Separation of Gadolinium (Gd) using Synergic Solvent Mixed Topo-D2EHPA with Extraction Method.

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Abstract. The main problem to obtain Gd with high purity is the similarity of chemical properties and physical properties with the other rare earth elements (REE) such as Y and Dy, it is necessary to do separation by the extraction process. The purpose of this research to determine the best solvent type, amount of solvent, feed and solvent ratio in the Gd extraction process, to determine the rate order and the value of the rate constant of Gd concentration based on experimental data of aqueous phase concentration as a function of time and to know the effect of temperature on the reaction speed constant. This research was conducted on variation of solvent, amount of solvent, feed and solvent ratio in the extraction process of Gd separation, extraction time to determine the order value and the rate constant of Gd concentration in extraction process based on the aqueous phase concentration data as a function of time, to the rate constant of decreasing concentration of Gd. Based on the calculation results, the solvent composition was obtained with the best feed to separate the rare earth elements Gd in the extraction process is 1 : 4 with 15% concentration of TOPO and 10% concentration of D2EHPA. The separation process of Gd using extraction method by solvent TOPO-D2EHPA 2 : 1 comparison is better than single solvent D2EHPA / TOPO because of the synergistic effect. The rate order of separation process of Gd follows order 1. The Arrhenius Gd equation becomes k = 1.46 x 10-7 exp (-6.96 kcal / mol / RT).

1. Introduction

One of the rare earth elements (REE) in senotim that have potential in the development of the nuclear industry is Gadolinium (Gd) with content 3.6% [1]. Rare Earth Elements in the form of Gd in the form of oxide (Gd2O3) is used as the main component of a nuclear reactor control rods because Gd has a neutron absorption cross section (σ) is very large [2]. The required Gd level as control rod is 99%. The main problem for obtaining high purity Gd is the similarity of chemical properties and physical characteristics with other Rare Earth elements such as Y and Dy, it is necessary to separate with the most technologically feasible and efficient to obtain Gd in REE [3].

Separation of Gd in the Rare Earth elements can be done with a liquid-liquid extraction process. Methods of liquid-liquid extraction is used to separate the elements or compounds from low levels to high levels, but it has advantages such as more efficient, effective, selective against certain ions, the solvent can be reused, the energy requirements are lower, and more equipment small [4]. So liquid-liquid extraction methods are considered feasible and efficient to obtain Gd from REE. In the process the selection of liquid-liquid extraction solvent, the amount of solvent, and the ratio of

the amount of feed and the solvent is very important, this is because the solvent play a role in determining the distribution coefficient value, increased efficiency, and the separation factor [5]. Solvents used in this study were Acid di- (2-ethylhexyl) Posfat (D2EHPA), Trioctylphosphine Oxide (TOPO), and solvent mixture of both. Mixed solvents need to be used to elicit synergistic effects that have the effect of strengthening the extraction process against organic solvents. Other factors that influence the extraction process are time and temperature extraction. Temperature and extraction time are used in determining the kinetics of reduction of Gd concentration (rGd) [6]. The variation of extraction temperature is carried out to determine the activation energy (E) and the frequency factor (A) by using the Arrhenius Equation. By doing research on the kinetics of the extraction process some important data such as the order of the reaction (n), the reaction rate constant (k), the activation energy (E),and frequency factor (A) can be known and useful as data and scientific information useful for research and design in the future.

So the purpose of this research is to determine the type, number of solvent, and the best ratio of feed and solvent in the Gd extraction process, and to determine the order and the value of the rate constant of the reduction of Gd concentration based on experimental data of aqueous phase concentration as a function of time and to know the effect of temperature on the reaction speed constant.

2. Method

2.1 Tools and Materials

The tools to be used in this research are beker, 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, porcelein plate, analytical balance, filter paper oven, glass funnel, thermometer. Materials to be used in this study are Tributyl Phosphate (TBP), Bis (2-ethylhexyl) Phosphate Acid (D2EHPA), REE(OH)$_3$, Aquadest, XAD-16 Resin, Nitric Acid (HNO$_3$) and Acetone.

The materials used in this study were TOPO (TOPO), Bis (2-ethylhexyl) Phosphate Acid (D2EHPA), Concentrated REE senotim (result of enhanced senotim cracker concentration of Rare Earth Metal with Gd concentration 15.45%), Aquadest , HNO3 65% pa (ex. Merck), Kerosene. The tool used in this research is glass beker as reactor that used as place of extraction process that is beaker. This tool is coupled with hot plate, stirrer, water batch and thermometer in kinetic study. XRF device for measuring quantitative and qualitative analysis, measuring glass, watch glass, stirrer, magnetic strirrer, measuring flask, dropper pipette, measuring pipette, spatula, analytical balance, purple spoon, erlenmeyer, bulpet, hotplate stirrer.

