Separation Factor of Y/Dy Emulsion on Membrane Process Using Nitric Acid and D2EHPA Solvent

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Received: May 24, 2018
Accepted: October 1, 2018

DOI: 10.22146/ijc.35783

Abstract: *Liquid extraction of Y that containing Dy using bis-2-Ethylhexyl phosphoric acid (D2EHPA) extractant has been conducted. The purpose of this study is to determine the optimum parameter in a separation process that uses membrane emulsion. As the aqueous phase, a mixed solution of Y_2O_3 and Gd_2O_3 containing Y 10 g/L and Gd 250 mg/L was used. D2EHPA as extractant or organic phase with a variety of concentration was diluted with kerosene. Emulsifier Span-80 was used to make an emulsion of membrane liquid. The internal phase of the liquid membrane used 0.20–0.50 M nitric acid, and the external phase used 1–5 M nitric acid. The studied parameters were extractant concentration, stirring speed, stirring time, and the ratio of the internal and external phase. X-Ray Fluorescence (XRF) was used for the analysis of Y and Dy. The analysis of Y and Dy used the X-Ray Fluorescence (XRF). The optimization results of the extraction process of Y with emulsion membrane using D2EHPA extractants obtained the following conclusions: the optimum stirring rate was 8500 rpm, the D2EHPA concentration was 4.5% in kerosene, the internal concentration was 0.45 M nitric acid, the external concentration was 4 M nitric acid, the stirring time was 10 min that fixed stirring rate was 500 rpm, and the ratio of internal and external phase was 1:1. This conditions acquired a separation factor (SF) Y-Gd of 7.57.*

Keywords: *stripping; yttrium; gadolinium; membrane emulsion*

■ INTRODUCTION

Senotim sand is phosphate rare earth elements (REEs) which is contained $(Y,LTJ)PO_4$. It obtained from byproducts of tin mining by PT Timah in Bangka and Belitung Island, Indonesia [1]. Rare Earth Elements (REEs) containing in the xenotime sand are Ittrium (Y), Gadolinium (Gd), Dysprosium (Dy), Cerium (Ce), Samarium (Sm), Lanthanum (La), and Neodymium (Nd) [2-4]. The total concentration of REEs range is 55% until 70% of REEs Oxide (RE_2O_3) which the dominant elements are Y, Dy, and Gd contained in senotim sands approximately 29.53%, 7.76%, and 2.58% [2-4].

The various by-product elements of REEs have enormous benefits both in the non-nuclear and nuclear fields [5-8]. For example in the non-nuclear field, REEs in the form of oxide plays a very important role in the needs of advanced materials such as superconductors, lasers, electronic optics, LED applications and iPAD [5,8-9]. In terms of usefulness in the nuclear field, for example, Y_2O_3 has a very important benefit and role that can be used as a dopant of control rod made from hafnium or yttria-stabilized [2,10-11] as well as a radiopharmaceutical for cancer therapy [9], Dy_2O_3 and Gd_2O_3 as control rod materials. The ability of control rod is to capture thermal neutrons due to its large neutron absorption (σ) (σ Dy = 2840 barns and σ Gd = 259000 barns) [1-2,12].

For both applications in the field of nuclear and non-nuclear science and technology, Y_2O_3 must be in the pure state of its impurity. The presence of impurities or additional compounds may modify the behavior and efficiency in application. Hence, it required prior to the preparation of Y_2O_3. Y has been separated from the impurities; then the calcination process obtained Y_2O_3 [13-15].

The separation process is carried out in two stages: precipitation and extraction-stripping. The precipitation process is carried out for the initial separation that obtained Y concentrate, so the feed used in the extraction process is slightly pure. Furthermore, Y_2O_3 is obtained after the calcination process. It gives effect in the separation process by precipitation, which is the optimum pH difference [16-18]. The extraction process is carried out for selective separation and purification of Y. If the separation process is only a non-precipitated extraction process, then the feed used in the extraction process is still containing impurities. Thus, it will reduce the separation efficiency in the extraction process. Similarly, if the separation process is only carried out by the precipitation process and without extraction, the presence of impurities on the formed oxide is still abundant and uneven [18-20]. In the extraction process-stripping, which is the success effect of separation of rare earth elements are the type of acidity and concentration medium [21].

