the decreasing trend of the leaching curve gradually disappeared with the decrease of the (La+Nd+Dy)/P ratio.

The individual REE recoveries of La, Nd, and Dy were also compared as a function of the molar ratio of (La+Nd+Dy)/P. As shown in Figure 5.3b, a decreasing trend of the recovery was found for each REE with the reduction of the (La+Nd+Dy)/P ratio, which was consistent with the TREE recovery. In each test, the order of the REE recovery from large to small was: La > Nd > Dy. For instance, the REE recoveries were 82.0%, 80.2%, and 71.6%, respectively when the ratio was 0.94. This trend may be explained by the

lanthanide contraction effect (Moldoveanu and Papangelakis, 2012). With the increase of atomic number, the ionic radius of REE^{3+} gradually decreases, which enables HREEs to be more strongly adsorbed on the negatively charged basal surface of kaolinite due to the increased charge density. As such, HREEs are more difficult to desorb relative to LREEs.

The model for the REEs in IACs proposed by Borst et al. (2020) indicates that REEs adsorb onto the surface of clays with 8-9 coordinated water molecules, which are readily leachable. The leaching mechanism of the IACs mined in South China by ammonium sulfate is normally written as follows,



which reveals that one mole of Ln^{3+} ions can be replaced by three moles of NH_4^+ ions. However, previous results in this study suggested that the ion exchangeability was impaired after doping with phosphate, and

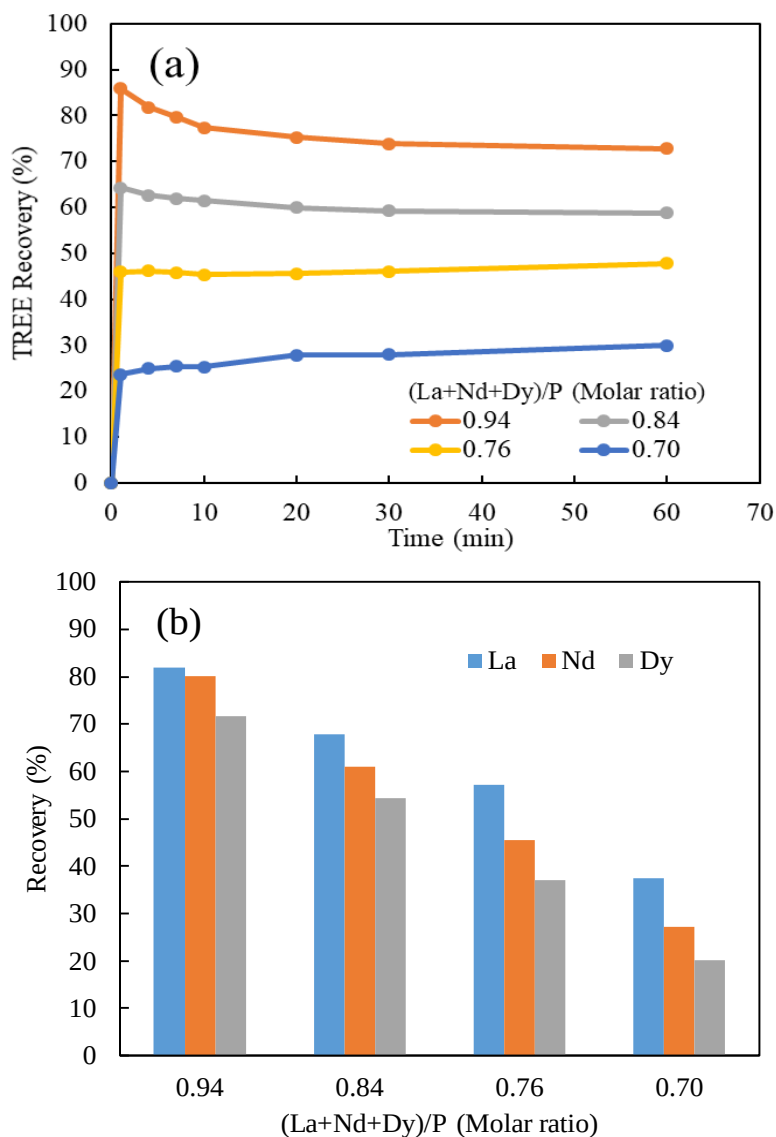


Figure 5.3 TREE recovery (a) and individual REE recovery (b) in the leaching of the synthesized kaolinite samples by 0.5 M ammonium sulfate at pH 4 and room temperature for 1 h.

the recovery was highly dependent on the amount of phosphate adsorbed on the surface of IACs. It is mainly due to that the presence of phosphate may chemically interact with the adsorbed REEs by favoring the formation of “clay-RE-PO₄” species due to the strong affinity between phosphate and REEs, which will be confirmed by the XPS study shown in later this study. This finding corroborated the hypothesis regarding the passivation effect of phosphate on the REEs in IACs in this study. Even for the IACs found in South China, it was found that the fraction of ion-adsorbed REEs is sample-dependent (ranging from 60 to 90%) due to the existence of different REE-host minerals in the parent rock and their varying resistance to the rock weathering (Sanematsu et al., 2016). In the granites, the higher the fraction of weathering-resistant REMs such as monazite and zircon, the lower the fraction of ion-adsorbed REEs in the weathered regolith. Besides the REMs, the phosphate-passivated REEs may also be another reason for the poor ion exchangeability of some IACs. Only ammonium sulfate leaching conducted at pH 4 could not desorb those phosphate-passivated REEs, i.e., surface-deposited REPO₄ species.

The passivation effect may also be partially responsible for the poor ion-exchange leaching efficiency of REEs associated with coal-derived clays. Only one coal-based clay sample collected from the Upper Kittanning Bed had distinctively high fractions (70-90%) of ion-exchangeable REEs (Rozelle et al.,

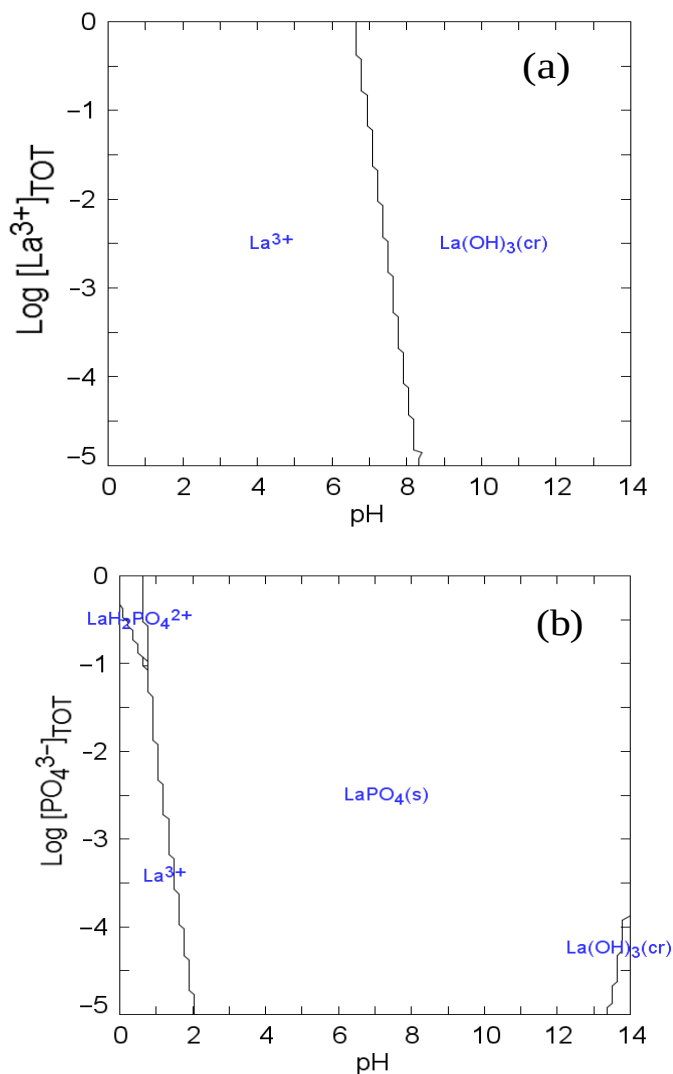


Figure 5.4 Stability diagrams for La in the systems of (a) La³⁺-H₂O and (b) La³⁺-PO₄³⁻-H₂O system (b) at 25 °C, condition: [La³⁺] = [PO₄³⁻] = 10⁻⁵ M.

2016), which were comparable to the IACs in South China. However, direct ammonium sulfate leaching at acidic pH usually recovered negligible fractions of REEs (<2%) for most US coal-derived clays that have been tested so far. Essentially, coal-derived clays may be assumed as poorly weathered IAC to some extent, given their similarity in the dominant mineral (i.e., clays). Accordingly, except for the rare earth phosphate minerals, the proposed phosphate passivation mechanism may also be a potential reason to explain the poor ion exchangeability of the REEs in the US coal-derived clays.

5.3.3 REE Speciation of the Synthesized Kaolinite Samples

5.3.3.1 Thermodynamic Simulation Results

The stability diagrams of La in the La-H₂O and La-PO₄-H₂O systems were constructed in the present study by Medusa software and its Hydra database (Puigdomenech et al., 2013) to gain insights into the possible interactions between REEs with phosphate on the surface of kaolinite. The concentration of La³⁺ ion was set as 10⁻⁵ M, which was the approximate concentration estimated based on the La content in the artificial kaolinite sample. The stability diagram of the La³⁺ ions in the La-H₂O system is shown in Figure 5.4a, which explains how the Ln³⁺ ions are extracted by NH₄⁺ ions via an ion-exchange mechanism. At acidic and near-neutral pH, lanthanum exists as La³⁺ ions. As the pH increases, La(OH)₃(s) is formed. The critical pH, at which the free La³⁺ ion transforms into La(OH)₃, decreases with the increase of La³⁺ ion concentration. This finding is consistent with how REE ions adsorb on clay surfaces. The dominant species of REEs is “clay-REE” or “clay-REE (H₂O)_n” at acidic and near-neutral pH (Papangelakis et al., 2014; Borst et al., 2020). In this case, REEs can be readily displaced at acidic pH using monovalent cations like NH₄⁺ as a lixiviant. In neutral and alkaline pH, REEs occur as “clay-O-REE²⁺” species by complexing with the amphoteric surface hydroxyl groups, making it difficult to be extracted by the ion-exchange mechanism. Therefore, REEs are extracted from IACs at acidic pH values.

The stability diagram changes drastically in the presence of PO₄³⁻ ion as shown in Figure 5.4b. Even with the presence of 10⁻⁵ M PO₄³⁻ ions, free La³⁺ ions exist only at pH < 2.0, suggesting that REE ions can be preferentially extracted by acid leaching, which may explain why only 29.9% of TREE were extracted from the synthesized clay sample with the ratio of (La+Nd+Dy)/P being 0.70. Note also that as the PO₄³⁻

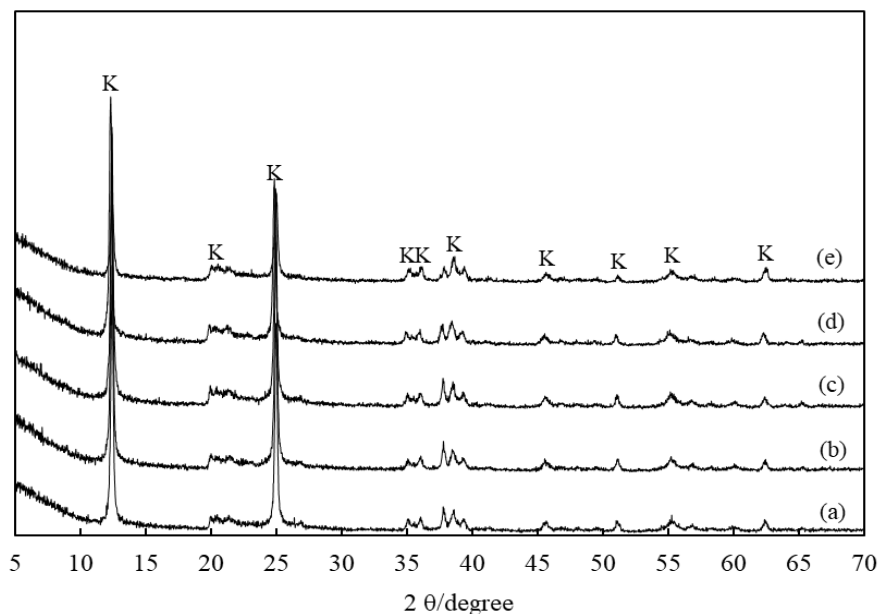


Figure 5.5 XRD patterns of (a) the blank kaolinite and artificial kaolinite samples with the molar ratio of (La+Nd+Dy)/P being (b) 0.94; (c) 0.84; (d) 0.76; (e) 0.70.

ion concentration increases, the region of free La^{3+} ions disappears almost completely, suggesting that most of the REEs on the surface of kaolinite probably exist as REPO_4 (e.g., $\text{LaH}_2\text{PO}_4^{2+}$). In this work, the HCl leachate of hydroxyapatite was used as a source of P to simulate the weathering process of apatite. Attia et al. (1988) investigated the equilibrium composition of hydroxyapatite and fluorapatite in water and constructed the solubility diagram for hydroxyapatite as a function of pH (2-12) at 25 °C. The solubility diagram shows that H_2PO_4^- is the dominant species from pH 3 to 7. Given this finding, it might be the formation of $\text{LnPO}_4(\text{s})$ (e.g., $\text{LaH}_2\text{PO}_4^{2+}$) on the surface clays that deteriorated the ion-exchange leaching efficiency of ammonium sulfate in this study. This assertion will be further supported by the XRD and XPS characterization results shown in the next section.

5.3.3.2 XRD and XPS Analysis

Initially, the mineralogical changes of the kaolinite samples before and after REE and/or phosphate doping were studied by XRD. Figure 5.5 shows the XRD patterns of the blank kaolinite (i.e., the feed sample without any doping) and the four artificial clay samples. As presented, kaolinite was the dominant species for all the blank kaolinite and those synthesized samples. The finding suggested that the adsorption of REEs and/or phosphate did not alter the crystal structure of kaolinite. The adsorption mainly occurred on the surface of kaolinite (Feng et al., 2021). The only impure mineral in the kaolinite sample was illite, with a small peak being noticed at $2\theta = 36^\circ$. As suggested by Feng et al. (2021), the presence of illite in the kaolinite sample does not influence the adsorption process since this mineral is also an ideal absorbent for REEs.

XPS characterization was employed to determine the speciation of REEs and P on the artificially prepared IACs. Figure 5.6 shows the $3d_{5/2}$ region of La and P_{2p} region of P of the clay samples. In the blank kaolinite sample, the signals of La $3d_{5/2}$ and P_{2p} were not detected due to their extremely low concentrations. After being doped with REEs, the XPS spectra of La $3d_{5/2}$ appeared, with photoemission and satellite peaks at 836.3 and 839.7 eV, respectively. Unlike La, the P_{2p} signal was still undetected. This comparison suggested that La adsorbed on the surface of kaolinite. Once the REE-doped clay was subsequently treated by the HCl leachate of hydroxyapatite, both the La $3d_{5/2}$ and P_{2p} signals were detected, suggesting that REEs and P were adsorbed onto the kaolinite surface. The La $3d_{5/2}$ feature exhibited a similar multiplet splitting to the REE-doped sample. In addition to the P source derived from apatite, pure Na_3PO_4 was also used to

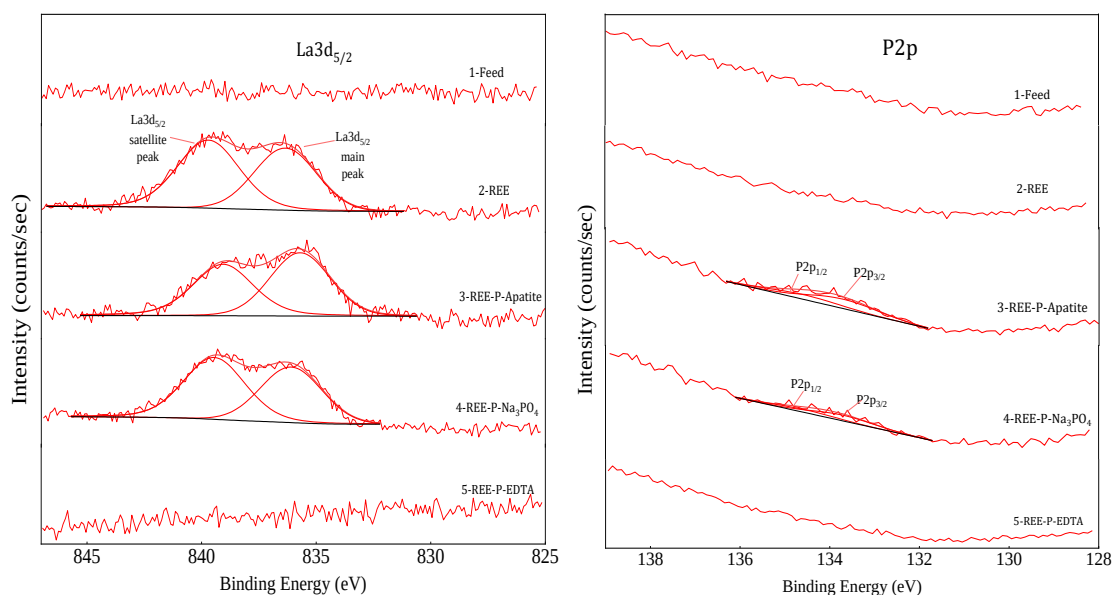


Figure 5.6 XPS spectra of $\text{La}3d_{5/2}$ and P_{2p} of the feed and artificial kaolinite samples.

treat the REE-doped kaolinite as a reference. As shown, the La $3d_{5/2}$ and P_{2p} features are very close to the ones treated by apatite-derived P. Their photoemission peaks were at around 836.0 and 133.7 eV, respectively, and the magnitudes of multiplet splitting (i.e., ΔE) were all 3.4 eV.

To further confirm the REE speciation, the La $3d_{5/2}$ feature characteristic values of the artificial kaolinite samples and several standard La compounds are compared in Table 5.2. Among the standard lanthanum compounds, it can be found that the photoemission peaks of La (835.3 eV) and P (133 eV) from LaPO_4 matched those artificial clay samples to a greater extent than others. The multiplet splitting (3.3 eV) of the REE-P-treated samples was also close to that of standard LaPO_4 (3.4 eV). Such characteristics confirmed the previous hypothesis that the speciation of the REE and P adsorbed on the surface of kaolinite is mainly in the form of $\text{LaPO}_4(\text{s})$. Accordingly, the proposed mechanism for the formation of the passivation layer may be written as Eq. (5.3), showing that $\text{LaPO}_4(\text{s})$ adsorbs on the surface of kaolinite. It should be noticed that the one treated by apatite-derived P had a smaller satellite: main ratio (0.81) compared to that of Na_3PO_4 -treated one (1.11). This difference may be because various species of LaPO_4 (such as LaPO_4 , LaHPO_4^+ , and $\text{LaH}_2\text{PO}_4^{2+}$) were formed. However, it was difficult to determine the specific forms of LaPO_4 by XPS due to their minor differences in the chemical environments (Feng et al., 2021).



Also shown in Figure 5.6 are the XPS spectra of the leaching residue of the REE-P-adsorbed sample after being leached by 0.1 M EDTA at pH 10. It shows that both the La $3d_{5/2}$ and P_{2p} signals disappeared since the REEs and P adsorbed on the surface of kaolinite were removed after the EDTA leaching. This finding agreed with the high TREE recovery obtained by the EDTA leaching, which will be further described later in this study.

Table 5.2 $\text{La}3d_{5/2}$ characteristic values for REE and/or phosphate-doped kaolinite samples at pH 4 and several standard La compounds.

Sample	La $3d_{5/2}$ BE (eV)		ΔE (eV)	satellite:main ratio	P $2p_{3/2}$ BE (eV)
	main	satellite			
1-Feed	-	-	-	-	-
2-REE	836.3	839.7	3.4	1.1	-
3-REE-P- Apatite	835.7	839.1	3.4	0.81	133.7
4-REE-P- Na_3PO_4	836.1	839.5	3.4	1.11	133.7
5-REE-P- EDTA	-	-	-	-	-
$\text{La}(\text{OH})_3$	834.7	838.4	3.7	0.71	-
La_2O_3	834.1	838.6	4.5	0.77	-
$\text{La}_2(\text{CO}_3)_3$	834.5	838.1	3.6	1.01	-
LaCl_3	835.6	839.1	3.5	1.43	-
LaPO_4	835.3	838.6	3.3	0.71	133

According to the thermodynamic simulation and XPS characterization results, the proposed passivation mechanism of phosphate on the ion-adsorbed REEs is shown in Figure 5.7. It is commonly acknowledged that the basal surface of kaolinite is negatively charged due to the isomorphous substitution of Si^{4+} and Al^{3+} by cations with lower valency. The negatively charged basal surface serves as a driving force for the adsorption of REE^{3+} ions via electrostatic attraction at pH 4. Those physically adsorbed REEs can be easily desorbed by ammonium sulfate leaching. However, the subsequently introduced phosphate at pH 4 undermines the ion exchangeability of the ion-adsorbed REEs doped on kaolinite (i.e., the IAC) caused by the formation of “clay-RE- PO_4 ” complexes. The passivation layer should mainly occur on the basal surface of clay instead of the edge surface since the latter one is positively charged, which inhibits the adsorption of REEs due to electrostatic repulsion.

