

## RECOVERY OF CERIUM, NEODYMIUM AND LANTHANUM FROM MALAYSIAN MONAZITE USING OXIDATION AND SELECTIVE PRECIPITATION METHOD

Jacqueline Kones\*, Roshasnorlyza Hazan, Khaironie Mohamed Takip and Nur Aqilah Sapiee

Industrial Technology Division, Agensi Nuklear Malaysia, Bangi,  
43000 Kajang, Selangor, Malaysia.

\*Correspondence author: jacqueline@nm.gov.my

### ABSTRACT

*This study utilises a mixture of rare earth elements obtained from the Malaysian monazite through a series of processes from digestion to separation of non-radioactive and radioactive elements. The non-radioactive elements are the mixture of rare earth elements, mainly cerium, neodymium, and lanthanum. It is possible to separate cerium from other elements due to its ability to form +3 and +4 oxidation state compared to others. Therefore, the objective of this study was to compare the effectiveness of nitric acid  $HNO_3$  and hydrochloric acid (HCl) as dissolution media for the separation of cerium from mixed rare earth hydroxide concentrates. The oxidation using nitric acid media was found to be incomplete hence leading to poor separation. 2 M HCl was proven to be more effective, yielding a cerium concentrate of approximately 71.2% purity. The remaining neodymium and lanthanum were separated through selective precipitation and the products obtained were analysed using Energy Dispersive X-ray Fluorescence (ED-XRF).*

**Keyword:** Rare earth elements, cerium, neodymium, lanthanum.

### INTRODUCTION

Rare earth elements (REEs) can be found naturally in the earth's crust. In Malaysia, it can be retrieved from the heavy mineral sand from processed tin tailing like xenotime and monazite. Other than that, REEs can also be obtained from adsorption clay minerals. Each source contains certain groups of elements, for example xenotime has more yttrium (Y) followed by heavy rare earth (HREE) and some light rare earth elements (LREE). Monazite, on the other hand, contains more LREEs namely cerium, neodymium, lanthanum, and praseodymium with presence of some HREEs.

In mineral processing, separation is a technique to isolate the substance of interest from others by using suitable techniques. For example, phosphate in monazite was removed using alkali digestion process. Separation is crucial as it facilitates the separation and concentration of the elements before extraction and purification can be done. The purpose to do extraction and purification is to obtain the highest concentration of the element of interest by minimising the presence of other elements. RE separation is commonly performed using the selective precipitation method. It means the desired elements will be removed by forming precipitate at a certain pH level. This method was used to separate REEs from thorium and uranium that are also present in monazite. After the REEs were concentrated, each REE can be separated too.

Another way that can be done to separate REE is to manipulate the property of the oxidation state. REEs generally have the oxidation state of +3 but in the case of cerium, it can also form +4 oxidation state. This is because, Ce has four valence electrons while others have three. The distinct oxidation state of  $Ce^{4+}$  allows for selective separation from trivalent REEs (Vapnik et al., 2025). It is important

to remove Ce from the mixed RE compound first before other elements can be purified because the presence of Ce will interfere with the purity of the final products (McNeice, 2018).

Oxidation of Ce can be done by reacting the mix rare earth solution with oxidising agent. Some oxidising agents that can be used are such as potassium permanganate ( $\text{KMnO}_4$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), and sodium hypochlorite ( $\text{NaOCl}$ ). Among these oxidants,  $\text{KMnO}_4$  was found to be the most suitable to oxidise Ce (III) to Ce (IV) since  $\text{H}_2\text{O}_2$  and  $\text{NaOCl}$  usually will decompose rapidly prior to reacting with Ce (III) (Sauber, 2018 & Morais et al, 2003). The oxidation of Ce (III) to Ce (IV) using  $\text{KMnO}_4$  in acidic media is a robust method for high-purity separation, provided pH is strictly controlled to prevent manganese dioxide interference (Suyanti et al., 2025). Other than that, air oxidation method can also be done by drying the  $\text{RE}(\text{OH})_3$  cake obtained through precipitation RE in sulphate solution with  $\text{NaOH}$  at 120 °C (Rice, 1959). Oxygen at high temperature will oxidise Ce (III) (Formiga, & Morais, 2016).

