Separation of Cerium from Neodymium Hydroxide Concentrate Through Decomposition and Leaching Using HNO₃

MV Purwani¹*, Triyono¹, M Setyadjji¹, RA Amiliana¹,
¹Center for Accelerator Science and Technology
National Nuclear Energy Agency, Jalan Babarsari PO Box 6101 ykbb
Yogyakarta 55281

purwani@batan.go.id

Abstract. The thermal decomposition or calcination of neodymium hydroxide concentrate product by pilot plant of REOH into CeO₂, La₂O₃ and Nd hydroxide concentrate in Center for Accelerator Science and Technology has been performed. From the result of start-up and validation was obtained neodymium hydroxide concentrate which still containing of impurities especially Ce. The purpose of this research to separate Ce from Nd(OH)₃ concentrate by thermal decomposition to form Nd oxide (Nd₂O₃). Calcination temperature was 1000°C, and variation of time. The result of calcination were dissolved using aqueous HNO₃ with molarity variation and the level of leaching was five times. From the results, it can be stated that calcination could convert Nd(OH)₃ concentrate to Nd₂O₃ concentrate. Cerium hydroxide was easy dissolve in aqueous HNO₃ while CeO₂ couldn’t. The longer of calcination time, the formed of Nd₂O₃ is more perfect. The results of 3 hours calcination for the %weight of La increase until 12,50%, Ce increase to 10,42% and Nd increase to 52,08%. The composition of La in solid of leaching products use 1 M HNO₃ with five leaching times is 3,57%, while Ce is 50,26% and Nd is 0,36%. The kinetic calcination and leaching followed reaction control.

Keywords: neodymium hydroxide concentrate, separation, calcination, leaching, aqueous HNO₃

1. Introduction
Neodymium hydroxide concentrate was a REOH (rare earth hydroxide) process products at pilot plant of REOH to form CeO₂, La₂O₃ and Nd hydroxide concentrate in Center for Accelerator Science and Technology that containing REEs namely Ce, La, Pr, Y, Sm and Gd [1]. There is a growing demand of the high-tech rare earth metals such as Nd, Pr and Dy in daily life because their numerous usages in various electronic and mechanical devices like computers, audio-visual components, magnetic separators, cranking motor of automobiles, military and aerospace system [2-6]. Cerium oxide (CeO₂) has many applications, such as solid electrolytes in solid oxide fuel cells, catalysts, optical additives. For example, catalysts based on CeO₂ are widely used as efficient oxidation systems in heterogeneous catalysis such as in oxidation of CO in oxygen-rich and in hydrogen-rich atmospheres [7].

For the separation of Ce of La and Nd, neodymium hydroxide concentrate should be calcined and leached, so that the solution is formed. Leaching was a liquid-solid extraction which is the process of extraction of a soluble constituent (solute) on the solid compound by using the solvent. The leaching of
Nd using mineral acid were investigated for substantial recovery of Nd [8-12]. The leaching reaction that occurs could be between base and an acid. The base will react with the acidic solution to form salt and water [13]. Leaching of the rare earth metals with various organic and inorganic acids have been investigated by some researchers [9-11]. K Stonea et al., who studied comparison of H₃PO₄, HCl, HClO₄ and HNO₃ usage leading to the leaching, had proven the leaching process can use H₃PO₄, HCl, and HNO₃. Using of HNO₃, resulting in the greatest leaching efficiency [14].

The obtained cerium oxide, depending on the synthesis procedure, had the following values of calcination temperature [15]. Leonid et al. was produced of high porosity nanoparticles of cerium oxide that was calcined at 550°C [7]. Cerium is largely used in various applications such as phosphor lamps, polishing media, automotive three way emission catalyst, nickel metal hydride batteries and ceramics and is always found as a mixture with most of the REEs (Rare Earth Elements) and numerous transition metals [3,16]. Leaching of metals present in such devices was previously reported using sulfuric acid [17-19]. The separation of transition metals from lanthanides was carried out by hydrometallurgical techniques, REEs precipitating under the form of sulphate salts [20,21]. The separation of cerium (III) from lanthanum(III), neodymium(III) and praseodymium (III) can be done by oxidation and liquid-liquid extraction using ionic liquids [22].

