Extraction Development for the Separation of Gadolinium from Yttrium and Dysprosium Concentrate in Nitric Acid using Cyanex 572

Kris Tri Basuki[1*], Alfiyatur Rohmaniyyah[1], Wahyu Rachmi Pusparini[2], Andri Saputra[1]

[1]*Department of Nuclear Chemical Engineering, Polytechnic Institute of Nuclear Technology (STTN), Jl. Babarsari, Yogyakarta 55821, Indonesia*
[2]*Accelerator Science and Technology Center (PSTA) - National Nuclear Energy Agency (BATAN), Jl. Babarsari, Yogyakarta 55821, Indonesia*

Abstract. Xenotime sand, a byproduct of the tin mining process of PT Timah, is one of the potential gadolinium (Gd) resources. Because of similarities in their physical and chemical properties, it is difficult to separate and purify Gd from rare earth elements (REEs) in xenotime sand (i.e., yttrium and dysprosium). In the present work, Gd was separated through an extraction process using Cyanex 572. The extraction feed solution was prepared by digesting the REE oxalate in NaOH to obtain $REE(OH)_3$. The effects of the extraction parameters (i.e., stirring time and rate, feed pH and concentration, and Cyanex 572 concentration) were examined via a batch experiment. The optimum results of Gd separation from yttrium concentrate were achieved when the process conditions included a 250-rpm stirring rate for 30 minutes, a 150×10^3-ppm feed concentration at pH 3, and a 30% Cyanex 572 concentration. These conditions gave distribution coefficient results for Y, Gd, and Dy of about 0.031, 0.827, and 1.060, respectively; separation factors of Gd-Y and Gd-Dy of about 26.482 and 0.780, respectively; and extraction efficiencies for Y, Gd, and Dy of about 3.119%, 46.627%, and 53.007%, respectively.

Keywords: Cyanex 572; Dysprosium; Extraction; Gadolinium; Separation; Yttrium

1. Introduction

Gadolinium (Gd), yttrium (Y), and dysprosium (Dy) are included in a group of 17 chemically similar metallic elements called rare earth elements (REEs). Gd has excellent scintillation properties and a high magnetic moment compared with other REEs. In the nuclear industry, gadolinium oxide is used for radiation-shielding ceramic compositions (Gupta and Krishnamurthy, 2005) and control rods (Jaworski and Gawlowski, 2015) as well as in making optical fibers. Gd is also added to optical glasses for use in electro-optical and magneto-optical systems. Gd (1%) in iron, chromium, and related alloys improves resistance to oxidation and high temperatures (Xu et al., 2014). Y is also an important element used in electrical material (Rahmawati et al., 2015), for example, to increase ionic conductivity (Shakthinathan et al., 2012).

Data from 2014 shows that China is the world's largest REE deposit, containing about 58% of the total global deposit of 154,135 tons. Meanwhile, the Indonesian REE deposit hypothesis shows a very small amount, about <1% of the total world deposit (Gunradi et al., 2019). The main minerals containing REEs found in Indonesia are xenotime, monazite,

and zircon, associated with cassiterite obtained from alluvial tin mining. Granite, pegmatite, and metamorphic, ultramafic, and alluvial rocks are among the types of rocks that may contain REEs in Indonesia. These REE minerals are concentrated in the Riau Islands, Bangka Belitung, and parts of West Kalimantan (Virdhian and Afrilinda, 2014; Gunradi et al., 2019). Xenotime sand, a byproduct of the tin mining process of PT Timah, is one of the potential gadolinium resources of REEs. It contains rare earth phosphate minerals such as 29.53% Gd, 7.76% Y, and 2.58% Dy (Atmawinata et al., 2014). In Indonesia, xenotime has not been further processed to obtain pure REEs or to obtain its oxides. If Gd, Y, and Dy can be separated from other materials properly, this will increase xenotime's economic value.

Because of similarities in REEs' physical and chemical properties, it is difficult to separate and purify Gd from other REEs (other lanthanides). To separate Gd in high purity, it is necessary to find the most efficient and feasible technology (Fisher and Kara, 2016). High-purity REEs like Gd have received considerable attention in recent years due to various industrial applications, limited supply, significant price fluctuations, and market availability (Hasan et al., 2009; Torkaman et al., 2013).