Yttrium (Y), a silver transition metal, is a chemical metal similar to lanthanide and often classified as "rare earth elements". Y is almost found in combination with lanthanide elements of rare earth minerals and is never found in nature as a free element. Y also has a very important role in some applications in the field of advanced industry, for example, as superconductor [1-2,5].

Membrane processing for the separation of chemical or chemical element mixtures is very important, and it is an alternative to conventional chemical separation processes. The liquid emulsion membrane technique is highly favored from the separation technology, and it is high potential to be applied to several fields of science, i.e., hydrometallurgy, environmental engineering, biochemical engineering, pharmaceutical technology, and food technology [23-28].

The many benefits of membrane technology include easy phase separation, fairly rapid reaction, and widely used for separation of REEs in the industry as in the process of using mixer-settlers [26]. However, these traditional tools have many drawbacks, such as large-area equipment occupancy and large solvent bullets [27]. Several types of methods and equipment are devised To solve the problem such as hollow fiber contactor [29], impregnated, polymer beads and resin [30-31] ionic liquid [32-33], magnetic absorption [34], polymer sorbent [35] and others.

Emulsion liquid membran separations (ELMs) technique [26,28] has been regarded as an emerging technology with considerable potential for a variety of applications such as recovery and concentration of metal ions and biochemical products and the removal of pollutants from wastewaters. ELMs exhibit several attractive features in comparison with solvent extraction. These include a large specific surface area for extraction, simultaneous extraction, and re-extraction in a single stage, and the requirement is only small quantities of an expensive carrier [36-37]. In view of all these advantages, the separation of metals by the ELMs techniques has drawn considerable attention [26].

In the present work, Emulsion liquid membrane is investigated to select the suitable conditions for extraction of Y and Dy ions from acidic nitric solutions using D2EHPA as the extractant. The effects of extractant and surfactant concentrations, mixing speed, concentration and type of stripping solution, phase ratio, treatment ratio, and nature of diluent on the extraction rate were studied. Under the optimum conditions, extraction of Y and Dy ions has also been studied for different feed mixture solution [38].

The configuration supported liquid membranes system. Globules are granular of the organic phase in the emulsion solution. Solvent extraction and stripping of Y and Dy ions were carried out in order to study the influence of the concentration of the aqueous solution, the concentration of D2EHPA, the equilibrium time on the extraction percent of Y and Dy ions and stripping percent of this metal ions from the loaded organic phase by the hydrochloric acid solution.

In general, liquid membranes can be held in porous structure or bounded on either side by two thin polymeric films. Emulsion (unsupported) liquid membranes are usually in the form of double emulsion drop. In Water/Oil/Water (W/O/W) system, immiscible in the oil phase, separating the two aqueous phases, while in an O/W/O system, the liquid membrane is the immiscible water phase which separates the two oil phases [26].

Initial studies were done to study the effect of stirring rate by using stable Ultra Turrax, which is producing membranes 5% Span-80. In the producing of emulsion membrane, the selected stirring rate is 8500 rpm, because the membrane was relative stability and recovered energy efficiency.

The metals are present in the external aqueous phase to be extracted by the extractors that exist in the organic phase by forming complex compounds. Complex compounds are further decomposed by the internal water phase. Therefore the extraction and re-extraction or stripping occur simultaneously [26-27].

■ EXPERIMENTAL SECTION

Materials

The materials used in this study were Bis(2-Ethylhexyl) Phosphate Acid (D2EHPA) PA Merck, Yttrium concentrate containing 90.51% Y that obtained yttria sand process and dysprosium 6.38%, HNO_3 PA 37% Merck, Kerosene PA Merck, Span-80 PA Merck.

Instrumentation

Heating and magnetic stirrer, stirrer Ultra Turrax, appliance glass, and XRF (X-Ray Fluorescence) spectrophotometer) EG&G ORTEX 7010.

Procedure

The membrane emulsion preparation

Membrane phase and internal water phase (FAi) and 10 mL of 5% surfactant Span-80 were dissolved in 10 mL. The formed emulsion as membrane phase (FM) is used for the extraction of 20 mL of the feed solution. The feed or external aqueous phase is 1 g/L Y solution of nitric acid was mixed with 20 mL FM for 10 min with stirring rate extraction at 500 rpm. % D2EHPA-Kerosene) as the organic phase plus10 mL HNO_3 4 M as an external phase (FAe). Ultra Turrax was stirred for 20 min with a stirring speed varies from 5000 to 10000 rpm. The formed emulsion as membrane phase (FM) is used for the extraction of 20 mL of the feed solution. The feed or external aqueous phase is 1 g/L Y solution of nitric acid that was mixed with 20 mL FM for 10 min with stirring extraction at 500 rpm.

