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## Solvent Selection for Extraction of Neodymium Concentrates of Monazite Sand Processed Product

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# Solvent Selection for Extraction of Neodymium Concentrates of Monazite Sand Processed Product

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**Abstract.** The extraction of neodymium concentrates of monazite sand processed product has been done. The objective of this investigation was to determine the best solvent to separate Nd from Nd concentrate. As an aqueous phase was  $\text{Nd}(\text{OH})_3$  concentrated in  $\text{HNO}_3$  and as solvent or the organic phase was trioctylamine (TOA), tributyl phosphate (TBP), trioctylphosphine oxide (TOPO) and di-ethyl hexyl phosphoric acid (D2EHPA) in kerosene. The investigated variables were  $\text{HNO}_3$  concentration, feed concentration, solvent concentration or solvent in kerosene, time and stirring speeds. From the investigation on the selection of solvent for the extraction of  $\text{Nd}(\text{OH})_3$  concentrate with various solvents, it was concluded that the extraction of Nd could be carried out by using TBP or TOA. Extraction of Nd using TOA at the optimum  $\text{HNO}_3$  concentration of 2M, feed concentration of 5 gram/10 mL, TOA in kerosene concentration of 6 %, stirring time of 15 minutes, stirring speed of 200 rpm was chosen if the Y concentration in Nd concentrate is small. In these condition  $D_{\text{Nd}}$  obtained was 0.65; extraction efficiency of Nd ( $E_{\text{Nd}}$ )=37.10%, the concentrations of  $\text{Nd}_2(\text{C}_2\text{O}_4)_3 = 67.14\%$ ,  $\text{Ce}_2(\text{C}_2\text{O}_4)_3 = 1.79\%$ ,  $\text{La}_2(\text{C}_2\text{O}_4)_3 = 1.37\%$  and  $\text{Y}_2(\text{C}_2\text{O}_4)_3 = 24.70\%$ . Extraction of Nd using TBP at the optimum  $\text{HNO}_3$  concentration of 1M, feed concentration of 5 gram/10 mL, the TBP concentration in kerosene of 15%, stirring time of 15 minutes and stirring speed of 200 rpm was chosen if the Ce concentration in Nd concentrate is small. In these condition  $D_{\text{Nd}}$  obtained was 0.20, extraction efficiency of Nd ( $E_{\text{Nd}}$ )=17%, concentration of  $\text{Nd}_2(\text{C}_2\text{O}_4)_3 = 70.84\%$ ,  $\text{Ce}_2(\text{C}_2\text{O}_4)_3 = 15.53\%$ ,  $\text{La}_2(\text{C}_2\text{O}_4)_3 = 0.00\%$  and  $\text{Y}_2(\text{C}_2\text{O}_4)_3 = 8.63\%$ .

**Keywords:** Solvent selection, neodymium concentrates, tri octyl amine (TOA), tributyl phosphate (TBP), diethyl hexyl phosphoric acid (D2EHPA) dan trioxthyl phosphone oxide (TOPO)

## 1. Introduction

Neodymium is a chemical element in the periodic table having atomic number of 60. Neodymium was discovered by Welsbach in 1885. It has an atomic mass of 144.2 g mol<sup>-1</sup>, a density of 7.0 g cm<sup>-3</sup>, a melting point of 1024 °C and a point Boiling 3047°C. Neodymium is including rare earth metals element whose abundant presence after cerium, belonging to the lanthanide group and can be found in monazite sands. Neodymium is one of the rare earth elements that can be used in home appliances



such as color television, incandescent lamps, and energy saving lamps. 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 [1].

Monazite sand is a mineral which has a phosphate bond form containing thorium (Th) and rare earth metals such as yttrium (Y), cerium (Ce), lanthanum (La), gadolinium (Gd), dysprosium (Dy), neodymium (Nd) and samarium (Sm). The chemical formula of monazite sand is generally written as  $(RRE.Th) PO_4$  [1,2]. The concentrate of  $Nd(OH)_3$  of the processed monazite sand was obtained through several stages of the process from leaching of monazite by using  $H_2SO_4$ . Th separation by precipitation, Ce separation by oxidation and precipitation, the separation of La by fractional precipitation to obtain  $Nd(OH)_3$  concentrate. This  $Nd(OH)_3$  concentrate still contains other RRE elements[3].

The separation of Nd from the  $Nd(OH)_3$  concentrate of the processed monazite 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 more simple. 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[4,5].

Solvent extraction involves the distribution of a solute between the two immiscible liquid phases[6,7]. 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 (water phase).

The mass transfer mechanism on extraction[8]

-Mass transfer or metallic ion diffusion (A) from aqueous phase bodies through the film boundary layer to the interface between the water phase and the organic phase

-The metallic ion (A) reacts with the carrier or solvent (carrier = B) in the organic phase on the interface of water and organic phase.

-Mass transfer or diffusion of reaction products between metal and solvent in an organic phase from the water phase-organic phases interface to the organic phase body.