Many methods, such as solvent extraction, fractional crystallization, ion exchange, and chemical precipitation, are used to purify and separate REEs. A well-known method of purification and separation is solvent extraction (Andriayani et al., 2015; Wahab et al., 2016). On an industrial scale, solvent extraction is the most successful method for the extraction and separation of REEs (Wang et al., 2014). The development of new extractants and more efficient extraction techniques is essential for maintaining a stable supply of REEs to meet rapidly increasing demand on a global scale (Tunsu et al., 2016).

Organophosphorus and amine are extractants commonly used to extract REEs in acid solutions. Cytec Industries, Inc., introduced a new extractant, known as Cyanex 572, which belongs to the type of organophosphorus extractant whose active ingredient is a mixture of phosphinic and phosphonic acid with the active group of POOH. This type of extractant is known for its selectivity to certain metals, and one such extractant is used for the separation of metals from heavy REE groups using the liquid-liquid extraction separation method (solvent extraction). Cyanex 572 is specifically designed to extract heavy REEs under the required operating conditions of low acidity (Cytec, 2014). Cyanex 572 has been studied for extracting REEs and Th from waste residues, including ion-absorbed minerals or fluorescent lamps (Tunsu et al., 2016). Cyanex 572 synergized with n-octyl diphenyl phosphate (ODP) has also been studied for extracting Th from leaching solutions of rare earth residues (Zhou et al., 2019). El-Hefny et al. (2018) used Cyanex 572 to separate Y(III) and Dy(III) in hydrochloric and nitric acid solutions.

Gd extraction was studied by Vijayalakshmi et al. (2014) using EHEHPA as a solvent and by Taufan et al. (2008) using DBDTC. Torkaman et al. (2016) also studied Gd extraction using D2EHPA and Cyanex 301. This study proposes to investigate the separation of Gd from xenotime sand by an extraction process using Cyanex 572 solvent in nitric acid solution. Nitric acid has been used to dilute $REE(OH)_3$ or Gd and other elements in $REE(OH)_3$ (Taufan et al., 2008).

2. Methods

Xenotime sand (REE Oxalate) was obtained as a byproduct of the tin mining process of PT Timah on Bangka Island. The chemicals used for preparing the feed solution were NAOH (Merck), HNO_3 (Merck), NH_4OH (Merck), and distilled water. For the batch extraction, the chemicals used were Cyanex 572 and dodecane.

X-ray fluorescence (XRF) (Rigaku NEX QC) was used to measure the final concentrations of Y, Dy, and Gd in the aqueous phase.

2.1. Preparation of Feed Solution of REEs in Hydroxide Form

The feed solution of REE(OH)$_3$ was prepared by digesting the REE Oxalate 427.6173 g in NaOH 425 g and then filtering by hot water until the pH of the filtrate was neutral. The obtained REE(OH)$_3$ was dissolved in HNO$_3$ 500 mL at a ratio of 1:3 (w/v) and evaporated at 120°C until the gas from the HNO$_3$ ran out and then was combined with distilled water 1.5 L. REE(NO$_3$)$_3$ was deposited by NH$_4$OH 15% until the pH reached 6.5, then the sediment was filtered and dried in an oven to form the solid REE(OH)$_3$.

## 2.2. Extraction Process

The effects of extraction parameters (i.e., stirring time and rate, feed pH and concentration, and Cyanex 572 concentration) were examined via a batch experiment. A solution with 100×10^3 ppm of REE(OH)$_3$ was prepared by dissolving REE(OH)$_3$ into HNO$_3$ at a ratio of 1:3 (w/v). The mixture was evaporated at 120°C until the gas from the HNO$_3$ ran out. Then, the mixture was supplemented with 0.5 M of HNO$_3$, and the pH was adjusted to 1 by adding 15% NH$_4$OH until the volume of the solution reached 100 mL (as aqueous phase). The organic phase was prepared using 30% of Cyanex 572 and dodecane (1:1 v/v). The aqueous phase was extracted by stirring the organic phase at 150 rpm for 10 minutes. Then, the solution was allowed to stand for 1 hour until the aqueous phase and the organic phase were separated. As much as 5 mL of the aqueous phase was taken to be analyzed using XRF. The steps were repeated using different stirring times (10, 15, 20, 30, and 40 minutes), different stirring rates (100, 150, 200, 250, and 300 rpm), different pH levels (0.5, 1, 2, 3, and 4), different feed concentrations (25×10^3, 50×10^3, 100×10^3, 150×10^3, and 200×10^3 ppm), and different Cyanex 572 concentrations (20%, 30%, 40%, 50%, and 60%).