For this study, the  $\text{RE}(\text{OH})_3$  used contains mixtures of Ce, Nd, La, Pr, some HRE, and other elements. This study aims to separate Ce mixed  $\text{RE}(\text{OH})_3$  by using two different acidic media, that is nitric acid ( $\text{HNO}_3$ ) and hydrochloric acid ( $\text{HCl}$ ) followed by separation of Nd and La through selective precipitation.

## METHODS

$\text{RE}(\text{OH})_3$  used in this study was obtained from Malaysia monazite through alkali digestion process. Finely ground monazite was digested with sodium hydroxide solution, then washed with hot water to remove trisodium phosphate that was formed. The hydrous monazite cake then reacted with concentrated hydrochloric acid solution for leaching process. After that, thorium and uranium elements were separated by conducting selective precipitation using ammonia solution at pH 5.8. The remaining elements in the filtrate was finally obtained as  $\text{REE}(\text{OH})_3$  by continuing the precipitation with excess ammonia. It contains mixtures of Ce, Nd, La, Pr, some HRE, and other elements.

### a. Oxidation of Ce (III) in nitric acid.

Dried  $\text{RE}(\text{OH})_3$  was slowly added into concentrated nitric acid and heated until it fully dissolved. Water was added to dilute the acidic liquid, producing a yellow coloured solution.  $\text{KMnO}_4$  solution was prepared by dissolving  $\text{KMnO}_4$  into water. This solution was then added into the acidic solution. Solution of  $\text{Na}_2\text{CO}_3$  was then added to precipitate Ce (IV) until pH 5. The solid compound formed was filtered while the remaining elements in the acidic solution were then precipitated by adding ammonia solution until pH 8. The solid compounds formed were dried and analysed using ED-XRF for their elemental content.

### b. Oxidation of Ce (III) in hydrochloric acid.

Dried  $\text{RE}(\text{OH})_3$  was dissolved in hydrochloric acid with concentrations of 2 M and 37 % (v/v) until it was fully dissolved and then diluted with water for dilution. The pH of the acidic solutions was adjusted to pH 3 by adding  $\text{Na}_2\text{CO}_3$  before a solution of  $\text{KMnO}_4$  was added slowly. The pH of the reaction was maintained at pH 3 – 5 by adding more  $\text{Na}_2\text{CO}_3$  when it dropped below pH 3. Addition of  $\text{KMnO}_4$  was ceased only after the purple colour did not disappear. The solid compound formed was filtered and the remaining elements in the filtrate were precipitated with ammonia. The precipitated elements were dried and analysed using ED-XRF and X-ray diffraction (XRD).

### c. Separation of Nd and La.

For this step, Nd and La remaining in the nitric acid solution were separated by adding  $\text{NH}_4\text{OH}$  solution until pH 7.5. The precipitated  $\text{Nd}(\text{OH})_3$  concentrate was filtered and washed followed by drying. More  $\text{NH}_4\text{OH}$  then added into the filtrant to retrieve La until no further precipitation was observed at around pH 10.30. Slurry of  $\text{La}(\text{OH})_3$  obtained was filtered, washed and dried. Both dried precipitates obtained were analysed by using ED-XRF.

## RESULTS AND DISCUSSION

Monazite contains more cerium followed by neodymium, lanthanum and praseodymium. These are also known as the light RE elements. Other REEs that were detected are dysprosium and thulium. Thorium and uranium were also detected, and it can be separated by using the selective precipitation at pH-5.8 that the remaining elements were retrieved by adding ammonia solution in excess until no more precipitation observed. Separating the REEs is one way to increase the concentration of the elements individually. This will enable the enhancement of the extraction process as few elements were present in the mixture.  $\text{RE}(\text{OH})_3$  obtained previously will need to be dissolved in acidic media – for this study, nitric acid and hydrochloric acid were selected. Separation of Nd and La can be done after Ce was isolated.