In this investigation it would be investigated the comparison of the efficiency of Nd extraction on various solvents. Extraction of Nd could be done by dissolving  $Nd(OH)_3$  concentrate into nitric acid. This solvent selection is aimed to investigate the properties of each solvent and determine the best solvent for Nd extraction.

The reaction mechanism in the extraction process[9]:

• *Solvation*

Solvent extraction by solvation mechanism is used to extract uranium, plutonium, or thorium from acid solution. One of the solvents used for this purpose is the tributyl phosphate organophosphate (TBP) in the PUREX process commonly used in nuclear reprocessing. Shahryar Jafari Nejad[10] has studied the use of TBP for the extraction of  $La^{3+}$ ,  $Ce^{3+}$  and  $Sm^{3+}$  ions. Siu Hua Chang et al[11], studied the efficiency, stoichiometry and structure of Cu (II) recovering from the water phase using di-2-ethylhexylphosphoric (D2EHPA) and TBP. Dessouky et al[12] separated Zn (II), Fe (II), Fe (III) and Cd (II) by the solvent extraction using TBP and CYANEX 921 in kerosene from the chloride media. Mohsen Aliakbari et al[13] separated hafnium and zirconium by using TBP modified with ferromagnetic nano particles: the effect of acidity and metal concentration. Xingbin Li et al.[14] conducted the solvent extraction of vanadium from the acidic leached carbon stone solution using D2EHPA / TBP.

- *Ion Exchange*

Another known mechanism of extraction is the ion exchange mechanism. The acid of di-2-ethyl hexyl phosphate with the solute will occur an ion-exchange reaction [15]. Man Seung Lee et al. separated Hf (IV) -Zr (IV) in H<sub>2</sub>SO<sub>4</sub> solution using D2EHPA or Cyanex 272. Diptendu et al[16] studied U (VI) extraction with a mineral acid from water phase using D2EHPA, PC88A and Cyanex 272. Torkaman et al[17] studied the solvent extraction kinetics of samarium in nitrate solution with D2EHPA and Cyanex 30. Mehdi Noori et al[18] recovered and separated nickel and vanadium in sulfate solution using a mixture of D2EHPA and Cyanex 272.

- *Ion pair*

The solute will form ion pairs with the tri-n-octylamine compound (TOA). Qi Wang et al[19] extracted 2-chloroethanol from the water phase using TOA. Mehdi Ghadiri et al[20] studied the extraction of Mo using TOA and stripping using ammonia solution.

- *Complex formation*

Solute with tri-n-octyl phosphine oxide (TOPO) forms a complex bond. Stas et al[21] studied the effects of uranium and iron co-extraction factors using DEHPA / TOPO- kerosen. Gadgil et al[22] studied the kinetics of uranium extraction in phosphoric acid using D2EHPA-TBP and D2EHPA-TOPO.

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 extraction process of Nd is very influenced by type and solvent concentration variations, concentration variation of HNO<sub>3</sub>, feed weight variation of Nd (OH)<sub>3</sub> concentrate, time and stirring speed variations, so that in this investigation the extraction was performed with various variations as mentioned above.

## 2. Materials and methods

Materials used were:

Monazite sand, H<sub>2</sub>SO<sub>4</sub> technical, NaOH technical, ammonia, H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> technical grade, HNO<sub>3</sub> technical grade solution, D<sub>2</sub>EHPA solution, TOA solution, TBP solution, TOPO crystalline, kerosene solution, aquadest, pure RRE materials for standard analysis.

Instrumentations used were:

X-ray or XRF (Ortec 7010) spectrometer, magnetic stirrer and heater (Ika® Werk), Analytical scales (Sartorius 2464), various size flasks, spray bottles, volumetric pipette, propipette, small bottle size of 10 mL vials, spex film, pH meter.

## 3. Experimental procedure

Preparation of Nd concentrate

Monazite sand of 100 grams was digested with 100 ml of concentrated H<sub>2</sub>SO<sub>4</sub> technical grade at a temperature of 210<sup>0</sup>C for 1 hour. The digested product was diluted with 2500 ml of water then it was filtered. The residue was disposed and the pH filtrate was adjusted by using 15% ammonia. The formed solid was the Th concentrate, then filtered. The filtrate was precipitated using 15% ammonia at a certain pH, then filtered and dried. The formed solids are RRE or RRE hydroxide (RREOH). Every 25 g of RREOH was dissolved in 70 mL of hot concentrated HNO<sub>3</sub> (165<sup>0</sup>C) for 2 hours. After cooling, it was added by 15% ammonia by adjusting the pH, the precipitate formed Ce concentrate was filtered and dried. The filtrate was added by 15% ammonia by adjusting the pH, the precipitate

formed was filtered and dried. The precipitate formed was Nd (OH)<sub>3</sub> concentrate and La concentrate filtrate. All the processed products were analyzed using XRF.

