Optimization Recovery of Yttrium Oxide in Precipitation, Extraction, and Stripping Process

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Abstract. Yttrium oxide can be used as a dopant control rod of nuclear reactors in YSH material and superconductors. Yttrium oxide is obtained in the Xenotime mineral derived from byproduct of tin mining PT Timah Bangka which contain rare earth elements (REE) dominant Y, Dy, and Gd whose content respectively about 29.53%, 7.76%, and 2.58%. Both usage in the field of nuclear and non-nuclear science and technology is need to pure from the impurities. The presence of impurities in the yttrium oxide may affect the characteristic of the material and the efficiency of its use. Thus it needs to be separated by precipitation and extraction-stripping and calcination in the making of the oxide. However, to obtain higher levels of Yttrium oxide, it is necessary to determine the optimum conditions for its separation. The purpose of this research was to determine the optimum pH of precipitation, determine acid media and concentration optimum in extraction and stripping process and determine the efficiency of the separation of Y from REE concentrate. This research was conducted with pH variation in the precipitation process that pHs were 4 - 8, the difference of acid media for the extraction process, i.e., HNO₃, HCl and H₂SO₄ with each concentration of 0.5 M; 1 M; 1.5 M; and 2 M and for stripping process were HNO₃, HCl, and H₂SO₄ with each concentration of 1 M; 2M; and 3 M. Based on the result, the optimum pH of precipitation process was 6.5, the optimum acid media was HNO₃ 0.5 M, and for stripping process media was HNO₃ 3 M. The efficiency of precipitation process at pH 6.5 was 69.53 %, extraction process was 96.39% and stripping process was 4.50%. The separation process from precipitation to extraction had increased the purity and the highest efficiency recovery of Y was in the extraction process and obtained Y₂O₃ purer compared to the feed with the Y₂O₃ content of 92.87%.

1 Introduction

Xenotime is a phosphate rare earth elements compound (Y, Dy, Gd) PO₄ obtained from byproducts of tin mining in PT Timah Bangka island which has not been widely developed for its separation [¹]. The rare earth metal elements (REE) contained in xenotime were Gadolinium (Gd), Dysprosium (Dy), Yttrium (Y), Samarium (Sm), Lanthanum (La), Cerium (Ce), and Neodymium (Nd) [¹,²,³]. Total of rare earth elements ranged from 55% to 70%. The Rare Earth Elements Oxides (REE₂O₃) with dominant elements Y, Dy, and Gd contained in Xenotime were 29.53%, 7.76%, and 2.58% [¹]. REE has been widely used especially in the field of advanced technology. In nuclear science and technology, REE such as Y in the form of an oxide (Y₂O₃) was used as a control rod dopant material at a nuclear reactor made from Yttria-stabilized hafnia [⁴]. The permitted impurities on Y₂O₃ as a control rod dopant material at a nuclear reactor made from Yttria-stabilized hafnia [⁴].
Dy and Gd level was 500 mg/g of powder$^{[5]}$. In the non-nuclear field, Y$_2$O$_3$ could be used as a superconducting material that is highly potent in the manufacture of fast trains$^{[6]}$

Both usage in the field of nuclear and non-nuclear science and technology, Y$_2$O$_3$ must be in the pure state of its impurity. The presence of impurities or additional compounds may modify the behavior and efficiency in its use a separation is necessary before the preparation of Y$_2$O$_3$. Yttrium that has been separated from the impurities, then calcined to obtain Y$_2$O$_3$. In this research, it was used the concentrate of xenotime in the form of REE hydroxide. The Y element contained in the concentrate still had a purity of 85.17%. However, these content could not be used for nuclear and non-nuclear science and technology application such as dopant material of Yttria-stabilized hafnia (YSH) and control rods for nuclear application and for non-nuclear application such as especially a superconducting material with purity requirement of Y$_2$O$_3$ > 90% thus it needed to be increased in purity. In this research, the study of REE purification including precipitation, extraction, and stripping process.

2 Research Method

2.1 Reagent

The Reagents used in this research were rare earth element hydroxide concentrate [REE(OH)$_3$] which had composition: Y = 85.17%, La = 0.71%, Ce = 5.81%, Gd = 2.33%, Dy = 5.98%, HNO$_3$ 65% p.a, NH$_4$OH 25%, HCl 32% p.a, H$_2$SO$_4$ 97% p.a, H$_2$C$_2$O$_4$ 15%, Bis(2-etilheksil) Phosphate Acid (D2EHPA) 97% and kerosene.

2.2 Tool

The tools used in this research were glass beaker as a reactor in the process of precipitation, extraction, and stripping, pH meter as an instrument for measurement pH of solution in settling process, and X-ray spectrophotometry as an instrument for quantitative and qualitative analysis, hot plate, volumetric flask, Volumetric pipette magnetic stirrer, Graduated cylinder, pipette, spatula, analytical balance, Erlenmeyer, bullet, oven, desiccator, and furnace.

