



## Characteristics and Performance of Cerium Extraction from Cerium Hydroxide Concentrate using Tri Butyl Phosphate

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**Abstract.** This study aims to develop a liquid-liquid equilibrium model to predict the Ce distribution in the extraction system based on experimental laboratory data. Extraction feed solution (Ce hydroxide in nitric acid media) and solvent (Tri Butyl Phosphate (TBP) in kerosene diluent) with a volume ratio of 1:1 at various concentrations of feed and solvent were contacted using a mechanical shaker at 150 rpm for 15 minutes. The solution was settled for 30 minutes to separate the aqueous and organic phases. Cerium concentration in the aqueous phase was analyzed using XRF, while cerium concentration in the organic phase was calculated using a mass balance. The results showed that the extraction of Ce from the Ce-hydroxide concentrate was successfully carried out using TBP 0.92 M in kerosene diluent so that the Ce extraction efficiency of 70% was obtained. The equilibrium model that has been developed was able to represent the phenomenon of the liquid-liquid equilibrium distribution in the extraction system, which was carried out with an average relative error of 8.53%. Five stages of extraction unit need to apply to achieve 90% of extraction efficiency.

**Keywords:** Cerium; Equilibrium; Extraction; TBP

### 1. Introduction

The availability of monazite minerals in Indonesia can be found in the Bangka Belitung and West Kalimantan regions. The volume of REE deposits reached 0.0023% of the total area of Bangka Belitung ([Ministry of Energy and Mineral Resources Republic of Indonesia, 2017](#)). The by-product of tin mining processing has so far not been utilized optimally. Research on the separation of REE from mining ore has been done a lot. Previous researchers have succeeded in developing solid-liquid extraction methods up to

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adsorption (Ji *et al.*, 2022; Trinopiawan *et al.*, 2020; Kusrini *et al.*, 2020; 2019; 2018).

Monazite, as a by-product associated with tin mining, is a radioactive mineral because it contains uranium (U) and thorium (Th). The method of removing U and Th involves a reasonably long process to obtain REE hydroxide (REOH) (Setiawan, Anggraini, and Sunanti, 2020; Migdisov *et al.*, 2019).

Generally, the separation of Ce from REOH is carried out by oxidation of Ce(III) to Ce(IV) and selective dissolution of trivalent REE (McNeice, Kim, and Ghahreman, 2020; Pusporini, Amiliana, and Poernomo, 2020; Li *et al.*, 2019; Ferdowsi and Yoozbashizadeh, 2017; Bulfin *et al.*, 2013). However, this technique results in low-purity products. Therefore, advanced separation and purification methods are still required. The Ce product resulting from the selective dissolution of REOH is a Ce-hydroxide concentrate which still contains other REE such as yttrium (Y), lanthanum (La), praseodymium (Pr), neodymium (Nd), promethium (Pm), and samarium (Sm). The separation of Ce from these elements can be done by liquid-liquid extraction. This method is easily applied with high selectivity in separating identical chemical properties of the elements (Neves *et al.*, 2022; Dan, Ji, and Deqian, 2014).

The concept of separating Ce from other elements is carried out by forming Ce-complex in the organic phase. Various studies have been conducted to determine the effectiveness of organic solvents such as Tri Butyl Phosphate (TBP), di-(2-Ethylhexyl) 2-Ethylhexyl phosphate (DEHEHP), di-2(2-Ethylhexyl) phosphate (D2EHPA), and Cyanex923 in the extraction process of Ce from other REE (Li *et al.*, 2018; Kuang *et al.*, 2017; Formiga and de Morais, 2016; Cheremisina *et al.*, 2015; Dan, Ji, and Deqian, 2014). The results showed that TBP was the most efficient solvent used in the industry to extract Ce from HNO<sub>3</sub> media (Dan, Ji, and Deqian, 2014).

Most organic solvents have high specific gravity and viscosity, so it is not easy to cause the solute transfer process from the aqueous phase to the organic phase. To simplify the process, the viscosity of the organic phase must be lowered by adding an organic diluent such as benzene, kerosene, and n-hexane (Hu *et al.*, 2022; Tang *et al.*, 2022; Shekaari, Zafarani-Moattar, and Mohammadi, 2020). Neither benzene nor n-heptane is inert. In addition, benzene and n-heptane are very volatile, toxic, and smelly, so they require special handling in terms of safety. It is different from kerosene diluent, which is inert, low volatility, and odorless.

The phenomenon of liquid-liquid equilibrium in a hybrid system involves interactions between the components. Mathematical models based on stoichiometry and non-stoichiometry to predict the distribution of neodymium (Nd) and yttrium (Y) in the extraction system with HNO<sub>3</sub> media and D2EHPA solvent have also been developed. The stoichiometric model was developed based on the reaction mechanism by considering the reaction coefficient. In contrast, the non-stoichiometric model is formulated by considering the phase equilibrium and chemical thermodynamics phenomenon. The non-stoichiometric model can describe the equilibrium phenomenon well (mean relative error is less than 10%) and is relatively simple (Pusporini *et al.*, 2021).