#### *Variation of HNO<sub>3</sub> concentration*

The preparation of the feed solution was carried out by dissolving each of 20 g of Nd (OH)<sub>3</sub> concentrate into 100 mL of 1. 2. 3. 4. and 5 M HNO<sub>3</sub> solutions. Each 10 mL of feed solution (FA = water phase) with various HNO<sub>3</sub> concentrations, was put into five 50 mL chemical glasses. A 10 mL of a 6% TOA solution - kerosene (FO = organic phase) was added to FA. then it was stirred with a magnetic stirring bar for 15 minutes at the speed of 200 rpm. This process is called the extraction process. The water phase (FA) and the organic phase (FO) of the extraction products were separated. Each 5 mL of water phase was taken for being analyzed with XRF. The works was repeated for TBP - kerosene = 15%. D2EHPA - kerosene = 6% and TOPO - kerosene = 6%. From the variation of HNO<sub>3</sub> concentration having the highest D (optimum) used for optimization of feed concentration variation.

#### *Variation of feed concentration*

Amount of 3, 4, 6 and 7 g of Nd (OH)<sub>3</sub> concentrate were dissolved into 25 mL of the optimized product of HNO<sub>3</sub> solution as the feed (FA). Each 10 mL of feed was added by 10 mL of a 6% TOA - kerosene solution (FO) was then stirred with a magnetic stirrer bar for 15 minutes at the stirring speed of 200 rpm. The aqueous phase (FA) and the extracted product FO were separated. Each 5 mL FA was taken for being analyzed using XRF. Work is repeated for TBP - kerosene = 15%. D2EHPA - kerosene = 6% and TOPO - kerosene = 6%. From the variation of HNO<sub>3</sub> concentration having the highest D(optimum) used for optimization of solvent concentration variation.

#### *Variation of solvent concentration*

Preparing a feed solution of the extraction optimized product of the feed concentration variation (FA). Each of 10 mL FA was added by 10 mL of TOA - kerosene solution with varying concentrations (2. 4. 8. and 10%). it was then stirred for 15 minutes at the stirring speed of 200 rpm. After extraction. FA and FO were separated. Each of 5 mL FA was taken for being analyzed using XRF. The works were repeated for TBP - kerosene = 5, 10, 20 and 25%. D2EHPA - kerosene = 2. 4. 8. and 10% and TOPO - kerosene = 2, 4, 8 and 10%. From the variation of HNO<sub>3</sub> concentration having the highest D(optimum) was used for the optimization of stirring speed variation.

#### *Variation of stirring speed*

Each 10 mL of feed solution from the optimized product of feed concentration (FA) was added by 10 mL of TOA - kerosene (FO) optimum solution. it was then stirred with a magnetic stirrer with a stirring time of 15 minutes. The stirring speed was varied by 100, 150, 250 and 300 rpm. Each 5 mL of water phase was taken for being analyzed using XRF. The work was repeated for % TBP - kerosene.% D2EHPA - kerosene and% TOPO - kerosene of the optimization products. From the variation of HNO<sub>3</sub> concentration having the highest D used for optimization of stirring time variation.

#### *Variation of stirring time*

Each 10 mL of feed solution of the optimized product of HNO<sub>3</sub> concentration and the feed was extracted by 10 ml of TOA-kerosene. TBP-kerosene. D2EHPA-kerosene and TOPO-kerosene of the optimized product of solvent concentration with the optimized product of stirring speed. The stirring time or extraction was varied for 5, 10, 15, 20 and 25 minutes. After the extraction. FA and FO were separated. Each 5 mL of water phase was taken for being analyzed using XRF. From the analysis results can be known the optimum stirring time.

*Stripping of the optimized products of extraction*

The optimized products of extraction were stripped using 15% oxalic acid (stripping phase). the volume ratio of 1: 1 and it was restripped using water in order the remaining solute in organic phase could be wholly recovered in the stripping phase.

*Precipitation of stripping products*

The stripping products used 15%  $\text{H}_2\text{C}_2\text{O}_4$  and water was mixed. added by 15%  $\text{H}_2\text{C}_2\text{O}_4$  until no precipitate was formed. The formed precipitate was filtered and dried and then was analyzed by using XRF.

Determining of the distribution coefficient value (D)

The distribution coefficient is expressed by the following formula[23]:

$$D = \frac{c_2}{c_1} \text{ or } D = \frac{c_o}{c_a} \quad (1)$$

Where 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 D is large, the solute will quantitatively tend to be more distributed into organic solvents, as well as the opposite.

The distribution coefficient value could be determined by comparing the organic phase with the water phase after the extraction.

$$D = \frac{\text{element concentration in FO}}{\text{element concentration in FA}} \quad (2)$$

The extraction efficiency could be determined by the following calculation:

$$\text{Extraction efficiency (\%E)} = \frac{\text{solute concentration in organic phase}}{\text{solute concentration in the feed}} \times 100\% \quad (3)$$

