Effect of Temperature to Adsorption Capacity and Coefficient Distribution on Rare Earth Elements Adsorption (Y, Gd, Dy) Using SIR

N Aziz¹, A Mindaryani¹, Supranto¹, A Taftazani², D Biyantoro²

¹ Chemical Engineering - Universitas Gadjah Mada
² Centre for Science and Accelerator Technology - National Nuclear Energy Agency of Indonesia (PSTA – BATAN), Yogyakarta, Indonesia

nofriadyaziz@gmail.com

Abstract. The use of REE like element of Yttrium (Y) as a superconducting material requires a purity of more than 90%, so it needs to increase the purity of Y from the settling process. The purpose of this research is to study the separation process of REE that is Y, Gd, Dy elements from REE hydroxide (REE(OH)₃) using SIR method are consisting of Amberlite XAD-16 resin impregnated with Di-(2-ethylhexyl) phosphate (D2EHPA) and Tributyl Phosphate (TBP) and determine the isotherm model on REE adsorption and determine the kinetic model of pseudo adsorption reaction. This research was started by activating XAD-16 resin and is mixed with TBP-D2EHPA solvents so it will form SIR, then it is conducted on variation of SIR composition, temperature variation of adsorption process, determination of equilibrium equation and kinetic sorption occurring in SIR adsorption based on experimental data of liquid concentration as function of time. Based on the calculation result, the most effective SIR composition for REE separation is 0.75 g, the equilibrium equation for Y, Gd and Dy follows the Henry equilibrium model and the pseudo kinetic model of the reaction order Y, Gd, and Dy is followed by the pseudo reaction of order 2. The result of separation of LTJ with SIR is said to be effective from another method because purity is obtained that is 96.73% and qualify as a super conductor material.

1 Introduction

Rare earth metals (REE) are very rare, in nature can be complex compounds, generally complex phosphate compounds and carbonates [1]. One of them is xenotime which is a rare earth elements phosphate compounds and is usually written with REEPO₄ or YPO₄ and containing the main elements that are Yttrium (Y), Gadolinium (Gd), and Dysprosium (Dy) with each content is 60%, 3.6%, and 7.5%. In Indonesia, xenotime is found on the islands of Bangka, Belitung and Singkep which is a by-product of tin mining of PT Timah, Tbk in Bangka [2].

Because of the prospect, potential and economic value of REE is very large, especially the use of a single REE like Y then it is necessary to separate the REE to obtain elements Y with high purity (more than 90%) to be used as a super conductor material. While processing xenotime before the purification process, Y only has content 79-80%, so it needs to be increased purity. However, the problems experienced by the REE elements have similar chemical properties and physical properties that are difficult to separate. REE separation is usually done by solvent extraction or ion exchange (resin).
However, solvent extraction and ion exchange techniques have some limitations. To solve the limitations of extraction and ion-exchange resins, Warshawsky in 1974 introduced a method called solvent impregnated resins (SIR) method for the separation of metal ions \cite{3}. This study purpose to study the separation process of REE (Y, Gd, Dy) from REE hydroxide (REE(OH)\textsubscript{3}) using SIR method and are consisting of Amberlite XAD-16 resin impregnated with Di-(2-ethylhexyl) phosphate (D2EHPA) and Tributyl Phosphate (TBP), to determine the isotherm model on REE adsorption and determine the kinetic model of pseudo adsorption reaction.

\section{Methods}

\subsection{Tools and Materials}

The tools to be used in this research are beaker glass, erlenmeyer, magnetic stirrer, hot plate, stirrer bar, pumpkin neck 3, measuring, bulpet, plastic bottle, XRF tool and the device where sample for XRF analysis, measuring cylinder, measuring pipette, volume pipette, porcelain plate, analytical balance, filter paper oven, glass funnel, thermometer. Materials to be used in this study are Tributyl Phosphat e (TBP), Bis (2-ethylhexyl) Phosphate Acid (D2EHPA), REE(OH)\textsubscript{3}, Aquadest, XAD-16 Resin, Nitric Acid (HNO\textsubscript{3}) and Acetone.

\subsection{Procedure}

\subsubsection{Activation of XAD – 16}

The process begins with activating XAD - 16 as much as 50 g XAD - 16 soaked HNO\textsubscript{3} 2 M for 2 hours then filtered. Then soaked again with 2 M NaOH for 2 hours then filtered. After it was rinsed with aquadest to neutral, soaked with acetone for 2 hours, and dried with oven for 50°C.

\subsubsection{Preparation of D2EHPA / TBP Solution (3: 1) and Resin Impregnation}

Prepared D2EHPA and TBP solution, then mixing to homogeneous with a ratio of 3: 1. Then 20 g solvent soaked with 100 mL of acetone and add 20 g of resin (50% / 50%) was stirred at 350 rpm at room temperature for 2 Hour and dried in 50°C oven for 24 hours.