3.   Results and Discussion

3.1. Variation of Stirring Time

The contact time between the aqueous phase (REE(OH)$_3$) and the organic phase (Cyanex 572 in dodecane) affects the distribution of Y, Gd, and Dy into the organic phase. The longer the contact time between the aqueous phase and the organic phase during the extraction process, the more Y, Gd, and Dy are bound by Cyanex 572.
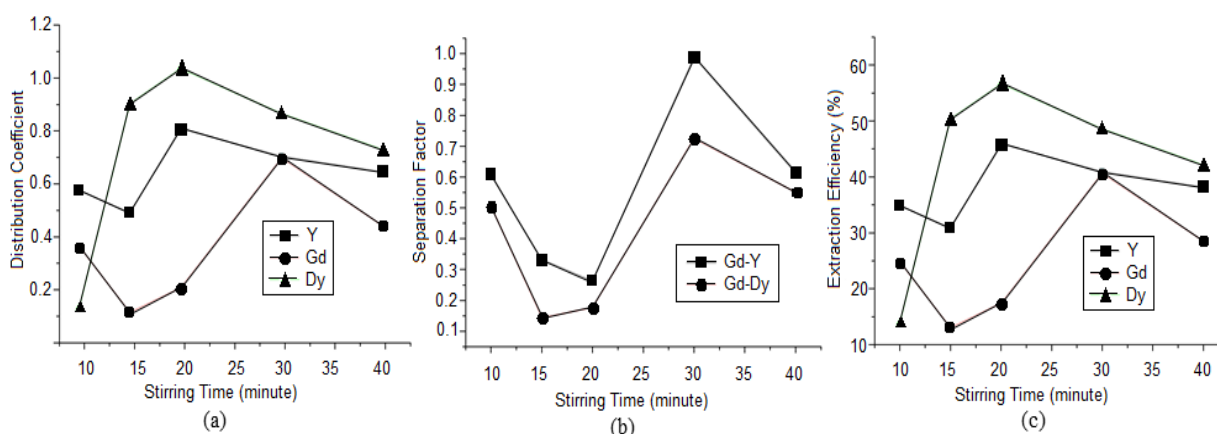

Figure 1 Correlations of stirring time to: (a) distribution coefficient; (b) separation factor; and (c) extraction efficiency of Y, Gd, and Dy

Figure 1a shows that the distribution coefficient value tended to increase with increasing stirring time until reaching the optimum value at 20 minutes. Figure 1a also shows that the distribution coefficient and extraction efficiency of Dy were higher than

those of Gd and Y, which indicates that Dy is more stable in the Cyanex 572 than the other elements. This result is in line with Aziz (2017) and Wang et al. (2015). The extraction efficiencies of REEs using Cyanex 572 were reported by Wang et al. (2015) to be in the following order: La < Ce < Pr < Nd < Sm < Eu < Gd < Tb < Dy < Er < Lu, which is consistent with decreasing ionic radii. In addition, Aziz (2017) stated that this result was due to the electronegativity of elements. Elements with greater electronegativity will more easily bind to the solvent. The electronegativity value of Dy is 1.22, while that of Gd is 1; therefore, we assumed that Dy more easily binds to the solvent or is more stable in Cyanex 572.