The process of extracting and stripping

Yttrium feed solution concentration (FAe) 10000 ppm by volume of 10 mL with 10 mL of FM was stirred for 10 min with a speed of 500 rpm. The mixture was silenced for a moment and then separated with a separating funnel. FAe volume was measured. FM heated briefly, the emulsion will separate into FO and FAi. FO and FAi were separated and measured its volume. FAe and FAi then were analyzed by XRF. This work was repeated to study the effects of the percentage of D2EHPA-kerosene and to study the influence of variations of the internal water phase molarity, the feed molarity, and the stirring time. The FAe, FO, and FAi data are used to calculate the efficiency of extraction and stripping efficiency Y, and Dy.

To determine the success of the process can be seen from the efficiency of extraction stripping efficiency and total efficiency.

M = Metal
FAe = External phase aqueous
FAi = Internal phase aqueous
FO = Organic phase

Efficiency calculation formula follows equation [26]:

$$\text{Extraction Efficiency} = \frac{(\text{VFAeo} \times \text{CFAeo}) - (\text{VFAe} \times \text{CFAe})}{(\text{FAeo.} \times \text{FAeo})} \times 100\% \quad (1)$$

$$\text{Total Effeciency} = \frac{(\text{VFAi} \times \text{CFAi})}{(\text{VFAeo} \times \text{CFAeo})} \times 100\% \quad (2)$$

$$\text{Stripping Efficiency} = \frac{(\text{VFAi} \times \text{CFAeo})}{(\text{VFAeo} \times \text{CFAeo}) - (\text{VFAe} \times \text{CFAe})} \times 100\% \quad (3)$$

where: VFAeo = the volume of the external aqueous phase before extraction (initial); VFAe = the volume of the external aqueous phase after extraction; VFAio = the volume of the internal aqueous phase before extraction (initial); VFAi = the volume of the internal aqueous phase after extraction; CFAe = the concentration of the internal aqueous phase before extraction (initial); CFAe = the concentration of the external aqueous phase after extraction; CFAio = the concentration of the internal aqueous phase before extraction (initial); CFAi = the concentration of the internal aqueous phase after extraction.

The success of the process is measured by looking at the magnitude of the distribution coefficient (DC) which is the ratio of element concentration in the organic phase compared to the element concentration in the water phase and the separator factor (SF), i.e., DC one with DC other elements.

$$DC = \frac{\text{Concentrations of elements in organic phase (FO)}}{\text{Concentrations of element in water phase (FA)}} \quad (4)$$

The concentration of an element in the organic phase (FO) = Concentration of element in (ratio– FA)

$$SFY - Dy = \frac{DCY}{DCDy} \quad (5)$$

RESULTS AND DISCUSSION

Effect of D2EHPA-kerosene percentage

In this part, the ratio FM:FAe was 1:1 (10 mL:10 mL); FAi was 0.5 M HNO_3; FAe was 4 M HNO_3; Stirring speed was 500 rpm, and time of extraction was 15 min. The type of membrane emulsion was a water-in-oil emulsion, i.e., HNO_3 in D2EHPA-kerosene. This emulsion can be formed due to existing Span-8. The previous studies [26] had investigated the parameters that the emulsion formed becoming stable by using Span-80 as much as 5% by the volume of the emulsion.

