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

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Abstract. In this report, we describe the selective and effective separation of Ce, La, and Nd rare-earth (RE) elements from the concentrate of a RE hydroxide (REOH) feedstock. The separation steps included dissolving the feedstock into a nitric acid solution and oxidizing the solution with potassium bromate (KBrO_3) 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 PTBGN-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 ($(\text{RE})\text{PO}_4$), bastnasite ($(\text{RE})\text{CO}_3\text{F}$), xenotime (YPO_4), 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



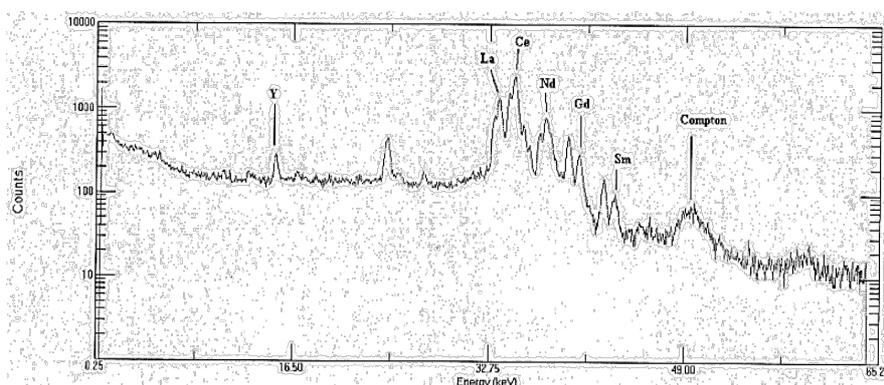


Figure 1. XRF analysis result during reprocessing and reduction of the chlorine and phosphate contents.

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 REs 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 CeO₂, La₂O₃, and Nd(OH)₃ 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

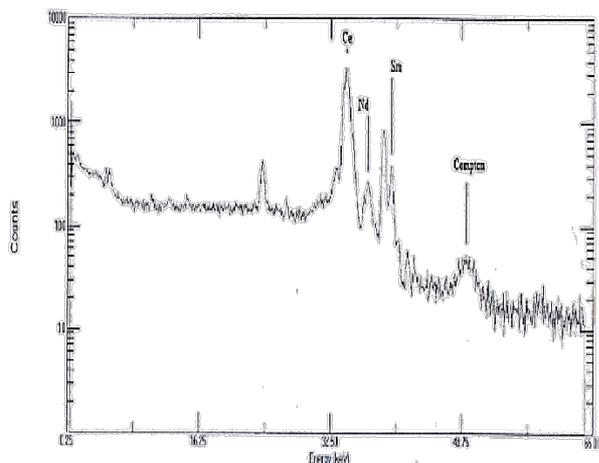


Figure 2. XRF spectrum of the Ce-dominant precipitate formed at pH 4

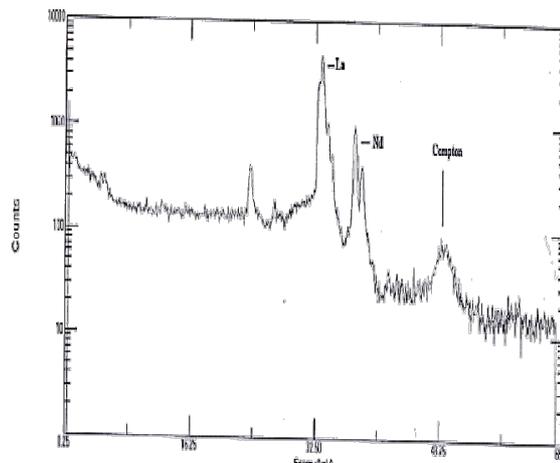


Figure 3. XRF spectrum of the of La-dominant precipitate formed by oxalate addition

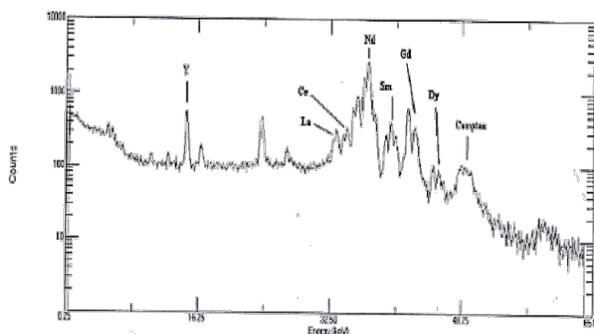


Figure 4. XRF spectrum of the Nd-dominant precipitate formed at pH 8.5

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 $\text{Nd}(\text{OH})_3$ 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 $\text{La}(\text{OH})_3$ at 33.44 keV.

3.3. Identification of cerium oxide

Figure 5 shows the FT-IR spectrum of the prepared CeO_2 precipitate. The spectrum of the CeO_2 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 CeO_2 stretching vibration, and at 1632 cm^{-1} with H_2O (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.