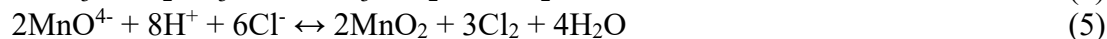
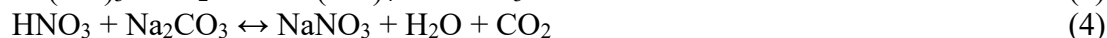
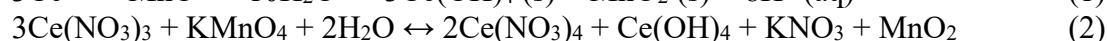
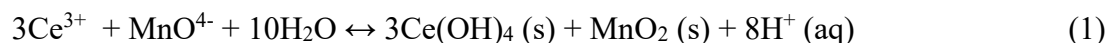
### a. Nitric acid as dissolution medium.

Dissolving  $\text{RE}(\text{OH})_3$  in  $\text{HNO}_3$  was demonstrated in some reports (Wai, 2018; Purwani & Trinopiawan, 2019). The method used for this study was adapted from method by (Wai, 2018) in which the separation of cerium was done in two stages. In the first stage, some of cerium was reported to form a solid state after dilution of the acidic solution. As for the second stage, it happens after the reaction with potassium permanganate in excess followed by the addition of sodium carbonate. The filtrate remained then proceed to the next steps for the separation of the neodymium by continuing adding  $\text{Na}_2\text{CO}_3$  solution until pH 8. Cerium was expected to be separated completely by this method. However, in this study it was found that cerium concentrate started to form only after addition of  $\text{Na}_2\text{CO}_3$  solution at around pH 3. The analysis content of cerium concentrate was as shown in Table 1 where Ce was the most abundant element followed by Nd, La, and Pr that were co-precipitated. After the filtrate was further added with more  $\text{Na}_2\text{CO}_3$ , cerium was also detected in what was expected to be the other RE concentrate. Ce was the most concentrated element although it was expected that it should be less than that. This suggests that Ce (III) oxidation in this study was not completed. This observation can be caused by the chemical dynamics of the oxidation-hydrolysis reaction and the resulting pH instability. As in Equation (1), the oxidation of  $\text{Ce}^{3+}$  to  $\text{Ce}^{4+}$  using permanganate is accompanied by the release of  $\text{H}^+$  ion, which rapidly lowers the pH of the solution. For effective separation, cerium must precipitate as  $\text{Ce}(\text{OH})_4$  which is also highly soluble in highly acidic conditions. Rapid generation of  $\text{H}^+$  ion is likely to overwhelm the buffering capacity of the added  $\text{Na}_2\text{CO}_3$ , resulting in drop in pH to below threshold required for stable precipitate formation. This eventually makes it difficult to complete the hydrolysis of  $\text{Ce}^{4+}$ ; therefore, a significant portion of cerium remained in the filtrate. As reported in recent kinetic studies, Ce (IV) species are highly sensitive to re-dissolution in acidic nitrate media compared to chloride systems where complexation stability differs significantly (Abdulvaliyev et al., 2024). Hence, a significant amount of cerium remained in the filtrate. Table 1 displayed the incomplete separation where cerium can still be detected after the process.

Table 1: Elemental composition of Ce and other RE concentrate obtained from the separation of the elements dissolved in nitric acid solution

Element	Concentration in Ce concentrate	concentration in other RE concentrate
Ce	45.5 %	43.9 %
Nd	13.7 %	18.8 %
La	8.4 %	20.3 %
Pr	3.6 %	4.3 %
Mn	18.5 %	(not detected)
Others	9.3 %	12.6 %

KMnO<sub>4</sub> is more stable at pH more than 2.5. However, the more KMnO<sub>4</sub> added, the pH of the solution will be reduced and eventually will affect the oxidation process. This could be explained by the formation of H<sup>+</sup> ions as described in Equation (1). Therefore, to maintain the pH, Na<sub>2</sub>CO<sub>3</sub> needs to be added. The oxidation process of Ce (III) with KMnO<sub>4</sub> was described in Equation (2) – (4). It showed that apart from forming Ce (IV) as Ce(OH)<sub>4</sub>, manganese (IV) oxide will be produced as impurity, hence affecting the purity of cerium. Fortunately, MnO<sub>2</sub> can be removed by dissolving it in dilute HCl.