\subsubsection{Making Feed Solution REE(OH)\textsubscript{3}}

The REE(OH)\textsubscript{3} feedstock standard solution was prepared by weighing as much as 25 g of REE(OH)\textsubscript{3} dissolved in concentrated HNO\textsubscript{3} and then heated to 120°C until the acidity of the depleted HNO\textsubscript{3} vapor was then dissolved in 0.5 M.

\subsubsection{Determination of Adsorption Optimization Y, Gd, Dy}

The SIR variation is made by a certain ratio with a fixed feed amount of 10 mL as in Table 1.

\begin{table}[h]
\centering
\caption{Variation of SIR}
\begin{tabular}{|c|c|}
\hline
Solution & SIR  \\
\hline
Feed & 0  \\
A & 0.25 g  \\
B & 0.5 g  \\
C & 0.75 g  \\
D & 1 g  \\
E & 1.5 g  \\
\hline
\end{tabular}
\end{table}

In each variation, the SIR was then mixed with feed at 30 °C and atmospheric pressure stirred at 350 rpm for 30 minutes. Then separated by filter paper. The filtrate was taken as much as 5 mL to be analyzed using XRF. This process is also carried out at temperatures of 30°C, 40°C, 50°C, and 60°C.
2.2.5 Kinetics of sorption

Comparison of 0.75 g SIR composition: 10 mL of feed then mixed at 30°C and atmospheric pressure stirred at 350 rpm for 30 minutes. Then separated by filter paper. The filtrate was taken as much as 5 mL to be analyzed using XRF. This adsorption action is carried out for temperature variations of 30°C, 40°C, 50°C, 60°C with mixing time variation of 2 minutes, 5 minutes, 10 minutes, 20 minutes, 30 minutes.

3. Result and Discussion

3.1. Rare Earth Separation Mechanisms

After processing from leaching to settling obtained levels of Y, Gd and Dy of 79.4%; 12.1% and 8.5%. However, the use of Y as a superconductor material requires a purity of Y of 90%, so it needs to be increased Y purity. After the calculation is done the results Table 2.

| Type of Separation | % purity | % taken |
|--------------------|----------|---------|
|                    | Y   | Gd     | Dy   | Y   | Gd | Dy   |
| Adsorption         |     |        |      |     |    |      |
| Activated Carbon   | 77.15| 10.08  | 12.77| 7.27| 4.85 | 31.76 |
| Silica             | 81.98| 7.09   | 10.93| 6.19| 2.73 | 21.78 |
| Extraction         |     |        |      |     |    |      |
| Solvent D2EHPA     | 91.11| 6.33   | 2.57 | 60.27| 39.45 | 55.88 |
| Solvent TBP        | 90.57| 6.91   | 2.53 | 23.27| 16.72 | 21.36 |
| Solvent Mixture TBP-D2EHPA | 91.87 | 5.26 | 2.87 | 66.38 | 35.85 | 68.23 |
| Resin XAD -16      | 92.20| 6.30   | 1.50 | 17.29| 6.03 | 7.42  |
| SIR                |     |        |      |     |    |      |
| SIR Solvent D2EHPA | 93.91| 3.62   | 2.47 | 22.69| 4.46 | 15.73 |
| SIR Solvent TBP    | 90.95| 7.21   | 1.84 | 14.20| 5.75 | 7.57  |
| SIR Solvent TBP - D2EHPA | 96.733 | 2.743 | 0.524 | 31.57 | 4.57 | 4.51  |

In Table 2, the separation by using SIR obtained by Y purity over 90% with Gd and Dy of 2.743% and 0.524% compared with adsorption using activated carbon or silica, extraction and ion exchange resin and qualified to be used as the superconductor material is Y 89.76%. The analysis used XRF with 99.95% accuracy and 90.43% precision using Merck Yttrium Oxide standard with 99.99%. In addition, based on the results of previous research, it can be seen that the separation by using SIR is much greater than using liquid-liquid extraction and ion exchange resin. The results of this study were compared using the extraction method, ion-exchange resin, and SIR and presented in Table 3. Table 3 shows the synergistic effect of the solvent mix of D2EHPA and TBP that is greater than 1.
Table 3 Separation Method of REE