**4. Research results and discussions***Concentrate of Nd(OH)<sub>3</sub>*

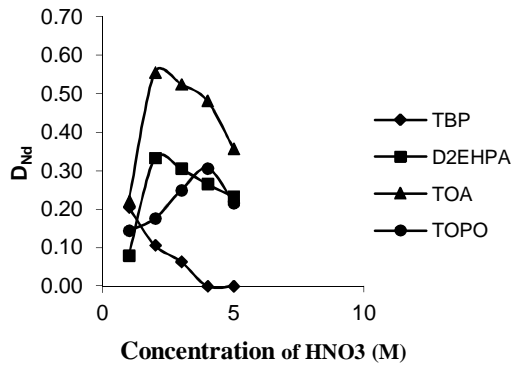
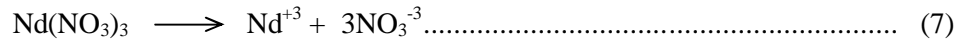
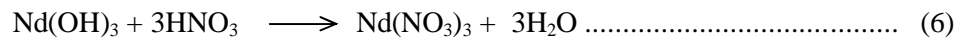
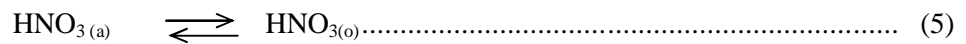
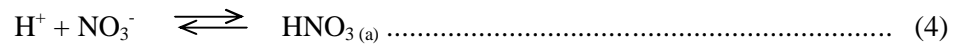
The result of analysis using XRF of monazite processing into the concentrate of  $\text{Nd}(\text{OH})_3$  is presented in Table 1. The concentrate of  $\text{Nd}(\text{OH})_3$  contains Ce, Y, La, water etc. (Sm, Pr)

**Table 1.** Element concentration and compound of  $\text{Nd}(\text{OH})_3$  concentrate of the processed product of monazite

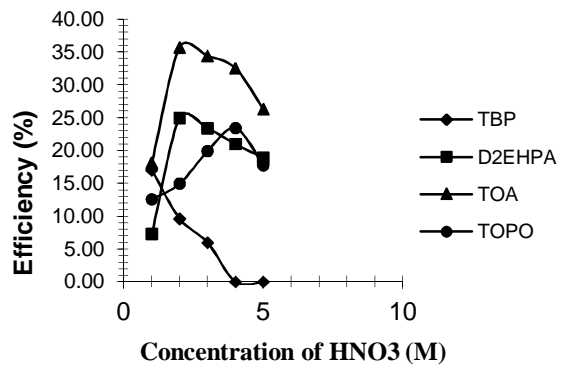
Element concentration, %				
Ce	Y	La	Nd	Water
2.87	14.94	3.61	39.42	2.87
Compound concentration, %				
$\text{Ce}(\text{OH})_3$	$\text{Y}(\text{OH})_3$	$\text{La}(\text{OH})_3$	$\text{Nd}(\text{OH})_3$	Water
3.91	22.63	4.93	53.37	15.15

*Variation of HNO<sub>3</sub> Concentrations*

The graph of the correlation between the distribution coefficient (D) with the concentration of  $\text{HNO}_3$ , as well as the graph of the correlation of the extraction efficiency (% E) to the  $\text{HNO}_3$  concentration, are shown in Figure 1 and Figure 2. In the extraction process, the acidity of the water phase is a very important factor. The addition of  $\text{HNO}_3$  causes the increase of  $\text{H}^+$  ions and  $\text{NO}_3^-$  ions complying with the following reactions[11]:

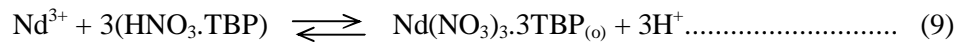


**Figure 1.** Graph of correlation of HNO<sub>3</sub> concentration with D<sub>Nd</sub> using the solvents of TBP, D2EHPA, TOA, and TOPO



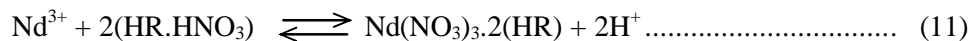
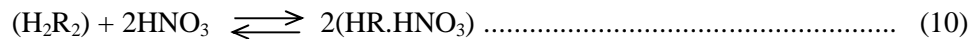
**Figure 2.** Graph of correlation of HNO<sub>3</sub> concentration with the extraction efficiency of Nd using the solvents of TBP, D2EHPA, TOA, and TOPO

Reaction with TBP[12-14]



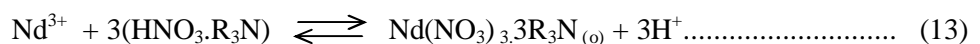
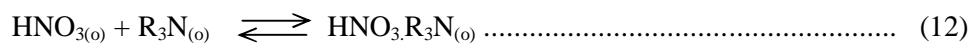
Nitric acid was used to form (HNO<sub>3</sub>.TBP) complex which functions as a complex intermediate-forming agent with metals as seen in the reactions (8) and (9). Excessive concentrations of HNO<sub>3</sub> could cause TBP degradation to Mono Butyl Phosphate (MBP) and Di Butyl Phosphate (DBP), thereby decreasing K<sub>d</sub>. Mono Butyl Phosphate (MBP) and Di Butyl Phosphate (DBP) dissolve in the organic phase. Besides, if the DBP forms a complex compound with metal will become a strong bond so it will be difficult to be re-extracted. The highest value D= 0.2 at HNO<sub>3</sub> concentration of 1 M.