5.3.4 Activation of the P-passivated IACs

The results presented in the preceding sections have shown that phosphate adsorption can passivate the REEs adsorbed on the surface of kaolinite, thus poorly responding to ion-exchange leaching. The passivation layer (i.e., LnPO_4) formed on the kaolinite surface may be comparable to the nanoparticles of secondary phosphate deposited on the surface of clays during the weathering process. Two different activation methods were applied in this section to activate the passivation layer.

5.3.4.1 EDTA Leaching of the Synthesized IACs

In this section, a set of direct EDTA leaching tests was performed to activate the P-passivated REEs on the synthesized clays. EDTA has been widely used to chelate metal ions by virtue of its unique complexing ability, which is ascribed to its high density of ligands. The coordination typically occurs through its two amine and four carboxylate groups. It showed promising potential for the dissolution of phosphate rock (Paschalidou et al., 2019; Argotte-Ibarra et al., 2022). EDTA normally complexes with nearly all the metal ions with a valence larger than one, and the resulting water-soluble complexes are stable over a wide pH range (West, 1969; Lazo et al., 2018).

To determine the impact of phosphate amount on the EDTA leaching, the stability diagram of La in the $\text{La-PO}_4\text{-EDTA-H}_2\text{O}$ system as a function of pH at 25 °C was also constructed by the Medusa software and its Hydra database (Puigdomenech et al., 2013). The concentration of La^{3+} was still fixed at 10^{-5} M, while the phosphate concentration was altered to investigate its influence on the speciation of La. As shown in Figure 5.8(a), when $[\text{La}^{3+}] = [\text{PO}_4^{3-}] = 10^{-5}$ M, the free La^{3+} ion is the dominant species of lanthanum as

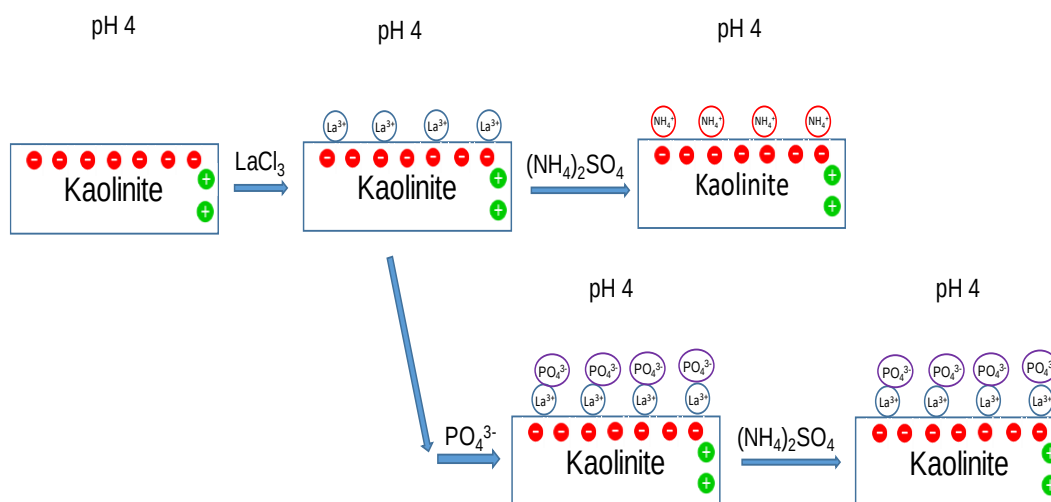


Figure 5.7 Proposed mechanism for the phosphate-passivated REEs in the synthesized IACs phosphate and the involved leaching process.

the pH is less than 2.0. The critical EDTA concentration, at which $\text{LaPO}_4(\text{s})$ converts to LaEDTA^- , gradually increases with the pH. When EDTA concentration is less than the critical value, the transformation of $\text{LaPO}_4(\text{s})$ to $\text{La}(\text{OH})_3(\text{s})$ mainly occurs at alkaline pH (above pH 13). In contrast, above the critical concentration (i.e., $[\text{EDTA}] > 10^{-3.5} \text{ M}$), $\text{LaPO}_4(\text{s})$ can be dissolved and form a soluble complex (LaEDTA^-) as pH ranges from 2.5 to 14.0. It exhibits that EDTA has the potential to decompose $\text{LaPO}_4(\text{s})$. When the $[\text{PO}_4^{3-}]$ is further increased to 5×10^{-5} (Figure 5.8b) and 10^{-4} M (Figure 5.8c), respectively, the region of $\text{LaPO}_4(\text{s})$ gradually expands, especially between pH 2 and 4. It is also accompanied by the elevated critical EDTA concentration required for the formation of LaEDTA^- . These two characteristics indicate that introducing more phosphate renders the leaching process more difficult. This simulation work provides a thermodynamic basis for the EDTA leaching tests in this study.

Based on the simulation work, the pH and EDTA concentrations were selected as 10 and 0.1 M, respectively, which are sufficient to dissolve the $\text{LaPO}_4(\text{s})$. Figure 5.9 shows the leaching results of the REE-P-kaolinite sample with the ratio of $(\text{La}+\text{Nd}+\text{Dy})/\text{P}$ being 0.70 by 0.1 M EDTA at pH 10. Also presented in Figure 5.9 are the ammonium sulfate leaching results conducted on the REE-doped and the REE-P-kaolinite sample ($(\text{La}+\text{Nd}+\text{Dy})/\text{P} = 0.70$), respectively, which can be used as references to evaluate

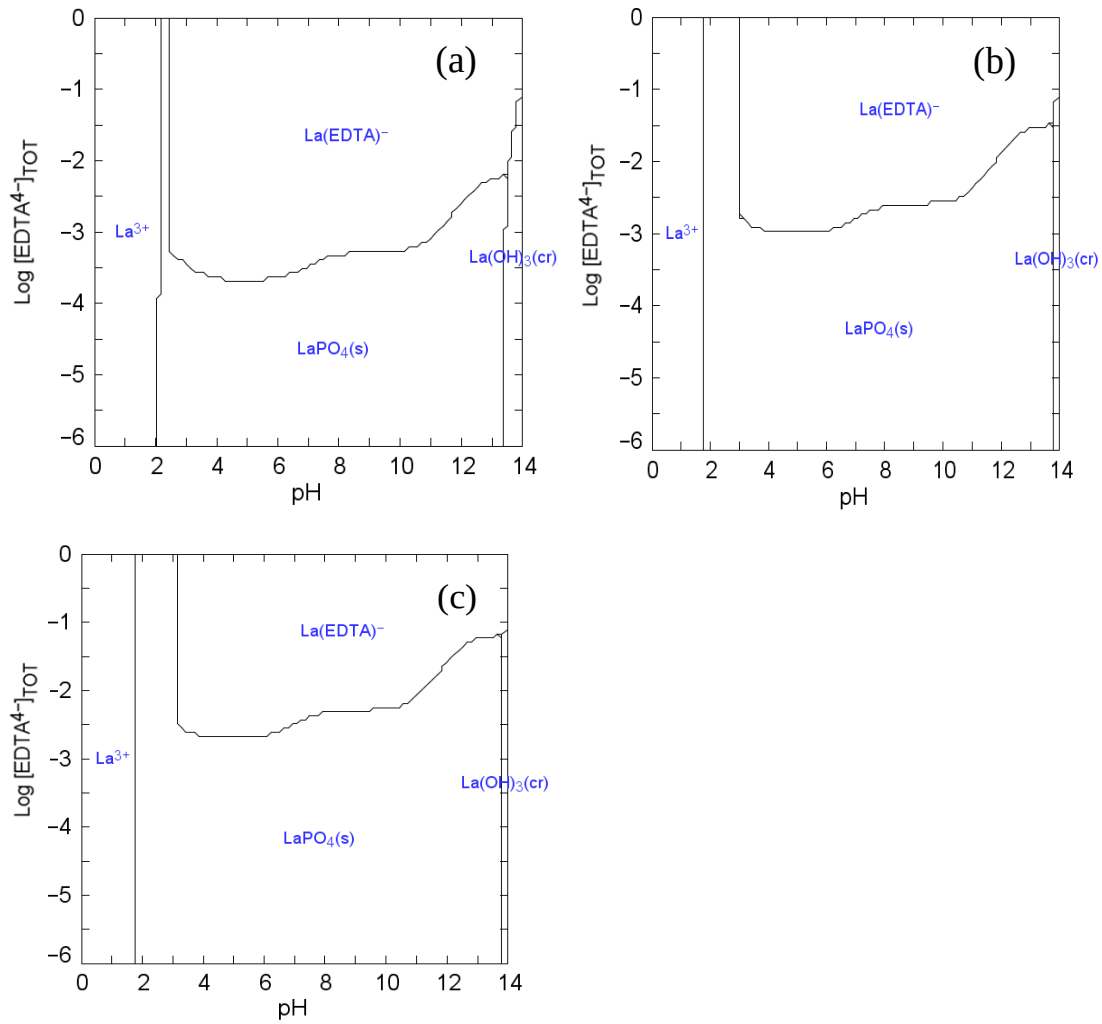


Figure 5.8 Stability diagrams of La in La- PO_4 -EDTA- H_2O system with varying phosphate concentrations at 25 °C. $[\text{La}^{3+}] = 10^{-5} \text{ M}$, $[\text{PO}_4^{3-}] = 10^{-5} \text{ M}$ (a); $[\text{PO}_4^{3-}] = 5 \times 10^{-5} \text{ M}$ (b); $[\text{PO}_4^{3-}] = 10^{-4} \text{ M}$ (c).

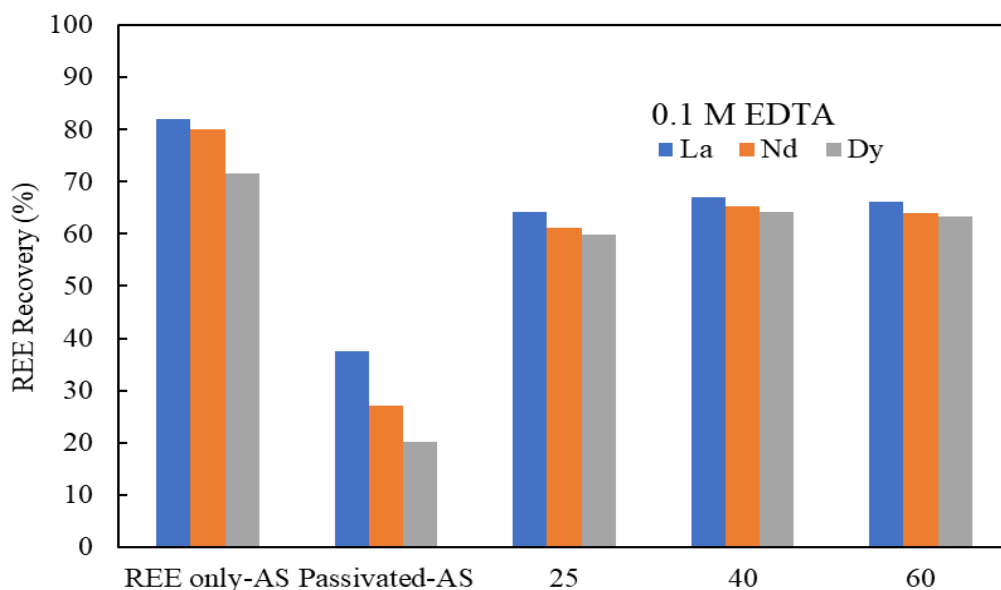


Figure 5.9 Effect of temperature on the REE recovery of the EDTA leaching from the REE-P-kaolinite sample with $(La+Nd+Dy)/P = 0.70$, conditions: 0.1 M EDTA, pH 10, 1 h. “AS” refers to ammonium sulfate.

the performance of the EDTA leaching. Those two tests were labeled as “REE only-AS” and “Passivated-AS” in Figure 5.9, respectively. It shows that leaching temperature had a slight influence on REE recovery in general. A slight improvement in the La recovery (from 64 to 67%) was observed when the leaching temperature increased from 25 to 40 °C. The recoveries of the other two REEs were 2-4 absolute percent points lower than those of La. After that, the recovery remained stable with the further increase of leaching temperature to 60 °C. The recoveries of EDTA leaching were 14-17 absolute percentage points lower than one of the REE-doped kaolinite. It indicated that only relying on the complexing ability of EDTA under the experimental conditions was not sufficient to activate all the passivated REEs.

5.3.4.2 Ammonium Sulfate Leaching after NaOH Pretreatment

Other than direct EDTA leaching, a series of ammonium sulfate leaching after NaOH pretreatment with and without the presence of EDTA was carried out to maximize the TREE recovery. The alkali pretreatment technique performed under aggressive conditions (e.g., high temperature, concentrated NaOH) has been commercially used to decompose high-grade REMs such as monazite and xenotime, which are extremely stable in thermodynamics. After the pretreatment step, acid leaching is usually used to dissolve the resulting rare earth hydroxides. Herein, the pretreatment step was conducted with dilute NaOH solutions to reduce alkali consumption, and the conventional acid leaching was replaced by ammonium sulfate leaching, a standard leaching process applied in the processing of the IACs mined in South China. This leaching method has also been used to extract REEs from NaOH-treated monazite at pH 4 (Liu et al., 2022). Furthermore, EDTA was added in the pretreatment step to evaluate its performance in the dissolution of $REPO_4(s)$ by NaOH solution with relatively higher concentrations (i.e., 2, 5, and 10%).

Figure 5.10a shows the REE recovery of ammonium sulfate leaching as a function of NaOH concentration. Generally, the REE recovery gradually increased as the NaOH concentration varied from 2 to 10%. Except for La (53.9%) by 10% NaOH, the REE recoveries in other cases were all <50.0% in the absence of EDTA. On the other hand, the recovery of Dy gradually increased from 28.5 to 43.5% with the increase in NaOH concentration. Similar to the direct ammonium sulfate leaching (see Figure 5.3b), the order of the individual REE recovery from large to small was: La > Nd > Dy.

After the NaOH pretreatment with the addition of EDTA, the leaching efficiency was significantly improved. With only 2% NaOH, La, Nd, and Dy recoveries reached 72.4%, 70.2%, and 63.1%, respectively. When the NaOH concentration increased to 10%, the recoveries of the three REEs increased to 88.1%, 88.9%, and 76.0%, which were even higher than the recovery of the REE-kaolinite sample leached by ammonium sulfate (see Figure 5.9), indicating that all the surface-deposited REEs may be recovered. Besides that, a fraction of REEs may result from the dissolution of the intrinsic REE-bearing minerals in the blank kaolinite, causing relatively higher recovery.

REEs partitioned into the used-NaOH solution and the ammonium sulfate leachate were also analyzed, with the results being summarized in Table 5.3. As shown, the fraction of REEs reported to the used NaOH solution was negligible in the NaOH pretreatment without EDTA, and nearly all the REEs were reported to ammonium sulfate solutions. This partition was expected since NaOH can convert $\text{REPO}_4(\text{s})$ to its hydroxides after NaOH pretreatment. Feng et al. (2021) found that the dominant REE species in the artificial IAC synthesized at pH =10 is $\text{REE}(\text{OH})_2^+$, which is electrostatically adsorbed on the surface of kaolinite. They can be readily recovered by ammonium sulfate leaching via an ion-exchange leaching

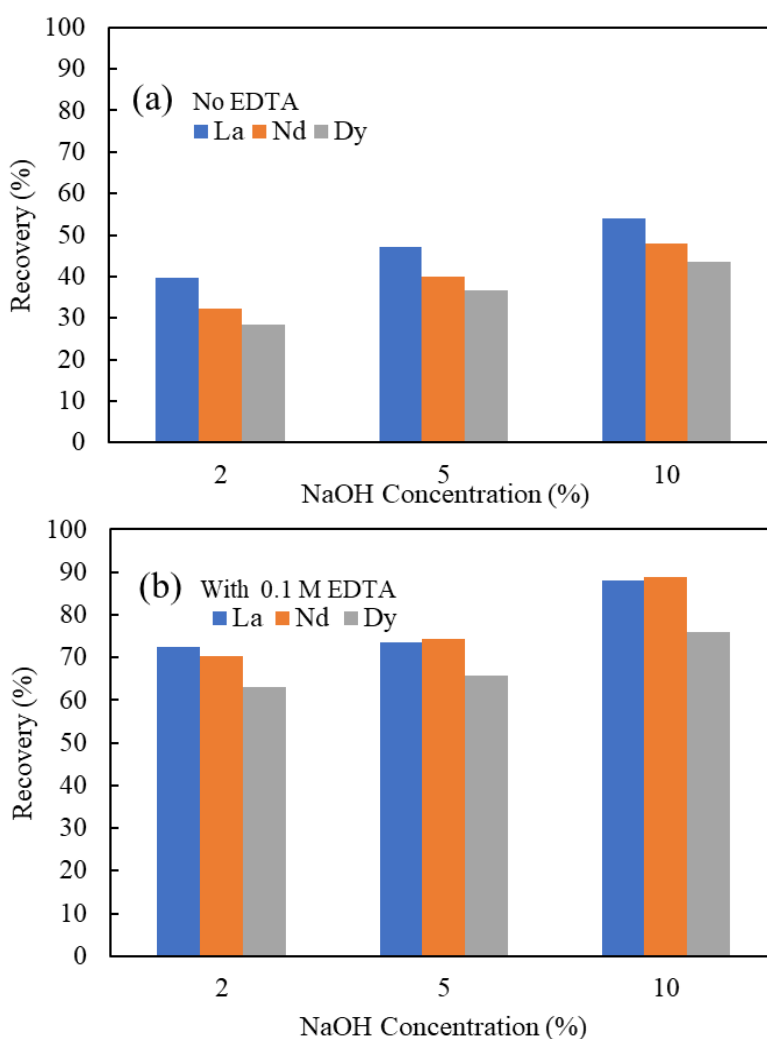


Figure 5.10 Ammonium sulfate leaching of REEs from the REE-P-kaolinite sample with (La+Nd +Dy)/P = 0.70 after NaOH pretreatment in the absence (a) and presence (b) of 0.1 M EDTA. Pretreatment: 2-10% NaOH, 60 °C, 1 h. Leaching: 0.5 M ammonium sulfate, pH 4, room temperature.

Table 5.3 Partition of REE recovery in the NaOH solution and the leachate of ammonium sulfate in the leaching of the REE-P-kaolinite sample (REE/P = 0.70). Pretreatment: 2-10% NaOH, 60 °C, 1 h. leaching: 0.5 M ammonium sulfate (AS), pH 4, room temperature.

NaOH Conc. (%)	REE recovery (%) in NaOH solution					
	Without EDTA			With EDTA		
	2	5	10	2	5	10
La	0.08	0.05	0.10	62.59	69.62	86.87
Nd	0.14	0.15	0.20	54.29	67.52	85.54
Dy	0.20	0.21	0.30	39.11	53.69	67.06
REE recovery (%) in AS solution						
La	39.52	47.15	53.78	9.82	3.92	1.31
Nd	32.22	39.93	47.74	15.93	6.86	3.39
Dy	28.34	36.37	43.24	23.97	12.18	8.98
Total REE recovery in both steps (%)						
La	39.60	47.21	53.88	72.40	73.53	88.18
Nd	32.36	40.08	47.94	70.22	74.38	88.93
Dy	28.54	36.59	43.54	63.08	65.87	76.04

mechanism. Accordingly, after NaOH pretreatment, the phosphate passivation layer, i.e., REPO_4 , was transformed into $\text{RE}(\text{OH})_3(\text{s})$. REE^{3+} ions can be released from $\text{RE}(\text{OH})_3(\text{s})$ at pH 4 and physically adsorb on the surface of kaolinite during the ammonium sulfate leaching step. Subsequently, those REEs were displaced by NH_4^+ ions via an ion exchange mechanism.

However, a contrasting leaching characteristic was noticed with the presence of EDTA. Instead of forming $\text{RE}(\text{OH})_3(\text{s})$, it was found that most of the REEs were partitioned into the NaOH solutions, probably in the form of Ln-EDTA^- , as suggested by the simulation results (see Figure 5.8). Moreover, the fraction of REEs in the NaOH solution increased (e.g., La: from 62 to 87%) as a function of NaOH concentration. Only a small fraction of REEs was extracted by ammonium sulfate. It suggested that Ln-EDTA^- was preferentially formed rather than $\text{RE}(\text{OH})_3(\text{s})$ during the NaOH pretreatment stage. The high REE recoveries suggested that the passivation layer was all removed by the proposed NaOH pretreatment and ammonium sulfate leaching process. In addition, the leaching method proposed in this study may also be used to extract REEs from IACs with low fractions of ion-exchangeable REEs as well as coal-derived clays.

