Improved separation of Ce, La, and Nd from a concentrate of rare-earth hydroxide via fractional precipitation

I Haritsah, W A Adi, M V Purwani and A Manaf

Centre for Science and Technology of Advanced Materials, National Nuclear Energy Agency (BATAN), Kawasan Puspiptek Serpong, Banten 15314, Indonesia

Corresponding author: azwar@ui.ac.id

Abstract. In this report, we describe the selective and effective separation of Ce, La, and Nd from the concentrate of rare-earth (RE) elements in a hydroxide (REOH) feedstock. The separation steps included dissolving the feedstock into a nitric acid solution and oxidizing the solution with potassium bromate (KBrO₃) as an oxidizing agent to enable precipitation under the addition of sodium hydroxide (NaOH). The yellow precipitates consisted of a concentrate of Ce precipitates, and the filtrate contained La and Nd. The adjustment of the pH of the filtrate to 8.5 with ammonia solution led to the precipitation of Nd and an La concentrate in the filtrate. The developed method was demonstrated to be selective and adequate for the qualification separation of Ce, La, and Nd. This study demonstrates the identification and analysis of REOH from PTBN-G-BATAN, Indonesia, and can be used as a reference for further processing at both the laboratory and industrial scale.

1. Introduction
Rare-earth (RE) elements have low natural abundance, and their reserves are likely to be exhausted. With the development of materials technology, demand for RE elements (REE), which are mostly used in high-technology industries, has increased. RE oxides play important roles in the modern production of materials such as those used in optical, electronic, magnetic, and LED applications [1,2]. In short, REE are expected to play a central role in the development of a huge number of technologies. The pursuit of this aim necessitates the development of separation technologies for various worldwide natural resources [3,4]. Currently, more than 100 RE-bearing minerals are known, but only four are used for the commercial production of RE oxides: monazite ((RE)PO₄), bastnasite ((RE)CO₃)F, xenotime (YPO₄), and RE-bearing clay [5,6].

In recent years, investigators have developed and investigated various separation methods such as solvent extraction, ion exchange, chromatographic extraction, and fractional precipitation. However, the most common method is solvent extraction because of its high efficiency and simple operation. Moreover, various solvents, including di-(2-ethylhexyl) phosphoric acid [7], 2-ethylhexylphosphonic mono-2-ethylhexyl ester [8], bis-2,4,4-tri-methylpentyl phosphinic acid [9], tributylphosphate [10], bis(2-ethylhexyl) (2-ethylhexyl)phosphonate [11], di(1-methyl-heptyl)methyl phosphonate [12], and primary amine N1923 [13,14], have been used to separate Th and other REs. In the process of element
separation in monazite, researchers in India noted the potential benefit of Cyanex 923 in separating La, U, and Th [15]. Furthermore, a mixture of TBP and D2EHPA in a nitric acid medium has been used to successfully purify Th, U, and REEs by supercritical fluid extraction with carbon dioxide [7]. TEHP and TiAP have also been used to separate Th, U, and REE of monazite in a nitric acid medium [16]. The separation of Th and REE in monazite has also been carried out using phosphorylated calixarene in a nitric acid medium [17].

In this paper, we report a selective and effective method for separating Ce, La, and Nd from a concentrate of rare-earth hydroxide (REOH) by fractional precipitation and our identification and analysis of monazite sand acquired from PTBGN-BATAN.

2. Experimental
REOH was supplied by PTBGN-BATAN; all other reagents were acquired from PSTA-Batan Yogyakarta. A 100-g sample of REOH was dissolved in 280 mL of a nitric acid solution for 30 min at 150 °C. Afterwards, the RE nitrate was dissolved with oxalic acid 15% in 5 L of demineralized water; the precipitate that formed was then filtered. Furthermore, the RE oxalate was added to demineralized water containing sodium hydroxide, and the resulting mixture was stirred and heated at 140 °C for 1 h. The REOH precipitate was filtered, washed with hot water until pH 7, and then dried at 110 °C. The REOH concentrate was dissolved in concentrated nitric acid, potassium bromate was added, and the solution was heated at 100 °C. After the oxidation process, 15% ammonia solution was added to the RE nitrate solution to adjust the pH to 4. The precipitate formed was filtered and analyzed. The filtrate was added to 15% aqueous ammonia solution, and the pH was adjusted to 8.5. Oxalic acid (15%) solution was then added to the pH 8.5 solution until precipitate formation ceased. The precipitation process was performed three times. The resulting precipitates were characterized by X-ray fluorescence (XRF) spectroscopy, Fourier transform infrared (FT-IR) spectroscopy, and X-ray diffraction (XRD) analysis.