#### b. HCl as the dissolution medium.

HNO<sub>3</sub> was then substituted with hydrochloric acid. This method was reported by McNeice (2018) & Sauber (2018). RE(OH)<sub>3</sub> were dissolved in 2 M and 37 % (v/v) concentration and it was found that 2 M HCl is sufficient to dissolve RE(OH)<sub>3</sub>. Therefore, it is recommended that highly concentrated HCl should not be used since it can give more risks in terms of environment, health and safety if not handled properly. Besides that, there were dark coloured particles observed in both acidic concentrations, but it will dissolve upon addition of water for dilution.

Unlike before, the pH for this reaction was controlled and kept above pH 2.5. This is because, under low pH, MnO<sub>4</sub><sup>-</sup> will react with H<sup>+</sup> and Cl<sup>-</sup> ions to form solid MnO<sub>2</sub> (Eq. 5), hence affecting the oxidation process as no MnO<sub>4</sub><sup>-</sup> ions will be available to oxidise Ce (III). Meanwhile, KMnO<sub>4</sub> was added until the purple colour did not disappear, indicating no more Ce (III) to be oxidized. Table 2 illustrates the percentage concentration of elements found in the products formed from both solutions and Figure 1 illustrated the elements presence in the concentrate as hydroxides. As expected, Ce was not found in the other RE concentrate. This suggested that Ce successfully separated through oxidation process. The concentration of Ce in the Ce concentrated was at around 70% together with 15.2 % Nd, Mn and some REEs. As for the REE concentrate, more Nd detected with concentration of more than 30 % together with La (>20 %), Pr (> 10 %) and other elements.

Table 2: Elemental composition of Ce and other concentrate obtained from dissolving the rare earth hydroxide concentrate in 2M and 37 % HCl.

Elements	2 M HCl acid		37 %(v/v) HCl	
	(Ce concentrate)	(other REE concentrate)	(Ce concentrate)	(other REE concentrate)
Ce	71.2 %	(Not detected)	70.6 %	(Not detected)
Nd	15.2 %	37.6 %	15.2 %	30.9 %
Mn	7.7 %	(Not detected)	7.5 %	(Not detected)
La	(Not detected)	31.1 %	(Not detected)	22.1 %
Pr	(Not detected)	12.6 %	(Not detected)	10.2 %
Cl	4.2 %	11.6 %	3.2 %	26.5 %
Other REEs	0.8 %	6.8 %	1.0 %	9.8 %
Other elements	0.7 %	0.3 %	2.5 %	0.6 %