5.4 Summary and Conclusions

In this study, the passivation effect of apatite-derived phosphate on the ion exchangeability of ion adsorption clays was investigated by synthesizing a series of rare earth ion-adsorption clays at pH 4 with varying concentrations of phosphate being doped. Direct ammonium sulfate leaching results suggested that phosphate can significantly impair the ion-exchange leaching efficiency of the IACs by forming a passivation layer, i.e., $\text{LnPO}_4(\text{s})$. The XPS characterization showed that the association of REEs and phosphate on the surface of the synthesized clays was mainly in the form of “clay-RE- PO_4 ”. The direct EDTA leaching at pH 10 can recover 60 to 66% of the passivated REEs due to its strong affinity for REEs, and temperature exhibited a minor influence on the recovery. Another activation technique using dilute NaOH solution with the addition of EDTA followed by ammonium sulfate leaching can recover all the passivated REEs, with most REEs partitioning into the used NaOH solution as Ln-EDTA^- complexes. This

study demonstrated that phosphate can immobilize the REEs absorbed on the surface of clays, thereby undermining the ion exchangeability of IACs and coal-based clays. Thus, the surface-deposited $\text{REPO}_4(\text{s})$ could be an occurrence of REEs on the surface of clays, which is comparable to secondary rare earth phosphate. The activation technique proposed in this study can be used to extract REEs from the IACs or coal-based clays with poor leachability.

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Chapter 6 Rare Earth Element Extraction from a Kaolinite Mining Waste after Physical Preconcentration

Abstract

Rare earth element (REE) extraction from alternative resources such as mining wastes has been extensively explored due to the increasing demands and supply risks. In this study, the preconcentration of REEs from a kaolinite flotation reject by flotation and the hydrophobic-hydrophilic separation (HHS) using octanohydroxamic acid as a collector was investigated. The occurrences of REEs in the upgraded concentrate were determined by microscopic analyses such as scanning electron microscopy- and transmission electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS and TEM-EDS). Moreover, a series of ammonium sulfate leaching tests after NaOH pretreatment at 80 °C was performed to recover REEs from a flotation concentrate with a total REE (TREE) content assaying 8,868.4 ppm. The leaching results were compared to those of 1 M HCl leaching.

It has been found that REEs in the kaolinite flotation reject can be directly upgraded by flotation and the HHS process without grinding. Anatase was found to be the dominant mineral in the concentrate. A final concentrate assayed 10,765 ppm of REEs and 71.6% of recovery was obtained by the HHS process due to its advantage of separating ultrafine particles. The microscopic characterization found that crandallite group minerals and xenotime were the dominant REE-bearing minerals in the concentrate. Monazite and zircon were also found but rare in number. Ammonium sulfate leaching results suggested that the leachability of light REEs (LREEs) was more significantly enhanced relative to heavy REEs (HREEs) after being treated with 30% NaOH at 80 °C for only 1 h due to the high crystallinity of the xenotime and zircon. Around 70% of La, Pr, Nd, and Sm were extracted by ammonium sulfate leaching at pH 3 and room temperature. The leaching residue can be used to produce high-grade anatase. The findings from this study suggest that kaolinite flotation reject is a promising feedstock for both REEs and Ti.

6.1 Introduction

Kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), also known as Chinese clay, is a versatile mineral used in the paper, ceramics, and fiberglass industries. It is also critical to the production of advanced building materials, photocatalysts, etc. (Kogel et al., 2014; Cao et al., 2021). The United States Geological Survey report (USGS, 2021) shows that the total world production of kaolinite in 2020 reached 45 million metric tons, of which 4.1 million metric tons were produced in the US. The gangue minerals associated with the run-of-mine kaolinite normally contain quartz, mica, iron oxide (Fe_2O_3), anatase (TiO_2), etc. (Yoon et al., 1992; Pruett et al., 2012). In the kaolinite industry, different processing circuits, such as wet, dry, and thermal processing, have been applied to produce high-brightness kaolinite (Prasad et al., 1991; Kogel et al., 2014). In a wet processing flowsheet, the raw kaolinite is dispersed into water by a continuous blunger, after which the resulting slurry is deagglomerated by size classification equipment such as screens and hydrocyclones. The gangue minerals are removed by one of the methods, such as high-intensity magnetic separation, selective flocculation, froth flotation, and reductive leaching. The reject material with coarse grains from this step, which is normally discarded to impoundment, is called kaolinite sludge (Longhi et al., 2016).

Due to the intense kaolinite production, the annual production of the mining wastes and the quantities of those wastes stored in tailing dams are huge in volume, which occupies large storage areas and threatens the local environment (da Silva et al., 2021). For instance, the annual waste production in Brazil's kaolinite industry was found to be ~0.5 million ton per year, and more than 10 million tons has been discarded into the impoundment (Longhi et al., 2016). In the UK, the production of each ton of kaolinite leads to the generation of nine tons of other minerals, including sand, rock, overburden, and micaceous residues (Highley et al., 2009). Under such circumstances, the valorization of those waste

materials has been explored by many researchers. Lqbal (2015) found that a kaolinite waste sample from the UK can be used to recover lithium by bioleaching after proper preconcentration. They have also been used as feedstocks to produce geopolymers (Longhi et al., 2016; Longhi et al., 2022), zeolite (Schwanke et al., 2022), low-carbon cement (da Silva et al., 2021), and rare earth elements (REEs) (Dehaine et al. 2015).

It is widely acknowledged that REEs, consisting of 15 lanthanides (Ln), scandium (Sc), and yttrium (Y), play critical roles in green energy production, national defense, civil commodity items, etc. (Chowdhury et al., 2021). The vulnerable supply chain of REEs and their increasing demands have stimulated studies on the extraction of REEs from secondary rare earth resources such as electronic wastes (e.g., battery waste and spent magnets), industrial byproducts (e.g., slags and phosphogypsum), and mining wastes (e.g., coal byproducts and red mud) (Akcil et al., 2018; Jyothi et al., 2020; Gaustad et al., 2021). Mining wastes such as coal byproducts have received intensive attention (Zhang et al., 2020; Eterigho-Ikelegbe et al., 2021). Compared to the commercialized rare earth minerals (REMs), the advantages of extracting REEs from coal-derived materials mainly include large reserves, eliminated mining costs, lower contents of radionuclides (e.g., Th and U), and higher fractions of critical and heavy REEs (Zhang et al., 2020). However, the total REE (TREE) contents in those alternative resources are normally low (~300 ppm), and the majority of the REEs exist in difficult-to-leach forms (e.g., rare earth phosphate minerals). Rozelle et al. (2019) suggested that the relative production cost significantly decreases with the increase of the head grade of REEs. As such, it is important to explore the possibility of preconcentrating REEs by physical beneficiation. It can also reduce the sample volume subjected to hydrometallurgical extraction step, which is economically inhibitive for those low-grade materials.

Several studies have been performed to upgrade REEs from coal-derived clay materials by physical separation methods such as magnetic separation, flotation, and density separation, as reviewed by Zhang et al. (2020) and Eterigho-Ikelegbe et al. (2021). Although REE-bearing minerals can be enriched from coal-based clays (Lin et al., 2017), the ultrafine grain size of REMs (<10 μm) and their poor liberation enable most of the physical methods to be less cost-effective, with only limited mass recovery and enrichment ratio being obtained. Li (2019) conducted a series of REE preconcentration tests from a thickener underflow of a Fire Clay coal by the hydrophobic-hydrophilic separation (HHS), which is an innovative froth flotation technique. A final REE concentrate assayed 15,590 ppm TREE on an ash basis was obtained by the author.

Besides coal-derived materials, Jha et al. (2008) found that anatase accumulates in secondary placer deposits (e.g., kaolinite) along with zircon, monazite, leucoxene, and magnetite minerals in the form of sand. The existence of these REMs provides a basis for the physical preconcentration of REEs from kaolinite mining wastes. Dehaine et al. (2015) suggested that the micaceous residue stream from a kaolinite plant in the UK (using a dry mining process) contained higher concentrations of rare metals (Sn (139 ppm), Nb (94 ppm), and W (69 ppm)) and light REEs (170 ppm) than other output streams. Dehaine et al. (2017) performed gravity separation techniques (a spiral and a shaking table) to upgrade rare metals and REEs from a kaolinite processing waste (180–53 μm). A final REE concentrate containing 1.6% of light REEs (LREEs) was obtained using a shaking table. In the third paper of the series (Filippov et al., 2016), the fine size fraction (<53 μm) of the micaceous residue was upgraded for REEs and rare metals by flotation. The results showed that flotation outperformed Falcon Ultra-Fine concentrator in the preconcentration of LREEs, with a flotation concentrate assaying 5,350 ppm of REEs and 80% of recovery being obtained. These studies suggest that kaolinite mining waste is a promising source for REEs and rare metals after preconcentration. However, other than the micaceous residue, the feasibility of preconcentrating REEs from the kaolinite sludge of kaolinite plants using a wet processing method has rarely been reported. On the other hand, literature about the leachability of those upgraded REE concentrate is limited.

In this study, froth flotation and the HHS process have been used to upgrade REEs from a kaolinite flotation reject material. The mineralogical changes before and after the separation were characterized by X-ray diffraction (XRD). Meanwhile, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were employed to study the REE mineralogy of the upgraded concentrate. In addition,

to recover REEs from the REE concentrate, several chemical leaching tests by ammonium sulfate and hydrochloride acid were performed after NaOH pretreatment under mild conditions (<100 °C). Results obtained from this study provide a novel approach, i.e., physical preconcentration followed by chemical leaching, regarding the REE extraction from kaolinite flotation reject materials.

6.2 Experimental

6.2.1 Sample Preparation and Reagents

The kaolinite flotation reject material used in this study was collected from a kaolinite processing plant in eastern Georgia, US. The sample was received as a dense slurry in a 5-gallon bucket. The feed material for the preconcentration tests was the remaining wet solid after decanting the top supernatant (i.e., water). The particle size of the feed was measured to be 80% passing (d_{80}) 12.0 μm . ICP-MS was used to measure the rare earth contents of the products of interest after lithium metaborate fusion at 1000 °C for 15 min. In addition, a flotation concentrate assaying 8,865.6 ppm of REEs was used as a feed material for a series of chemical leaching tests. The major element compositions and individual REE contents of each flotation product are shown in Tables 6.1 and 6.2, respectively. Moreover, a representative split of the flotation concentrate was ground by a planetary ball mill for 90 min to examine the effect of particle size on the leaching efficiency.

Methyl isobutyl carbinol (MIBC, Fisher Scientific), sodium metasilicate nonahydrate (SMN, Fisher Scientific), and octanohydroxamic acid (OHA) of >99.0% purity (TCI American) were used as received. Heptane, sodium hydroxide, and ammonium sulfate were purchased from Fisher Scientific in reagent grade. Hydrochloride acid (HCl) and nitric acid (HNO_3) were of trace metal grade from Fisher Scientific. Tap water was used for the HHS and flotation tests, while deionized water with a resistivity of 18.2 $\text{M}\Omega\cdot\text{cm}$ at 298.15 K was employed for all the solution preparation and leaching tests.

6.2.2 Physical Beneficiation

6.2.2.1 Flotation Test

A flotation test was conducted using a bench-top Denver D-12 laboratory flotation machine with a 1 L flotation cell. The detailed flowsheet and reagent dosage are shown in Figure 6.1. OHA was used as a collector due to its high affinity for transition metals (Fe^{3+}) and REEs (Yoon et al., 1992; Filippov et al., 2016). In the flotation test, 1 L pulp with a solid concentration of 20% by weight was prepared. After sufficient dispersion of the slurry in the flotation cell at 1,200 rpm for 3 min, NaOH was added to adjust the pH of the pulp to 9.5. Subsequently, OHA with a dosage of 100g/ton was added as a collector. The slurry was conditioned for 10 min, followed by adding 0.1 mL MIBC and agitating for another 2 min. Air was introduced after slurry conditioning, and the particles in the froth were collected using a scraper for 3 min. The rougher concentrate was then subjected to 4 stages of cleaning. After flotation, each flotation product was collected, dried, and weighed. 1 g of representative sample was taken from each product for the assay of TREE content by means of the lithium metaborate fusion.

Table 6.1 Major element concentrations of the feed and flotation products (in wt.%).

Sample	Mg	Al	Si	P	Ca	Fe	Ti
Feed	0.45	17.94	19.22	0.05	1.05	1.03	9.69
Flotation Concentrate	0.29	3.79	3.29	0.45	0.81	2.41	34.95
Rougher Tail	0.22	22.4	24.75	0.04	0.57	0.43	1.34
Cleaner Tail	0.24	15.03	16.11	0.21	0.67	1.36	13.89

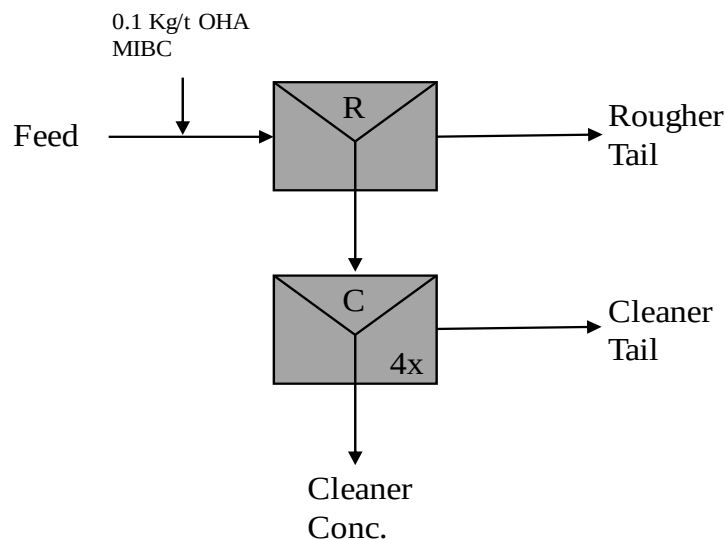


Figure 6.1 Flowsheet for the flotation and HHS tests performed on the kaolinite flotation reject material (Note: “Conc.” refers to concentrate).

6.2.2.2 Hydrophobic-hydrophilic Separation (HHS) Test

The HHS separation test was conducted following the same flowsheet and reagent dosage, as shown in Figure 6.1. The only difference is that two stages of cleaning were performed due to the high separation efficiency of the HHS process. At the beginning of the test, 1 L slurry with 20% solid concentration was initially dispersed at 300 rpm in a mixer (Cafrmo Constant-Torque Brushless Mixer, USA) for pH adjustment and OHA conditioning (dosage: 100 g/ton). Subsequently, 200 mL heptane was added to the conditioned slurry and mixed in a high-shear blender (Waring MX1050XTX Countertop Drink Blender, USA) for 1 min. Then, the agitated slurry was transferred into a 2 L separation funnel and set aside for 10 min, during which the oil droplets that collected the hydrophobic particles floated on top and formed an oil phase, while the hydrophilic particles were left in the aqueous phase. Phase separation was performed by slowly discharging the water and hydrophilic particles into a beaker. The rougher concentrate was further cleaned twice by washing it with 500 mL of tap water, by which the entrained gangue minerals can be further removed (Zambrana et al., 1974; Li, 2019). Finally, each product was also collected, dried, weighted, and assayed for TREE content.

6.2.3 Sample Characterization

In order to determine the mineralogy changes of the samples produced from preconcentration and chemical leaching, a series of XRD characterizations was conducted on a Bruker D8 instrument with a Cu X-ray source. The XRD patterns were acquired over a 2θ range of $5-70^\circ$ with a step time of 0.02° . MDI Jade 6 software was used to analyze the XRD spectra.

REE mineralogy and surface morphology of the flotation concentrate and samples from leaching steps were investigated by a JSM-IT500 SEM (JEOL, MA, USA), which is in conjunction with an Ultim Max EDS detector (Oxford Instruments, UK). For the SEM specimen preparation, solid particles were sprinkled onto the double-sided carbon tape fixed on SEM stubs. Before characterization, the specimens were coated by a layer of Pt/Pd (10 nm in thickness) via a Sputter Coater to obtain high-quality SEM images (Leica EM ACE600, Leica Microsystems, IL, USA). The AZtech software (Oxford Instruments, UK) was used to control the EDS detector. The SEM-EDS spectra were obtained by the “Point & ID” mode, providing the elemental information of a point of interest. In the backscattered electron (BSE) mode, REE-enriched particles normally appear to be bright due to the large atomic numbers, which can be easily

Table 6.2 TREE and individual REE concentrations in the feed and flotation products (in ppm).

Sample	TREE	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd
Feed	2,362.4	93.0	262.8	394.4	826.4	99.2	382.8	80.4	14.9	63.5
FC	8,868.4	292.7	1,052.5	1,507.5	3,100.5	369.8	1,404.4	283.8	55.8	236.4
Ro. Tail.	372.8	24.6	19.4	68.0	142.2	17.2	63.9	12.9	2.8	9.6
Cln. Tail.	3,221.3	131.5	309.7	558.8	1,160.6	138.7	533.1	107.2	20.2	86.8
Tb	Dy	Ho	Er	Tm	Yb	Lu	Th	U	LREEs	HREEs
9.4	58.7	10.6	29.6	4.2	28.2	4.2	194.4	42.2	1876.2	486.1
37.6	220.3	42.4	115.5	17.2	114.9	17.0	633.8	132.7	6958.7	1909.6
1.2	6.1	0.8	1.9	0.2	1.7	0.2	28.2	4.2	328.8	43.9
12.8	71.9	13	35.3	4.8	32.4	4.6	243	47.0	2629.9	591.5

Note: “FC”, “Ro. Tail”, and “Cln. Tail.” refer to flotation concentrate, rougher tailings, and cleaner tailings, respectively. LREEs include Sc, La, Ce, Pr, Nd, and Sm; HREEs contain Y, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu.

identified.

Additionally, the mineralogy of REE particles of interest in the flotation concentrate was also determined using a JEM-2100 Transmission Electron Microscope (JEOL, MA, USA) in conjunction with an EDS detector. The TEM images, diffraction patterns, and EDS spectra of REE-enriched particles were acquired, respectively. DM DiffTolls software was used to determine the interplanar spacing of each diffraction pattern.

6.2.4 Alkali Pretreatment and Chemical Leaching

6.2.4.1 NaOH Pretreatment

NaOH pretreatment was used to enhance the REE leachability of the flotation concentrate. Our previous study showed that ammonium sulfate leaching is capable of recovering REEs from NaOH-treated monazite under less aggressive conditions (pH 4 and room temperature) compared to HCl leaching (Liu et al., 2022). Accordingly, this work also used the NaOH pretreatment followed by the ammonium sulfate process to extract REEs from the flotation concentrate. One difference is that the leaching tests were conducted at pH 3 to maximize the leaching efficiency in this study. 1 M HCl leaching was performed to evaluate the performance of ammonium sulfate leaching. The effects of experimental variables such as NaOH concentration (10 to 50%), particle size, and pretreatment contact time (1, 2, 3, and 24 h) on the leaching efficiency were systematically examined. In a given pretreatment test, 0.5 g flotation concentrate sample and 20 mL NaOH solution were mixed in a 50 mL alkali-resistant polytetrafluoroethylene (PTFE) beaker. The mixture was heated and magnetically stirred (600 rpm) on a hot plate at 80 °C (± 1 °C) with varying contact times. To minimize the evaporative loss of water, the beaker was sealed by paraffin film. The pretreated slurry was centrifuged at 5,000 rpm for 10 min to separate the treated sample from the NaOH solution. The residue was washed with deionized water three times to remove the residual NaOH. The NaOH solutions used were collected and saved for further analysis.

6.2.4.2 Ammonium Sulfate and Hydrochloride Acid Leaching Tests

The NaOH-treated flotation concentrate samples were leached by 0.5 M ammonium sulfate and 1

M HCl at room temperature. In each experiment, a 0.5 g sample was mixed with 40 mL of a lixiviant solution in a 50 mL polypropylene beaker. The mixture was then magnetically agitated at 600 rpm for 1 h. During the ammonium sulfate leaching, HCl and NaOH solutions both of 0.5 M were utilized to maintain the pH at 3.0 ± 0.05 . 0.3 mL slurry samples were periodically taken from the beaker using a 1 mL disposable syringe to examine the extraction kinetics. Each slurry sample was immediately filtered by a disposable syringe filter with a particle size of 0.22 μm for solid-liquid separation. Subsequently, the filtrate was diluted 100 times with a mixed HNO_3 (2.5%) and HCl (0.5%) solution for ICP-MS analysis. The TREE recovery (R) was determined according to Eq. (6.1),

$$R = 100 \times \frac{C_l V}{C_f M} \quad (6.1)$$

in which C_l and V are the REE concentration and volume of the leachate, 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.