2.3 Procedure

2.3.1 Optimization pH of Precipitation Process

An amount of 20 g REE(OH)$_3$ was dissolved in 250 mL HNO$_3$ 0.5 M. Then it was settled by adding 15% NH$_4$OH solution to pH = 4. A Filtrate I and a precipitate I were separated. The precipitate was dried at 110°C and stored in the desiccator for 30 minutes. The precipitate and the filter paper were weighed until had a constant weight. Process a) was repeated for simultaneous precipitation, starting pH = 5 until Y did not re-form the precipitate. Each of the precipitation process results in different pH (filtrate (n) and precipitate (n) was separated. The filtrate (n) and precipitate (n) at various pH were analyzed using XRF. After analyzed, it would be known the optimum pHs to recovery concentrate Y(OH)$_3$.

2.3.2 Optimization Acidity of Feed Extraction

An amount of 1 g precipitate of Y(OH)$_3$ in the precipitation process was dissolved in the acidity media of HNO$_3$ 0.5 M, 25 mL. Preparations for variation acidity on extraction process were performed by making of HNO$_3$, H$_2$SO$_4$ and HCl acidic media at concentrations of 0.5 M; 1 M; 1.5M; and 2M. Then, solution Y(NO$_3$)$_3$ was extracted using 30% D2EHPA in Kerosene (organic phase v/v) with a water phases on volume (FA) and an organic phase (FO) ratio was 1: 1. The mixture was stirred on a hot plate stirrer at 30 ± 1 °C for 30 minutes then allowed for 15 minutes until it formed two phases that was the water phase and the organic phase and could be separated using a separation funnel. The aqueous phase were analyzed using XRF.
The processes were repeated for variations of the acidity media of HNO₃, H₂SO₄, and HCl with each concentration of 0.5 M; 1 M; 1.5M; and 2M.

2.3.3 Optimization Acidity of Stripping Process

An amount of 5 g precipitate of Y(OH)₃ in the precipitation process was dissolved in the optimum acidity at 100 mL extraction process. Then, solution Y was extracted using 30% D2EHPA in kerosene (organic phase v/v) with a water phase (FA) and an organic phase (FO) volume was 1: 1. The mixture was stirred on a hotplate for 30 minutes then allowed for 15 minutes until the water phase and the organic phase was separate. Two phases which were formed separated by a separation funnel.

The extracted organic phase (FO) was stripped with 3 M H₂SO₄ with the volume ratio of the water phase (FA) and the organic phase (FO) was 1: 1. The mixture was stirred using a stirrer hot plate at 30 °C ± 1°C at 4 °C for 30 minutes, then allowed until it formed two phases that were the water phase and the organic phase and could be separated using a separation funnel to obtain a stripping phase (FSwater) and an organic phase (FO). Process b) was repeated for variations of the acidity media of stripping HNO₃, H₂SO₄ and HCl with each concentration of 1 M; 2M; and 3M.

The stripping phase (FSwater) was added 15% H₂C₂O₄ (b/v) hence, forming precipitate Yttrium Oxalate (Y₂(C₂O₄)₃). FSwater in each variation was analyzed using XRF to find the type of acidity media and the optimum concentration. The precipitate Y₂(C₂O₄)₃ was filtered and dried at 110°C then stored in the desiccator.

3 Result and Discussion

3.1 Optimization of Precipitation pH

The occurrence of element precipitation could be predicted by calculating from the pKsp data of each element hence it could be seen that each element would settle to a certain pH.

| Type     | Y  | La | Ce | Gd | Dy | Mass of precipitate (g) | Total Efficiency (%) |
|----------|----|----|----|----|----|-------------------------|----------------------|
| Feed     | 85.17 | 0.71 | 5.81 | 2.33 | 5.98 | 20.3102 | - |
| pH 4     | 0   | 0   | 0   | 0   | 0   | 0           | 0            |
| pH 5     | 0   | 0   | 0   | 0   | 0   | 0           | 0            |
| pH 6     | 37.69 | 0.75 | 55.63 | 0   | 5.93 | 0.1537 | 0.76 |
| pH 6.5   | 89.57 | 0   | 0.03 | 1.09 | 9.31 | 14.1209 | 69.53 |
| pH 6.8   | 89.77 | 0.42 | 1.59 | 5.31 | 2.91 | 2.4207 | 11.92 |
| pH 7     | 97.35 | 2.65 | 0   | 0   | 0   | 0.0088 | 0.04 |
| pH 7.5   | 70.59 | 0.27 | 25.12 | 4.02 | 0   | 1.2611 | 6.21 |
| pH 8     | 0   | 0   | 0   | 0   | 0   | 0           | 0            |

Note: Feed Volume was 250 mL, Temperature was 30 ± 1 °C

Based on Table 1, it was known that the largest efficiency of precipitation was at pH 6.5 with a total efficiency was 69.53% and Y content was 89.57%.