Process optimization and kinetics for leaching of cerium, lanthanum and neodymium elements from iron ore waste's apatite by nitric acid. The maximum REE leaching recoveries of 66.1%, 56.8% and 51.7% for Ce, La and Nd, respectively were achieved at the optimum leaching condition with 18% nitric acid concentration, 0.06 solid to liquid ratio and 38 min leaching time [23]. Extraction of Nd and Fe are quantitative using dilute CH₃COOH (0.4 M) solution and the result of the extraction was 89.76% of Nd [24]. The purpose of this work is to combine thermal decomposition or calcination and leaching to recover Ce, La and Nd component from neodymium hydroxide concentrate. Thermal decomposition or calcination to form Nd oxide (Nd₂O₃) containing Ce and La oxide and leaching using aqueous HNO₃. Neodymium oxide and La₂O₃ dissolved in aqueous HNO₃ while Ce oxide (CeO₂) was insoluble in aqueous HNO₃.

2. Experimental method

2.1. Materials and Reagents
Neodymium hydroxide concentrate was a REOH process products at pilot plant of REOH to form CeO₂, La₂O₃ and Nd hydroxide concentrate in National Nuclear Energy Agency using nitric acid solution.

2.2. Thermal decomposition or calcination conditions
The calcination experiment was carried out in furnace. The prepared sample was calcined at 1000 °C for 1, 2, and 3 hours.

2.3. Leaching procedure conditions
The results of calcination were leached or dissolved in HNO₃. The leaching experiment was carried out in a three necked round bottom flask which was placed on a heating mantle (set at desired temperature). The solution was kept under agitation using an externally connected agitator. The nitric acid concentration was studied at the concentration range of 0.2 M – 1 M. The ratio of neodymium hydroxide concentrate weight with volume of nitric acid (w/v) was 2.5. Time of leaching was 5 minutes with stirring speed 150 rpm. The stage of leaching was five times. The sample is analyzed using XRF.

3. Results and discussion

3.1. Calcination of Neodymium hydroxide concentrate
3.1.1. Effect of time of calcination on weight fraction and conversion of Solid Weight. The calcination was conducted at various temperatures. The weight conversion calculation uses following formula [1].
\[ \alpha = \frac{m_0 - m}{m_0 - m_f} \]  

(1)

Where \( m_0 \) is the initial mass, \( m \) is the mass at time \( t \), and \( m_f \) is the final mass when it has turned into Nd oxide. The weight of each fraction was characterized using XRF (X-ray fluorescence spectrometry), so we can calculate the conversion of the compound. Effect of increasing time is the decreasing of weight fraction, but the weight conversion of \( \alpha \) is increase [25,26]. The reaction that occurred in this process can be seen in this following equation and the relationship between calcination time and weight fraction and conversion is shown at Figure 1.

\[ RE(OH)_3(s) \rightarrow RE_2O_3(s) + H_2O(g) \]  

(2)

3.1.2. Effect of time of calcination on %weight of RE element and %weight of RE compounds. The calcination was conducted at various temperatures too. The %weight of RE element after calcination is shown in Figure 2 and the %weight of RE compounds is shown in Figure 3. The %weight of RE element and RE compounds is increase with increasing calcination time. But for water and hydroxide are decreasing. In calcination for 1 to 2 hours the RE oxide that is formed, but it is not perfect yet because it still contains H\(_2\)O and hydroxide. In 3-hour calcination, the %weight of La is increase from 3.50% to 12.50%, Ce content increase from 3.33% to 10.42% and %weight of Nd increase from 16.67% to 52.08%. All water content in Nd hydroxide became vapor. Before calcination, the %weight of La compound (La(OH)\(_3\)) was 5.47%, and %weight of Ce compound (Ce(OH)\(_3\)) was 4.55%. After calcination, the %weight of La compound (La\(_2\)O\(_3\)) was 14.66%.

3.2. Leaching for separation of Ce, La and Nd
3.2.1. Effect of HNO₃ molarity on leaching efficiency of Ce, La and Nd. The leaching of La and Nd was investigated at varying HNO₃ concentration in the range of 0.2 M – 1 M while keeping other parameters constant. The leaching efficiency of La and Nd was increased with the increase in the HNO₃ concentration as shown in Figure 4. The leaching efficiency of La is 11.16% and the leaching efficiency of Nd is 30.72%, while Ce could not leach.