6.3 Results and Discussion

6.3.1 Physical Beneficiation

The kaolinite flotation reject sample was beneficiated by the HHS process and flotation, respectively. The material balances of the tests are shown in Table 6.3. The sub-sampling bias in the sample preparation step may be responsible for the inconsistent feed grades for both tests (Filippov et al., 2016). Figure 6.2 compares the recovery versus grade curves for flotation and the HHS process. The performance of the HHS process was superior to flotation in terms of the final grade. After one rougher and one stage of cleaning, although the recovery of the HHS process (71.6%) was 4% lower than the flotation test (75.5%), the REE assay of the former (10,765 ppm) was 2,235 ppm higher than the latter. In the flotation test, the REE recovery dramatically decreased from 75.5% to 29.5% after the fourth stage of cleaning, while the TREE content only slightly increased from 8,529 to 9,873 ppm, indicating that the cleaning operation should not continue. As such, performing one rougher and one stage of cleaning may be optimal for

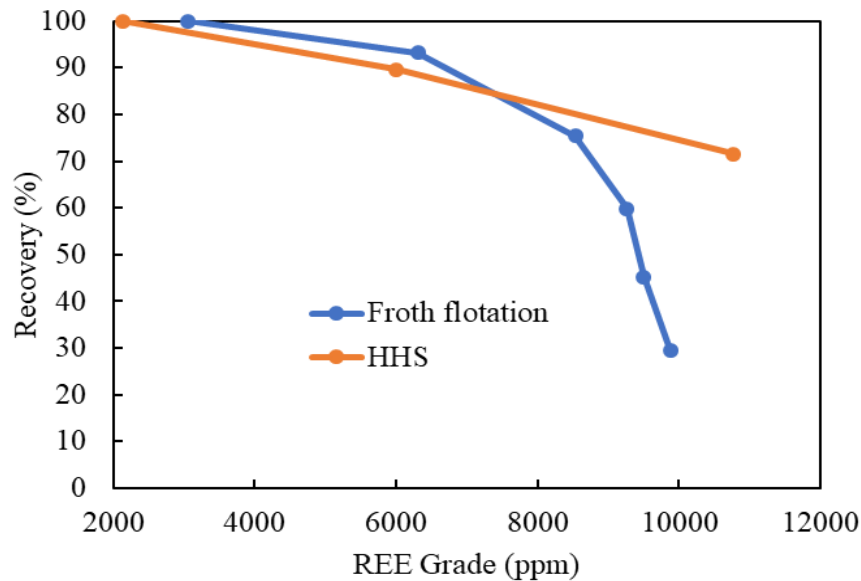


Figure 6.2 Recovery versus grade curves of the flotation and the HHS tests performed on the kaolinite flotation reject material for REE preconcentration.

flotation, by which a balance between recovery and REE grade can be achieved. In addition, the TREE contents in the rougher tailing products of the HHS and flotation only assayed 326 and 373 ppm (see Table 6.3), respectively, which were significantly lower than their feed grades.

Compared to the HHS process, the lower final grade of flotation may be explained by its inefficiency in separating ultrafine particles. Li (2019) systematically investigated the application of the HHS process and other flotation methods (column and conventional flotation) in the preconcentration of REEs from a thickener underflow of a Fire Clay coal sample. It was also found that the HHS process far outperformed other conventional flotation techniques regarding the final concentrate grade. According to Huang and Yoon (2019) and Li (2019), compared to conventional flotation, which uses air bubbles as a carrier, the advantages of the HHS process were mainly attributed to the larger contact angles between oil and the target minerals as well as less hydraulic entrainment. However, the REE recovery (<10% in the final concentrate) of each separation test was much lower than the concentrates obtained from the kaolinite waste material in this study. This is mainly due to the extremely small sizes of REMs in coal-derived materials and their poor liberation (Zhang et al., 2020). Some REE-bearing minerals may be encapsulated by the dominant minerals such as clays. Thus, the collector molecules can hardly render the target minerals hydrophobic, thereby leading to poor separation efficiency. As such, ultrafine grinding (e.g., 3 μm) was required to liberate them, undermining the economic viability of physical separation.

Differing from the coal-based clay, the d_{80} of the kaolinite flotation reject was 12.0 μm . Even with this size, the majority of the REE-bearing species can be readily recovered by flotation without grinding, which is one of the advantages of upgrading REEs from the kaolinite flotation reject. This may be mainly due to the enhanced liberation of REMs via the blunging step, and the initial preconcentration of REEs in the kaolinite flotation reject. The REE content in the kaolinite flotation feed assays ~500 ppm, which is increased to around 2,000 ppm in the kaolinite flotation reject. This may suggest that the easy-to-float REMs had been initially preconcentrated into the kaolinite flotation reject material, and thus a good separation performance was observed in the preconcentration of REEs from the kaolinite reject material. After upgrading by flotation, which is a low-cost technique, the volume of the sample subjected to the following chemical leaching step can be significantly reduced.

6.3.2 Sample Characterization of the Upgraded Concentrate

Table 6.3 Material balances for the flotation and HHS tests.

Flotation				HHS process			
Product	Weight (%)	TREE Grade (ppm)	REE Recovery (%)	Product	Weight (%)	TREE Grade (ppm)	REE Recovery (%)
Cln. Conc.4	9.2	9873.5	29.5	Cln. Conc.	14.2	10765.0	71.6
Cln. Tail 4	5.4	8865.6	45.2	Cln. Tail	17.7	2174.0	82.0
Cln. Tail 3	5.2	8607.2	59.9	Ro. Tail	68.2	326.2	
Cln. Tail 2	7.3	6535.4	75.5	Feed	100.0	2133.9	100.0
Cln. Tail 1	18.2	2988.5	93.2				
Ro. Tail	54.7	372.8					
Feed	100.0	3065.3	100.0				

Note: “Cln.” and “Ro.” refer to cleaner and rougher, respectively.

6.3.2.1 XRD Characterization and Particle Size Measurements

XRD was employed to characterize the mineralogical compositions of the feed sample, flotation concentrate, and flotation tailing, respectively. As shown in Figure 6.3, kaolinite was the dominant species in the feed sample, with anatase, rutile, and zircon being the minor components. After the preconcentration, kaolinite was the dominant mineral in the tailing product, which can be recovered as a byproduct for extra revenue, whereas anatase, rutile, and zircon were reported to the flotation concentrate. This finding was consistent with the ICP-MS results, as shown in Tables 6.1 and 6.2, respectively. It indicates that the total content of anatase and rutile was 58.3 wt.% (in TiO_2), while the contents of Al and Si were only ~3.3wt.%, which was lower than the detection limit of XRD (~5%). Other than kaolinite, the concentrate also contained a small fraction of Fe (2.41wt.%), primarily associated with anatase by isomorphous substitution and iron oxide. REE-bearing species were not detected by XRD in the concentrate due to the low concentration. Particle size measurements indicated that the d_{80} of the feed sample also changed before and after flotation. The particle size of the feed materials was 12.02 μm . In comparison, the d_{80} of the flotation concentrate increased to 15.45 μm , suggesting that the coarse particles such as anatase and REE-bearing species were reported to the concentrate. This observation is expected since the d_{80} of the rougher tailing product was only 3.2 μm , indicating that fine particles, i.e., kaolinite, were reported to the tailings. Therefore, the concentrate is not only a source for REEs but also may be a potential feedstock to produce high-grade anatase after the removal of impure elements.

6.3.2.2 SEM and TEM Analysis

It has been reported that rare earth phosphate minerals (e.g., monazite and aluminum phosphate) and zirconium silicate are the primary REE-bearing species in bomar ilmenite and anatase (Sanchez-Segado et al., 2015; Ephraim et al., 2015). Although the dominant mineral in the flotation concentrate beneficiated in this study was also anatase, which is similar to the bomar anatase, it is still worth determining its REE mineralogy since their differences in geological origin. Initially, SEM-EDS was used to determine the REE-containing species. Due to the relatively higher REE grade in the flotation concentrate, REE-containing particles are readily detectable by SEM. In total, 34 REE-bearing particles (numbered from P1 to P34) were

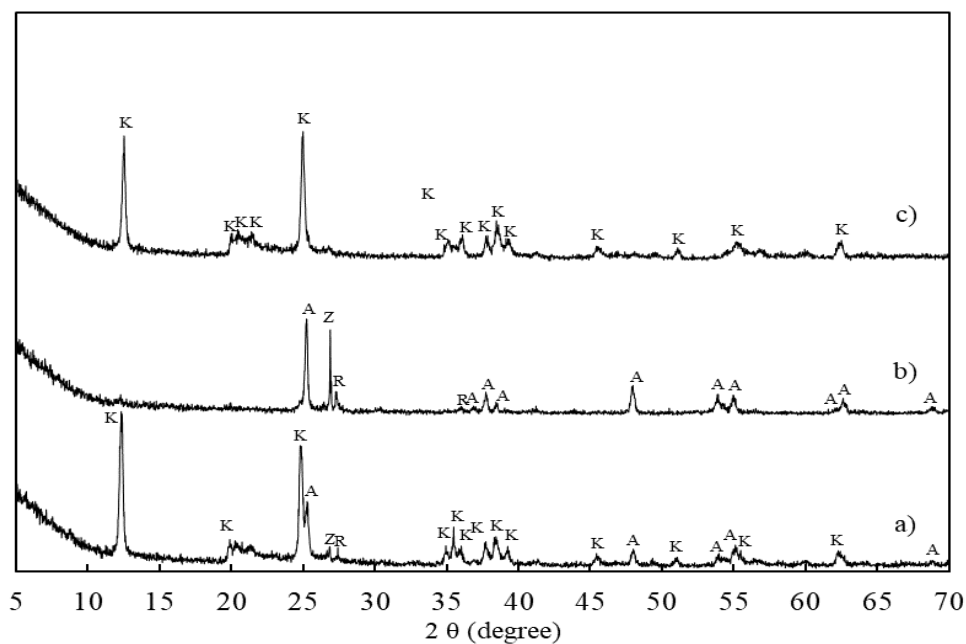


Figure 6.3 XRD spectra of a) the kaolinite flotation reject feed, b) flotation concentrate, and c) flotation tailing. Note: A: anatase; Z: zircon; R: rutile; K: kaolinite.

corroborated by the TEM-EDS characterization.

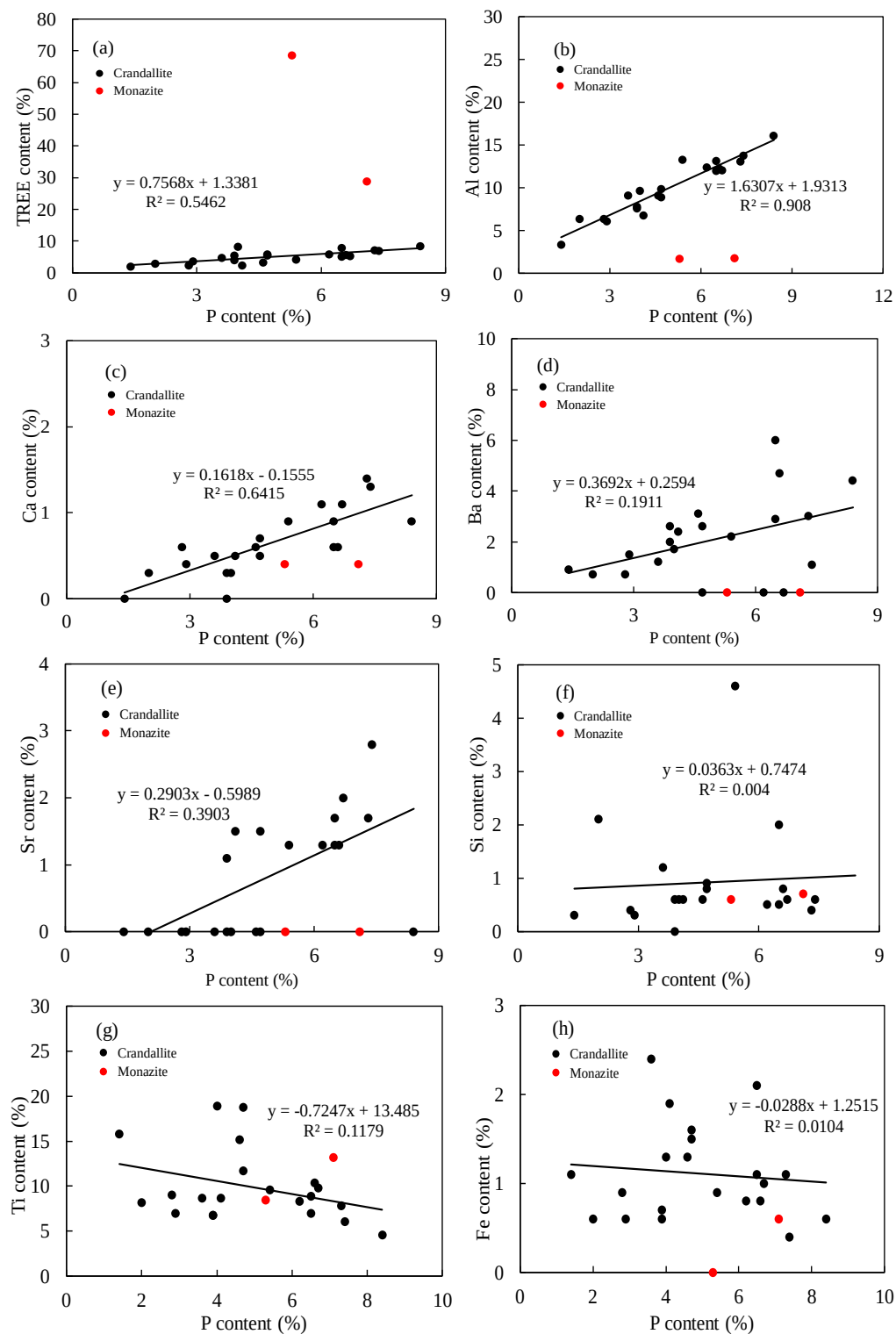


Figure 6.5 Statistical analysis of the elemental compositions of the LREE-enriched particles identified from the flotation concentrate by SEM-EDS.

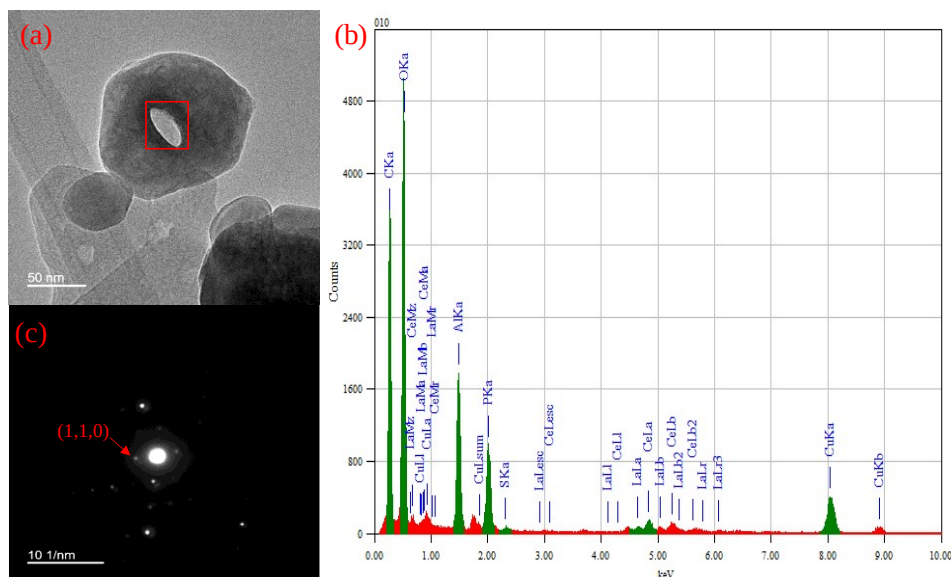


Figure 6.6 TEM image (a), EDS spectrum (b), and diffraction pattern (c) of a crandallite group mineral particle identified in the flotation concentrate.

Figure 6.6 shows the TEM image (a), EDS spectra (b), and diffraction pattern (c) of a REE-bearing particle. The hole marked by the red rectangle in Figure 6.6a was caused by the electron beam, which penetrated the specimen for collecting the EDS spectrum and diffraction pattern. As suggested by the EDS spectrum (see Figure 6.6b), the peaks of Al (~1.5 keV), P (~2.0 keV), La (4.7 keV), and Ce (4.8 keV) were detected. Ca was not found in the EDS spectrum. As indicated in the SEM analysis, the content of Ca determined in the REE-rich particles only ranged from 0 to 2% (Figure 6.5c), which was lower than that of TREEs (0-10%). As such, the undetected peak of Ca by TEM was mainly due to its weak signal. After

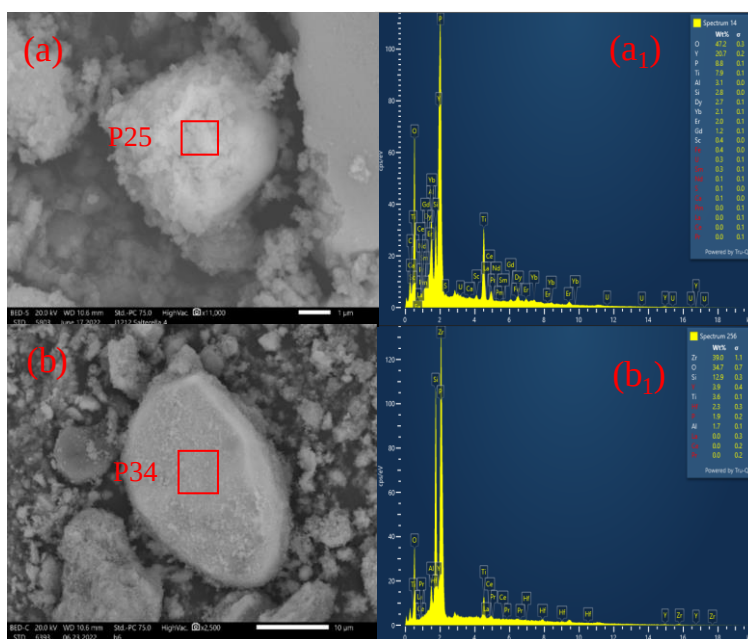


Figure 6.7 SEM images of two HREE-enriched particles and their EDS spectra of the selected areas. (a): xenotime; (b): zircon. (a1) and (b1) are the corresponding EDS spectra of the selected areas in (a) and (b), respectively.

measuring the d-spacing values of the diffraction spots in Figure 6.6c, it was found that 3.609, 2.734, 2.483, 2.050, and 1.841 Å corresponded to the (1,1,0), (0,0,6), (0,2,4), (2,1,4), and (0,2,7) lattice planes of pure crandallite. Another two crandallite particles were also identified by TEM (not shown here), while monazite was not detected by TEM during the scanning period due to its scarcity in number. Accordingly, the TEM-EDS characterization confirmed the existence of the crandallite group mineral, thus supporting the findings from the SEM-EDS characterization and the statistical regression of the data acquired from the EDS spectra. Although the REE content in monazite is much higher than that of crandallite group minerals, its scarcity in number may suggest that it contributed less to the TREE content of the sample.

