Extraction of Neodymium (III) from Neodymium Concentrate Using Synergistic Solvent D2EHPA, TOPO and TBP

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Abstract. Solvent extraction was performed on Nd (III) concentrate by using synergistic solvents D2EHPA, TOPO and TBP. The aim of this research is to know the effect of synergistic solvent on the extraction result. The extraction process of the Nd (III) concentrate was carried out at the feed pH of 1.0. The first extraction was carried out using a mixture of D2EHPA and TOPO extractants while the second extraction used a mixture of D2EHPA and TBP at various concentrations (10: 0, 8: 2, 6: 4, 4: 6, 2: 8 and 0:10) and variation of feed and solvent volume ratio (0.5: 1.0; 0.75: 1.0; 1.0: 1.0; 1.0: 0.5; 1.0: 0.75) at constant stirring speed of 250 rpm and extraction time of 30 minute. The results showed that the concentration and volume of synergistic solvents greatly influenced the distribution coefficient (Kd), extraction efficiency (E) and separation factor (α). From all parameters studied the highest separation factor was obtained using the synergistic % ratio of D2EHPA-TOPO 4: 6 solvent and the volume ratio of feed and solvent 1: 0.5 ie α Nd-Pr = 2.55 and α Nd-Sm = 1.47 but the distribution coefficient and efficiency of the three elements are low so they are not selected. The recommended condition is to use a 4% -6% D2EHPA-TOPO synergistic solvent and a 0.5: 1.0 solvent and solvent ratio. In this condition obtained Kd Nd = 0.46 Kd Pr = 0.27 Kd Sm = 0.72, E Nd = 31.5% E Pr = 21.3% E Sm = 41.8 with the separation factor α Nd-Pr = 1.7 and αNd-Sm = 0.84.

Keywords: Extraction, Nd (III), synergistic solvents, D2EHPA, TBP, TOPO

1. Introduction

Rare-earth elements (REEs) are a group of 17 elements, consisting of the 15 lanthanides plus scandium and yttrium. REEs are used in a wide range of products, such as fluorescent lamps, magnets, superconductors, lasers, ceramics, semiconductors, catalysts, and thermal neutron absorbents. REEs occur together in nature in some minerals, e.g. bastnasite, monazite and xenotime [1]. The rare earth metals (REMs) are progressively establishing themselves as ecisive industrial materials, with inimitable applications in copious fields, such as the permanent magnets, electronics, superconductor, hydrogen storage, medical and nuclear technologies [2][3]. Different rare earths are needed to supply the required functionality in these applications. In some cases, a single rare earth element may be required, such as La for nickelmetal hydride batteries, but other applications require a mixture of rare earths, for example Nd and Pr for rare earth magnets and Eu (or Tb) and Y for rare earth phosphors.[4][5].

A mixture of neodymium, iron, and boron metal is used in the manufacture of permanent magnets. This magnet is part of the vehicle component, also used on the loudspeaker and for data storage on the computer. Neodymium is an important technological metal due to its widespread use in
neodymium–iron–boron permanent magnets (NdFeB magnets or neomagnets). The ever-increasing use of NdFeB magnets and possible supply risk of neodymium makes recycling of neodymium from end-of-life NdFeB magnets an important economic issue [6][7]. Since these metals are found in resource as a mixture, they should be separated into each other. This separation is difficult especially in the case between neighbouring elements in the periodic table, because they have the similar chemical features due to the same electric configuration of outermost husks. Solvent extraction is presently one of the commercialized techniques for the separation [8]. The development of sustainable recycling schemes for neodymium is a technological challenge. An important technique for the recovery of neodymium and other rare earths is solvent extraction (SX), because this technique allows the separation of rare earths from other metals as well as the separation of mixtures of rare earths into the individual elements [4][8].

The separation of Nd from the Nd (OH)₃ concentrate of the processed monasite sand product is necessary conducted considering the usefulness and the expensive price of Nd. The separation of Nd from Nd(OH)₃ concentrate was conducted by using solvent extraction process. The separation by using extraction is due to the greater advantages of this process, among of which is time saving/efficient, and that the equipment used is simpler. Based on the description, from this investigation it is expected to know the optimum condition of the extraction process to separate neodymium (Nd) from Nd (OH)₃ concentrate [3]. Solvent extraction involves the distribution of a solute between the two immiscible liquid phases. Extraction techniques are useful for rapid and "clean" separations both for organic and inorganic substances. This way could be used for macro and micro analysis. Through the extraction process, the metal ion in the water solvent is pulled out by an organic solvent (organic phase). In general, extraction is the process of withdrawing a solute from its solution in water by another solvent which is immiscible with water phase [3][4].