Figure 1b shows that the best separation factors were 0.989 for Gd-Y and 0.752 for Gd-Dy, both at a 30-minute stirring time. With stirring times of over 30 minutes, the separation factor decreased due to the solvent's optimum ability and a competing reaction between elements. As a result, the resulting separation product fluctuated due to the reversible reaction shown in Equation 1 (Kislik, 2012; El-Hefny et al., 2018). In addition, an excessive extraction time will lead to poor yields, poor selectivity, and longer phase separation time (Nejad and Kazemeini, 2012), so it will decrease the separation factor.

$$Gd^{3+}_{(aq)} + 3HA_{(org)} \leftrightarrow GdA_{3(org)} + 3H^+_{(aq)} \tag{1}$$
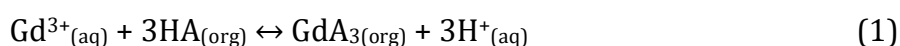
Gd^{3+} represents the gadolinium ion, and $HA_{(org)}$ represents the dimer of Cyanex 572 in the organic phase species.

Increasing the stirring time will increase the mass transfer from the aqueous phase to the organic phase, which increases the solutes extracted into the organic phase. As a result, the extraction efficiency increases (Soeezi et al., 2015). After reaching the optimum value, the amount of solute extracted will be constant, and more stirring time has no further effect. The optimum extraction efficiency value is shown when the stirring time is 20–30 minutes, which is sufficient for the optimum reaction, as presented in Figure 1c.

3.2. Variation of Stirring Rate

Figure 2a shows that the distribution coefficient value tended to increase by increasing the stirring rate because the intensity of collisions between reactants increases and becomes faster (Soeezi et al., 2015).
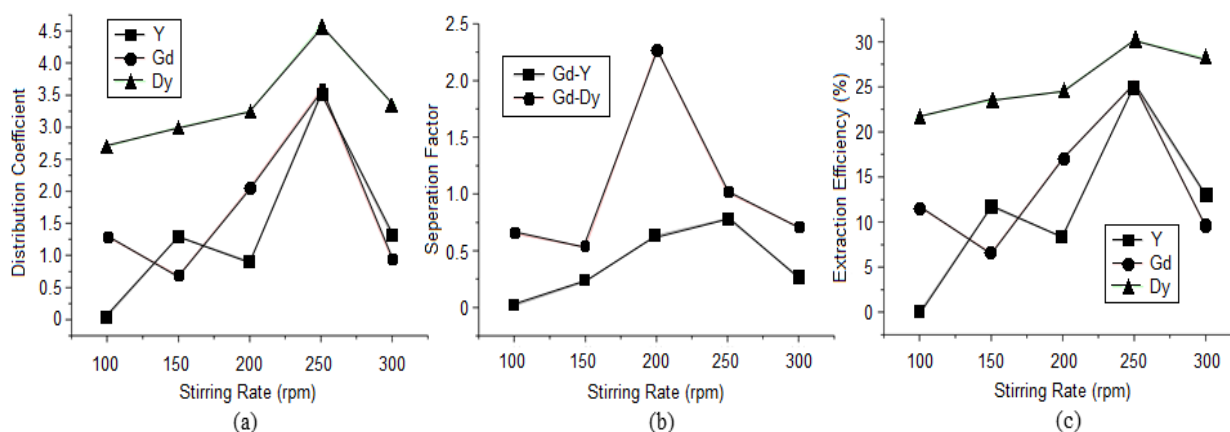
Figure 2 Correlations of stirring rate to: (a) distribution coefficient; (b) separation factor; and (c) extraction efficiency of Y, Gd, and Dy

The highest distribution coefficient for Gd separation was at 250 rpm. Stirring rates over 250 rpm decreased the distribution coefficient because at these rates, the aqueous

phase and the organic phase become an emulsion, making them hard to separate. Liquid emulsions involve two liquids that are mixed, but it cannot dissolve each other; the two liquids are a polar liquid (aqueous phase) and a non-polar liquid (organic phase).

The highest separation factor was achieved at the stirring rate of 250 rpm, at which the obtained separation factor of Gd-Y was 0.782 and the obtained separation factor of Gd-Dy was 1.011, as shown in Figure 2b. In determining the optimization value to be applied in the next step, the stirring speed of 250 rpm was chosen based on the separation factor of Gd-Y. It was expected to obtain purer Gd than Y (the impurities element), which is high in the feed solution. The obtained results decreased at 300 rpm. This decrease occurred because the temperature was not measured at each process condition, and temperature differences affect the distribution coefficient value and, as a result, the obtained separation factor value.