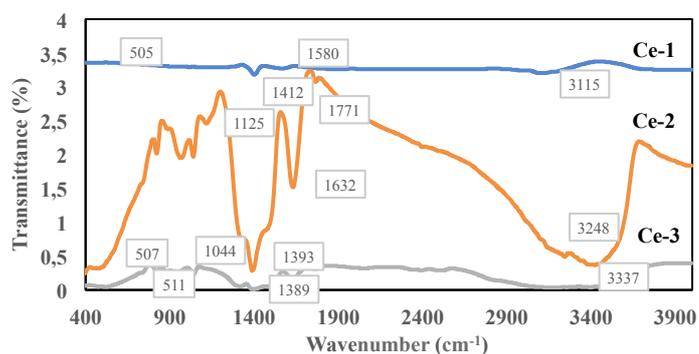


Figure 5. FTIR spectrum of the Ce fractional precipitate

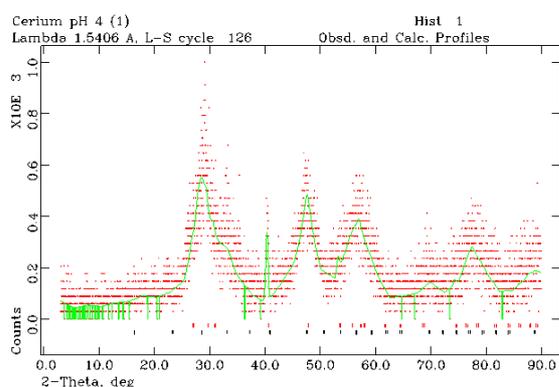


Figure 6. XRD pattern of sample Ce-1 obtained by fractional precipitation of the cerium sample

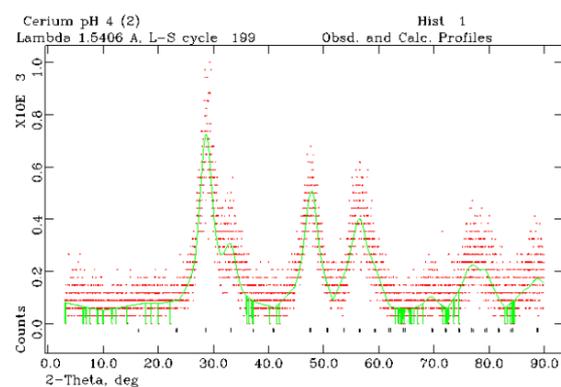


Figure 7. XRD pattern of sample Ce-2 obtained by fractional precipitation of the cerium sample

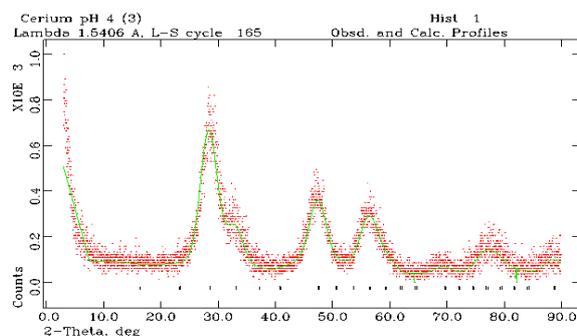


Figure 8. XRD pattern of sample Ce-3 obtained by fractional precipitation of the cerium sample

3.4. Identification of lanthanum oxide

Figure 9 shows the FT-IR spectra of the prepared La_2O_3 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 CO_3^{2-} groups. The absorption at 802–810 cm^{-1} is assigned to bending vibration modes of out-of-plane and in-plane of water and CO_2 adsorbed onto the $\text{La}(\text{OH})_3$ surface. The sharp peak observed at approximately at 500–507 cm^{-1} is attributed to a stretching vibration of La–O bonds.

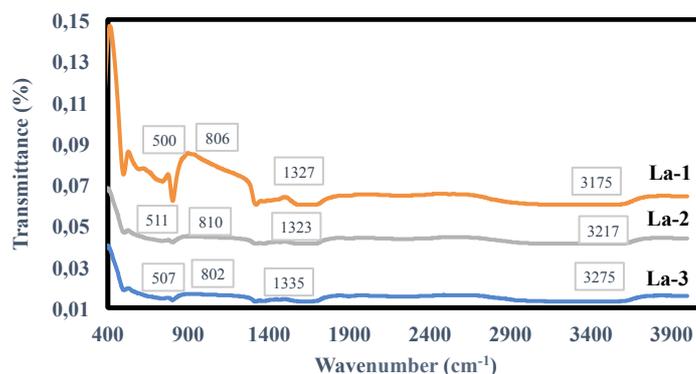


Figure 9. FT-IR spectra of the lanthanum fractional precipitates

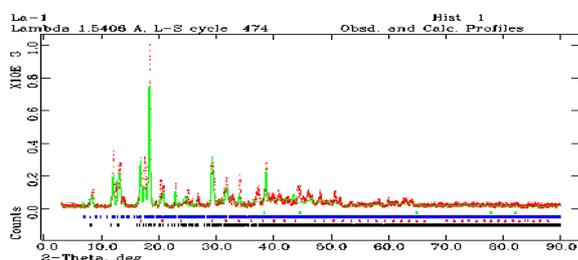


Figure 10. XRD pattern of sample La-1 obtained by fractional precipitation of the lanthanum sample