Researcher M.Setyadji et al previously conducted the solvent extraction of neodymium concentrates of monazite sand processed product using extractants of trioctylamine (TOA), tryibuthyl phosphate (TBP), trioctylphosphine oxyde (TOPO) and di-ethyl hexyl phosphoric acid (D2EHPA) in kerosene [4]. Konaem Wasamonet al., studied the modeling of neodymium ions extraction from the mixture of D2EHPA and TOPO by the hollow fiber supported liquid membrane[6]. J.Kraikaew et al., studied the application of isomolar mixtures of tributylphosphate(TBP) and di-(2-ethylhexyl)phosphoric acid(D2EHPA) in kerosene at room temperature for extractive separation of individual rare earths from mixed rare earth nitrate feed solution compared with 50%TBP in kerosene[9]. M.O. Andropov et al., carried out according to the method by shaking the organic and aqueous phases in separating funnels with subsequent slicing. REE were extracted in the presence of salting-out agents by extraction with100 % tributyl phosphate[10].

According to Nerst's distribution law, when into two immiscible solvents was entered the soluble solutes in both solvents there would be a solubility division. Both solvents are generally organic solvents and water solvents. In practice the solute would be distributed by itself into the two solvents after being shaken and left separately. The ratio of the solute concentration in both solvents remains constant, and it would be a constant at a fixed temperature. Those constants are called distribution constants or distribution coefficients. The distribution coefficient is expressed by the following formula [4][5][9]:

\[
K_d = \frac{C_2}{C_1} \quad \text{or} \quad K_d = \frac{C_o}{C_a}
\]

where \( K_d \) = distribution coefficient and \( C_1 \), \( C_2 \), \( C_o \), and \( C_a \) respectively are solute concentrations in solvents 1, 2, organic, and water.

In accordance with the agreement, the solute concentration in the organic solvent is written above and the solute concentration in the water solvent is written below. From the formula if the value of \( K_d \) is large, the solute will quantitatively tend to be more distributed into organic solvents, as well as the opposite. The distribution coefficient can also be expressed as the distribution ratio. The distribution ratio (D) is the most important parameter involved in the solvent extraction along with the separation factor (\( \alpha \)). These are determined using Eqs. 1 and 2, respectively [1][11]:
\[ D_A = \frac{[A]_{\text{org}}}{A_{\text{aq}}} \]  
(2)

\[ \alpha_{A/B} = \frac{D_A}{D_B} \]  
(3)

where \([A]_{\text{org}}\) and \([A]_{\text{aq}}\) are the equilibrium concentrations of the metal of interest in all its existing species in the organic and aqueous phases, respectively. Consequently, the separation factor is the ratio between the distribution ratios of the metal 1 and 2 that are of interest. The separation factor represents the selectivity between these two metals in the extraction. The extractability of neodymium ions in this research can be calculated by the percentage of extraction [12]:

\[ \% \text{Extraction} = \frac{[C]_{f,\text{in}} - [C]_{f,\text{out}}}{[C]_{f,\text{in}}} \]  
(4)

where \([C]_{f,\text{in}}\) denotes the initial concentration in the feed phase and \([C]_{f,\text{out}}\) denote the outlet concentration in the feed.

2. Materials and methods

Materials used were:

Monazite sand derived of side products tin industrial processing Bangka-Belitung Island, technical chemicals \(\text{H}_2\text{SO}_4\), \(\text{NaOH}\), ammonia, \(\text{H}_2\text{C}_2\text{O}_4\) and \(\text{HNO}_3\). The solvents used are D2EHPA, TBP, TOPO, kerosen solution, aquadest and pure RRE material for standard analysis. All chemicals are obtained from Process Technology Laboratory, PSTA-BATAN Yogyakarta.

Instrumentations used were:

Glass beaker, ball mill, sieve, analytical scales, glassware, porcelain crucible, muffle furnace, magnetic stirrer and heater, various size flasks, spray bottles, volumetric pipette, propipette, small bottle size of 10 mL vials, spex film, pH meter, X-ray or XRF (Ortec 7010) spectrometer.

Experimental procedure

Preparation of Nd concentrate

REOH concentrate of 100 grams plus 50 g of \(\text{NaOH}\) and 200 mL of water was heated at 200 °C for 2 hours. After washing with hot water until the pH is neutral, filtered, dried and weighed. The resultant REOH concentrate was 60 g dissolved in 80 mL of \(\text{HNO}_3\) plus \(\text{KBrO}_3\) 2 g, heated to boiling while stirring for 30 minutes. The solution is then precipitated by adding ammonia to pH of 2.4. The precipitate formed is the Ce concentrate (Ce hydroxide) subsequently filtered, the filtrate RE nitrate (low Ce content). The Ce concentrate is dried, weighed and analyzed using XRF. The filtrate of RE nitrate was precipitated by increasing the ammonia 15% to pH to 6.5. The precipitate formed is filtered, dried, weighed and analyzed using XRF. The filtrate produced from the deposition of pH 6.5 plus ammonia 15% to pH to 8. The precipitate formed was filtered, dried, weighed and analyzed using XRF. The precipitate formed is Nd concentrate.