(2) HREE-enriched particles

Figure 6.7 shows the SEM images and EDS spectra of two HREE-bearing particles (i.e., P25 and P34). The elevated contents of Y and P as well as other HREEs (e.g., Dy, Yb, and Er) in particles P25 to

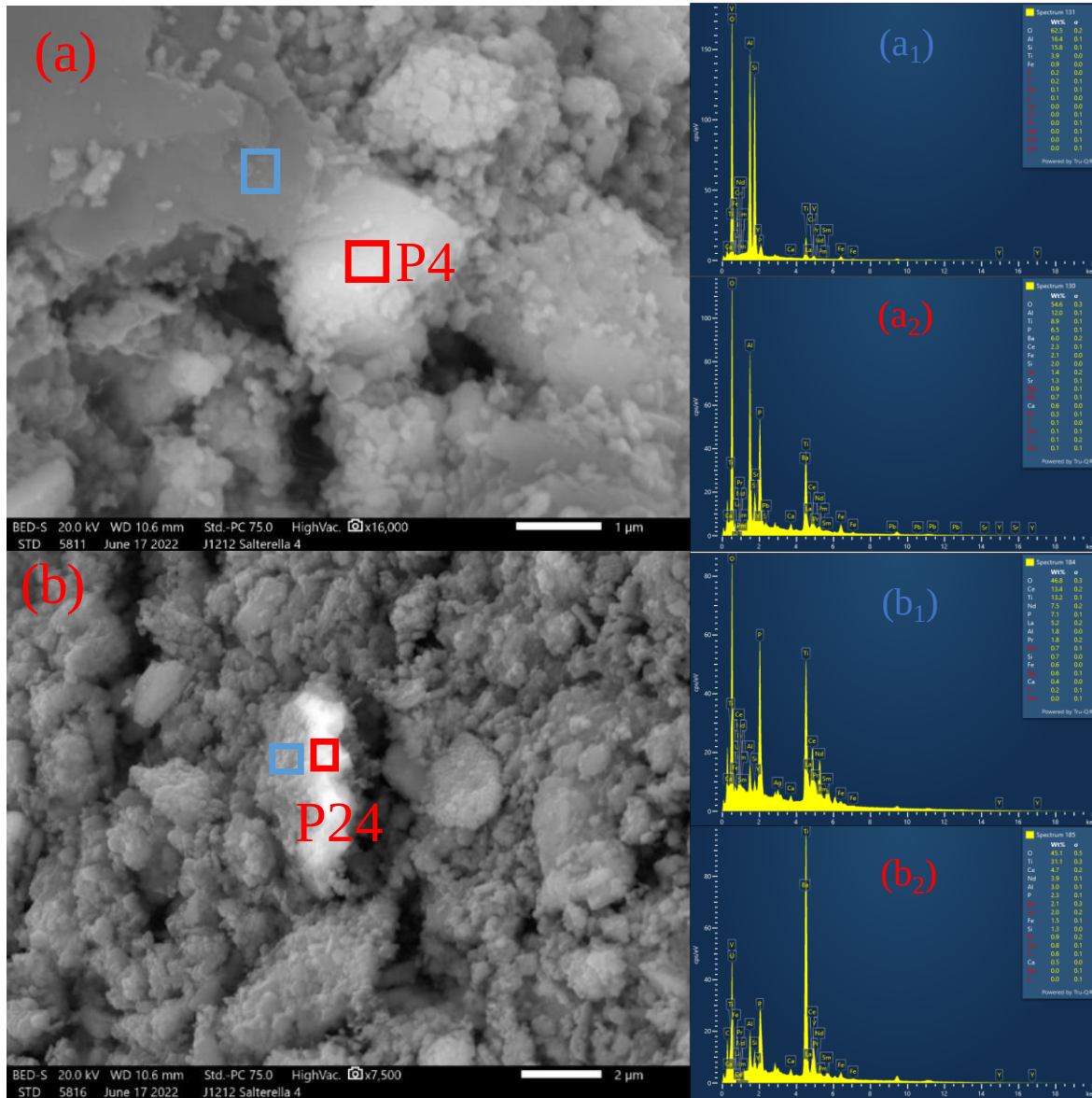


Figure 6.8 SEM images of two REE-enriched particles co-existed with other minerals. (a): a REM particle (a2) associated with clay (a1); (b): a REM particle (b2) intergrown with TiO₂ (b1).

P32 suggested that they were xenotime particles, which is a critical HREE-hosting mineral. Many zircon particles were also detected by SEM; however, they normally did not contain SEM-detectable REEs. Only two zircon particles (P33 and P34) were found to contain small fractions of REEs, with one having Y (3.9%) and the other having Y (0.6%) and Sc (0.6%). It suggested that the occurrence of REEs in zircon was limited in the concentrate, which can benefit the leaching process since zircon is one of the most difficult-to-decompose REMs.

6.3.2.3 REE Occurrences and Physical Associations

The elemental composition (see Table 6.2) of the flotation concentrate suggests that Ce, La, Nd, and Y are the most abundant REEs in the sample since the total amount of those four REEs accounted for nearly 80% of the TREE content. This agrees with the observation that REE particles containing Ce, La, Nd, and Y were frequently identified by SEM. It is true that the spatial resolution of SEM-EDS is only 0.1%, and the REE-bearing species (e.g., REEs in ion substitution form) with a content <0.1% cannot be detected. However, those REEs may only contribute to a small fraction of the TREE content. Therefore, it is still reasonable to conclude that monazite and crandallite group minerals are the dominant host minerals of LREEs, while xenotime and a small amount of zircon are the HREE-bearing minerals in the flotation concentrate.

A similar conclusion has been drawn by Ji et al. (2022), who systematically investigated the REE mineralogy in two coal wastes of the Western Kentucky No. 13 and Fire Clay Seam by SEM- and TEM-EDS. In the former sample, crandallite group minerals and monazite were the dominant REE-bearing minerals. The similar REE mineralogy of the coal-based clay and the kaolinite waste material may suggest that they have a similar geochemical origin. As reported in previous literature, both the Georgia kaolinite and the coal-derived kaolinite were derived from the weathering of feldspar. Crandallite group minerals and rhabdophane, resulting from apatite dissolution, are normally found to be secondary REMs in weathered rocks and soil (Sanematsu et al., 2015).

According to the SEM images, most of the REE-bearing particles are liberated. Only a small fraction of REE particles were found to have associations with other minerals. Figure 6.8a and -b show that LREE-containing particles intergrew with an aluminosilicate particle (probably kaolinite, spectrum a₁) and TiO₂ (probably anatase, spectrum b₁). In the latter case, REE particle was trapped in the grain of an anatase particle. This finding was not surprising since the REM particles in the crude kaolinite were liberated after the blunging and the kaolinite flotation steps in the processing plant. The liberated REE-bearing particles are beneficial to the following leaching step since they can be directly exposed to the chemicals.

6.3.3 Chemical Leaching

6.3.3.1 Effect of NaOH Concentration on the TREE Recovery

Figure 6.9 compares the TREE recovery of ammonium sulfate and HCl leaching from the flotation concentrate after being treated by NaOH with varying concentrations. In the blank test (i.e., no NaOH pretreatment), only 1.76 and 5.26% of REEs were extracted by ammonium sulfate and HCl, respectively. Such low recoveries indicated that the fraction of ion-exchangeable REEs in the concentrate was minor, and the majority of REEs in the sample were in difficult-to-leach form (e.g., rare earth phosphates), which agreed with the findings from the SEM and TEM characterization. However, the overall REE recovery gradually increased with the NaOH concentration. It underwent considerable improvements for both ammonium sulfate (from 1.8% to 38.0%) and HCl (from 5.3% to 59.0%) leaching when the NaOH concentration increased from 0 to 20%. Only slight improvements in the TREE recovery were found when the NaOH concentration varied from 30% to 50%. Consequently, it can be concluded that 30% may be the optimal NaOH concentration under the pretreatment conditions tested.

The corresponding individual REE recovery of each test shown in Figure 6.9 is presented in Figure 6.10. Th and U were also listed to have an in-depth insight into the involved leaching mechanisms. As

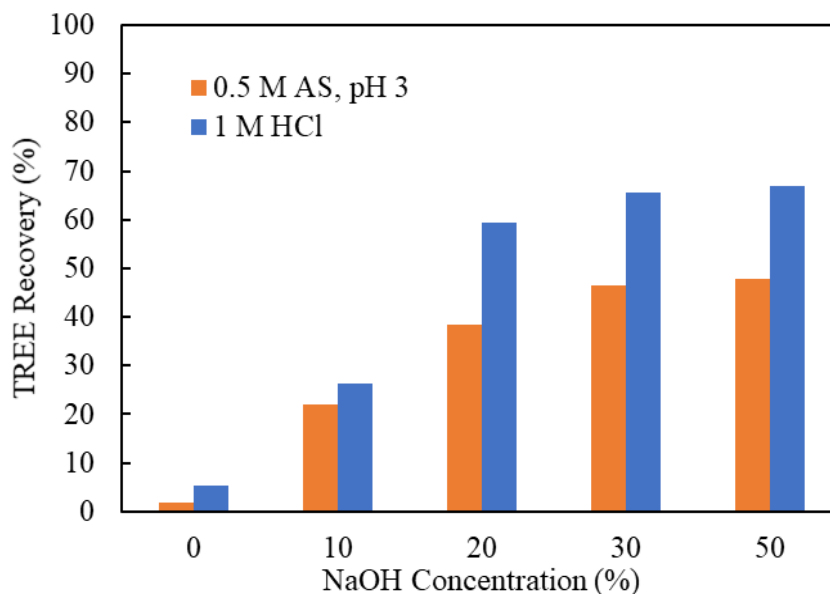


Figure 6.9 Effect of NaOH concentration on the TREE recovery of ammonium sulfate and 1 M HCl leaching from the flotation concentrate ($d_{80} = 15.0 \mu\text{m}$ after NaOH pretreatment conducted at 80 °C for 1 h. The leaching tests were all conducted at room temperature.

shown, although the TREE recoveries were poor for the samples without NaOH pretreatment, relatively higher recoveries of Sc, Y, and the REEs located from Gd to Lu were obtained by both two lixiviants (Figure 6.10a and -b). For the 1 M HCl leaching (Figure 6.10b), the recoveries of Er, Tm, Yb, and Lu were comparable to those from 10% NaOH-treated samples. It indicated that only a small fraction of HREEs was in ion-exchangeable and acid-soluble forms. After being treated with 10% NaOH, the recoveries of LREEs (from La to Sm) were increased to 20-25% by those two lixiviants. Except for Eu and Gd, the recoveries of LREEs were higher than those of HREEs (from Tb to Lu). Regarding the higher NaOH concentrations, the leachability of LREEs was enhanced to a greater extent than HREEs. Except for Ce, the recoveries of La, Pr to Sm were significantly increased to around ~70% by ammonium sulfate leaching and ~80% by HCl leaching. This is particularly true for Nd (86% by HCl), a critical REE for cleaner energy production. Such high recoveries revealed that most of the readily leachable REE-bearing minerals (e.g., crandallite) had been decomposed by 30% NaOH solution, and the remaining REE-enriched minerals (e.g., monazite, xenotime) were more resistant, thereby only slight improvement in the leaching efficiency was achieved by 50% NaOH at 80 °C.

Yang et al. (2021) reported that the existence of rare earth phosphate with lower crystallinity in coal-derived clays could facilitate the REE extraction process. Compared to monazite, whose melting temperature is over 2,000 °C (Hikichi et al., 1987), crandallite group minerals are less stable thermodynamically. Frost et al. (2012) investigated the thermal stability of crandallite by thermogravimetry and found that this mineral became unstable when the temperature was >139 °C. Moreover, crandallite lost OH units at around 416 °C, after which the alteration of the mineral structure occurred. This difference suggested that crandallite is more leachable than monazite under the same condition. Similar to monazite, xenotime and zircon are also difficult-to-leach REMs (Franken et al., 1995; Abdelkader et al., 2008). By characterizing the HCl leaching residue after being treated with 50% NaOH by SEM, a xenotime particle (>10 μm in grain size) with a minor fraction of Zr was identified (Figure 6.11). The smooth and compact surface morphology indicated that it had a well-crystalline structure and was resistant to the chemical extraction step. Therefore, the lower recoveries of HREEs achieved were not unexpected.

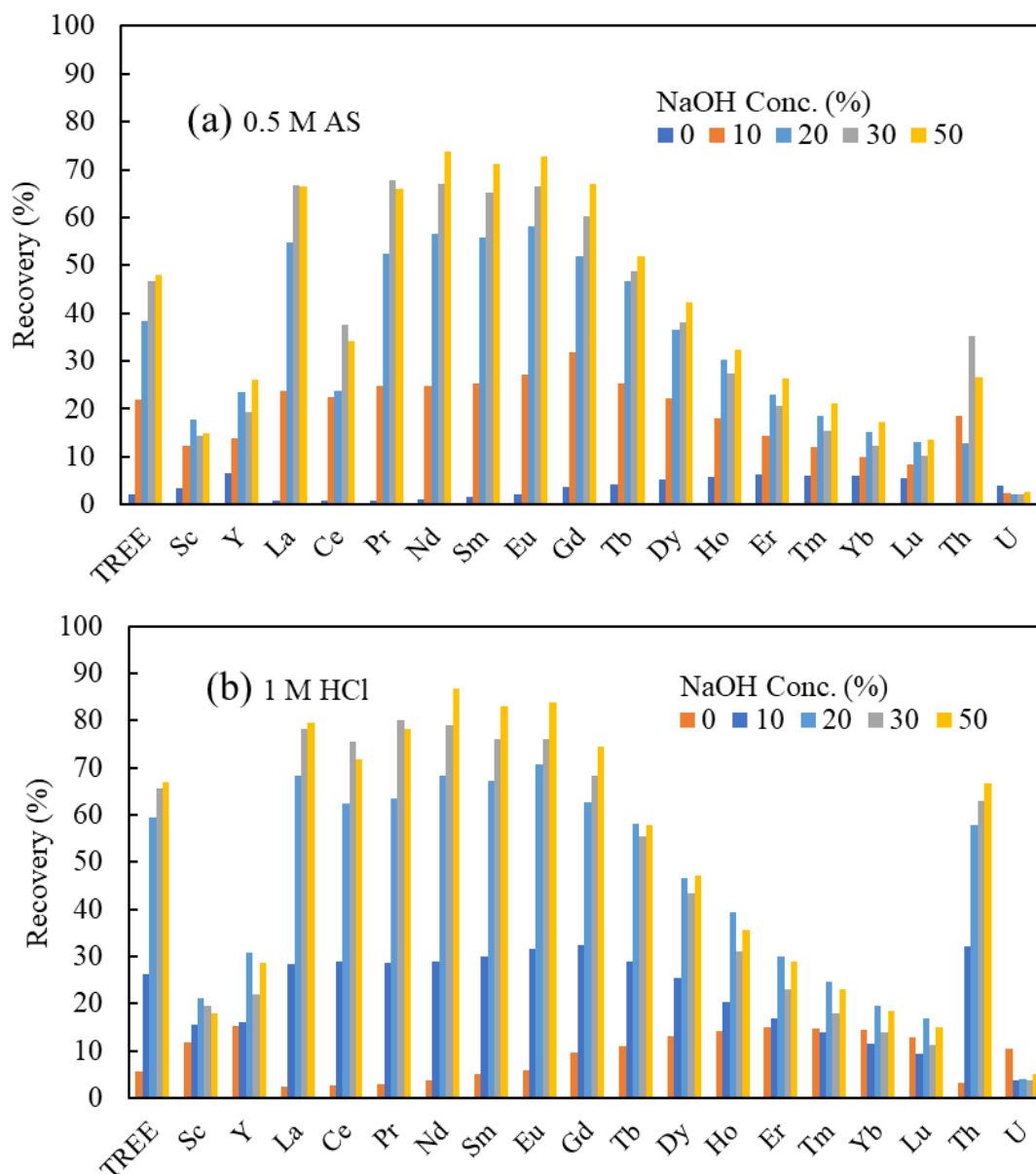


Figure 6.10 Effect of NaOH concentration on the individual REE recovery of ammonium sulfate (a) and 1 M HCl leaching (b) from the flotation concentrate ($d_{80} = 15.0$ μm after NaOH pretreatment conducted at 80 °C for 1 h. The leaching tests were all conducted at room temperature.

After being treated by 30 and 50% NaOH, it can be found that 1 M HCl leaching outperformed ammonium sulfate leaching by only 11-13% absolute percentage points. The difference in recovery was mainly attributed to the improvements in the recoveries of LREEs, especially for Ce, which is the most abundant REE in the flotation concentrate. Ce recovery (34.26%) obtained by ammonium sulfate was two times less compared to the one (71.78%) in the case of 1 M HCl leaching from the 30% NaOH-treated sample. It is known that $\text{Ce}(\text{OH})_3(\text{s})$ can be readily oxidized into $\text{CeO}_2(\text{s})$, which is difficult to be dissolved by a weak acid. However, it can be dissolved by 1 M HCl due to its strong acidity. At pH 3, the dissolution of $\text{CeO}_2(\text{s})$ was not complete, and thus the ion-exchange process between the Ce^{3+} ions and NH_4^+ ions was less favored. For the critical REEs such as Nd and Dy, the recoveries of ammonium sulfate were only 13%

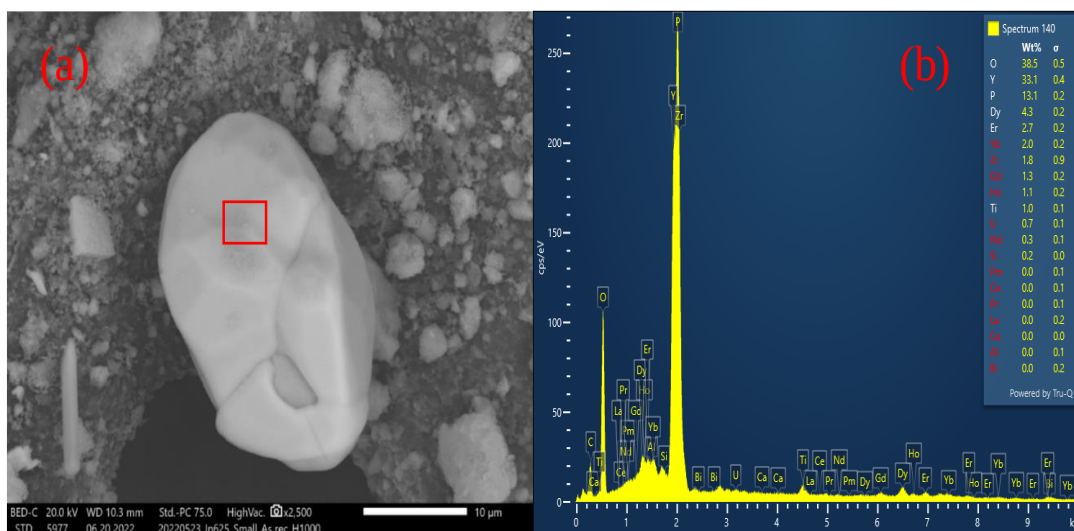


Figure 6.11 SEM image (a) and EDS spectrum (b) of a xenotime particle found in the leaching residue of 1 M HCl after 50% NaOH pretreatment at 80 °C for 1 h.

lower or even comparable to those of the HCl leaching. The leaching behavior of Th was found to be parallel with that of TREE recovery. The high Th recovery also suggested that most LREE-containing minerals had been dissolved. Moreover, compared to 1 M HCl, the partition of Th in the leachates of ammonium sulfate was lower, which may be another benefit of the ammonium sulfate leaching. Hence, it indicates that ammonium sulfate leaching still has the potential to be an alternative lixiviant to HCl in terms of extracting REEs from the upgraded concentrate.