The reaction with D<sub>2</sub>EHPA could be seen in the following equation <sup>(14-16)</sup>



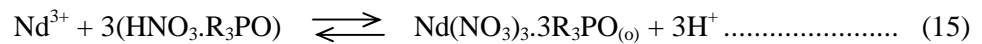
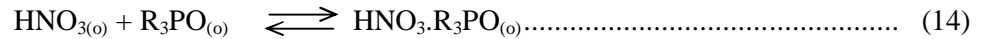
The existence of excessive HNO<sub>3</sub> would react with D2EHPA and cause a decrease in the amount of D2EHPA which reacts with the metal. Thereby reducing the reactivity of the element to the organic phase and causing a decrease in the value of D. In the use of HNO<sub>3</sub> concentrations above 2 M, the value of decreases more and the highest D= 0.35.

The reaction with TOA (R<sub>3</sub>N) is as follows[18,19]:



The addition of HNO<sub>3</sub> as an intermediate for the formation of Nd (NO<sub>3</sub>)<sub>3</sub>.3R<sub>3</sub>N ions pair. For the addition of HNO<sub>3</sub> H<sup>+</sup> ions would subsequently increase in the system causing the equilibrium of the reaction shifts to the left. so that the formation of Nd (NO<sub>3</sub>)<sub>3</sub>.3R<sub>3</sub>N ions pair would decrease and the distribution coefficient would decrease as shown in Figure 1.

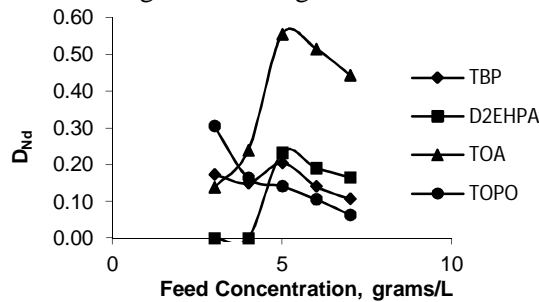
The reaction with TOPO as the following[20,21]



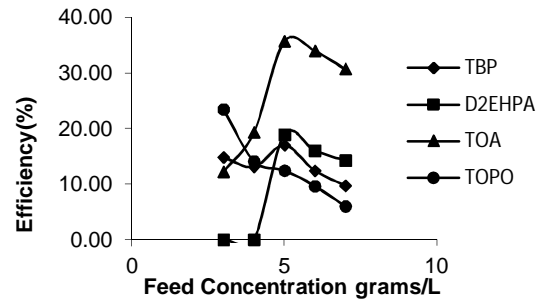
In Figure 3 and Figure 4 it could be seen that the distribution coefficient and Nd efficiency are greatest when using TOA solvents. compared to the use of TBP. TOPO and D2EHPA. At concentration of HNO<sub>3</sub>2M. Nd has D= 0.56 and extraction efficiency = 35.70%.

*Variation of Feed Concentration*

The result of the extraction process of the weight variation of Nd (OH)<sub>3</sub> concentrate in the feed. hereinafter referred to as the feed concentration variation. the calculation result of D and % E are shown in Figure 3 and Figure 4



**Figure 3.** Graph of correlation of feed concentration with D<sub>Nd</sub> using the solvents of TBP, D2EHPA, TOA, and TOPO.



**Figure 4.** Graph of correlation of feed concentration with the extraction efficiency of Nd using the solvents of TBP, D2EHPA, TOA, and TOPO.

One of the most influential factors for the mass transfer rate from the water phase (FA) to the organic phase (FO) is the amount of solute concentration in the feed. The greater the solute concentration in the feed. the greater the mass transfer rate will be. In Figure 6 it can be seen that the extraction conditions will tend to increase as the feed increases. At a 6 g / 10 mL feed concentration. it is likely to give the highest distribution coefficient. but under these conditions Nd was not well separated from its impurities. hence based on the greatest its separation factor the concentration of the feed taken was 5 g / 10 mL. In Figures 3 and 4 it could be seen that the distribution coefficient and Nd efficiency are greatest when using TOA solvents. compared to the use of TBP and D2EHPA. At 5 g / 10 mL feed concentration. D<sub>Nd</sub> = 0.56 and extraction efficiency (E<sub>Nd</sub>)= 35.70%.

*Solvent Concentration Variation*

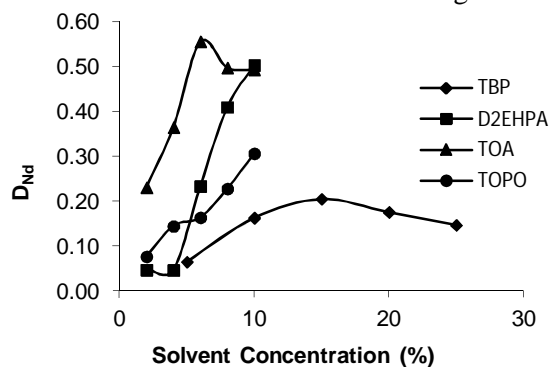
The use of solvents greatly affects the separation of the elements in the feed in the form of Nd (OH)<sub>3</sub> concentrate. The greater the use of the solvent concentration so the better the extraction of elements in the feed. which is marked by the increase of the value of D. But after reaching a certain concentration. the value of D will more decrease because at the greater solvent concentration the solute transfer greater the transfer of the solute from the water phase to the organic phase will be more difficult. This can be explained by the Stokes-Einstein equation as follows[22]:

$$D_{AB} = \frac{k T}{6\pi r\mu_B} \dots\dots\dots (16)$$

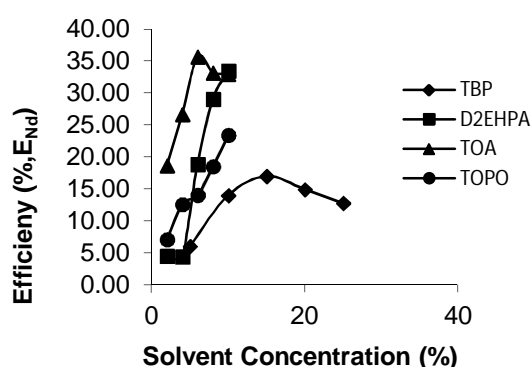


$D_{AB}$  = diffusivity of A in dilute solution in B.  $k$  = Boltzmann constant.  $T$  = temperature.  $r$  = radius of solute particle.  $\mu_B$  = solvent viscosity. From the equation (16) it could be seen that the diffusivity was inversely proportional to the solvent viscosity. so the greater the solvent viscosity the more difficult it is to diffuse from the water phase to the organic phase. thereby lowering the value of  $D$ .

In Figure 5 it can be seen that Nd has the highest distribution coefficient at the solvent concentration of 20%. After passing the concentration of TBP 20%  $D$  value tends to decrease because the solvent is getting more viscous so it is difficult to diffuse into the organic phase and forms a complex with Ce, TBP, D2EHPA, TOA and TOPO solvents which gave a sufficiently good Nd extraction conditions can be seen in Figure 5.



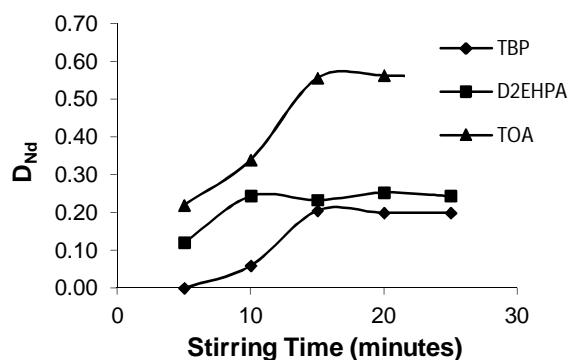
**Figure 5.** Correlation of solvent concentration with  $D_{Nd}$  using the solvents of TBP, D2EHPA, TOA, and TOPO.



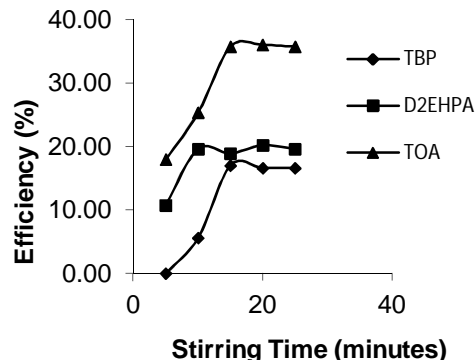
**Figure 6.** Correlation of solvent concentration with extraction efficiency of Nd using the solvents of TBP, D2EHPA, TOA, and TOPO.

#### Variation of Reaction Time

The stirring time is also related to the amount of stirred volume, so to vary the stirring time to the volume of 20 mL is reasonably sufficient to give an effective contact time. especially in the transfer of solutes from the water phase to the organic phase. Solvent TBP, D2EHPA and TOA gave the conditions of Nd extraction was good enough can be seen in Figure 7.



**Figure 7.** Correlation of stirring time with  $D_{Nd}$  with solvents of TBP, D2EHPA, and TOA.



**Figure 8.** Correlation of extraction time with the extraction efficiency of Nd with solvents of TBP, D2EHPA, and TOA.

It was required a sufficient stirring time for the reaction to occur and the formation of the reaction products. so that the reaction and reaction products obtained was maximum. The reaction rate, the reduced reactants, or the increased of reaction products can be formulated mathematically as the following:

$$[A] = [A]_0 - kt \quad (17)$$

$[A]$  = concentration of A after reacting.  $[A]_0$  = initial concentration of A (before reacting).

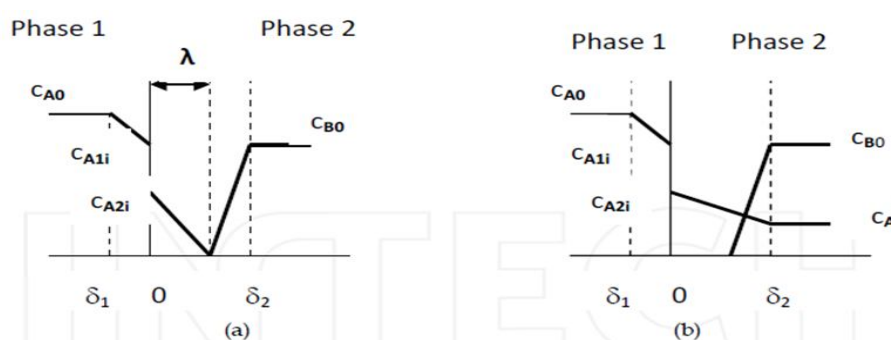
$k$  = reaction rate constant and  $t$  = reaction time.