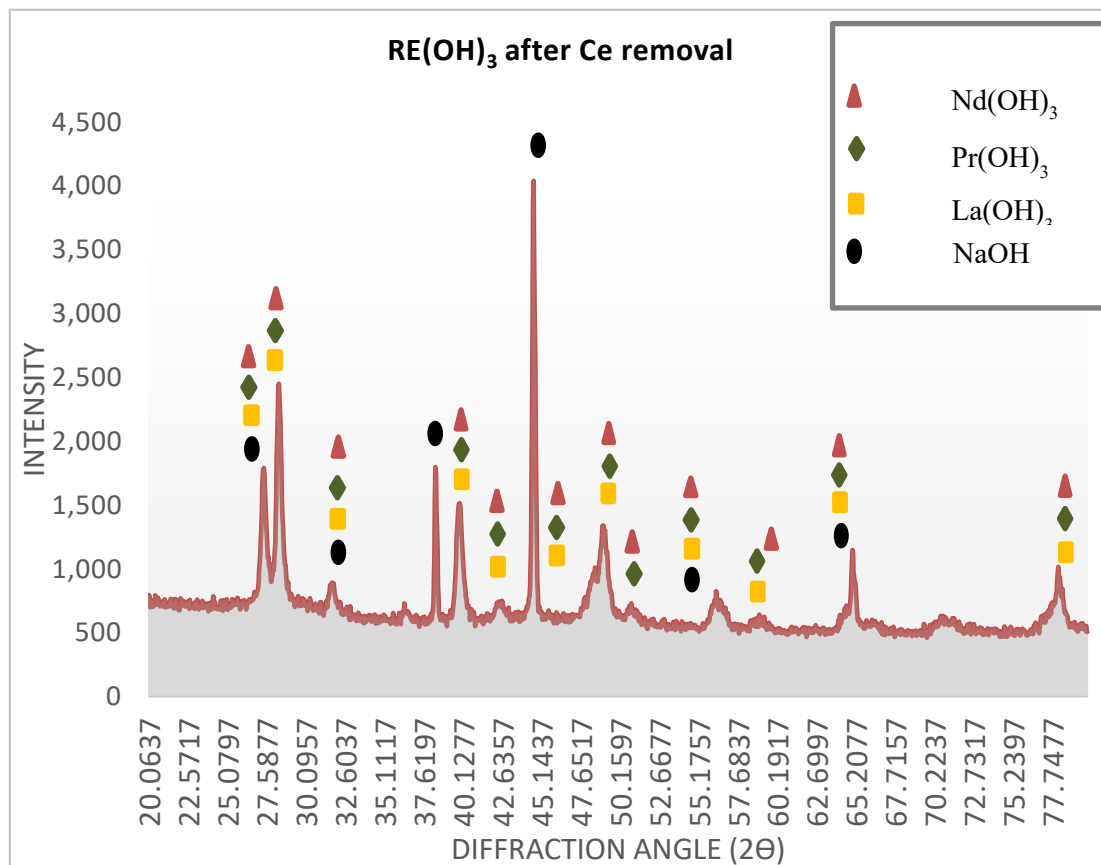


Figure 1: X-ray Diffraction (XRD) analysis on the RE(OH)<sub>3</sub> after Ce separation shows no Ce(OH)<sub>4</sub> detected indicating cerium was removed completely from the mixed rare earth hydroxide concentrate.

### c. Separation of Nd and La.

Separation of Nd and La were obtained by precipitating  $\text{Nd}(\text{OH})_3$  before  $\text{La}(\text{OH})_3$ . This is due to the difference in the solubility product constants ( $K_{sp}$ ) of both hydroxides (Wai, 2018).  $\text{Nd}(\text{OH})_3$  has a smaller  $K_{sp}$  value than  $\text{La}(\text{OH})_3$ , suggesting that  $\text{Nd}(\text{OH})_3$  is less soluble in ammonia solution, hence it will precipitate first. ED-XRF analysis of both concentrates in Figure 2 showed that Nd can be fully separated from La at pH 7.5 with 9.9% La present. Meanwhile, Sm prefers to be separated along with Nd while Pr prefers to be with La.

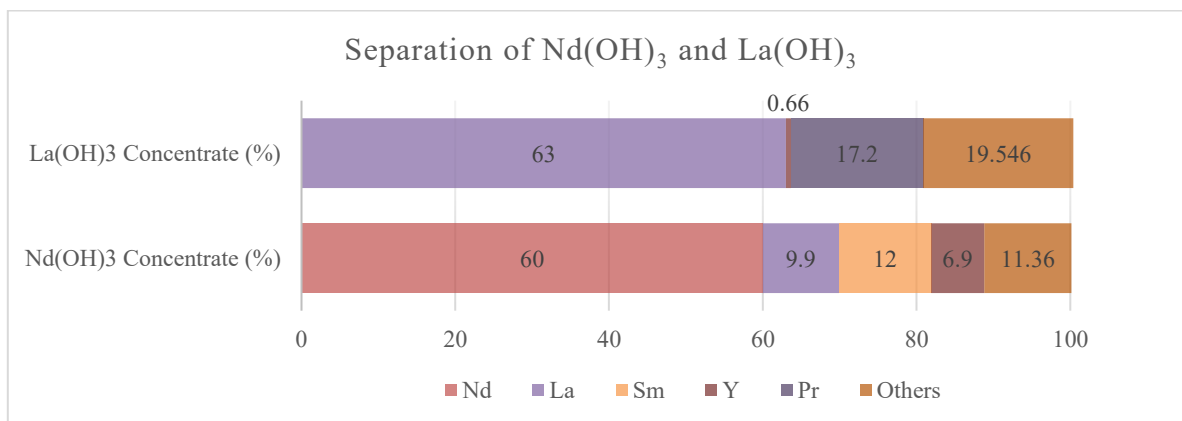


Figure 2: Major elements obtained through analysis result of analysis using ED-XRF for  $\text{Nd}(\text{OH})_3$  and  $\text{La}(\text{OH})_3$  concentrate