Figure 2c shows that the extraction efficiency value tended to increase with increased stirring rate, with the optimum extraction efficiency at 250 rpm. Diffusion and chemical reactions cause mass transfer from the aqueous phase to the organic phase. From the diffusion point of view, the diffusion rate is influenced by the distance or width taken up by the element that will diffuse from the aqueous phase to the organic phase. The wider the distance traveled, the slower the mass transfer will be. These distances become shorter when the stirring rate is increased. From the chemical reaction point of view, the reaction more likely will occur at increased stirring rates because the area of the collision is also growing.

3.3. Variation of Feed pH

Increased solution pH led to a proportionally increased distribution coefficient value, as shown in Figure 3a, and the distribution coefficient of Dy was higher than those of Gd and Y due to an increase in the atomic number of each element The greater the atomic number of an element, the smaller the atomic radius of the element. Because the radius of the REE atom is smaller, the interaction of ion exchange from the solute and solvent to form complex compounds will progress better as atomic numbers increase (Rohiman et al., 2008). The atomic radius of Dy is 178 pm, and that of both Gd and Y is 180 pm; the atomic numbers of Dy, Gd, and Y are 66, 64, and 39, respectively.
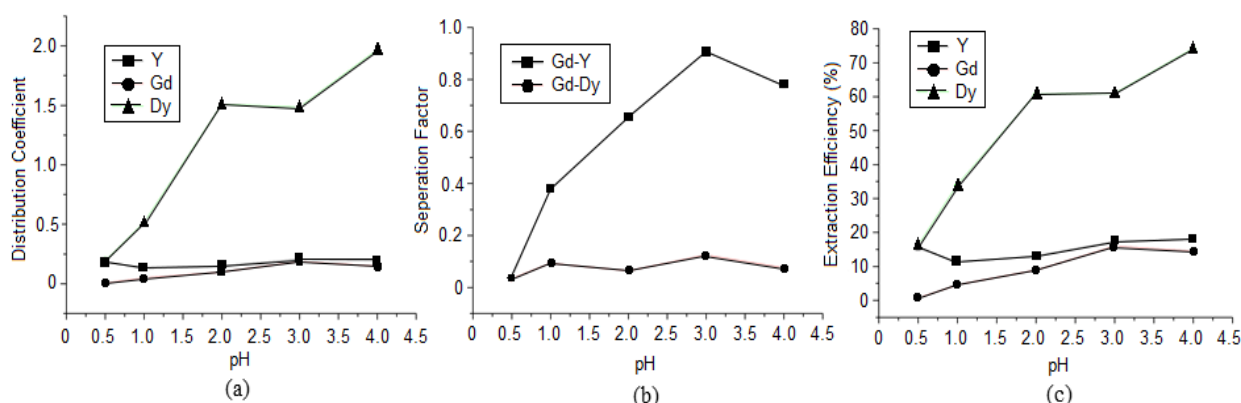
Figure 3 Correlations of feed pH to: (a) distribution coefficient; (b) separation factor; and (c) extraction efficiency of Y, Gd, and Dy

Nitric acid was chosen as the solvent in the aqueous phase because its lower acidity compared with hydrochloric acid increases the reactivity of Cyanex 572 (Ma et al., 2017). The first reaction is the cation exchange between $H^+_{(aq)}$ of the aqueous phase and $H^+_{(org)}$ from the organic phase; both of them contribute H^+, which means there is no significant

change in the reaction. The second reaction is the exchange of $H^+_{(org)}$ with Gd^{3+}. As a result, Gd^{3+} tends to react with Cyanex 572 and $3H^+$ donated to the aqueous phase according to the reaction in Equation 2. Sulfuric acid was not used because H_2SO_4 has $2H^+$ ions, which will cause Cyanex 572 to prefer to exchange ions with H_2SO_4 rather than binding complexes on REE ions. The low concentration of nitric acid was chosen because Cyanex 572 works under low acid concentration conditions. Under low acid concentration conditions, H^+ ions will exchange with REE ions, while in high acid concentration conditions, Cyanex 572 will form a complex with NO_3 and become $3GdL_6NO_33HA_{(org)}$ according to the reaction in Equation 2.