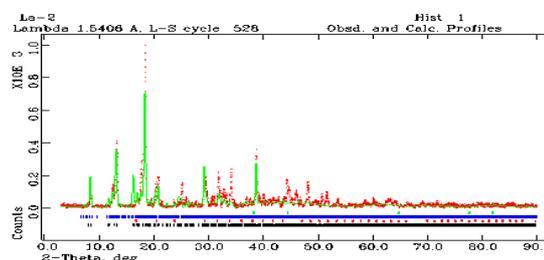


Figure 11. XRD pattern of sample La-2 obtained by fractional precipitation of the lanthanum sample

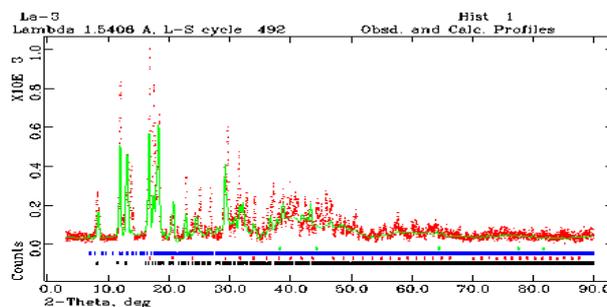


Figure 12. XRD pattern of sample La-3 obtained by fractional precipitation of the lanthanum sample

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-nepthanoate) trihydrate.

3.5. Identification of neodymium oxide

Figure 13 shows the FT-IR spectra of the prepared Nd_2O_3 precipitates. The peak at 1327 cm^{-1} is ascribed to carbonate groups. The peak at $3100\text{--}3400\text{ cm}^{-1}$ 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.

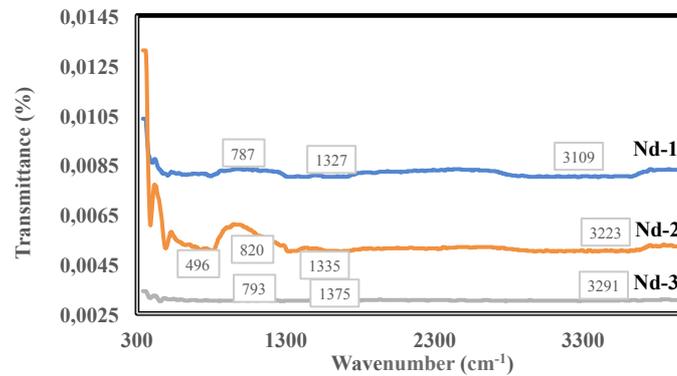


Figure 13. Spectrum FTIR of fractional precipitation of Neodymium

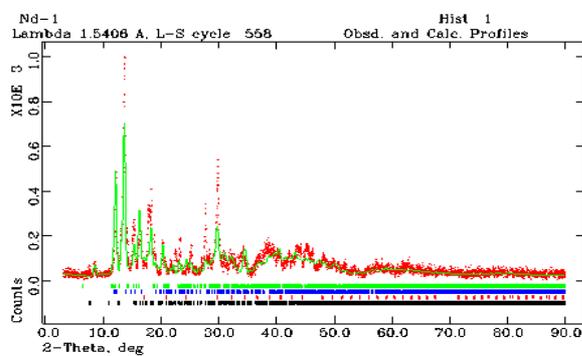


Figure 14. XRD pattern of sample Nd-1 obtained by fractional precipitation of the neodymium sample

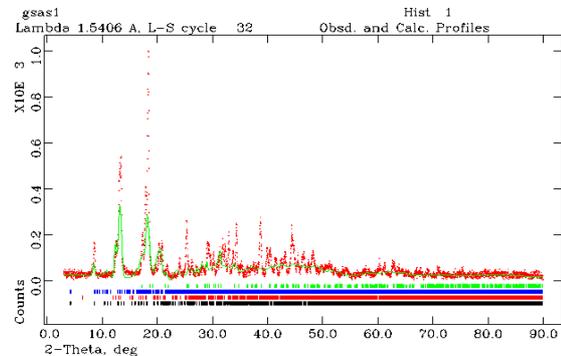


Figure 15. XRD pattern of sample Nd-2 obtained by fractional precipitation of the neodymium sample

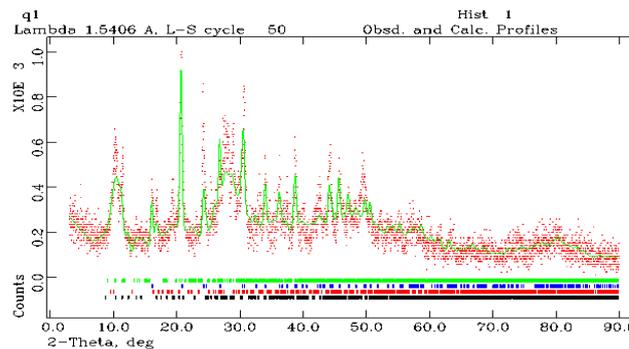


Figure 16. XRD pattern of sample Nd-3 obtained by fractional precipitation of the neodymium sample

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 CeO_2 , 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

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