Synergistic solvent extraction

Solvant extraction of Nd concentrate using synergistic solvents D2EHPA and TOPO, the solution of Nd (OH)\(_3\) with Nd concentration of 100 g / L was included in erlenmeyer and then added D2EHPA of 5 mL (variation of concentration 0.8, 0.6, 0.4 and 0.2 M) and added TOPO of 5 mL (variation of concentration 0.2, 0.4, 0.6, and 0.8 M). The extraction was carried out at 250 rpm stirring speed and reaction time 30 min. In the same way, solvent extraction of Nd concentrate using a synergistic solvent of D2EHPA and TBP. After equilibration, the mixture was transferred to a separation funnel where the phases were allowed to separate. The concentrations of metal ions in the aqueous solutions were determined by XRF and the concentrations of metal ions in the organic phase were calculated by a mass balance. The final volumes of aqueous and organic solutions after the complete separation of phases were measured and no changes in volumes were detected during the extraction. All the experiments were performed at room temperature.
3. Results and discussions

The overall research investigating the effect of % and volum ratio of synergistic solvent D2EHPA-TOPO and D2EHPA-TBP on distribution coefficients, extraction efficiency and separation factors of Nd, Pr and Sm. The variables investigated were % ratio of synergistic solvent: 10:0, 8:2, 6:4, 4:6, 2:8 and 0:10 and the variation of synergistic solvent volume ratio was 0.5:1; 0.75:1; 1:1; 1:0.5; 1:0.75. The graph of the correlation between the distribution coefficient (Kd), the extraction efficiency (E) and separation factor (α) to the % ratio of synergistic solvent, as well as the graph of the correlation of Kd, E and α to the volum ratio of synergistic solvent, are shown in Fig. 1 to Fig. 12.

Neodymium extraction with synergistic solvent D2EHPA-TOPO

![Graph of correlation of synergistic solvent (% ratio D2EHPA-TOPO) to distribution coefficient (Kd) Nd, Pr, Sm](image)

**Figure 1.** Graph of correlation of synergistic solvent (% ratio D2EHPA-TOPO) to distribution coefficient (Kd) Nd, Pr, Sm

![Graph of correlation of synergistic solvent (% ratio D2EHPA-TOPO) to extraction efficiency (%) Nd, Pr, Sm](image)

**Figure 2.** Graph of correlation of synergistic solvent (% ratio D2EHPA-TOPO) to extraction efficiency (%) Nd, Pr, Sm

![Graph of correlation of synergistic solvent (% ratio D2EHPA-TOPO) to separation factor (α Nd-Pr and αNd-Sm)](image)

**Figure 3.** Graph of correlation of synergistic solvent (% ratio D2EHPA-TOPO) to separation factor (α Nd-Pr and αNd-Sm)

![Graph of correlation of synergistic solvent (volum ratio D2EHPA-TOPO) to distribution coefficient (Kd) Nd, Pr, Sm](image)

**Figure 4.** Graph of correlation of synergistic solvent (volum ratio D2EHPA-TOPO) to distribution coefficient (Kd) Nd, Pr, Sm
Figure 5. Graph of correlation of synergistic solvent (volum ratio D2EHPA-TOPO) to extraction efficiency (%) Nd, Pr, Sm

Figure 6. Graph of correlation of synergistic solvent (volum ratio D2EHPA-TOPO) to separation factor (αNd-Pr and αNd-Sm)

Neodymium extraction with synergistic solvent D2EHPA-TBP

Figure 7. Graph of correlation of synergistic solvent (% ratio D2EHPA-TBP) to distribution coefficient (Kd) Nd, Pr, Sm

Figure 8. Graph of correlation of synergistic solvent (% ratio D2EHPA-TBP) to extraction efficiency (%) Nd, Pr, Sm

Figure 9. Graph of correlation of synergistic solvent (% ratio D2EHPA-TBP) to separation factor (αNd-Pr and αNd-Sm)