| Type of Separation | Kd  | β    | Effect of Synergism |
|--------------------|-----|------|---------------------|
|                    | Y   | Gd   | Dy                  | Dy    |
| Adsorption         |     |      |                     |       |
| Activated Carbon   | 0.08| 0.05 | 0.47                | 1.54  | 0.17 |
| Silica             | 0.07| 0.03 | 0.28                | 2.35  | 0.24 |
| Extraction         |     |      |                     |       |
| Solvent D2EHPA     | 1.52| 0.65 | 1.27                | 2.33  | 1.20 |
| Solvent TBP        | 0.30| 0.20 | 0.27                | 1.51  | 1.12 |
| Solvent MixtureTBP-D2EHPA | 1.97 | 0.56 | 2.15                | 3.53  | 0.92 | 1.08 |
| Resin              |     |      |                     |       |
| SIR Solvent D2EHPA | 0.29| 0.05 | 0.19                | 6.28  | 1.57 |
| SIR Solvent TBP    | 0.17| 0.06 | 0.08                | 2.72  | 2.02 |
| SIR Solvent TBP-D2EHPA | 0.46 | 0.048| 0.047               | 10.00 | 9.76 | 1.22 |

3.2 Effect of Composition Variation SIR

3.2.1 Effect of Weight SIR against Kd and separation factor (β)

Based on the calculations, we obtain the weight relationship SIR (g) Vs. Kd is presented in Figure 1, and relationship the weight of SIR (g) Vs separation factor (β) is presented in Figure 2. Based on Figure 1 and 2 it can be seen that with the increasing weight of SIR used in the separation of REE the distribution coefficients of each element (Kd_Y, Kd_Gd, Kd_Dy) will also increase. The largest distribution coefficient is owned by Y indicating that the Y^{3+} ion is absorbed larger than Gd and Dy.

Figure 1. Relations mass of SIR (g) vs Kd

Figure 2. Relations mass of SIR (g) vs Separation factor

3.2.2 The Effect of Temperature on Kd and separation factor (β)

Plot of temperature (g) Vs Kd is presented in Figure 1, and temperature SIR (g) Vs separation (β) is presented in Figure 2. Based on Figure 3 it can be seen that with the decreasing temperature used in the separation of REE the distribution coefficients of each element (Kd_Y, Kd_Gd, Kd_Dy) will also increase. In
Figure 4 it can be seen that with the decreasing temperature used in the separation of the REE, the separation factor ($\beta$) of Y-Gd and Y-Dy increases, so that the optimum temperature is 30°C.

![Figure 3: Relations Temperature (°C) vs. Kd](image)

![Figure 4: Relations Temperature (°C) Vs Separation Factor (\(\beta\))](image)

### 3.3 Adsorption Equilibrium Equation

#### 3.3.1 Determination of Equilibrium Time

![Figure 5: Equilibrium Time (min) for Yttrium ion sorption](image)

Figure 5 shows that there is a decrease in concentration and the equilibrium time has been reached in 30 minutes.

#### 3.3.2 Isotherms Adsorption

Through this research, SIR adsorption power will be exposed to REE to formulate the adsorption equilibrium behavior of Y, Gd and Dy ions in SIR.
Table 4 Adsorption Isotherm Equations

| Temperature | Y         | Gd   | Dy  |
|-------------|-----------|------|-----|
|             | Henry     |      |     |
|             | $r^2$     |      |     |
| 30          | 0.9824    | 0.9926 | 0.9894 |
| 40          | 0.9829    | 0.9946 | 0.9931 |
| 50          | 0.9977    | 0.9967 | 0.9953 |
| 60          | 0.9812    | 0.9887 | 0.9969 |
| error (%)   | 3.35      | 5.02  | 5.83 |
|             | Freundlich|      |     |
|             | $r^2$     |      |     |
| 30          | 0.9       | 0.8953 | 0.8789 |
| 40          | 0.8654    | 0.9106 | 0.9064 |
| 50          | 0.9515    | 0.9669 | 0.9221 |
| 60          | 0.9946    | 0.9872 | 0.9261 |
| Error (%)   | 5.59      | 7.75  | 13.49 |
|             | Langmuir  |      |     |
|             | $r^2$     |      |     |
| 30          | 0.9626    | 0.846 | 0.8422 |
| 40          | 0.9356    | 0.8534 | 0.848 |
| 50          | 0.9107    | 0.8499 | 0.8437 |
| 60          | 0.9538    | 0.8904 | 0.8132 |
| Error (%)   | 11.28     | 13.00 | 20.37 |

Based on Table 4 it can be stated that the adsorption of Y, Gd and Dy metals follows the Henry isotherm model because $r^2$ is close to 1 and the isotherm error of Henry is less than that of Langmuir isotherms and Freundlich isotherms.

3.3.3 Isotherms Adsorption of temperature function and van't Hoff equation

The van't Hoff equation can be done to find out the dependence of the equilibrium concentration of temperature and the results obtained in Table 5.