6.3.3.2 Effect of Particle Size on the Leaching Efficiency

A sample split with the $d_{80} = 1.90 \mu\text{m}$ was also subjected to ammonium sulfate leaching after NaOH

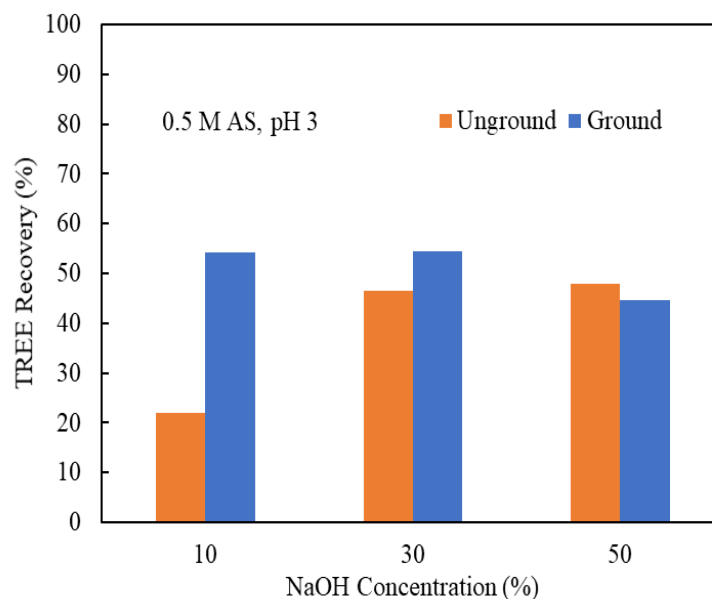


Figure 6.12 Effect of particle size on the TREE recovery of ammonium sulfate after NaOH pretreatment conducted at 80 °C for 1 h. The leaching tests were all conducted at room temperature.

pretreatment. The leaching results of the samples with and without grinding are compared in Figure 6.12. As shown, the enhancement of grinding on the REE leachability depended on the NaOH concentration. Compared to the unground sample, ultrafine grinding significantly improved the leaching efficiency by more than two times (i.e., from 22 to 56%) after 10% NaOH pretreatment, while a smaller increase (9%) was found at 30% NaOH. The recoveries for the ground and unground samples were comparable after 50% NaOH pretreatment. As mentioned in Figure 6.10, 30% and 50% NaOH solutions can decompose the majority of the LREE-containing particles in the unground sample, and the remaining REMs were difficult-to-leach. Therefore, only limited improvements in the TREE recovery were obtained at those two concentrations even after grinding, which can create more surface area and liberate the intergrown REMs. However, the conversion of REPO_4 to its readily leachable forms by 10% NaOH was limited due to its weak alkalinity. As such, the enhancement of particle size reduction on the leaching efficiency was more significant for the 10% NaOH-treated sample than in other cases. However, considering the considerable

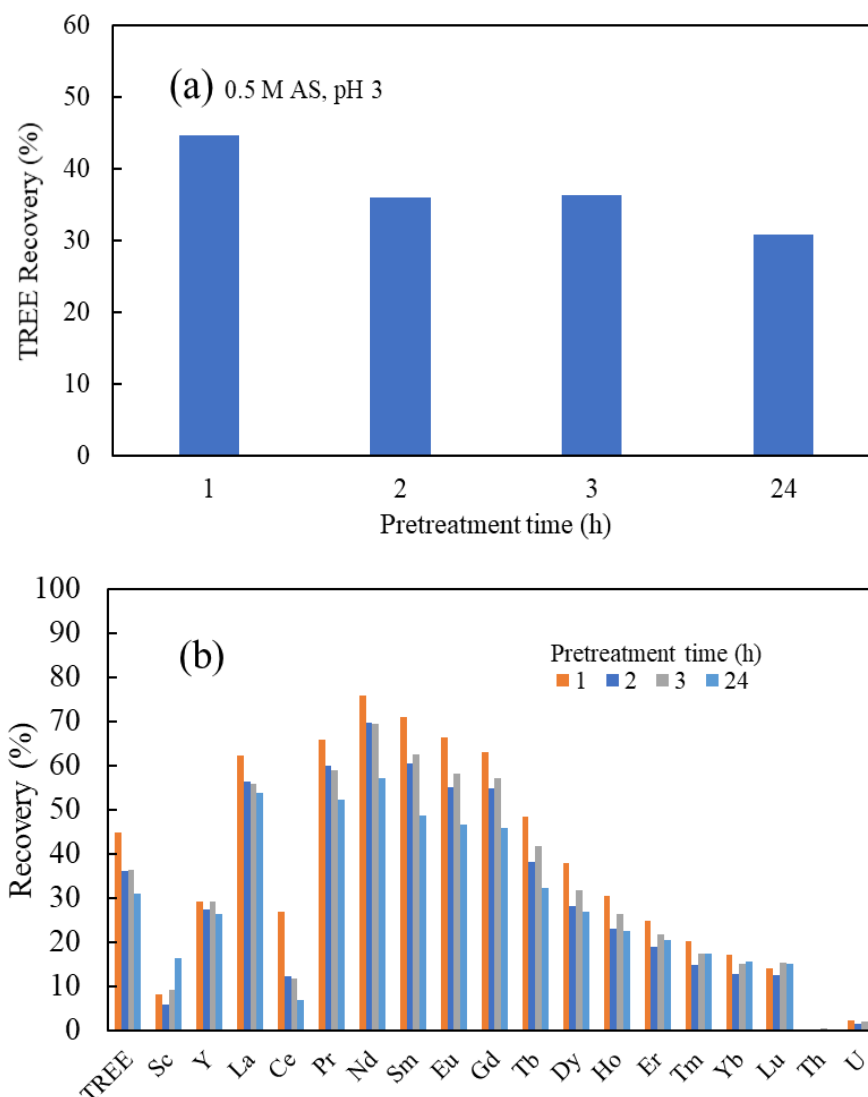


Figure 6.13 Effect of pretreatment time on the TREE recovery (a) and individual REE recovery (b) of 0.5 M ammonium sulfate, pH 3, room temperature. Pretreatment: 50% NaOH, 80 °C, 1-24 h; leaching conditions: 0.5 M ammonium sulfate, pH 3, and room temperature.

amount of energy consumption involved in ultrafine grinding, it may be more cost-effective to use 30% NaOH rather than grinding the sample to maximize the leaching efficiency.

6.3.3.3 Effect of Contact Time on the NaOH Pretreatment Step

The last section revealed that the reduction of particle size did not facilitate the leaching efficiency of the samples treated by 50% NaOH. To further maximize the leaching efficiency, the effect of pretreatment duration on the leaching efficiency of ammonium sulfate was studied in this section. Figure 6.13 shows the effect of pretreatment time on the TREE and individual REE recovery of ammonium sulfate leaching from the flotation concentrate. Instead of positively facilitating the leaching process, prolonging the pretreatment time deteriorated the leaching recovery since a decreasing trend of TREE recovery was noticed (see Figure 6.13a). Figure 6.13(b) shows that the reductions of LREE recoveries (i.e., La, Ce, Pr, Nd, and Sm) were more severe than those of HREEs. For instance, Ce recovery was negatively affected to a greater extent relative to other REEs, with its recovery reducing from 26.74% to merely 6.93% when the duration time varied from 1 to 24 h. Again, this was attributed to the oxidation of Ce (III) to its difficult-to-leach form, i.e., CeO₂(s), after more prolonged exposure to the dissolved oxygen in the NaOH solution. Yang et al. (2021) investigated the impact of NaOH pretreatment contact time on the leaching performance of REEs from coal-derived clays by HCl, and the results also indicated that the leaching recovery was not improved by prolonging contact time. Moreover, the authors found that extending the contact time caused the significant dissolution of dominant minerals such as clays, which released high fractions of Al and other contaminants into NaOH solutions. Therefore, 1 h would be the optimal contact time for the pretreatment step.

6.3.3.4 Chemical Compositions of the Used NaOH Solutions

In order to investigate the dissolution of the dominant minerals during the NaOH pretreatment step, the partitions of REEs and other impure elements (i.e., TREE, Sc, Al, Si, P, Ca, Fe, and Ti) in the used NaOH solutions of the tests shown in Figure 6.9 were analyzed and compared. As presented in Figure 6.14, the fraction of Ti in each of the used NaOH solution was negligible (<0.1%) since Ti was primarily in its oxide form under alkali conditions. The fraction of REEs partitioned into the NaOH solutions was less than 0.8%. However, higher fractions of Sc were partitioned into the NaOH solutions. The recovery gradually

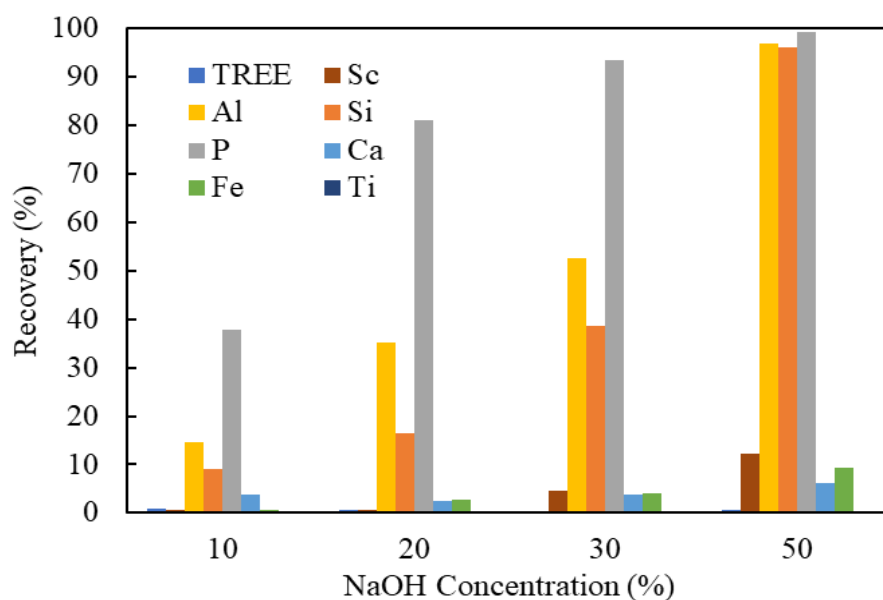


Figure 6.14 Partitions of TREE, Sc, and major impure elements (Al, Si, P, Ca, Fe, and Ti) in the used NaOH solutions of the leaching tests shown in Figure 6.9.

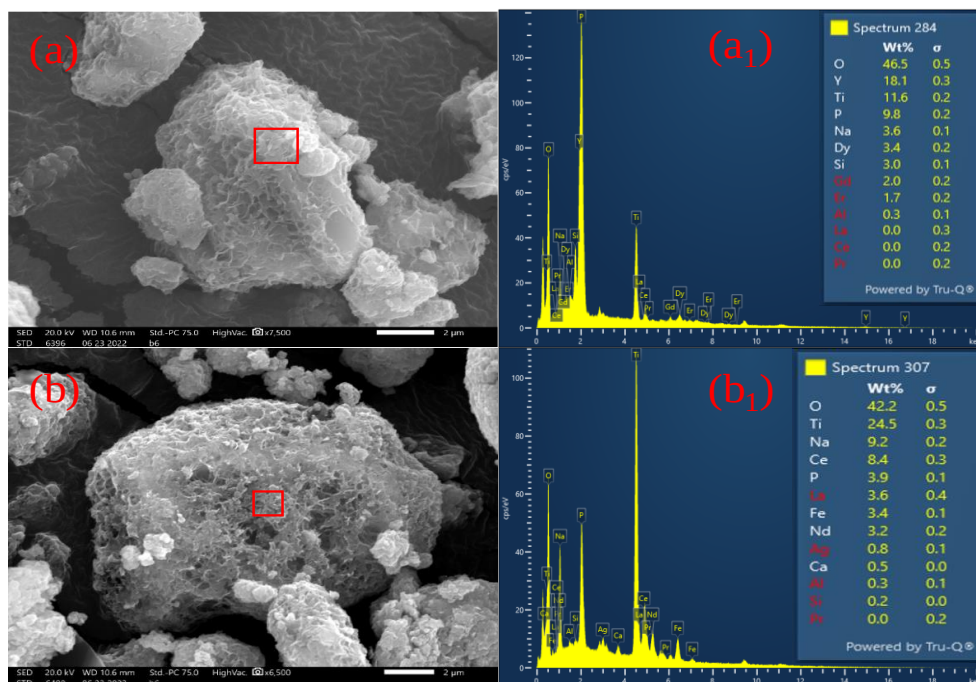


Figure 6.15 SED images and the EDS spectra of REMs found in the flotation concentrate after NaOH pretreatment (80 °C, 1 h). (a): xenotime; (b): probably monazite associated with $\text{TiO}_2(\text{s})$, and their corresponding EDS spectra (a₁) and (b₁), respectively.

increased from 0.5% to 12.1% as the alkali concentration increased from 10 to 50%. This can be explained by the formation of $\text{ScO}_2(\text{aq})$ above pH 12 and then left in the NaOH solution (Li et al., 2022). During the alkali pretreatment step, the majority of $\text{REPO}_4(\text{s})$ was converted to its insoluble hydroxide form. The SEM images of the NaOH-treated sample show that the surface morphology of the two selected REE-bearing particles became rough and porous (see Figure 6.15), by which the lixiviant molecules are more accessible to the inside of the REE-containing species.

Over 90% of P was partitioned into 30 and 50% NaOH solutions, probably in the form of Na_3PO_4 . Such high P recoveries were expected since the high TREE recoveries were achieved at those two NaOH concentrations. In the alkali cracking of monazite process, nearly all the P reported to the used NaOH solutions (Panda et al., 2014). It is known that phosphate ions have a strong affinity for RE^{3+} ions, and they can easily combine with REEs and reprecipitate as secondary REPO_4 , which can undermine the leaching efficiency once they are all in the leachate. As such, the high fraction of P left in the used NaOH solution will favor the following leaching step.

The dissolution of Al and Si also gradually increased from around 10% to 95% as the NaOH concentration varied from 10 to 50%. Those two elements mainly resulted from the dissolution of kaolinite, which only has 3.2% in the feed. Since the content of Ca was only 8,100 ppm in the flotation concentrate, the low partitions (3.8 to 6.2%) of Ca demonstrated that only a small amount of this element was left in the used NaOH solutions. In the flotation concentrate, Fe mainly associates with the anatase crystal by isomorph substitution and iron oxide (Yoon et al., 1992). Fe can occur in the form of $\text{Fe}(\text{OH})_4^-$ at basic pH conditions, which may be the reason for the increasing partition (from 0.6 to 9.4%) as a function of NaOH concentration. According to this section, the impurities left in the NaOH solutions were mainly P, Al, and Si.

6.3.3.5 Ratios of TREE Content versus Impurities in the Leaching Solutions.

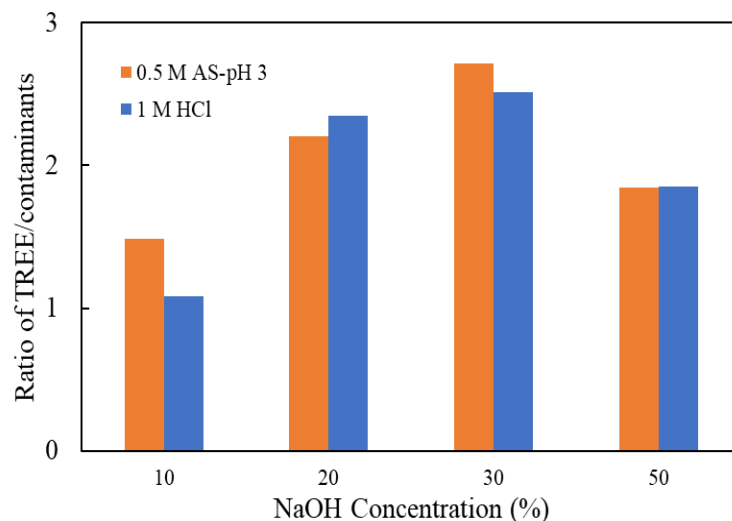


Figure 6.16 The Mass ratios of the amount of REEs over the total amounts of the contaminants (Mg, Ca, Al, Si, and Fe) in the leachates of the NaOH-treated samples shown in Figure 6.9 as a function of NaOH concentration.

Based on the experimental data of the leaching tests shown in Figure 6.9, the partitions of impurities in the leaching solutions were also investigated by calculating the ratio of the amount of REEs over the total amount of the contaminants (i.e., Mg, Ca, Al, Si, and Fe). On the other hand, this ratio can also evaluate the selectivity of REEs over impurities during the leaching process. If considerable amounts of those divalent and trivalent cations are co-extracted, it will render the downstream processes, such as solvent extraction, more complicated and expensive. As presented in Figure 6.16, the ratio gradually increased with the NaOH concentration. It peaked at 30% NaOH, after which it decreased to around 1.8. The highest ratio of 2.7 was achieved in the ammonium sulfate leaching solution of the 30% NaOH-treated sample, which was 0.2 higher than the one in HCl leachate at the same NaOH concentration. This indicated that the total

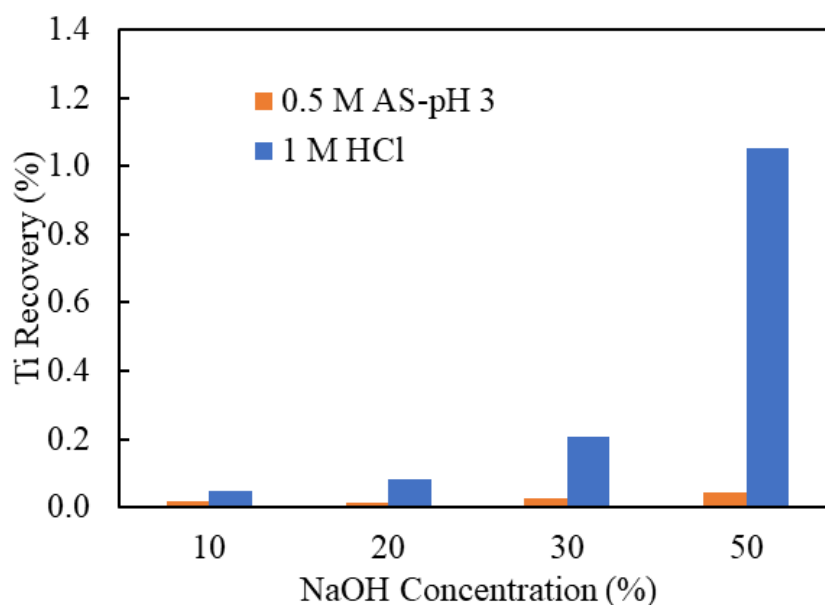


Figure 6.17 Partitions of Ti in the leachates as a function of NaOH concentration in the leachates of the tests shown in Figure 6.9.

amounts of REEs were 2.5 and 2.7 times more abundant than those of impure elements in the leachates, suggesting that the extraction was more selective in those two leaching tests than in other cases. The reduced ratios by 50% NaOH were mainly explained by the increased amounts of impure elements released into the leachates, while no extra REEs were extracted, leading to reduced selectivity. Due to the poor leaching efficiency achieved from the sample treated by 10% NaOH, the lowest ratio was found in the leachate of the 1 M HCl (1.1). Except for 20% NaOH, the selectivity of REEs over the impurities by ammonium sulfate was higher than that of HCl.

Additionally, the partition of Ti in each leachate was also examined (see Figure 6.17). As shown, minor fractions (<0.04%) of Ti were found in the leachates of ammonium sulfate. However, the fractions of Ti brought into the leachates by HCl leaching were 4 to 26 times higher depending on the NaOH concentrations. Compared to the HCl leaching, ammonium sulfate leaching reduced the dissolution of TiO_2 to a greater extent due to the higher leaching pH. Therefore, it can be concluded that the leaching tests conducted after 30% NaOH pretreatment were more selective for REEs over contaminants.

6.3.3.6 XRD Analysis of NaOH-treated Samples and Subsequent Leached Samples

XRD characterizations of the flotation concentrate, the NaOH-treated samples, and the leaching residues were performed in this section to determine the mineralogical changes before and after the chemical extraction process (see Figure 6.18). As presented, spectra b, c, and e show that nearly no mineralogical changes were observed from the samples treated with 10% and 30% NaOH as well as the leaching residue of ammonium sulfate of the 30% NaOH-treated sample. Anatase, rutile, and zircon were the major minerals akin to the feed material (see spectrum a). Moreover, several peak shifts to higher angles, as indicated by the brown areas in Figure 6.18, were noticed for the spectra of d, f, and g. Those peaks were assigned to aluminum titanium silicate ($\text{Al}_4\text{Ti}_2\text{SiO}_{12}$) instead of anatase by the Jade 6.0 software. However, Wang et al. (2016) suggested that those two minerals have very similar crystal structures, and the formation of $\text{Al}_4\text{Ti}_2\text{SiO}_{12}$ was due to the substitution of $10/3 \text{ Ti}^{4+}$ by $8/3 \text{ Al}^{3+}$ and $2/3 \text{ Si}^{4+}$ in the unit cell of anatase.

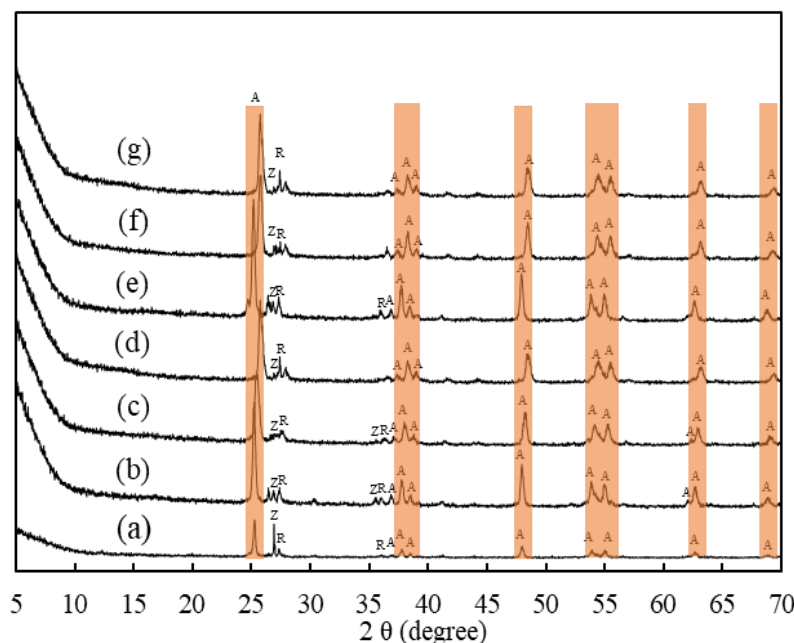


Figure 6.18 XRD spectra of a) flotation concentrate; b) 10% NaOH-treated; c) 30% NaOH-treated; d) 50% NaOH-treated; e) 30% NaOH-treated + AS leached; f) 30% NaOH-treated + 1 M HCl leached; g) 50% NaOH-treated + 1 M HCl leached flotation concentrate. Note: A: anatase; Z: zircon; R: rutile.

Such stoichiometry suggests that the massive formation of $\text{Al}_4\text{Ti}_2\text{SiO}_{12}$ was not favored in this study due to the lack of reactants (i.e., Al and Si). The authors also suggested that the XRD patterns of anatase and $\text{Al}_4\text{Ti}_2\text{SiO}_{12}$ are quite similar to each other. Therefore, it was less likely to assign the peaks to $\text{Al}_4\text{Ti}_2\text{SiO}_{12}$ since the amounts of Al (3.79%) and Si (3.29%) are much lower than that of Ti (35.0%) in the flotation concentrate. The peak shifts may be due to the variations of lattice parameters (e.g., d-spacing) caused by the NaOH pretreatment and leaching steps (Ishikawa et al., 2006; Nakaruk et al., 2010). Accordingly, it is still reasonable to attribute those peaks to anatase rather than $\text{Al}_4\text{Ti}_2\text{SiO}_{12}$ in the spectra d, f, and g. Additionally, the reduced peak intensity of zircon suggested that it was partially dissolved, especially in the leaching residues of HCl. Therefore, anatase was still the dominant mineral after the chemical extraction.