![Figure 4. Effect of nitric acid concentration on leaching efficiency of La, Ce, and Nd.](image)

3.2.2. Effect of leaching stage on leaching efficiency of La at various concentration of HNO₃. The stage of leaching was investigated at the range of I – V (1ˢᵗ – 5ᵗʰ) at varying HNO₃ concentration in the range of 0.2 M until 1 M. The leaching efficiency of La is increased with increase in the HNO₃ concentration as shown in Figure 5 and the leaching efficiency of La at the range of I – V (1ˢᵗ – 5ᵗʰ) in 0.2 M is 4.46% - 5.9%, while the leaching efficiency of La in 0.4 M is 8.13% - 7.98%, in 0.6 M is 10.89% - 10.53%, in 0.8 M is 8.87% - 12.78%, and the last in 1 M is 13.16% - 15.21%.

![Figure 5. Effect of leaching stage on La leaching efficiency.](image)

3.2.3. Effect of cumulative leaching stage on leaching efficiency of La at various concentration of HNO₃. The cumulative leaching efficiency of La was the amount of La leaching efficiency at each stage (I - V). The relationship between cumulative stage and cumulative leaching efficiency was presented in Figure 6.
Figure 6. Effect of cumulative leaching stage on La leaching efficiency.

The cumulative leaching efficiency is increase when the HNO₃ molarity is increase too. The cumulative leaching efficiency of La at 0.2 M is 22.62%, at 0.4 M is 41.54%, at 0.6 M is 50.66%, at 0.8 M is 54.62%, and at 1 M is 63.84%.

3.2.4. Effect of leaching stage on leaching efficiency of Nd at various concentration of HNO₃. The leaching efficiency of Nd was increased with the increase of HNO₃ concentration as shown in Figure 7. The leaching efficiency of Nd at the range of I – V (1ˢᵗ – 5ⁿᵈ) in 0.2 M is 0.75% - 5.9%, in 0.4 M was 2.23% - 7.98%, in 0.6 M is 15.86% - 18.02%, and in 0.8 M is 15.87% - 24.27%. Meanwhile the leaching efficiency of Nd at the range of I – III (1ˢᵗ – 3ⁿᵈ) in 1 M is 30.72% - 33.36%.

Figure 7. Effect of leaching stage on Nd leaching efficiency.

3.2.5. Effect of cumulative leaching stage on leaching efficiency of Nd various concentration of HNO₃. The cumulative leaching efficiency of Nd was the amount of Nd leaching efficiency at each stage (I - V). The relationship between cumulative stage and cumulative leaching efficiency was presented in Figure 8. The cumulative leaching efficiency is increase when the increasing of HNO₃ molarity. The cumulative leaching efficiency of Nd at 0.2 M is 17.40%, at 0.4M is 34.83%, at 0.6 M is 88.21%, and at 0.8 M is 97.65%. The cumulative leaching efficiency of Nd at 1 M was 99.44% at cumulative stage I – III (1ˢᵗ – 3ⁿᵈ), so the leaching of Nd only required 3 stage
3.3. Kinetic model

3.3.1. Thermal decomposition or calcination kinetic. Kinetic decomposition was studied by applying unreacted shrinking core model. The influence of different temperature regions upon the thermal behavior of chemical compounds can provide kinetic parameters indicating change in the reaction pathway. The extent of conversion, \(X\), is defined by the following equation [27].

\[
X = \frac{m_0 - m}{m_0 - m_f}
\]  

where \(m\) is the mass of the sample at a given time \(t\), \(m_0\) and \(m_f\) refer to masses at the beginning and the end of process. The result of the conversion at calcination of Nd Hydroxide concentrate can be seen in Figure 9.

The mechanisms occurring and mathematical models of thermal decomposition followed reaction control or ash diffusion control [25,26,28–30]. If the calcination process was controlled by the chemical reaction, the following expression can be used to describe the leaching kinetics of the process.

\[
1 - (1 - X)^\frac{1}{3} = k_1 t
\]  

Similarly, if the was controlled by diffusion, the following expression of the shrinking core model can be used.

\[
1 - 3(1 - X)^\frac{2}{3} + 2(1 - X) = -k_2 t
\]  

The using of these equation can be seen on Figure 10.
The relation between time and shrinking core equation at calcination process. The equations linearity ($R^2$) of the relationship between time ($t$) with $f(X)$ for the diffusion control and reaction control were shown in Table 1.