$$3Gd^{3+}_{(aq)} + 3NO^-_{(aq)} + 9HA_{(org)} \leftrightarrow 3GdA_3NO_33HA_{(org)} \tag{2}$$

Although the increased molarity of HNO_3 can increase the reactivity of the H^+ ion formation, acidity that is too high will reduce the reactivity of Cyanex 572. As a result, it will reduce the separation factor of REEs. This formed solvation reaction should be avoided because if the reaction mechanism occurs in a different reaction, it will produce different elements as a result. At a relatively high acidity concentration, the reaction that occurs in organophosphorus solvents is the formation of complexes, whereas at low concentrations the reactions that occur are ion exchanges (Braatz et al., 2016).

Figure 3b shows that the optimum separation factors of Gd-Y and Gd-Dy were in pH 3 because Y is the dominant element in yttrium concentrate. The value of the separation factor at low pH was low and tended to increase with increasing pH value because the extraction process begins at the solvent ionization stage. In this stage, the active group of solvents that have been ionized will bind with metal ions to form metal compounds that bind with a solvent. This happens based on the Le Chatelier principle, which states that if the concentration of one part (reactant or product) is increased, then the reaction will tend to shift toward the part that is not increased. At a low pH, H^+ ions are relatively higher, which encourages protonation reactions. The percentage of extraction will continue to increase until the pH of the solution reaches its optimum value.

Figure 3c shows that better extraction efficiency was achieved by increasing the pH value, and the optimum extraction efficiency for Gd was achieved at pH 3. Figure 3 also shows that there was a significant increase in extraction efficiency from pH 0.5 to pH 4. An increase in pH in the aqueous phase will cause an increase in extraction efficiency up to a certain pH value. After this, the extraction efficiency will decrease by increasing the pH value (Yuliusman, 2015). At a low pH, the low extraction value is due to protonation in the solvent that makes extraction hard to ionize and bind to metal ions in the aqueous phase solution.

When the feed pH has passed the optimum value of extraction efficiency, the extraction ability will decrease due to the hydrolysis of metal ions (e.g., Gd). The hydrolysis reaction is the breakdown reaction of the O-H bond in the hydrate ion $[Gd(H_2O)_6]^{n+}$, which forms when the salt of the metal cation is hydrated in water. The hydrolysis reaction will produce an insoluble gadolinium hydroxide $(Gd(OH)_3)$ compound. It puts the Gd into non-ion form, making it difficult to extract. Equation 3 shows the equation that occurs when Gd ions are hydrolyzed (Bentouhami et al., 2004) with Gd^{3+} as the Gd ion.

$$Gd^{3+} + 3H_2O \rightarrow Gd(OH)_3 + 3H^+ \tag{3}$$
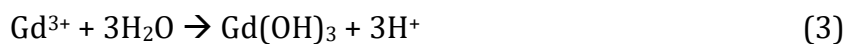
Gd^{3+} ions are not hydrolyzed below pH 7, which means Gd metals will continue to be extracted until the pH reaches the optimum value. After the pH of the aqueous phase ≥ 7, the extraction efficiency of Gd will decrease due to the hydrolysis reaction of Gd metal ions

(Kuila and Kundu, 2018). In this study, the variation of the feed pH was not raised to near 7 because precipitate is formed when the aqueous phase nears pH 5. The aqueous phase with pH 3 was chosen as the optimum condition for extraction based on the Gd-Y separation factor value, which was 0.9066.

3.4. Variation of Feed Concentration

Increasing feed concentration led to proportional increases in the distribution coefficient value, as shown in Figure 4a, and the distribution coefficient tended to decrease when the feed concentration was over 150,000 ppm due to the saturation of the organic phase, so that the diffusion of elements into the organic phase was reduced. By increasing the feed mass while the Cyanex 572 concentration remains constant, the amount of extraction will decrease.