6.3.4 Proposed Processing Circuit

Based on the current flowsheet used in the kaolinite plant, the conceptual flowsheet proposed for the processing of flotation reject material is shown in Figure 6.19. After flotation, kaolinite is the first byproduct that can be recovered. Subsequently, NaOH pretreatment followed by ammonium sulfate leaching is performed to recover most of the LREEs and a small fraction of HREEs. Furthermore, the leaching residue can be used to produce high-grade anatase and recover HREEs under more aggressive conditions. Future work will be conducted on the production of high-grade anatase and co-extraction of HREEs.

6.4 Summary and Conclusions

In the present work, the possibility of preconcentrating REEs from a kaolinite sludge by flotation and the HHS process was explored using octanohydroxamic acid as a collector. The results showed that the TREE contents of the final HHS and flotation concentrates were 10,765 and 6,535 ppm, respectively after one rougher and one cleaning stage, and the corresponding recoveries were 71.5% and 75.5%. Despite a relatively lower TREE content, the recovery versus grade curve of the flotation test suggested that

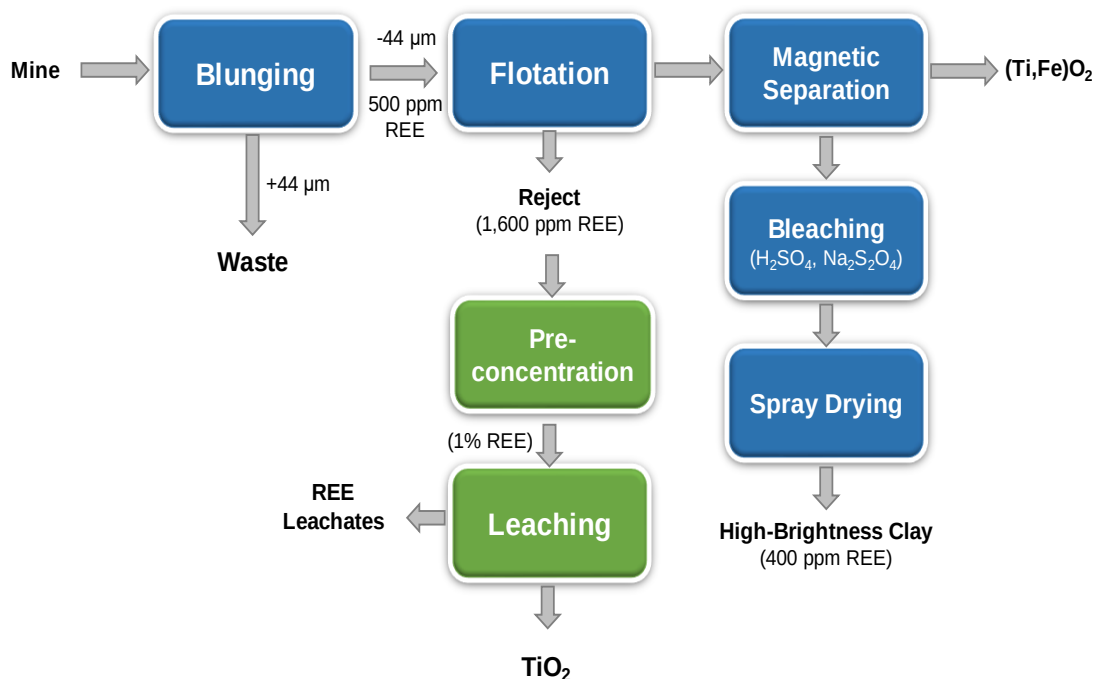


Figure 6.19 Proposed conceptual flowsheet for the processing of kaolinite flotation concentrate for the production of different products.

performing one rougher and one cleaning stage was optimal. The outstanding performance of the HHS process over conventional flotation was mainly due to the large contact angle and less hydraulic entrainment.

XRD characterization found that the final concentrate mainly consisted of anatase, rutile, and zircon, while most of the kaolinite was reported to the tailing product. The microscopic characterizations (SEM- and TEM-EDS) and statistical analysis of the elemental composition suggested that crandallite group minerals and monazite are the primary host minerals for LREEs, while HREEs are primarily enriched in xenotime and a small amount of zircon.

It has been indicated that 1 h of pretreatment by 30% NaOH at 80 °C was sufficient to decompose the majority of LREE-enriched minerals in a flotation concentrate, whereas the decomposition of HREE-bearing minerals (e.g., xenotime) was limited. Ammonium sulfate leaching conducted at pH 3 and room temperature can recover around 70% of La, Nd, Pr, Sm, and Gd, which were increased to about 80% when leached by 1 M HCl leaching. In addition, ultrafine grinding only significantly enhanced the leaching performance of the sample treated by 10% NaOH. However, the revenues from the improved recovery and reduced alkali consumption may not offset the high grinding cost.

Lastly, chemical composition analysis of the used NaOH and the leaching solutions, combined with the XRD characterization, revealed that ammonium sulfate leaching was more selective relative to the HCl leaching, even though the latter gave higher recovery. On the other hand, the leaching residue may be a potential feedstock for the preparation of high-grade anatase. Findings from this study indicate that kaolinite flotation reject can also be promising feedstocks for REEs and Ti after simply preconcentration by flotation.

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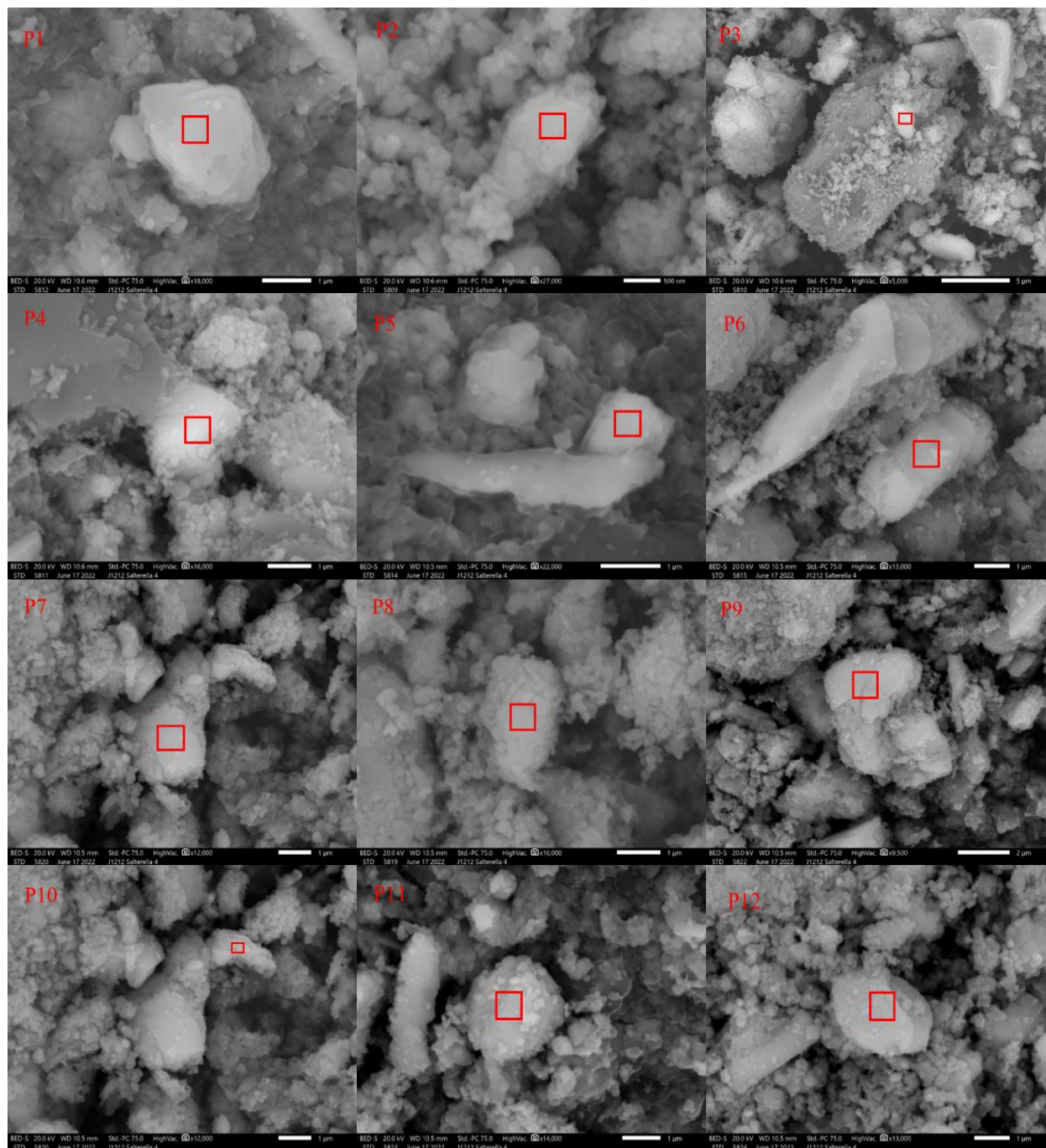
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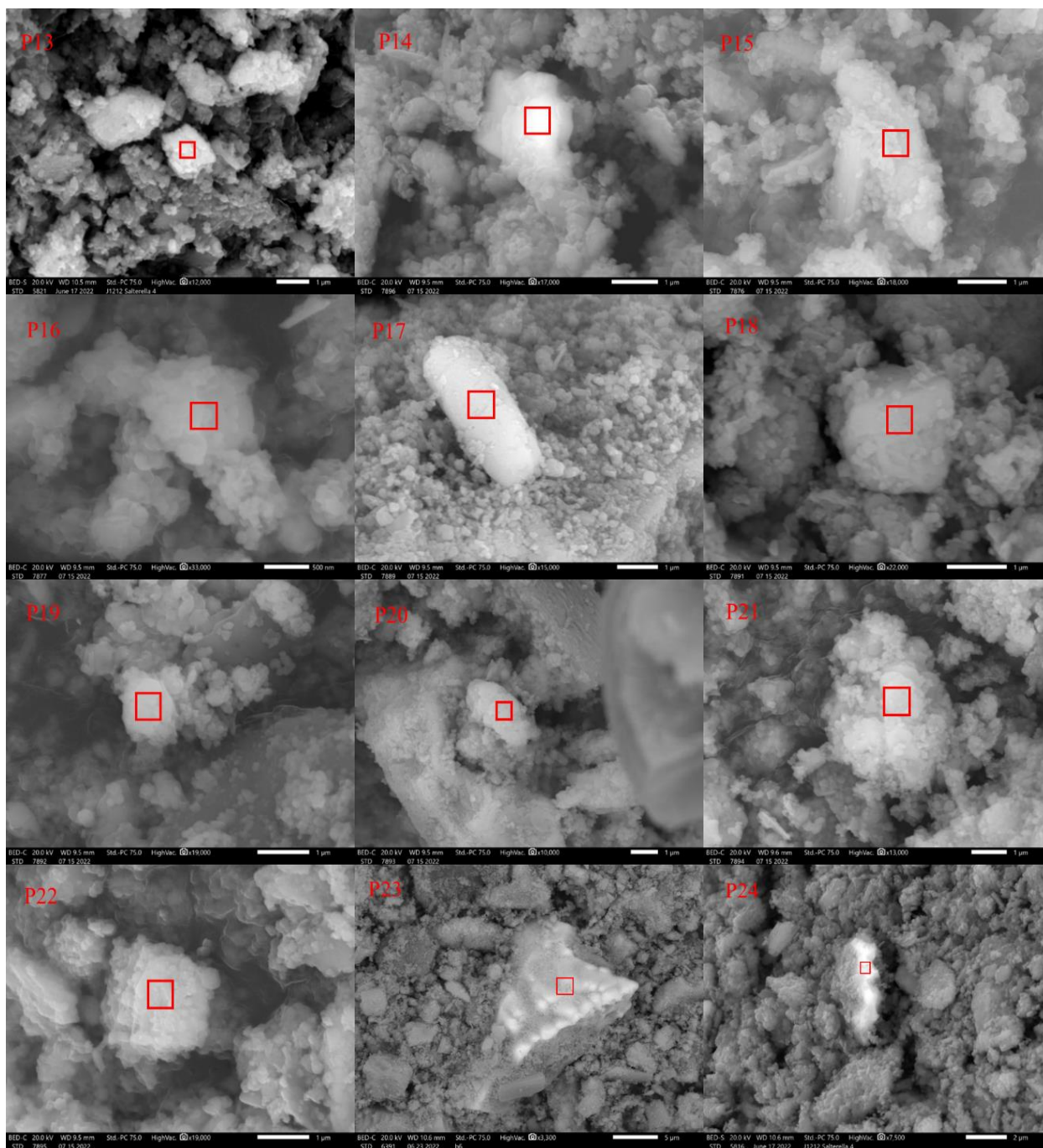
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Appendix A Summary of the SEM Characterization Results of the Flotation Concentrate

1. SEM images of the LREE-contained particles





2. SEM images of HREE-enriched particles

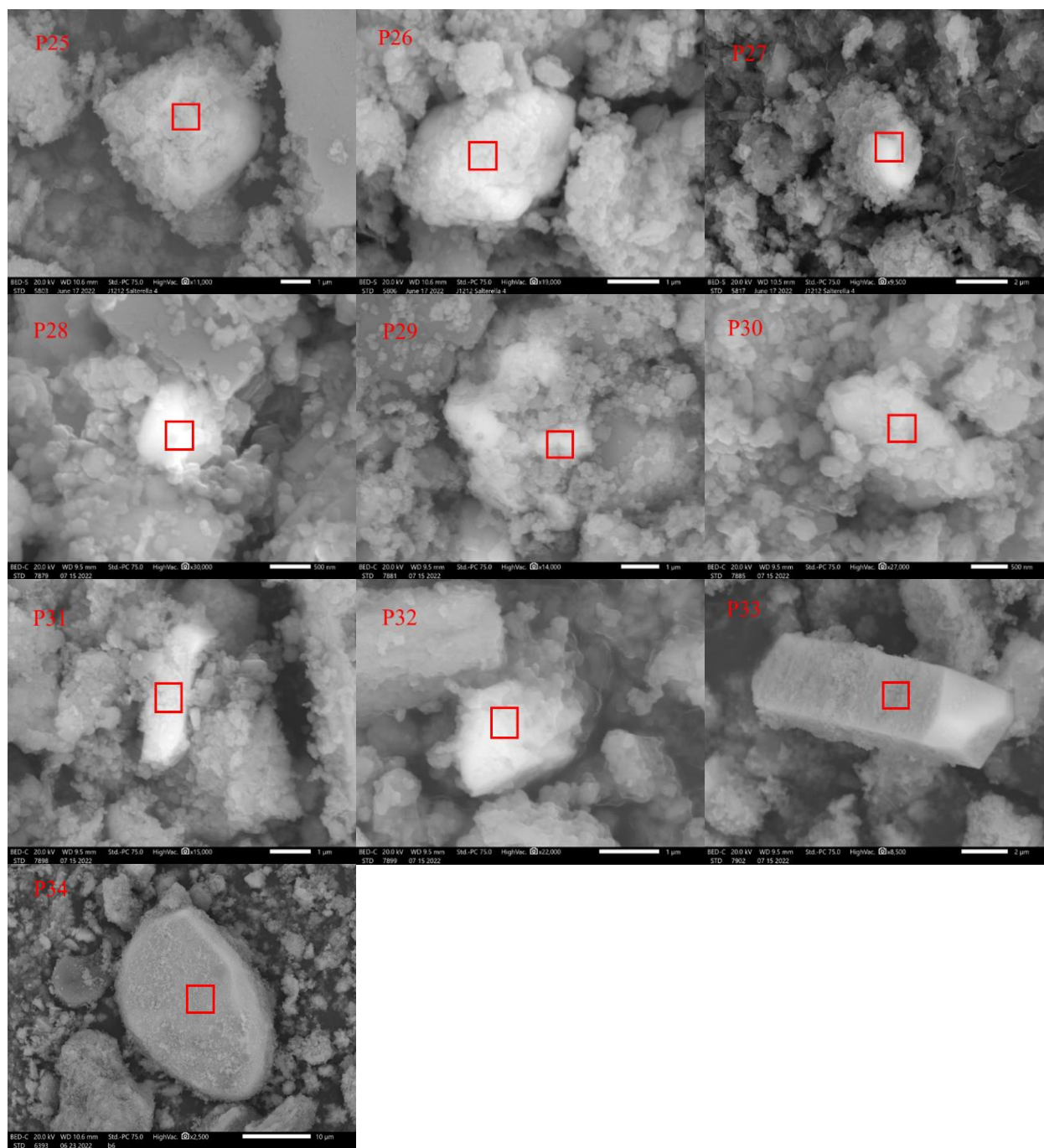
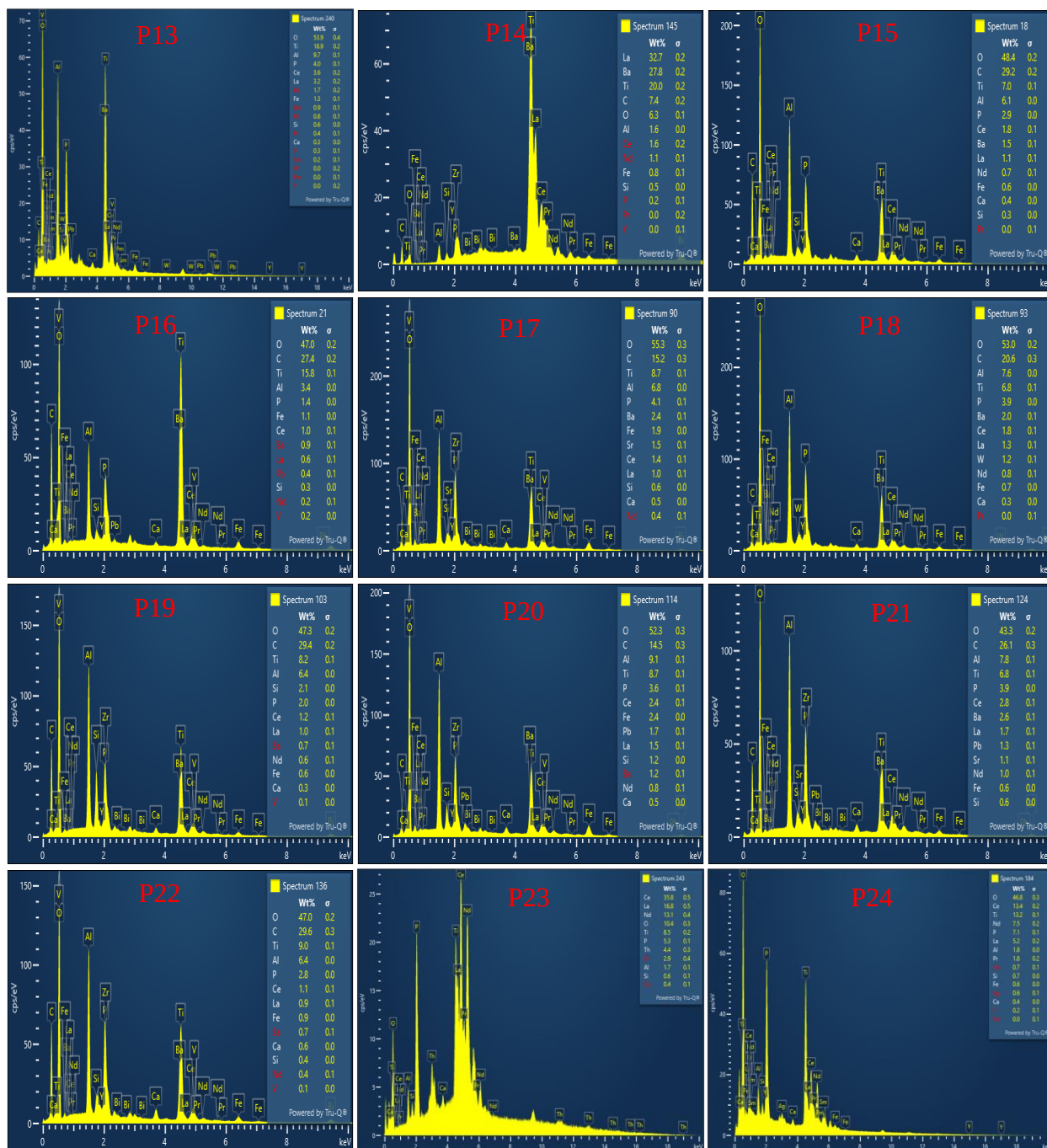


Figure 1 displays 12 XPS spectra (P1-P12) of the catalysts. Each panel shows intensity (counts) vs. binding energy (eV) from 0 to 18. The spectra are for: P1 (Spectrum 138), P2 (Spectrum 137), P3 (Spectrum 136), P4 (Spectrum 130), P5 (Spectrum 158), P6 (Spectrum 162), P7 (Spectrum 225), P8 (Spectrum 221), P9 (Spectrum 258), P10 (Spectrum 227), P11 (Spectrum 263), and P12 (Spectrum 281). Each panel includes a table of peak data (Element, Binding Energy, Intensity, Area) and a 'Powered by Thermo' label.