2.2 Procedures

Making of Feed Solution

20 g of REE (OH) $_3$ was dissolved into 50 mL of 65% HNO3 then heated at 120 °C until the gas from HNO$_3$ was depleted. Then the solution was diluted to 200 mL HNO$_3$ 0.5 M. The mother liquor was diluted to 900 ppm Gd.

Making of Solvent Solution

TOPO

TOPO 50% is prepared by weighing 1 g of pure TOPO solid then is added kerosene up to 200 mL. For 10 mL TOPO 5% is prepared by diluting 1 mL TOPO 50% then is added with kerosene up to 10 mL. This step is repeated for the preparation of TOPO solutions of 10%, 15%, and 30%.

D2EHPA

D2EHPA 50% is made by taking 100 mL of pure D2EHPA then diluted with kerosene to 200 mL. For 10 mL D2EHPA 5% was prepared by diluting 1 mL of D2EHPA 50% and then it is added with kerosene up to 10 mL. This step is repeated for the preparation of 10%, 20%, 30%, and 40% D2EHPA solution.

Extraction

a) The feed prepared on point 1 (water phase) was extracted using 10% D2EHPA in kerosene (v/-v) (organic phase). The ratio of the volume of the aqueous phase (FA) to the organic phase (FO) is 1: 1. The mixture is stirred at 350 rpm for 30 minutes and then is allowed to stand for 10 minutes until between the water phase and the organic phase separately. The two phases are separated by a separation funnel. Then the filtrate results is analyzed using XRF to know the concentration of Gd.

b) Process a) is performed for TOPO 5%, 10%, 15%, 20%, 30%, D2EHPA 5%, 10%, 15%, 20%, 30%, 40%, mix D2EHPA- TOPO 3: 1, 1 : 3, 2: 1, 1: 2, 1: 1 and the composition between the solvent and the feed with a ratio of 1: 1, 1: 2, 1: 3, 1: 4, 2: 1 with a mixture of D2EHPA - TOPO.

3. Result and Discussion

3.1 Variation of Solvent

Research conducted on the separation of Gd in the concentrate REE senotim by extraction process, has the dominant element content that is Y, Gd and Dy with the content 80.89%; 15.49%, and 3.62%. Solvents used in the extraction process consist of solvent solvents and mixed solvents. Single solven ie TOPO or D2EHPA and mixed solvent is a mixture of TOPO and D2EHPA. Solvent is diluted using kerosene to reduce the density of D2EHPA or TOPO so that separation can be done due to the formation of 2 perfect phases.

3.1.1 TOPO

From Table 1 can be seen that the greater the concentration of TOPO solves, the greater the distribution coefficient of each element due to the solvents used more and more so that the complex formed to bind each of the larger REE. However, to determine the optimum condition of TOPO on gadolinium it is necessary to note the separation factor against other elements, so that 15% concentration has the best disadvantage for gadolinium by considering the separation factor which shows the greatest value to Gd-Y is 0.538 and to Gd-Dy 0.548.

Table 1. Kd and β Variation of Solvent TOPO

	Kd			β	
TOPO	Y	Gd	Dy	Gd-Y	Gd-Dy
5%	0.180	0.197	0.461	1.096	0.427
10%	0.297	0.139	0.577	0.467	0.240
15%	0.554	0.298	0.544	0.538	0.548
30%	0.881	0.269	1.359	0.305	0.198
50%	1.695	0.695	3.475	0.410	0.200

3.1.2 D2EHPA

From Table 2 it can be seen that the greater the concentration of the D2EHPA solvent the greater the distribution coefficient of each element due to the solvent being used the more so that the complex formed to bind each of the REE is greater, especially in the Ittrium indicating the compatibility of D2EHPA solvent to Ittrium. However, to determine the optimum state of D2EHPA against gadolinium

it is necessary to note the separation factor against other elements, so that with 10% concentration has the best disadvantage for gadolinium by considering the distribution coefficient and separation factor. This optimum condition was chosen from the value of distribution coefficient to obtain more gadolinium quantity by considering good separation factor (β) to Gd-Y that is 0.281 and to Gd-Dy that is 0.061.