Determination percentage of D2EHPA was important in the mechanism of metal transfer in the internal water phase (FAi) because with increasing the percentage of D2EHPA, CFAi of Y and Dy would grow. Hence the reaction with D2EHPA and metal would be better. To determine the effect of the displacement of Y and Dy to the organic phase can be seen in the binding ability of D2EHPA, Y, and Dy. At first, the yttrium is at FAe in complex form solvated with water and nitrates. Due to the D2EHPA ligand through H_2O, the extraction process will be replaced by D2EHPA and form a neutral complex in the organic phase. The greater the concentration of D2EHPA, the higher the extraction efficiency would be. This suggests that the more Y and Dy were extracted, the more of a neutral complex form with D2EHPA in the membrane phase that is shown in Table 1. The reaction occurs in the Y extraction process on each acid medium can be written as equation 6 and 7 [25]:

For yttrium:

$$Y^{3+} + 3NO^{3-}{}_{(aq)} + 3H_2A_2 \leftrightarrow (HA_2)_{3(org)} + 3H^+ + 3NO^{3-} \quad (6)$$

For dysprosium:

$$Dy^{3+} + 3NO^{3-}{}_{(aq)} + 3H_2A_2 \leftrightarrow Dy(HA_2)_{3(org)} + 3H^+ + 3NO^{3-} \quad (7)$$

In Table 3, it is showed that the concentration of D2EHPA affected the efficiency of Y and Dy. The higher the concentration of D2EHPA, the higher the efficiency would be. Above 4 to 5%, the relative efficiency of D2EHPA has been steady due to the greater number of complex compounds of Y and Dy with increasing D2EHPA, while a limited number of stripping efficiency of Y slightly decreased. The reaction ability of HNO_3 and metal is still quite strong, so the stripping efficiency is relatively small. The effectiveness of the whole process of extraction method of emulsion liquid membrane can be known by looking at the distribution of coefficient and separation factor of Y and Dy.

The effectiveness of the whole process of extraction method of emulsion liquid membrane can be known by

Table 1. Correlation between %D2EHPA-Kerosene and extraction efficiency

%D2EHPA-Kerosene	Extraction Efficiency (EE), Distribution Coefficient (DC) and Separation Factor (SF)		
	Yttrium	Dysprosium	SF
2.5	EE=83.03; DC=4.89	EE=67.11; DC=2.04	2.40
3	EE=85.54; DC=5.92	EE=67.32; DC=2.06	2.87
3.5	EE=90.07; DC=9.72	EE=68.75; DC=2.20	4.23
4	EE=92.91; DC=13.10	EE=69.79; DC=2.31	5.67
4.5	EE=94.08; DC=15.97	EE=67.85; DC=2.11	7.57
5	EE=93.58; DC=14.53	EE=71.35; DC=2.49	5.83

Table 2. Correlation between % D2EHPA-Kerosene and stripping efficiency

%D2EHPA Kerosene	Stripping Efficiency (SE), Distribution Coefficient (DC) and Separation Factor (SF)		
	Yttrium	Dysprosium	SF
2.5	SE=87.03; DC=6.71	EE=58.85; DC=1.43	4.70
3	SE=91.57; DC=10.87	EE=79.70; DC=2.30	4.65
3.5	SE=91.68; DC=11.02	EE=70.55; DC=2.40	4.60
4	SE=91.91; DC=11.35	EE=70.33; DC=2.37	4.79
4.5	SE=92.28; DC=11.97	EE=70.06; DC=2.34	5.11
5	SE=92.02; DC=11.53	EE=65.52; DC=1.90	6.08

Table 3. Correlation between HNO_3molarity after extraction and extraction efficiency

HNO_3 M (FAi)	Extraction Efficiency (SE), Distribution Coefficient (DC) and Separation Factor (SF)		
	Yttrium	Dysprosium	SF
0.20	EE=64.54; DC=1.82	EE=35.90; DC=0.56	3.24
0.25	EE=89.29; DC=8.34	EE=71.09; DC=2.46	3.39
0.30	EE=89.12; DC=8.24	EE=72.60; DC=2.65	3.11
0.35	EE=90.02; DC=9.02	EE=84.32; DC=2.66	3.39
0.40	EE=91.91; DC=11.35	EE=79.55; DC=3.89	4.75
0.45	EE=92.28; DC=11.97	EE=67.32; DC=2.06	5.80
0.50	EE=92.02; DC=11.53	EE=69.88; DC=2.32	4.95

looking at the distribution of coefficient and separation factor of Y and Dy. Distribution coefficient is the ratio of concentrations of a compound in a mixture of two immiscible phases at equilibrium. The extraction efficiency is the percentage of solute moving into the extracting phase. Stripping efficiency is the ratio of concentration where one or more components are removed from the liquid stream by a vapor stream. Separation factor is identical to the ratio of the distribution factor organic phase into the aqueous phase.