3. Results and discussion
The REOH obtained from monazite through the alkaline-based processed contains Ce, La, and Nd. To increase the added value of REOH, each element contained therein, especially Ce, La, and Nd, should be separated and obtained as oxides. In this work, Ce, La, and Nd were obtained as CeO, LaO, and Nd(OH) concentrate.

3.1. Reprocessing and reducing chlorine and phosphate contents
Figure 1 shows that the intensities of the peaks of the three dominant elements of La, Ce, and Nd at 33.44 keV, 34.72 keV, and 37.36 keV, respectively, in the XRF spectrum do not substantially change. This lack of change demonstrates that the process of reducing the chlorine and phosphate contents does not substantially affect the main elements.

3.2. Fractional precipitation
After the oxidation process, the RE nitrate solution was adjusted to pH 4 by addition of 15% ammonia solution. The precipitates were filtered and characterized by XRF. The XRF spectrum in figure 2

---

Figure 1. XRF analysis result during reprocessing and reduction of the chlorine and phosphate contents.
shows that the Ce peak at 34.72 keV was the most intense. The filtrate was further adjusted to pH 8.5 by addition of more 15% ammonia solution; the obtained precipitate was collected by filtration and characterized by XRF. Figure 3 shows that the most intense peak in the spectrum is that of the Nd(OH)₃ concentrate at 37.36 keV. The reconstituted filtrate was mixed with oxalic acid until no other precipitates were formed; in the corresponding XRF spectrum in figure 4, the most intense peak is that of La(OH)₃ at 33.44 keV.

3.3. Identification of cerium oxide

Figure 5 shows the FT-IR spectrum of the prepared CeO₂ precipitate. The spectrum of the CeO₂ precipitate shows several absorption bands in the 400–4000 cm⁻¹ range, most notably those at 505–511 cm⁻¹, 1350–1400 cm⁻¹, 1632 cm⁻¹, and 3100–3400 cm⁻¹. The absorption band at 505–511 cm⁻¹ associated with CeO₂ stretching vibration, and at 1632 cm⁻¹ with H₂O (H–O–H) molecular bending frequency. The broad absorption band in the range of 3100–3400 cm⁻¹ represents water that is hydrated and physically adsorbed in the sample.

The XRD patterns used to identify the samples coded Ce-1, Ce-2, and Ce-3 are shown in figures 6, figure 7, and figure 8, respectively. Figure 6 indicates that sample Ce-1 contains cerianite and neodymium oxide phases. Figures 7 and figure 8 indicate that samples Ce-2 and Ce-3 contain only cerianite.
Figure 5. FTIR spectrum of the Ce fractional precipitate

Figure 6. XRD pattern of sample Ce-1 obtained by fractional precipitation of the cerium sample

Figure 7. XRD pattern of sample Ce-2 obtained by fractional precipitation of the cerium sample

Figure 8. XRD pattern of sample Ce-3 obtained by fractional precipitation of the cerium sample

3.4. Identification of lanthanum oxide

Figure 9 shows the FT-IR spectra of the prepared La₂O₃ precipitates. The absorption peak at 3100–3400 cm⁻¹ is related to vibrational modes of water molecules on the sample surface, namely H–O–H bending and the O–H stretching modes that may contribute during the spectra recording process. The weak broad absorption bands at 1320–1400 cm⁻¹ are correspond to the mode of asymmetric stretching vibration of CO₃²⁻ groups. The absorption at 802–810 cm⁻¹ is assigned to bending vibration modes of out-of-plane and in-plane of water and CO₂ adsorbed onto the La(OH)₃ surface. The sharp peak observed at approximately at 500–507 cm⁻¹ is attributed to a stretching vibration of La–O bonds.
The XRD patterns used to identify the phases in samples La-1, La-2, and La-3 are shown in figure 10, figure 11, and figure 12, respectively. The results indicate that the phases present in the samples are lanthanum oxalate hydrate, aluminum, yttrium oxide, yttrium tris(enanthate) dihydrate, and lanthanum tris(2-nephanolate) trihydrate.