The highest separation factor was achieved at the feed concentration of 150,000 ppm, at which the obtained separation factor of Gd-Y was 3.548 and that of Gd-Dy was 1.102, as shown in Figure 4b. Increasing feed concentration was proportional to the separation factor. According to the Le Chatelier principle, when the concentration of one part (reactant or product) is increased, the reaction tends to shift toward the part that is not increased, causing the value of the separation factor to tend to rise. However, when feed concentrations are more than 150,000 ppm, the separation factor value decreases because the organic phase is saturated.
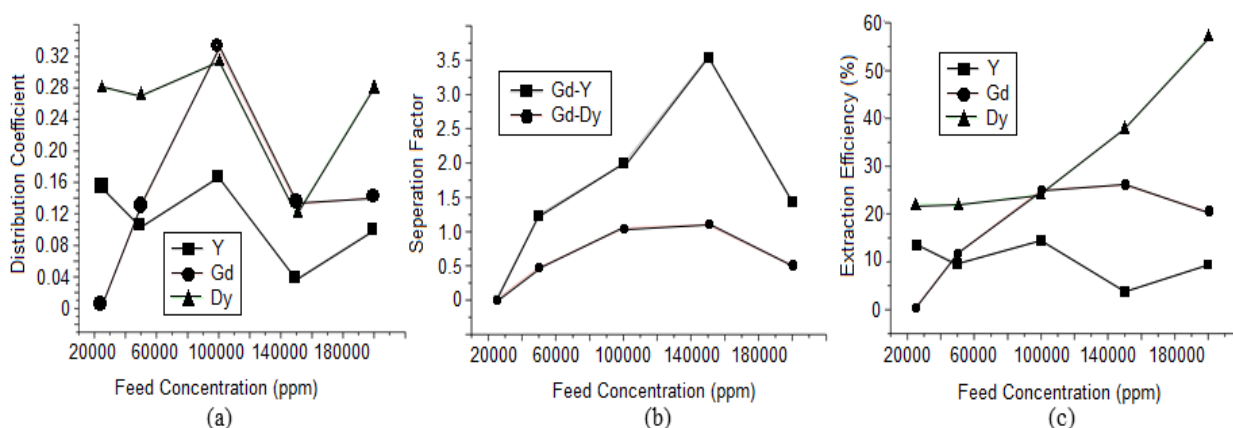
Figure 4 Correlations of feed concentration to: (a) distribution coefficient; (b) separation factor; and (c) extraction efficiency of Y, Gd, and Dy
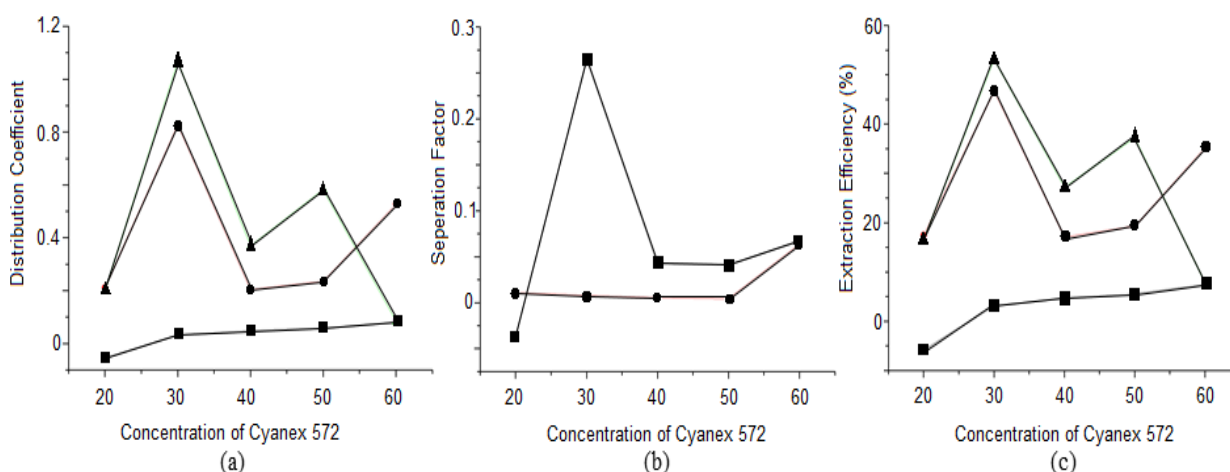
Figure 4c shows that the extraction efficiency tended to increase as the feed concentration increased. One factor that greatly influences the rate of mass transfer from the aqueous phase to the organic phase is the concentration of solute in the feed solution, which can be explained by Fick's law. The concentration variable is directly proportional to the rate of mass transfer; the greater the concentration, the greater the rate of mass transfer. As a result, the extraction efficiency value increases as the feed concentration increases (Ding et al., 2007).