The precipitation results in each pH 4 to 8 differed from the estimates in pKsp calculations. According to calculations, the precipitation for Y(OH)₃ would begin to settle at pH 8.14. However, this experiment
which was performed indicated that the yttrium was started to settle at pH 6 and the optimum precipitation for Y(OH)₃ was pH 6.5. This may occur because the solution deposited had content another rare earth metal elements which will cause a decrease in the solubility of Y in the solution.

3.2 Optimization of acid aqueous media extraction

The precipitate of Y(OH)₃ at pH 6.5 was selected as a feed for the variation of acidity media in the extraction process. The selected of acidity media types were HNO₃, HCl and H₂SO₄ with concentrations of 0.5 M, 1M, 1.5M and 2M respectively. The water phase as the extraction media was selected from acid solution because D2EHPA can extract REE at low pH state [14].

| Type of acidity media | Efficiency Y (%) | Purity of Y (%) |
|-----------------------|-----------------|----------------|
| HNO₃ 0.5 M            | 96.39           | 90.09          |
| HNO₃ 1 M              | 85.88           | 90.96          |
| HNO₃ 1.5 M            | 73.19           | 91.98          |
| HNO₃ 2 M              | 75.05           | 96.15          |
| H₂SO₄ 0.5 M           | 63.72           | 84.01          |
| H₂SO₄ 1 M             | 67.95           | 90.15          |
| H₂SO₄ 1.5 M           | 53.05           | 77.30          |
| H₂SO₄ 2 M             | 29.50           | 87.85          |
| HCl 0.5 M             | 95.62           | 89.68          |
| HCl 1 M               | 82.45           | 82.68          |
| HCl 1.5 M             | 70.03           | 92.57          |
| HCl 2 M               | 56.75           | 96.84          |

Note: temperature is 30°C ± 1, stirring time is 30 minute, D2EHPA: Kerosin 30%, FO: FA 1:1

Based on Table 2, the highest efficiency of recovery Y was obtained on the acidity medium of HNO₃ 0.5 M and the lowest efficiency was on H₂SO₄ 2M. The lower the acid concentration, it will get the higher the efficiency of recovery Y. This was occurred according to the following reaction equation,

\[
\text{HNO}_3^{(aq)} + \text{H}_2\text{A}_2^{(org)} \leftrightarrow \text{HNO}_3\cdot\text{H}_2\text{A}_2
\]

\[
\text{Y}^{3+^{(aq)}} + 3\text{HNO}_3\cdot\text{H}_2\text{A}_2 \leftrightarrow \text{Ln}((\text{H}_2\text{A}_2)_{3\text{org}} + 3\text{H}^+ + 3\text{NO}_3^{-}
\]

The first reaction was the exchange of cations between H⁺ (aq) water phase with H⁺ (org) organic phase, so that would equally donate H⁺ which means no significant change in the reaction. Furthermore, the second reaction was the exchange of H⁺ (org) with Y³⁺ which would cause Y³⁺ to react complex with D2EHPA ligands and 3H⁺ donated into the water phase. In the case of H₂SO₄, it was the most less effective because of the first reaction. H₂SO₄ had 2H⁺ which would cause D2EHPA prefer exchange H⁺ (org) in H₂SO₄ to binding complex at Y³⁺.

HCl had a lower efficiency compared to HNO₃ because HNO₃ had a lower acidity level than HCl. It was easier D2EHPA to react complex bonds with Y³⁺ at lower acidity than in high acidity. thus, the acidity media in the extraction of Y for the extraction process from the highest to the lowest which was according to the efficiency ie HNO₃ > HCl > H₂SO₄.
3.3 Optimization of acid aqueous media stripping

Feed of stripping process used organic phase which was extracted from HNO₃ 0.5 M. In the stripping experiment used variations of acidity type of HNO₃, H₂SO₄, and HCl with concentrations of 1 M, 2 M, and 3 M respectively. The stripping process results were obtained in Table 3.