3.5. Identification of neodymium oxide

Figure 13 shows the FT-IR spectra of the prepared NdO precipitates. The peak at 1327 cm\(^{-1}\) is ascribed to carbonate groups. The peak at 3100–3400 cm\(^{-1}\) corresponds to the stretching vibration of the O–H bond of absorbed water. The peak at approximately 820 cm\(^{-1}\) is due to neodymium oxide.
Figure 13. Spectrum FTIR of fractional precipitation of Neodymium

Figure 14. XRD pattern of sample Nd-1 obtained by fractional precipitation of the neodymium sample

Figure 15. XRD pattern of sample Nd-2 obtained by fractional precipitation of the neodymium sample

Figure 16. XRD pattern of sample Nd-3 obtained by fractional precipitation of the neodymium sample

The XRD phase analysis of the samples coded Nd-1, Nd-2, and Nd-3 samples are shown in figure 14, figure 15, and figure 16, respectively. Figures 14 and figure 15 indicate that the phases in the Nd-1 and Nd-2 samples were lanthanum oxide, neodymium oxalate hydrate, neodymium squarde hydrate, and neodymium aconite hydrate. Figure 16 indicates that the phases in sample Nd-3 are potassium neodymium silicate, trineodymium silicotetramolybdate, kazonite, and francosite.
4. Conclusions
In this study, we identified and analyze the composition of REOH from PTBGN-BATAN, Indonesia. The XRF spectra showed three dominant elements of La, Ce, and Nd at 33.44 keV, 34.72 keV, and 37.36 keV, respectively. The FT-IR spectra showed absorption bands at 497–510 cm⁻¹, 484–492 cm⁻¹, and 810 cm⁻¹ that correspond to stretching and vibration of CeO₂, a stretching vibration of La–O bonds, and to neodymium oxide. The results of both FTIR and XRF analyses were confirmed by XRD analysis, which showed that the Ce-, La-, and Nd-based precipitates consisted primarily of cerianite and neodymium oxide, lanthanum oxalate hydrate and yttrium oxide, and various neodymium oxide phases, respectively.

Acknowledgements
We are thankful for the financial support provided by Universitas Indonesia under a research grant program of International Publication Indexed for Final Project Student 2017 (PITTA 2017) no. 629/UN2.R3.1/HKP.05.00/2017. The authors would like to thank Einago (www.einago.com) for the English language review.

References
[1] Du Y P, Zhang Y W, Yan Z G, Sun L D and Yan C H 2009 J. Am. Chem. Soc. 131 16364–5
[2] Shen B G, Sun J R, Hu F X, Zhang H W and Cheng Z H 2011 Adv. Mater. 21 4545–64
[3] Binnemans K, Jones P T, Blanpain B, Van Gerven T and Pontikes Y 2015 J. Clean Prod. 99 17–38
[4] Abhilash S S, Meshram P and Pandey B D 2016 Hydrometallurg 160 47–59
[5] Xie F, Zhang T A, Dreisinger D and Doyle F 2014 Miner. Eng. 56 10–28
[6] Zhu Z W, Pranolo Y and Cheng C Y 2015 Miner. Eng. 77 185–96
[7] Samsonov M D, Trofimov T I, Kulyako Y M, Vinokurov S E, Malikov D A, Batorshin G S and Myasoedov B F 2015 Radiochem. 57 343–47
[8] Singh D K, Singh H, Gupta C K and Mathur J N 2001 J. Radioanal. Nucl. Chem. 250 123–8
[9] Tong H, Wang Y L, Liao W P and Li D Q 2013 Sep. Purif. Technol. 118 487–91
[10] Maiorov V G and Nikolaev A I 2006 Russ. J. Appl. Chem. 79 1196–9
[11] Wang Y L, Li Y L, Liao W P and Li D 2013 J. Radioanal. Nucl. Chem. 298 1651–7
[12] Zhu, T 1991 Hydrometallurgy 27 231–45
[13] Li D Q, Ji E R, Xu W and Ni J Z 1987 Chin. J. Appl. Chem. 4 36–41
[14] Zuo Y, Chen J, and Li D Q 2008 Sep. Purif. Technol. 63 684–90
[15] Gupta B, Malik P and Deep A 2002 J. Radioanal. Nucl. Chem. 251 451–6
[16] Biswas S, Rupawate V H, Hareendran K N, Parashar H and Roy S B 2015 Thorium Energy Conf. October 12-15, 2015 Mumbai ed Kumar N et al. (Trombay: Bhabha Atomic Research Centre) NCPth-2014/54
[17] Lu Y C, Wei H Q, Zhang Z F, Li Y L, Wu G L and Liao W P 2016 Hydrometallurgy 163 192–7