### Table 1. The equation of the relationship between $t$ and $f(X)$ at calcination process.

|                | Ash diffusion control       | Reaction control          |
|----------------|-----------------------------|---------------------------|
| Equation       | $Y = 0.3241x + 0.1338$      | $Y = 0.3185x + 0.1087$    |
| Linearity ($R^2$) | $R^2 = 0.8953$              | $R^2 = 0.9273$            |

Table 1 shows that the linearity ($R^2$) of Reaction control was greater than ash diffusion control. It can be concluded that calcination was controlled by reaction.

3.3.2. Kinetic of leaching. The major models that have been developed for kinetics of non-catalytic liquid–solid reactions are the shrinking (including shrinking particle and shrinking core), homogeneous, grain, uniform pore and random pore models [31]. The homogeneous, grain, uniform pore and random pore models applied to the porous solid–liquid system that were not suitable to our leaching process. The shrinking core is suitable to the reaction between an initially non-porous particle and a reagent, during which the unreacted core gradually shrinks. In this model, a solid product layer is formed around the unreacted grains. Same with shrinking core, the shrinking particle model also suitable to the reaction between an initially non-porous particle and a reagent, but no solid is produce [32].

In shrinking core model, the leaching process is controlled either by the diffusion of reactant through the solution boundary, or through a solid product layer, or by the surface chemical reaction rate [33]. If the leaching process is controlled by the chemical reaction, equation (4) can be used to describe the leaching kinetics of the process. Similarly, if the diffusion of the reagent through a product layer is the slowest step, the equation (5) of the shrinking core model can be used.

Figure 11 presents the fractional conversion during the leaching. As shown in Figure 11, Nd hydroxide concentrate was leached out to Nd(NO$_3$)$_3$ solution after the reaction of $25$ min at room temperature, with $0.8$ mol/L HNO$_3$ and the solid is Ce oxide concentrate. Meanwhile the relation between time ($t$) and the fractional conversion equation ($x = f(x)$) for the leaching process was shown in Figure 12.
Figure 1. The relationship between time and fractional conversion at leaching of Nd hydroxide concentrate.

Figure 2. The relationship between time with shrinking core equation at leaching process.

The equations line linearity (R²) of the relationship between time (t) with f (X) for the diffusion control and reaction control at leaching process was shown in Table 2.

| Equation Description           | Ash diffusion control | Reaction control |
|--------------------------------|-----------------------|------------------|
| y = 0.0218x - 0.1034           | y = 0.0215x - 0.0579  |                  |
| Linearity (R²)                 | R² = 0.7976           | R² = 0.9287      |

From Table 2, the linearity (R²) of reaction control was greater than ash diffusion control, it can be concluded that leaching was controlled by reaction.

3.4. The composition of solid product

The composition of raw material (REOH), product of calcination and product of leaching was shown at Figure 13. The %weight of Ce in REOH is 3.33%, after calcination increased to 9.00% and after leaching increased to 50.26%. The %weight of La in REOH is 3.50%, after calcination increased to 6.29% and after leaching decreased to 3.57 %. The %weight of Nd in REOH is 16.67%, after calcination increased to 45.01% and after leaching decreased to 0.36 %. It can be concluded that Ce difficult to dissolve in HNO₃, but Nd and La easy dissolve in HNO₃.
4. Conclusion

From the results of the study it can be stated that calcination could convert Nd(OH)$_3$ concentrate to Nd$_2$O$_3$ concentrate as evidenced by the solubility properties in aqueous HNO$_3$. Cerium hydroxide was easy dissolve in aqueous HNO$_3$ while CeO$_2$ could not soluble in aqueous HNO$_3$. The more of calcination time, the Nd$_2$O$_3$ formed was more perfect. The concentration La in Nd(OH)$_3$ concentrate before calcination is 3.50%, Ce is 3.33% and Nd is 16.67%. The results of 3 hours calcination, the %weight of La is 12.50 %, Ce is 10.42 % and Nd is 52.08 %. After leaching the result of 3 hour calcination, HNO$_3$ molarity was very influent on leaching La and Nd, but Ce can’t leach. The greater molararity of HNO$_3$ increase the efficiency leaching. The composition of La in solid of leaching product using 1 M HNO$_3$ with five leaching times is 3.57%, Ce is 50.26 % and Nd is 0.36 %. The kinetic calcination and leaching followed reaction control.

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