Table 5 Reaction Heat of REE

| Element | $\Delta H$ (kcal/mol) |
|---------|-----------------------|
| Y       | 1646.65 -3.05         |
| Gd      | 38368.80 -0.87        |
| Dy      | 48194.49 -0.74        |

In Table 4,4 it can be seen that the largest $\Delta H$ is owned by Yttrium that is 3.05 kcal/mol and $\Delta H$ is negative, i.e., the exothermic reaction due to $K$ decreases with temperature so that the metal sorption of Y in SIR is faster than Gd or Dy metal.
3.4 Kinetics of sorption

3.4.1 Compare Model

Result of rate constant adsorption speed based on some models can be seen in Table 6.

Table 6 Reaction Model of REE Pseudo Kinetics

| Pseudo Model/Temperature | Y 30 | 40 | 50 | 60 | Average |
|--------------------------|------|----|----|----|---------|
| Order 1                  |      |    |    |    |         |
| $r^2$                    | 0.7  | 0.6723 | 0.9557 | 0.8353 | 0.7908 |
| error (%)                | 25.58 | 31.45 | 16.75 | 29.51 | 25.82 |
| Order 2                  |      |    |    |    |         |
| $r^2$                    | 0.99996 | 0.9999 | 0.9996 | 0.9985 | 0.9995 |
| error (%)                | 1.89 | 0.96 | 2.23 | 5.69 | 2.69 |

Pseudo Model/Temperature | Gd 30 | 40 | 50 | 60 | Average |
|--------------------------|-------|----|----|----|---------|
| Order 1                  |       |    |    |    |         |
| $r^2$                    | 0.965 | 0.9955 | 0.9983 | 0.9959 | 0.9887 |
| error (%)                | 31.45 | 14.96 | -7.04 | -9.95 | 7.36 |
| Order 2                  |       |    |    |    |         |
| $r^2$                    | 0.9378 | 0.8626 | 0.7868 | 0.6433 | 0.8076 |
| error (%)                | 6.07 | 12.96 | 15.30 | 17.09 | 12.86 |

Pseudo Model/Temperature | Dy 30 | 40 | 50 | 60 | Average |
|--------------------------|-------|----|----|----|---------|
| Order 1                  |       |    |    |    |         |
| $r^2$                    | 0.9497 | 0.987 | 0.9821 | 0.9569 | 0.9689 |
| error (%)                | 18.72 | 20.17 | 13.01 | 17.74 | 17.41 |
| Order 2                  |       |    |    |    |         |
| $r^2$                    | 0.9206 | 0.9088 | 0.799 | 0.5481 | 0.7941 |
| error (%)                | 10.140 | 9.346 | 14.738 | 13.943 | 12.04 |

Table 6 shows that the REE adsorption kinetics of the SIRs are more suitably explained by the second order pseudo adsorption kinetics model because $r^2$ is close to 1 and the error by the 2nd order reaction kinetics is smaller than the order 1.

3.4.2 Effect of temperature on sorption kinetics

The effect of temperature on the value of the velocity constant (k) on the pseudo adsorption kinetics model 2 can be seen in Table 7, and Figure 6. It can be seen that the higher the temperature the constant value of the speed will be smaller because of the SIR resistance at temperatures below 60°C so that the REE will be bound complex and stable in the SIR at a temperature of 30°C. The largest reaction rate constant is owned by Y so that Y is more chemically stable in the SIR.
### Table 7: Kinetic Constants Reaction of Order 2 Pseudo REE

| Temperature (°C) | $k_2$ (mg/g adsorbent. min) |
|------------------|----------------------------|
|                  | Y  | Gd  | Dy  |
| 30               | 0.3872 | 0.3434 | 0.3533 |
| 40               | 0.3005 | 0.2660 | 0.2894 |
| 50               | 0.2344 | 0.2127 | 0.2188 |
| 60               | 0.2158 | 0.1911 | 0.2092 |

![Figure 6. Kinetic Constants Reaction of Order 2 Pseudo REE Temperature Relation (°C) and Order Rate Reaction Pseudo 2 (mg / g adsorbent.min)](image)

### 4. Conclusion

SIR method is more effective than extraction or adsorption. The most effective SIR composition for rare earth metal separation is 0.75 g with a temperature of 30 °C. Equilibrium equations for Y, Gd, Dy approach the Henry, equilibrium model. Y, Gd, Dy kinetic sorption follows the pseudo reaction kinetics of order 2 and the reaction kinetics constant belongs to Y that is 0.3872 mg / g of minute adsorbent at a temperature of 30 °C. The larger the temperature the absorption will be smaller and the greater the temperature then constant rate pseudo reaction order 2 will also be smaller.

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