Y and Dy were obtained with measurement by the value of the total yttrium. Table 2 shows the relatively good results in 4%-5% D2EHPA. The result showed that the stripping efficiency increased due to the greater the number of complex compounds.

Effect of FAi (HNO_3) Molarity

In this part, the volume ratio of FM:FAe was 1:1, 4.5% D2EHPA-kerosene, FAe was HNO_3, stirring speed was 500 rpm, and time of extraction was 15 min. To find out how much Y-Dy transferred to the organic phase it can be seen in Table 3, the relationship between FAi molarity with the extraction efficiency. From Table 3, it appeared that the extraction efficiency increased with the increase of nitric acid around 0.4-0.5 M HNO_3, but after that declined. The influence factors are the chemical reactions and change of negative volume emulsion membrane systems. The increase of HNO_3 concentration caused higher osmotic pressure on FAi that made, so more water coming into the FAi.

Effect of Fai acidity was investigated to determine the most optimum acidity, to elaborate on the complex FAi with ion complexes HNO_3.D2EHPA. The extraction efficiency increased that follows the increase of FAi acidity using nitric acid 0.4-0.5 M. Stripping efficiency rose with the increase of FAi acidity and was relatively steady above 4 M. Then, the increase of HNO_3 metal-D2EHPA caused the more perfected decomposition reaction and higher osmotic pressure on FAi by water to pour into FAi. Complex compounds $Y(NO_3)_3$-2D2EHPA and $Dy(NO_3)_3$-2D2EHPA are very strong. Table 3 shows how much metal is transferred to the organic phase, the relationship between the FAe acidity and extraction efficiency. At first, the FAe in complete form is solvated

Table 4. Correlation between HNO_3 molarity and stripping efficiency

HNO_3 M (FAe)	Stripping Efficiency (SE), Distribution Coefficient (DC) and Separation Factor (SF)		
	Yttrium	Dysprosium	SF
1	SE=45.06; DC=0.82	SE=54.75; DC=1.21	0.68
2	SE=57.98; DC=1.38	SE=52.61; DC=1.11	1.24
3	SE=84.50; DC=5,45	SE=66.33; DC=1.97	2.77
4	EE=90.02; DC=9.02	EE=62.41; DC=1.66	5.43
5	EE=89.30; DC=8.35	EE=66.22; DC=1.96	4.26

by water and nitrate. Due to the D2EHPA through the extraction process, H_2O ligands will be replaced by D2EHPA and a neutral complex form in the organic phase.

In Table 3, it appeared that at the acidity of 4 M, the efficiency of extraction started rising and reaching a maximum of 4 M after that declined. It caused a change of negative volume emulsion membrane systems.

Effect of molarity or acidity was great to the extraction of Y/Dy. The increase of the extraction system is solvation, especially for extractant D2EHPA, then D2EHPA will react with the acid solvent (HNO_3). The efficiency decreased in the acidity above 4 M, as a result of the reaction between D2EHPA with HNO_3 as a solvent feed. It is caused by the ability factor of D2EHPA that cannot extract the maximum Y-Dy at high acidity. Metal extraction in the extraction system is also influenced by the solvation of anions in the water phase. The increasing acidity is followed by the increasing of HNO_3 or NO_3^- ions in the solution.

■ CONCLUSION

In this work, the study to determine the optimum parameter in the extraction process that uses membrane emulsion is presented. The optimum parameters of extraction process showed that the feed solution extraction volume was 10 mL in an atmosphere of 4 M HNO_3, the membrane extraction volume was 10 mL of 4.5% D2EHPA-kerosene and 0.45 M HNO_3 for 10 min in stirring stage. The stirring rate parameters showed that the stirring rate of extraction was 500 rpm, and the rate of producing membrane was 8500 rpm. The use of span-80 was equal the 5%. The obtained separation factor (SF) of Y-Dy was 7.57 in this stage.

■ ACKNOWLEDGMENTS

The author would like to thank Dwi Biyantoro, Mulyono, Bambang EHB, Imam Prayogo, Sudarso and Trimohadi who have helped this work in the laboratory of the Center for Science and Technology Accelerator. The author also expressed his gratitude to Wulan, Luthfi, Novi, Puji for assisting in the implementation of this research working at the Polytechnic Institute of Nuclear Technology.

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