Table 2. Kd and β Variation of Solvent D2EHPA

D2EHPA	Kd			β	
	Y	Gd	Dy	Gd-Y	Gd-Dy
5%	0.477	0.276	10.034	0.572	0.027
10%	1.191	0.334	5.476	0.281	0.061
20%	24.577	0.633	11.019	0.026	0.057
30%	128.633	0.606	10.472	0.005	0.058
40%	843.967	0.567	243.564	0.001	0.002

3.1.3 Solvent TOPO – D2EHPA

The optimum concentration of TOPO - D2EHPA mixture for gadolinium is at 2: 1 with the highest distribution coefficient (Kd) value is 0.636 and the separation factor of Gd to Y and Dy is greater than other concentrations respectively is 1.014 and 1.181 (Table 3).

Table 3. Kd and β Variation of Solvent TOPO-D2EHPA

TOPO : D2EHPA	Kd			β	
	Y	Gd	Dy	Gd-Y	Gd-Dy
1;3	0.989	0.435	13.870	0.440	0.031
3;1	0.885	0.505	1.209	0.570	0.417
2;1	0.627	0.636	0.538	1.014	1.181
1;2	0.995	0.253	3.665	0.254	0.069
1;1	0.998	0.244	0.241	0.244	1.012

The value of Kd elements Y and Dy on D2EHPA is greater than Gd due to sole D2EHPA solvent more selective against elements Y and Dy shown by Table 4 so that Y and Dy elements are extracted more stable in solvent solvent extraction process D2EHPA, this is because what happens is ion exchange reactions, so that elements with greater electronegativity will be easier to bind to D2EHPA solvents whereas in the TOPO solvent is a Solvation reaction. Separation using a mixed solvent yields a larger Kd than a single solvent for Gd so that the 2: 1 mix ratio is optimized for the separation of gadolinium from the senotime REE concentrate. This optimum state is influenced by the synergistic effect of the TOPO and D2EHPA mixtures, in accordance with the theory that solvent solvent and ion exchange mixtures will produce a synergistic effect that will strengthen the bonding complex in the organic phase. The synergistic effect on Gd metal extraction is due to the role of TOPO in distributing the metal, the presence of this TOPO compound can increase the complex of metal formed between metals by D2EHPA. The synergistic effect of the TOPO and D2EHPA solvent mixtures is 1.01 indicating that there is a synergistic effect between the two solvents.

Table 4. REE Separation with variation solvent

Type of Solvent	Kd			B	
	Y	Gd	Dy	Gd-Y	Gd-Dy
Solvent D2EHPA	1.191	0.334	5.476	0.281	0.061
Solvent TOPO	0.554	0.298	0.544	0.538	0.548
Mixing Solvent TOPO-D2EHPA	0.627	0.636	0.538	1.014	1.181

3.2 Composition Feed and Solvent in Extraction process in Separation of REE

Based on Table 5 it can be seen that the greater the ratio of the solvent to the feed, the greater the REE is drawn, but it affects the distribution coefficients of each element (KdY, KdGd, KdDy) will vary depending on the number of mixed solvents. For gadolinium, the solvent mixture concentration: the optimum feed is 1: 4 because gadolinium is more competitive with TOPO-D2EHPA solvents in a 2: 1 ratio so that gadolinium is relatively stable compared to Y and Dy with 0.609 distribution coefficient and Gd to Y and Dy are 3.452 and 19.239 respectively.

Table 5. Kd and β Variation of Variasi Solvent : Feed

Solvent : Feed	Kd			β	
	Y	Gd	Dy	Gd-Y	Gd-Dy
2;1	2.376	0.845	138.72	0.356	0.007
1;1	0.610	0.636	0.551	1.043	1.815
1;2	0.384	0.611	0.257	1.590	3.893
1;3	0.286	0.576	0.187	2.011	5.337
1;4	0.176	0.609	0.052	3.452	19.239

3.3 Rate Process

3.3.1 Determination of Time Equilibrium

The extraction process occurs because of the separation of a particular component from a fluid to the organic phase.
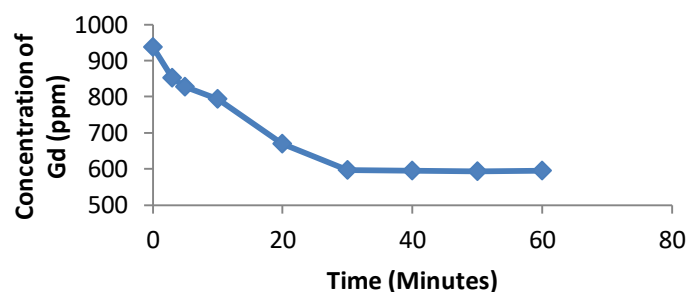

Figure 1. Time Equiblirium (minutes) foor Gd Extraction

Figure 1 shows that there is a decrease in the concentration of Gd in the liquid phase and the equilibrium time has been reached in the 30 minute meaning that the concentration reached in the time range is relatively constant, since the ability to bind the mixed solvent to Gd is maximum in other words the maximum solvent extract capacity has been reached. In addition, the decrease of Gd concentration in the extraction process proves that the solvent can be used to extract the Gd.