3.5. Variation of Cyanex 572 Concentration

The increase in the distribution coefficient achieved by raising the Cyanex 572 concentration from 20% to 30% as shown in Figure 5a is quite significant because the higher the concentration of solvent, the more ion exchange with the metal will happen. Increasing Cyanex 572 concentration will increase the number of phosphinic and phosphonic acid molecules in the dodecane solvent and the number of POOH groups in the

solution, so that the bound Gd and Dy metals will increase and the distribution coefficient will also increase. A Cyanex 572 concentration of over 30% will decrease the distribution coefficient because phosphinic acid compounds form dimers in the organic phase (Belabassi et al., 2008). The formation of dimers is triggered by the presence of hydrogen bonds and can cause the solvent performance to decrease in metal binding in high-solvent concentrations.

A significant separation factor increases occurred as the Cyanex 572 concentration increased because more POOH groups will bind Gd metal, but the separation factor decreased as the Cyanex 572 concentration exceeded 30%, as shown in Figure 5b. The separation factor result with the Cyanex 572 concentration at 60% was lower than when the Cyanex 572 concentration was at 30% because the aqueous phase approached the saturation point. Increasing the Cyanex 572 concentration beyond the optimum concentration will not increase the separation factor further. The value of the Gd-Y separation factor reached 26.48, while the Gd-Dy only reached 0.7800. Thus, Cyanex 572 is better used for the separation of Gd from Y.

Figure 5 Correlations of the concentration of Cyanex 572 to: (a) distribution coefficient; (b) separation factor; and (c) extraction efficiency of Y, Gd, and Dy

Figure 5c shows that the Cyanex 572 concentration was inversely proportional to the extraction efficiency. The extraction ability reached its optimum state after reaching a certain concentration because with a higher solvent concentration, the movement of solute from the aqueous phase to the organic phase becomes more difficult, which can be explained by the Stokes-Einstein equation. According to the Stokes-Einstein equation, diffusion is inversely proportional to the solvent viscosity, and with greater solvent viscosity, diffusion from the aqueous phase into the organic phase becomes more difficult, thereby reducing the extraction efficiency. In order to reduce the solvent viscosity, dodecane solution is used (Effendy et al., 2017) because it does not react to Cyanex 572 and is considered safer and relatively non-toxic in terms of dodecane profile in MSDS.

Figure 5c shows that the extraction efficiency values of Y, Dy, and Gd were 3.119%, 53.007%, and 46.662%, respectively, with Dy having the highest extraction efficiency. The extraction efficiencies of REEs using Cyanex 572 were reported by Wang et al. (2015) to be in the following order: La < Ce < Pr < Nd < Sm < Eu < Gd < Tb < Dy < Er < Lu, which is consistent with decreasing ionic radii. In addition, Aziz (2017) stated that this result was due to the electronegativity of elements. Elements with greater electronegativity will bind more easily to a solvent. The electronegativity value of Dy is 1.22, while that of Gd is 1, so we assumed that Dy would bind more easily to solvent or be more stable in Cyanex 572.

4.   Conclusions

Based on the results of the present research, the optimum conditions for the separation of Gd from yttrium concentrate were obtained at a 30-minute stirring time, a 250-rpm stirring rate, a feed concentration of 150×10^3 ppm with pH 3, and a 30% Cyanex 572 concentration. The distribution coefficient values of Y, Gd, and Dy of about 0.031, 0.827, and 1.060, respectively. The separation factor value of Gd-Y was 26.482, while that of Gd-Dy was 1.5276. The extraction efficiency values of Y, Dy, and Gd were 3.119%, 53.007%, and 46.662%, respectively.

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