Table 3. Efficiency and Purity of Stripping Process

| Type of acidity media | Efficiency Y (%) | Purity of Y (%) |
|-----------------------|------------------|-----------------|
| HNO₃ 1 M              | 0.00             | 0.00            |
| HNO₃ 2 M              | 18.59            | 83.01           |
| HNO₃ 3 M              | 40.50            | 92.64           |
| H₂SO₄ 1 M             | 5.17             | 73.53           |
| H₂SO₄ 2 M             | 9.55             | 90.95           |
| H₂SO₄ 3 M             | 15.79            | 94.13           |
| HCl 1 M               | 0.88             | 80.14           |
| HCl 2 M               | 6.92             | 92.74           |
| HCl 3 M               | 21.57            | 91.08           |

Note: temperature is 30°C ± 1, stirring time is 30 minute, FO: FA 1:1

Based on Table 3, the largest efficiency recovery of Y was obtained from the 3M HNO₃ stripping agent of 40.50% with a Y purity of 92.64%. The efficiency of stripping was still low. The higher acid concentration, the higher efficiency recovery of the Y in the stripping process. It was occurred because it would be easier to break down the complex at high acid concentration. If the acid concentration was high, the efficiency of the Y taken would be high in the stripping process. It occurred because process would be easier to break down the complex at high acid concentration. If D2EHPA was expected to form a complex in extraction process with metal by minimizing H⁺org reacts with H⁺aq hence H⁺org was more to bind metal complex, then on stripping process it was expected metal complex that has been bound would be split or decomplexation. At high concentrations, H⁺ dissociates in water was easier than low concentrations, hence the potential of Y³⁺ in the organic would be bind H⁺ higher in water phase than the low concentration. Thus in this study, if concentration was higher, so stripping efficiency also will be higher.

However, in the type of acid medium, HNO₃ was better than H₂SO₄ and HCl. This occurred because in the extraction process, it occurred the next solvent reaction was NO₃⁻ also slightly into the organic phase. When there was the addition of an acid with a similar anion of HNO₃, presence NO₃⁻ was in the organic phase also becomes a ligand in the complex Y bonds, hence it was easier to release into the water phase by carrying the Y metal than the acid with the unlike anions.

In this research, H₂SO₄ and HCl have low efficiency for Y so that agent stripping for metal Y was from high to low HNO₃ > HCl > H₂SO₄.

3.4 The Making of Yttrium Oxide

After the stripping process had performed, simultaneous precipitation with oxalic acid should be performed because all rare earth metals would settle by oxalic acid without treatment of pH variation. The results of simultaneous precipitation was shown in Table 4.
Table 4. Precipitation with Oxalate Acid

| Sample                      | ppm | Y   | Dy  |
|-----------------------------|-----|-----|-----|
| Aqueous Stripping HNO₃ 3M   | 5821| 462 |     |
| Filtrate                    | 0   | 0   |     |

In Table 4, it was shown that Y and Dy had simultaneous precipitation which was shown no concentration in the filtrate. Then, the oxalate precipitate formed was dried a temperature of 110°C before calcination was performed. The temperature of calcination was performed at 1100°C for 2 hours.

Table 5. Result of Yttrium Oxide from Calcination Process at 1100°C for 2 hours

| Sample                      | Content (%) |
|-----------------------------|-------------|
|                             | Y  |  | Dy  |
| Product 1 stripping HNO₃ 3 M | 92,87 | 7,13 |
| Product 2 stripping H₂SO₄ 3 M | 94,19 | 5,81 |

Ket: Temperature at 1100°C, t = 2 hours

In Table 5, it could be seen that the result of calcination product 1 had 92.87% content of Y and product had 94.19 content of Y. In Figure 1, product 2 had a white oxide color compared to product 1. It was occurred because Dy in product 1 was more than product 2 which caused a brownish-white color.

3.5 Efficiency of Each Process
The separation of Y from the rare earth metal concentrate in the experiments was performed by the precipitation process at various pH, extraction-stripping, and calcination process to obtain Y₂O₃. Efficiency and purity of the concentrate from the precipitation process to extraction - stripping with the optimum conditions were shown in Table 6.

Based on Table 6, each process from precipitation to extraction had increased the purity and the highest efficiency recovery of Y was in the extraction process and it can be obtained that Y₂O₃ purer than the feed with the Y₂O₃ content of 92.87%.
Table 6. Efficiency and Purity of Each Process

| Process                     | Efficiency Y (%) | Purity of Y (%) |
|-----------------------------|------------------|-----------------|
| Feed                        | -                | 85.17           |
| Precipitation (pH 6.5)      | 69.53            | 89.57           |
| Extraction (HNO₃ 0.5 M)     | 96.39            | 90.09           |
| Stripping (HNO₃ 3 M)        | 40.50            | 92.64           |

4 Conclusion
Based on this research, it could be concluded that the result of optimum precipitation of yttrium was pH 6.5, extraction with the highest effect that was on acidity type HNO₃ 0.5 M and stripping on acidity type HNO₃ 3 M. Efficiency of precipitation process at pH 6.5 was 69.53%, extraction process was 96.39%, stripping process was 40.50% and yield Y₂O₃ with purity 92.87%.

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