3.3.2 Reaction rate order and Constant Rate Reaction of Separation REE

The result of determination of extraction rate constant based on some models can be seen From Table 6. From Table 6 shows that the kinetics of extraction of Gd more in proportional with the model described first order reaction kinetics for r^2 close to 1 and error by a first-order reaction kinetics smaller than the order of 2.

Effect of temperature on extraction kinetics and the rate constant value (k) on the extraction kinetics model order 1 can be seen From Table 7. From Table 7 shows that the higher the temperature the separation factor will be smaller, this is not in accordance with the theory. This situation is due to a significant volume change in the process of taking the solution at any time on the temperature and time variations, so that the solvent becomes damaged due to rising temperature, causing the separation becomes less optimal.

Table 6. Kinetic Extraction Model of REE

Kinetic Model/Temperature	Gd			
	30 ºC	40 ºC	50 ºC	60 ºC
Orde 1				
r^2	0.983	0.978	0.979	0.991
error (%)	4.51	4.07	4.24	0.9
Orde 2				
r^2	0.990	0.976	0.988	0.995
error (%)	7.037	6.526	7.402	6.325

Table 7. Effect of Temperature on Kinetic Extraction of Gd Order 1

Temperature (ºC)	Gd Consentration (ppm)
30	340.24
40	321.20
50	228.23
60	135.61

From Table 8 shows that the higher the temperature of the reaction rate constants value will be smaller because of changes in the volume, which means the process of determining the kinetics causes the solvent resistance is reduced due to increased temperatures and increased impurities D2EHPA decomposed into M2HPA, causing the separation selectivity also reduced.

Table 8. Rate Constant First Order Reaction of Gd

Temperature (ºC)	k (1/minutes) Gd
30	0.014
40	0.012
50	0.008
60	0.005

3.3.3 Arrhenius Equation

The equilibrium constant will decrease with decreasing temperature as shown in Figure 2. This does not correspond to the kinetic theory due to damage of the solvents as described previously. The Arrhenius equation is performed to find out the energy dependence of activation (E) and the collision factor (A) on temperature and the results obtained as in Figure 2.
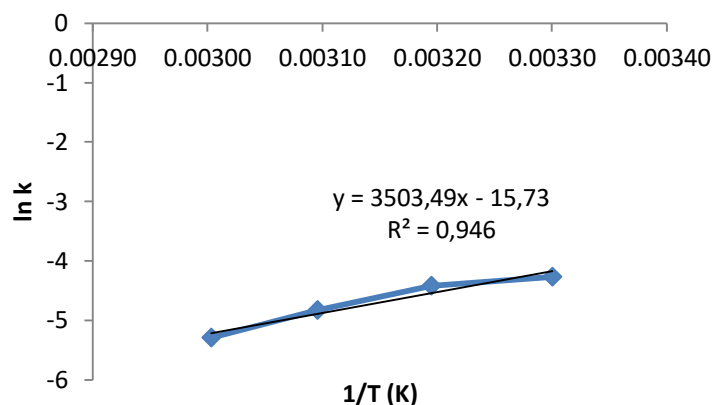

Figure 2. Curve ln k Vs 1/T

In Figure 2 it can be seen that the activation energy possessed by Gd is -6.96 kcal / mol and the collision factor owned by Gd is 1.46×10^{-7} so that the Arrhenius Gd equation becomes $k = 1.46 \times 10^{-7}$ exp (-6.96 kcal / mol / RT). Activation energy is negative due to the value of k and T is not in accordance with the theory. This event is experienced because of the significant volume changes in every solution taking during the kinetic determination process, so that the solvent capacity is reduced and the decomposition of D2EHPA into M2EHPA causes the separation selectivity also to decrease.

4 Conclusion

Based on this research, it can be concluded that the mixed solvent composition with the best feed to separate the rare earth metal Gd in the extraction process is 1: 4 with TOPO concentration of 15% and D2EHPA by 10%. The process of separation of the rare earth metals Gd with a solvent extraction method using a mixture of D2EHPA - TOPO better than a single solvent D2EHPA or TOPO with a mixture of TOPO-D2EHPA ratio is 2: 1.Orde reaction rate approaching Gd separation order 1 and Gd Arrhenius equation becomes $k = 1.46 \times 10^{-7}$ exp (-6.96 kcal / mol / RT).

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