## CONCLUSION

This study compared the effectiveness of  $\text{HNO}_3$  and  $\text{HCl}$  as dissolution media for the oxidative separation of cerium from rare earth hydroxides ( $\text{RE}(\text{OH})_3$ ). The investigation revealed that the nitric medium was less effective due to pH instability during the oxidation process, which hindered the complete precipitation of  $\text{Ce}(\text{IV})$ . Further optimization in terms of acid concentration and pH control would be necessary to make the nitrate route viable. Meanwhile, the use of 2 M  $\text{HCl}$  was proven to be more effective for dissolving  $\text{RE}(\text{OH})_3$  and facilitating cerium separation. This concentration is sufficient for dissolution while offering safer and greener separation processes for cerium and lanthanum, as emphasized in recent recovery studies (Vargas et al., 2021). Through this method, cerium was successfully separated with approximately 71.2% purity, although small amount of  $\text{MnO}_2$  impurities were present. Other than that, the following selective precipitation at pH 7.5 successfully isolated lanthanum from neodymium since neodymium was absent in the lanthanum concentrate. These findings suggest that the 2 M  $\text{HCl}$  route is a promising method for enhancing the extraction of individual rare earth elements from Malaysia monazite.

## ACKNOWLEDGEMENTS

This study is under the PQRD project NM-R&D-23-14 (Removal of Cerium from Malaysian Monazite for Neodymium Solvent Extraction Enhancement).

## REFERENCES

- Abdulvaliyev, R., Ultarakova, A., Mukangaliyeva, A., Lokhova, N., & Kassymzhanov, K. (2024). Comparative analysis of acid leaching for the efficient recovery of lanthanum and cerium from phosphate. *Separations*, 11(10), 288. <https://doi.org/10.3390/separations11100288>
- Formiga, T., & Morais, C.A., (2016). Cerium separation from light rare earth concentrate by liquid-liquid extraction. *World Journal of Engineering and Technology*. 4(1), 129-137.
- McNeice, J.A. (2018). An Investigation into cerium oxidation under acidic conditions [*Master's thesis, Queen's University*].
- Morais, C.A., Benedetto, J.S., & Ciminelli V.S.T. (2003). Recovery of cerium by oxidation/hydrolysis with  $\text{KMnO}_4 - \text{Na}_2\text{CO}_3$ , *Electrometallurgy and Environmental Hydrometallurgy*. 2.
- Purwani, M.V. & Trinopiawan, K. (2019). Separation of Ce, La, and Nd in rare earth hydroxide (REOH) by oxidation with potassium permanganate and precipitation, *Journal of Physics: Conference Series* 1198, 032003.
- Rice, A. C. (1959). *Preparation of rare earth chloride solutions* (Report of Investigations 5499). U.S. Department of the Interior, Bureau of Mines.
- Sauber, M.E. (2018). Oxidative removal of cerium from rare earth elements mixed chloride solution. In Davis, B., *et al.* (Eds.) *Extraction 2018*. (The Minerals, Metals & Materials Series. Springer, Cham) Springer.
- Suyanti, S., Daulay, A., Astuti, W., Widana, K. S., Petrus, H. T. B. M., & Adi, W. A. (2025). Separation of cerium from rare earth elements hydroxide using dilute nitric acid and potassium permanganate. *Canadian Metallurgical Quarterly*. Advance online publication. <https://doi.org/10.1080/00084433.2025.2609470>
- Vapnik, H., Kim, H.E., Kim, Y., Ooi, A.W.S., Vibbert, H. B., Park, A.H.A., Su, X. (2025). Selective electrochemical recovery of cerium over lanthanum from complex waste feedstocks by alternating current electro-precipitation, *Chemical Engineering Journal*, 504, 158537. <https://doi.org/10.1016/j.cej.2024.158537>
- Vargas, C., Crampon, M., Cognet, P., & Fermen-Coker, M. (2021). Green separation of lanthanum, cerium and nickel from waste nickel metal hydride battery leachate using aqueous biphasic systems. *Waste Management*, 125, 154-162.
- Wai, A.M. (2018) . Selective precipitation of neodymium oxide ( $\text{Nd}_2\text{O}_3$ ) from monazite, *International Journal of Science, Engineering and Technology Research (IJSER)* 8(8)