Figure 10. Graph of correlation of synergistic solvent (volume ratio D2EHPA-TBP) to distribution coefficient (Kd) Nd, Pr, Sm
In Figure 1 and Figure 2 it can be seen that the distribution coefficient and extraction efficiency of Nd and Sm are greatest when using synergistic solvent D2EHPA-TOPO of 0:10. In the synergistic solvent D2EHPA-TOPO of 0:10, Nd has Kd = 0.6 and the extraction efficiency = 36%, Sm has Kd = 2.5 and the extraction efficiency = 70%. While the coefficient of distribution and the extraction efficiency of Pr is greatest when using the synergistic solvent D2EHPA-TOPO 4: 6, the extraction efficiency = 50%. In Figure 3 shows the tendency of increasing the separation factor value to be proportional to the % ratio D2EHPA-TOPO increase. The maximum separation factor of Nd-Pr of 0.93 was obtained on the extraction using the synergistic solvent of D2EHPA-TOPO of 0:10 at volum ratio of 1:1. Whereas the maximum Nd-Sm separation factor value of 0.5 is obtained on the synergistic solvent D2EHPA-TOPO of 4: 6 at ratio of 1:1. While similar results of Nd extraction using the synergistic solvent of D2EHPA-TBP are shown in Figs. 7, 8, 9, 10, 11 and 12. From the figure it is shown that the highest yield using synergistic solvent D2EHPA-TBP 2:8, ie Kd Nd <0.1, the extraction efficiency of 5.9 and the separation factor (α) Nd-Pr = 0.23, αNd-Sm = 0.15. From all parameters studied the highest separation factor was obtained using the synergistic % ratio of D2EHPA-TOPO 4: 6 solvent and the volume ratio of feed and solvent 1: 0.5 ie α Nd-Pr = 2.55 and α Nd-Sm = 1.47 but the distribution coefficient and efficiency of the three elements are low so they are not selected. The recommended condition is to use a 4% -6% D2EHPA-TOPO syntactic solvent and a 0.5: 1.0 solvent and solvent ratio. In this condition obtained Kd Nd = 0.46 Kd Pr = 0.27 Kd Sm = 0.72, E Nd = 31.5% E Pr = 21.3% E Sm = 41.8 with the factor of α Nd-Pr = 1.7, α Nd-Sm = 0.84.

These results are very competitive even better when compared with research conducted by Kraikaew, J. et al [9]. In this investigation Nd extraction in rare earth using extractant 50% D_{2}EHPA 1.5 M in kerosene, Kd obtained = 0.162 and extraction efficiency= 13.84%. For extractant 50% TBP 1.5 M in kerosene Kd obtained = 0.473 and extraction efficiency = 31.97%. While for TBP 1.8 M in kerosene Kd obtained = 0.681 and extraction efficiency = 40.47%. Meanwhile, in the same investigation by using an extractant mixture of TBP 1.2 M and D_{2}EHPA 0.3 M, Kd obtained = 0.331 and extraction efficiency=24.87%. The researchers Panigrahi, M. et al [13] conducted an extraction of Nd ion using toluene extractant at various process conditions obtained the highest extraction efficiency of 33.56%. Another researcher, Gergoric, M. et al [14] carried out Nd extraction by using a 30% D_{2}EHPA extractant in hexane with the highest efficiency obtained was 50%. While the results of solvent extraction research on the REE solution feed using 100% tributyl phosphate solvent carried out by O. Andropov et al., it was obtained the extraction results shown by the REE distribution coefficient between 1 - 3 [10].

The results of this study are also better when compared with previous research by the same researchers. In the previous study, Setyadji, M. et al [4] optimized the neodymium concentrate extraction process resulting from the processing of monazite sand using various solvents, it can be concluded that Nd extraction can be done by using TBP or TOA solvent. The optimum condition of Nd extraction using TOA solvent in HNO_{3} of 2 M concentration, in this condition obtained the...
distribution coefficient of Nd is 0.65, Nd extraction efficiency is 37.10%, the content Nd$_2$(C$_2$O$_4$)$_3$ is 67.14%, Ce$_2$(C$_2$O$_4$)$_3$ is 1.79%, La$_2$(C$_2$O$_4$)$_3$ is 1.37% and Y$_2$(C$_2$O$_4$)$_3$ is 24.70%. While Nd extraction using TBP at optimum condition at concentration HNO$_3$ 1 M, Kd Nd obtained = 0.20, efficiency extraction Nd = 17%.

**Conclusion**

Neodymium extraction of the neodymium concentrate using two synergistic solvents D2EHPA-TOPO and D2EHPA-TBP did not provide much improved extraction results, either on the distribution coefficient, extraction efficiency and separation factors. The results showed that the concentration and volume of synergistic solvents greatly influenced the distribution coefficient, extraction efficiency and separation factors. From all parameters studied the highest separation factor was obtained using the synergistic % ratio of D2EHPA-TOPO 4: 6 solvent and the volume ratio of feed and solvent 1: 0.5 ie αNd-Pr = 2.55 and αNd-Sm = 1.47 but the distribution coefficient and efficiency of the three elements are low so they are not selected. The recommended condition is to use a 4% - 6% D2EHPA-TOPO synergistic solvent and a 0.5: 1.0 solvent and solvent ratio. In this condition obtained Kd Nd = 0.46 Kd Pr = 0.27 Kd Sm = 0.72, E Nd = 31.5% E Pr = 21.3% E Sm = 41.8 with the separation factor of Nd-Pr = 1.7 and the separation factor of Nd-Sm = 0.84.

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