When the reaction occurred was first order it would get the equation  $[A] = [A]_0 \cdot e^{-kt}$ . This equation shows that in the first order reaction the concentration of the reactants will decrease exponentially with time while the product will increase.

In Figure 7 and Figure 8 it can be seen that the distribution coefficient and extraction efficiency of Nd were the greatest when TOA solvent was used. compared with that of TBP and D2EHPA. At the stirring time of 15 minutes.  $D_{Nd} = 0.56$  and the extraction efficiency ( $E_{Nd}$ ) = 35.70%.

#### Variation of Stirring Speed

The extraction process was also a phenomenon of mass transfer of two insoluble liquids, so that if there were not external forces as an assistance in the form of stirring. then the mass transfer both of the two liquids would be very slow. This stirring process would help the intermixture of water phase and organic phase where the stirring process would disperse the solute into the organic phase solution resulting in inter-phase contact. This phenomenon would increase the mass transfer of the solute from the feed into the organic phase solution. Profile of reactant concentration in the extraction with the chemical reaction is shown in Figure 8.



**Figure 9.** Profile of reactant concentration in the extraction with the chemical reaction

a) irreversible spontaneous reaction occurred in the film layer of phase 2

b) slow reaction occurred in the film layer of phase 2

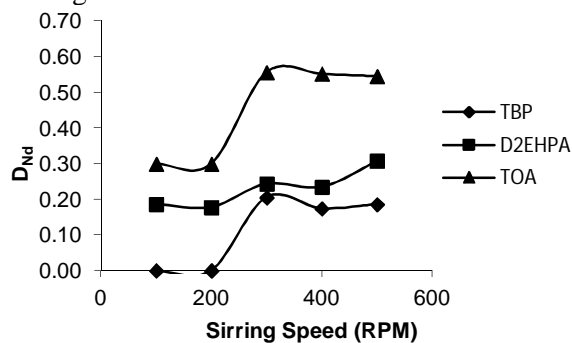
Notes: Phase 1 : water phase. Phase 2 : organic phase .  $\lambda$  :film layer thickness

The occurrence of mass transfer from FA to FO is caused. due to chemical reactions and diffusion. Between FA and FO there was a layer of interface with certain imaginary thickness which is the resistance to the mass transfer rate from FA to FO or vice versa. The thickness of this thin layer of interfaces depends on the speed of stirring. The faster the stirring. the thinner is the layer thickness for the occurring of mass transfer. This layer thickness could be reduced by increasing the intensity of stirring. The  $D$  value will increase with the increase of stirring speed. because the intensity of the occurring inter-reactants collision is getting more extensive and faster.

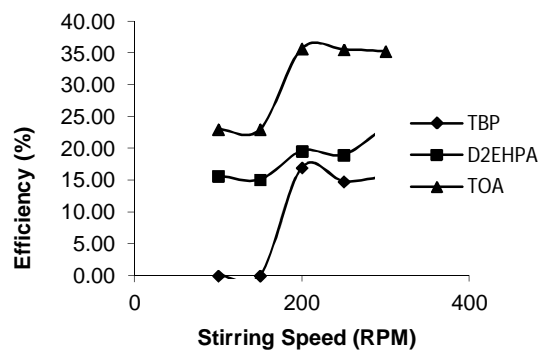
With faster stirring. the layer thickness that inhibits the occurring of mass transfer due to smaller diffusion. but if the stirring intensity was enhanced. the layer thickness that inhibits the occurring of diffusion was already very thin and almost has not any more obstruction because it does not affect the mass transfer anymore. The optimum condition chosen was based on the largest separation factor value at 200 rpm. In Figure 10 shows the tendency of  $D$  value increases as the increase of stirring speed. The greater the stirring speed. the more extraction results will be obtained.

After experiencing a significantly increase.  $D$  value was slightly decline. this indicates that there was no increase of extracted solute to FO. Parameter of stirring speed is important carried out in

order to know the optimum speed. In terms of diffusion, the diffusion rate =  $D_A \partial^2 C_A / \partial z^2$ . where  $z$  was the distance or the width traveled by elements or compounds that would diffuse from the water phase to the organic phase or vice versa. The wider  $z$  the diffusion will be slower. to shorten  $z$  the stirring was accelerated.



**Figure 10.** Correlation of stirring speed with  $D_{Nd}$  using the solvents of TBP, D2EHPA, and TOA.



**Figure 11.** Correlation of stirring speed with the extraction efficiency of Nd using the solvents of TBP, D2EHPA, and TOA.