4. EDS spectra of HREE-enriched particles

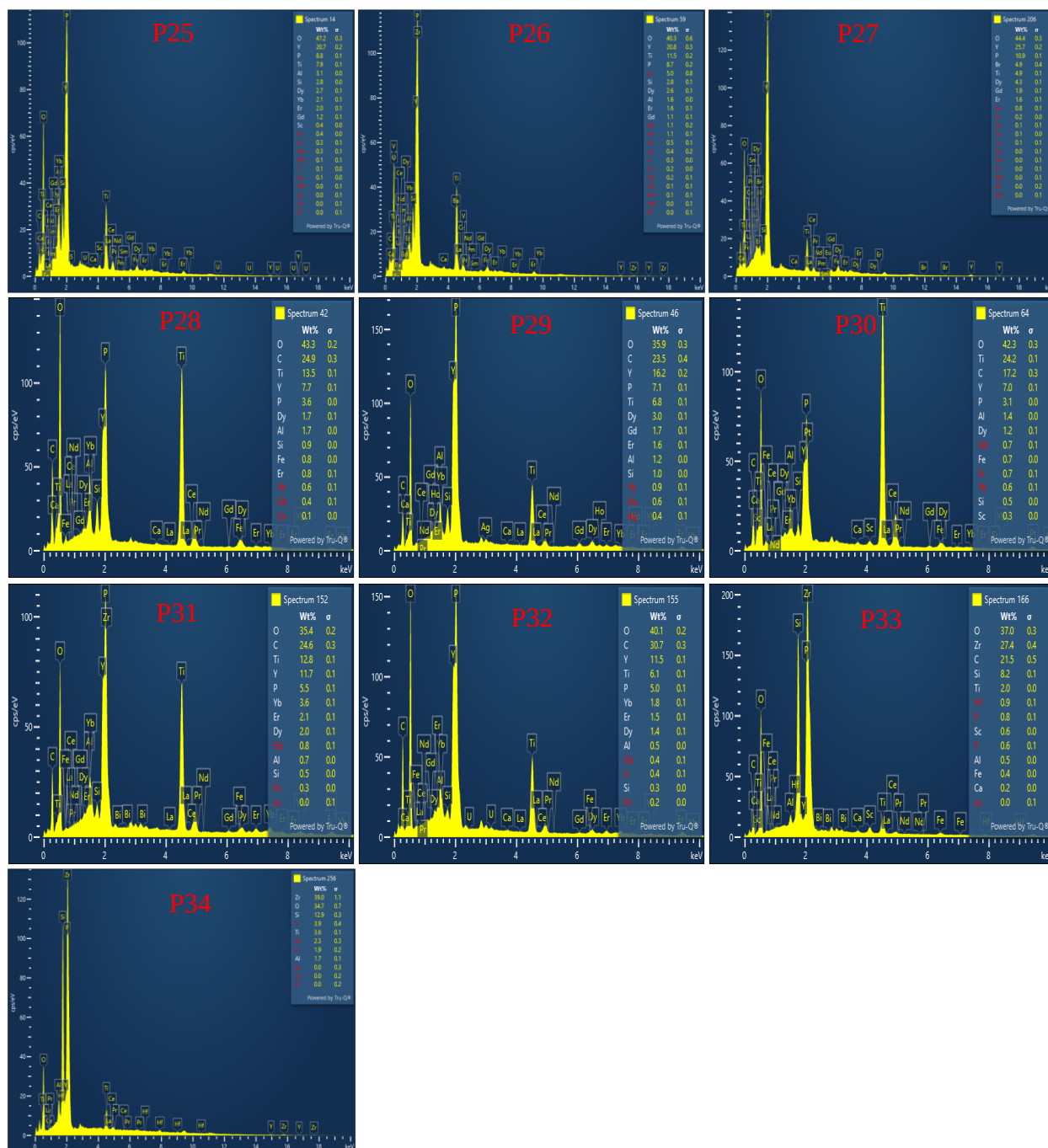


Table A1. Summary of the EDS spectra for the REE-bearing particles.

Particle	REE bearing minerals	P	Al	Si	Ca	Sr	Ba	Sc	Ti	Fe	Zr	Y	La	Ce	Pr	Nd
1	Cra.	7.4	13.8	0.6	1.3	2.8	1.1	0.0	6.1	0.4	0.0	0.4	1.8	3.1	0.3	1.1
2	Cra.	4.7	8.9	0.8	0.7	1.5	2.6	0.0	18.8	1.6	0.0	0.3	1.2	2.0	0.0	1.5
3	Cra.	5.4	13.3	4.6	0.9	1.3	2.2	0.0	9.6	0.9	0.0	0.0	1.0	1.7	0.2	1.0
4	Cra.	6.5	12.0	2.0	0.6	1.3	6.0	0.0	8.9	2.1	0.0	0.0	1.4	2.3	0.3	0.9
5	Cra.	4.7	9.9	0.9	0.5	0.0	0.0	0.0	11.7	1.5	0.0	0.0	1.6	2.3	0.4	1.5
6	Cra.	6.5	13.2	0.5	0.9	1.7	2.9	0.0	7.0	1.1	0.0	0.4	2.0	3.3	0.4	1.3
7	Cra.	7.3	13.1	0.4	1.4	1.7	3.0	0.0	7.8	1.1	0.0	0.3	2.4	2.4	0.3	1.4
8	Cra.	6.6	12.3	0.8	0.6	1.3	4.7	0.0	10.4	0.8	0.0	0.2	1.7	2.8	0.2	0.8
9	Cra.	8.4	16.1	0.3	0.9	0.0	4.4	0.0	4.6	0.6	0.0	0.0	2.5	3.2	0.3	2.3
10	Cra.	4.6	9.1	0.6	0.6	0.0	3.1	0.0	15.2	1.3	0.0	0.0	1.0	1.4	0.1	0.7
11	Cra.	6.7	12.1	0.6	1.1	2.0	0.0	0.0	9.8	1.0	0.0	0.4	1.1	2.8	0.2	0.8
12	Cra.	6.2	12.4	0.5	1.1	1.3	0.0	0.0	8.3	0.8	0.0	0.3	1.8	2.1	0.3	1.3
13	Cra.	4.0	9.7	0.6	0.3	0.0	1.7	0.0	18.9	1.3	0.0	0.0	3.2	3.6	0.4	0.9
14	Cra.	0.2	1.6	0.5	0.0	0.0	27.8	0.0	20.0	0.0	0.0	0.0	32.7	1.6	0.0	1.1
15	Cra.	18.0	2.9	6.1	0.3	0.4	0.0	1.5	0.0	7.0	0.0	0.6	0.0	1.1	1.8	0.0
16	Cra.	21.0	1.4	3.4	0.3	0.0	0.0	0.9	0.0	15.8	0.0	1.1	0.2	0.6	1.0	0.0
17	Cra.	90.0	4.1	6.8	0.6	0.5	1.5	2.4	0.0	8.7	0.0	1.9	0.0	1.0	1.4	0.0
18	Cra.	93.0	3.9	7.6	0.0	0.3	0.0	2.0	0.0	6.8	0.0	0.7	0.0	1.3	1.8	0.0
19	Cra.	2.0	6.4	2.1	0.3	0.0	0.7	0.0	8.2	0.6	0.0	1.0	1.2	0.0	0.6	0.0
20	Cra.	3.6	9.1	1.2	0.5	0.0	1.2	0.0	8.7	2.4	0.0	1.5	2.4	0.0	0.8	0.0
21	Cra.	3.9	7.8	0.6	0.0	1.1	2.6	0.0	6.8	0.6	0.0	1.7	2.8	0.0	1.0	0.0
22	Cra.	2.8	6.4	0.4	0.6	0.0	0.7	0.0	9.0	0.9	0.0	0.9	1.1	0.0	0.4	0.0
23	Mon	5.3	1.7	0.6	0.4	0.0	0.0	0.0	8.5	0.0	0.0	16.8	35.8	2.9	13.1	0.0
24	Mon	7.1	1.8	0.7	0.4	0.0	0.0	0.0	13.2	0.6	0.2	5.2	13.4	1.8	7.5	0.0
25	Xen.	8.8	3.1	2.8	0.1	0.0	0.0	0.4	7.9	0.4	0.0	20.7	0.0	0.0	0.0	0.0
26	Xen.	8.7	1.6	2.8	0.2	0.0	0.0	0.0	11.5	0.5	0.5	20.8	0.4	0.0	0.0	0.0
27	Xen.	10.9	0.0	0.2	0.1	0.0	0.0	0.0	4.9	0.1	0.0	25.7	0.1	0.0	0.0	0.0
28	Xen.	3.6	1.7	0.9	0.1	0.0	0.0	0.0	13.5	0.8	0.0	7.7	0.0	0.0	0.0	0.0
29	Xen.	7.1	1.2	1.0	0.0	0.0	0.0	0.0	6.8	0.0	0.0	16.2	0.0	0.0	0.0	0.0
30	Xen.	7.0	1.4	0.5	0.0	0.0	0.0	0.3	24.2	0.7	0.0	7.0	0.0	0.0	0.0	0.0
31	Xen.	5.5	0.7	0.5	0.0	0.0	0.0	0.0	12.8	0.3	0.0	11.7	0.0	0.0	0.0	0.0
32	Xen.	5.0	0.5	0.3	0.0	0.0	0.0	0.0	6.1	0.2	0.0	11.5	0.0	0.0	0.0	0.0
33	Zir	1.9	1.7	12.9	0.0	0.0	0.0	0.0	3.9	0.0	39.0	3.9	0.0	0.0	0.0	0.0
34	Zir	0.8	0.5	8.2	0.2	0.0	0.0	0.6	2.0	0.4	27.4	0.6	0.0	0.0	0.0	0.0

Note: Cra.: crandallite; Mon.: monazite; Zir.: zircon.

Table A1. Summary of the EDS spectra for the REE-bearing particles (continued).

Particle	REE bearing minerals	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	TREE	P/Ca	Ba+Sr
1	Cra.	0.1	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	7.0	5.7	3.9
2	Cra.	0.2	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.5	6.7	4.1
3	Cra.	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.1	6.0	3.5
4	Cra.	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.1	10.8	7.3
5	Cra.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.8	9.4	0.0
6	Cra.	0.1	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	7.8	7.2	4.6
7	Cra.	0.1	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	7.1	5.2	4.7
8	Cra.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.7	11.0	6.0
9	Cra.	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.4	9.3	4.4
10	Cra.	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.3	7.7	3.1
11	Cra.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.3	6.1	2.0
12	Cra.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.8	5.6	1.3
13	Cra.	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.3	13.3	1.7
14	Cra.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	35.4	None	27.8
15	Cra.	0.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	15.3	7.3
16	Cra.	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
17	Cra.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	13.6	8.2
18	Cra.	0.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	25.3	13.0
19	Cra.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.8	1.4	0.7	6.7
20	Cra.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.7	1.3	1.2	7.2
21	Cra.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.5	1.4	3.7	0.0
22	Cra.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.4	0.9	0.7	4.7
23	Mon	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	68.6	12.9	0.0	13.3
24	Mon	0.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	28.8	4.1	0.0	17.8
25	Xen.	0.0	0.3	0.0	1.2	0.0	2.7	0.0	2.0	0.0	2.1	0.0	29.4	88.0	0.0
26	Xen.	0.0	0.1	0.0	1.1	0.0	2.6	0.0	0.0	0.0	1.1	0.0	26.1	43.5	0.0
27	Xen.	0.0	0.0	0.0	1.9	0.0	4.3	0.0	1.6	0.0	0.0	0.0	33.6	109.0	0.0
28	Xen.	0.0	0.0	0.0	0.4	0.0	1.7	0.0	0.8	0.0	0.6	0.0	11.2	36.0	0.0
29	Xen.	0.0	0.0	0.0	1.7	0.0	3.0	0.6	1.6	0.0	0.9	0.0	24.0	None	0.0
30	Xen.	0.0	0.0	0.0	0.7	0.0	1.2	0.0	0.7	0.0	0.6	0.0	10.5	None	0.0
31	Xen.	0.0	0.0	0.0	0.8	0.0	2.0	0.0	0.0	0.0	3.6	0.0	18.1	None	0.0
32	Xen.	0.0	0.0	0.0	0.4	0.0	1.4	0.0	1.5	0.0	1.8	0.0	16.6	None	0.0
33	Zir	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.9	None	0.0
34	Zir	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.2	4.0	0.0

Note: Cra.: crandallite; Mon.: monazite; Zir.: zircon.

Chapter 7 Conclusions, Original Contributions, and Recommendations

7.1 Conclusions

Based on the findings in the present work, the conclusions obtained may be summarized as follows:

1. A novel method of extracting rare earth elements (REEs) from monazite has been developed. It consists of displacing the PO_4^{3-} ions by OH^- ions under mild conditions ($<100^\circ\text{C}$) and ammonium sulfate $((\text{NH}_4)_2\text{SO}_4)$ leaching at pH 4 and room temperature. Increasing the leaching temperature and reducing particle size can significantly benefit the leaching performances of ammonium sulfate. ζ -potential measurements coupled with thermodynamic studies suggest that the $(\text{NH}_4)_2\text{SO}_4$ leaching may be explained by an ion exchange leaching mechanism after releasing RE^{3+} ions by acid from $\text{RE}(\text{OH})_3(\text{s})$. The RE^{3+} ions in the vicinity of the NaOH-treated monazite are displaced by the NH_4^+ ions, which is further illustrated by a conceptual model. The rare earth leaching rate from NaOH-treated monazite by ammonium sulfate was found to be controlled by a chemical process, with the determined activation energy being 61.28 kJ/mol. An empirical equation developed for the leaching process is $1 - (1 - x)^{\frac{1}{3}} = 4.79 \cdot r_0^{-2} e^{-\frac{61280}{RT}}$.

2. Except for formate, it was found that the carboxylate ligands (i.e., acetate, citrate, EDTA, and DTPA) are ineffective to recover REEs from NaOH-treated monazite at room temperature. The leaching kinetics of $\text{La}(\text{OH})_3(\text{s})$ by ammonium acetate and EDTA at pH 4 was inner diffusion-controlled, and the corresponding activation energies were 77.95 and 101.87 kJ/mol, respectively. The kinetic type and high activation energies suggested the formation of a passivation layer on the surface of rare earth hydroxide. The passivating effect was more likely to be the binuclear surface complexes of the carboxylate ligands and REEs, which significantly constrained the dissolution kinetics of $\text{RE}(\text{OH})_3(\text{s})$.

3. Thermodynamic simulation results suggest that EDTA can enhance the dissolution of $\text{REPO}_4(\text{s})$ over a wide pH range (2-13) by initially forming soluble RE-EDTA complexes and subsequently being converted to $\text{RE}(\text{OH})_3(\text{s})$. The ammonium sulfate leaching results showed that the TREE recovery of the samples pretreated by NaOH with EDTA could be substantially improved compared to those without EDTA. The determined optimal conditions for alkali pretreatment are 0.1 M EDTA, 10% NaOH, 40°C , and 24 h, under which the dissolution of the dominant minerals can be significantly reduced. Ammonium sulfate leaching conducted at pH 3 achieved comparable recovery values with 1 M HCl, and exhibited better selectivity for REEs over impure elements (Al, Si, and Fe). The linear correlation between TREE and P recovery indicated that rare earth phosphates are the dominant REE-bearing minerals, and the differences in crystallinity caused varying leaching characteristics of light REEs and heavy REEs.

4. A series of artificial ion adsorption clays (IACs) doping with and without phosphate showed that phosphate resulting from the dissolution of apatite could significantly undermine the ion exchangeability of REEs adsorbed on IACs by passivation. The passivating effect was more severe with the increase of phosphate concentration. It demonstrated that secondary rare earth phosphate might also deposit on the surface of clays in nanoparticle size during the formation of IACs. XPS analysis revealed that the association of the passivation layer should be “clay-RE- PO_4 ”.

5. Physical beneficiation (i.e., flotation and the HHS process) of REE-bearing species from a Georgia kaolinite flotation reject was successful mainly due to the improved liberation of REM particles from the gangue minerals during the blunging step. The mineralogy studies of the HHS concentrate (mainly anatase) showed that LREEs are mainly enriched in crandallite group minerals and monazite, while xenotime and zircon are the HREE-bearing minerals. The application of the proposed ammonium sulfate leaching after NaOH pretreatment can also recover around 80% of the LREEs. The leaching residue can be used to recover Ti as a byproduct. Other than coal-based clay, clayey waste materials from kaolinite industry may also be a promising feedstock for REEs.

7.2 Original Contributions

1. A process consisting of NaOH pretreatment and ammonium sulfate leaching has been found to be effective for extracting REEs from monazite and other clayey waste materials. It can be performed under mild conditions. For instance, the pretreatment step can be conducted at $<100\text{ }^{\circ}\text{C}$ and the following ammonium sulfate leaching can be carried out at pH 3-4 and room temperature. The involved leaching mechanism of ammonium sulfate may be an ion exchange process after the proton attack of $\text{Ln}(\text{OH})_3(\text{s})$.

2. Previous studies have shown that carboxylate ligands can enhance the decomposition of rare earth minerals due to their stronger complexing ability. However, this work found that, except for ammonium formate, other carboxylate ligands (e.g., acetate, citrate, EDTA, and DTPA) are ineffective lixivants for NaOH-treated monazite at room temperature due to the formation of a passivation layer (probably binuclear surface complexes), which significantly reduce the dissolution kinetics. This work is the first to determine the involved kinetic type and activation energy.

3. This study also proposed a novel NaOH pretreatment technique to extract REEs from coal-based clays using dilute NaOH solutions (5-10%) and 0.1 M EDTA. No previous study has been conducted on using EDTA as an additive to enhance the conversion of REPO_4 to $\text{RE}(\text{OH})_3$ in coal-derived clays. The optimal pretreatment conditions, under which relatively high TREE recovery and low mass loss can be achieved, have also been determined. This process can reduce alkali consumption and the decomposition of gangue minerals.

4. Besides primary and secondary rare earth phosphate mineral particles (e.g., monazite, xenotime, crandallite group minerals), this study is also the first to study the possibility that REEs adsorbed on the surface of clays can be passivated by phosphate in the form of “clay-RE- PO_4 ”. The phosphate-passivated REEs may exist in coal-based clays and IACs and undermine the ion-exchange leaching efficiency.

5. A HHS concentrate assaying 10,765 ppm of REEs and 71% recovery was successfully upgraded from a Georgia kaolinite flotation reject material assayed 2,000 ppm. The modes of occurrence of REEs in the final concentrate were mainly rare earth phosphates (e.g., crandallite group minerals, monazite, and xenotime) and zircon. In addition, the leachability of REEs in the concentrate was systematically evaluated. Based on alkali pretreatment technique, an extraction process that can co-extract REEs and Ti has been proposed.

7.3 Recommendations

According to the results obtained in this study, the recommendations for future work may be shown as follows:

1. REE extraction from coal-based clays and the upgraded kaolinite flotation reject have been carried out in this work after NaOH pretreatment. However, compared to LREEs, relatively lower leaching recoveries of HREEs were achieved from both sources. Future studies should be performed to enhance the leachability of HREEs, which are more critical raw materials compared to LREEs.

2. This work showed that NaOH pretreatment can be performed using 2-10% NaOH solutions with the presence of EDTA. However, a proportion of REEs ($<10\%$) partitioned into NaOH solution. It is suggested to study how to recover those REEs lost in the used NaOH solutions.

3. After physical preconcentration of the Georgia kaolinite flotation reject, the REE assay in the final concentrate can be improved to $\sim 1.0\%$, which significantly reduces the cost in the chemical extraction step. Continuous leaching tests should be conducted on the concentrate to obtain data for industrial process design. For instance, the effects of experimental variables such as ammonium sulfate flow rate, solid concentration, and retention time on the leaching efficiency need to be determined and optimized.

4. As suggested by XRD analysis in chapter 6, the dominant mineral in the upgraded flotation concentrate is anatase (58.3%), which is also an important source of Ti. It is, therefore, recommended to explore the possibility of extracting Ti as a co-byproduct from the leaching residue after REE extraction. The revenue from Ti may increase the economic attractiveness of using the kaolinite flotation reject material as a REE feedstock.