From the point of view of chemical reaction,  $k \cdot [A] = -d \frac{[A]}{dt}$ , with  $k$  = the reaction rate constant.

which is the value according to Arrhenius,  $k = Ae^{-E/RT}$ ,  $A$  = collision frequency,  $E$  = activation energy,  $T$  = temperature and  $R$  = ideal gas constants. The faster the stirring of the reaction will be more perfect because the area of impact would also be greater. In Figure 10 and Figure 11 it could be seen that the distribution coefficient and Nd efficiency were greatest when TOA solvents was used, compared with the use of TBP and D2EHPA. At a stirring speed of 200 rpm,  $D_{Nd} = 0.65$  and extraction efficiency = 37.10%.

This result was competitive when compared with research results conducted by Kraikaew, J. et al[23]. In this investigation Nd extraction in rare earth using extractant 50% D2EHPA 1.5 M in kerosene,  $D_{Nd}$  obtained = 0.162 and extraction efficiency= 13.84%. For extractant 50% TBP 1.5 M in kerosene  $D_{Nd}$  obtained = 0.473 and extraction efficiency = 31.97%. While for TBP 1.8 M in kerosene  $D_{Nd}$  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<sub>2</sub>EHPA 0.3 M,  $D_{Nd}$  obtained = 0.331 and extraction efficiency=24.87%. While the researchers Panigraha, M. et al[24] 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.[25] carried out Nd extraction by using a 30% D2EHPA extractant in hexane with the highest efficiency obtained was 50%. The result of FO stripping using H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>15% was RRE<sub>2</sub> (C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> solid with the composition shown in Table 2.

**Table 2.** Products of FO stripping of extraction optimization results of various solvent and precipitation of stripping products

Solvent	Condi- tion		Extraction efficiency of elements. %						
	M	g/10mL	%	min	rpm	Ce	Y	La	Nd
TBP	1	5	15	15	200	50.5	4.49	0	17
D2EHPA	5	5	6	25	300	44.9	18	0	23.5
TOPO	4	3	10	15	200	28.1	18.1	1.3	23.45
TOA	2	5	6	15	200	13	28.7	7.89	36

	Element concentration, %			
	Ce	Y	La	Nd
TBP	7.99	3.70	0.00	36.96
D2EHPA	4.61	9.63	0.00	33.17
TOPO	2.98	10.00	0.17	34.19
TOA	0.92	10.58	0.70	35.03

	Compound concentration, %			
	Ce <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub>	Y <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub>	La <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub>	Nd <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub>
TBP	15.53	8.63	0.00	70.84
D2EHPA	8.96	22.47	0.00	63.57
TOPO	5.79	23.34	0.34	65.53
TOA	1.79	24.70	1.37	67.14

M: concentration of HNO<sub>3</sub>, g / 10mL: Feed Concentration, %: solvent concentration, minute: Stirring time, rpm: Stirring speed.

Extraction efficiency of Nd with 15% TBP-kerosene of 17%, but the concentration of Nd<sub>2</sub> (C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> obtained = 70.84% although the extraction efficiency of Ce was also great (50.5%) but because Ce concentration in Nd concentrate was insignificant, so the effect of Ce oxalate concentration in the products was insignificant (7.99%). Extraction efficiency of with 6% of TOA-kerosene was 36% , but the concentration of Nd<sub>2</sub> (C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> obtained simply = 67.14%, , due to extraction efficiency of Y = 28.7% its effect was great on Y oxalate concentration in the product namely 24.70 % , since the number in Y in the Nd concentrate was large (the second largest after Nd). The largest impurities in extraction with TBP was Ce, while the largest impurities in extraction with TOA was Y. Thus if in the Nd concentrate containing Ce and Y it must be cleaned from Ce and Y.

## 5. Conclusion

The results of optimization of neodymium concentrate extraction process producing from processing of monazite sand using various solvents, it could be concluded that Nd extraction could be done by using TBP or TOA solvent. The optimum condition of Nd extraction using TOA solvent in HNO<sub>3</sub> concentration of 2 M, feed concentration of 5 g / 10 mL, TOA concentration in 6% kerosene, stirring time of 15 minutes, stirring speed of 200 rpm selected when Nd concentration has a small Y content. In this condition the distribution coefficient of Nd ( $D_{Nd}$ ) was 0.65, the extraction efficiency of Nd ( $E_{Nd}$ ) was 37.10%, the content of Nd<sub>2</sub> (C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> was 67.14%, Ce<sub>2</sub> (C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> was 1.79%, La<sub>2</sub> (C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> was

1.37% and  $Y_2(C_2O_4)_3$  was 24.70%. While Nd extraction using TBP at the optimum condition at  $HNO_3$  concentration of 1 M, feed concentration of 5 g / 10 mL, TBP concentration in kerosene of 15%, stirring time of 15 minutes, stirring rate of 200 rpm selected if the concentrate of Nd has a insignificant Ce concentration. In this condition  $D_{Nd}$  obtained = 0.20, extraction efficiency of Nd ( $E_{Nd}$ )= 17%, concentration of  $Nd_2(C_2O_4)_3$  = 70.84%,  $Ce_2(C_2O_4)_3$  = 15.53%,  $La_2(C_2O_4)_3$  = 0,00 % And  $Y_2(C_2O_4)_3$  = 8.63%.

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