This study aims to develop a liquid-liquid equilibrium model that can represent the distribution of Ce in the Ce extraction system from the Ce-hydroxide concentrate. The equilibrium model was developed through a thermodynamic approach based on phase and chemical equilibrium. The simulation results were then validated with laboratory research data at various concentrations of feed and solvent. The results of this study can be applied to determine the number of mixer settler stages.

## 2. Methods

### 2.1. Materials and Equipment

The primary material used in this study was the Ce-hydroxide concentrate leached from REOH monazite, HNO<sub>3</sub> solution (Merck, 65% w/w concentration), Tri Butyl Phosphate (Sigma Aldrich, 97%), and kerosene from Fischer Chemical. X-ray Fluorescence (XRF) using Ortec 7010 series. The composition of the Ce-hydroxide concentrate is shown in Table 1. Based on X-ray Fluorescence (XRF) using Ortec 7010 series analysis, the primary components in this sample were Ce, La, and Nd, with concentrations of 72.923%, 3.088%, and 6.081%, respectively. The cerium dominates the REE contents. Monazite contains REEs with the largest element being Ce 18%, in the form of a 37.32% phosphate compound (Setiawan, Anggraini, and Sunanti, 2020). Monazite was decomposed and separated from the radioactive elements and phosphates to obtain REOH with the composition Ce 30%, La, 20%, Nd 14%, Y 1.7%, Sm 1.1% and Gd 0.22%. Separation of Ce from other REEs is by leaching REOH using dilute nitric acid. The Ce is insoluble and most of the Ce is in the solid residue, while the other REEs are mostly soluble according to the composition in table 1. A small number of other REEs are still left in the residue because the dilute nitric acid used has not dissolved all the REEs present.

**Table 1** The composition of Ce-hydroxide concentrate leached from REOH monazite

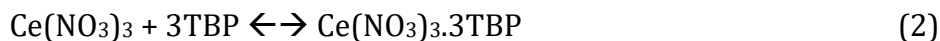
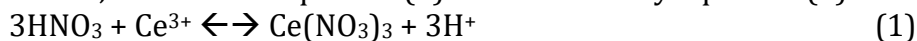
Compound	Si	p	Cl	Ca	Y	Sn	Te	La	Ce	Pr	Nd	Pm	Sm
Percentage, %	0.402	0.298	0.590	0.148	0.981	0.209	0.117	3.088	72.923	1.399	6.081	0.318	0.230

### 2.2. Method

The extraction process begins with a feed solution production, a dissolving Ce-hydroxide concentrate in HNO<sub>3</sub> (the S/L was 120 g/L). The effect of HNO<sub>3</sub> concentration, Ce concentration in feed solution, and solvent concentration were evaluated to investigate the effect of those parameters on the efficiencies of Ce extraction using liquid-liquid extraction. The concentration of Ce in the feed solution varied from 63.55 g/L to 86.75 g/L, analyzed using XRF, while the HNO<sub>3</sub> concentration ranged from 3M to 7 M. The feed and solvent solution (TBP in kerosene) with a volume ratio of (FA:FO) 1:1 was added to the Erlenmeyer. TBP concentration variation in kerosene varied from 5% to 25% (or 0.18 M to 0.92 M). The Erlenmeyer was shaken using a mechanical shaker at a speed of 150 rpm for 15 minutes. Then the mixture was allowed to stand for 30 minutes so that the aqueous and organic phases were separated. The aqueous and organic phases are separated using a separatory funnel, and then the final volume of each step is measured. The Ce concentration in the aqueous phase was analyzed using XRF. While the concentration of Ce in the organic phase was calculated using a mass balance.

### 2.3. Theory

The extraction process of the elements by using a neutral organophosphorus solvent follows the solvation reaction mechanism as the extraction of Ce in HNO<sub>3</sub> media using TBP (Xie *et al.*, 2014; Gagliardi and Cashion, 2012). The mechanism is assumed to take place as a pseudo-single-step reaction, as stated in equation (1) and followed by equation (2).



The assumptions used to formulate a mathematical model for the distribution of Ce at equilibrium are 1) the organic phase and the aqueous phase are insoluble; 2) TBP solvent is only present in the organic phase; 3) no third layer is formed, and 4) the feed solution is

conditioned as a dilute solution so that the Ce only interacts with TBP thus the result is Ce pure equilibrium.

A mathematical model is a thermodynamic approach based on phase and chemical equilibrium. This model focuses on an equilibrium between free Ce and Ce complex in the organic phase, as described in equation (3). As a form of simplification, chemical equilibrium can be expressed as an analogy to phase equilibrium (Pusporini *et al.*, 2021; Wiratni, Tyoso and Sediawan, 2001). The expression is stated in equation (4). The number of complexes formed depends on the number of free elements in the organic phase. This relationship is indicated in equation (5). Furthermore, the equilibrium constant is also estimated to be influenced by the solvent concentration, as shown in equation (6).

$$C_{Ce,tot(org)} = C_{Ce(org)} + C_{Cekomp} \quad (3)$$

$$K_{fCe} = \frac{C_{Ce,tot(org)}}{C_{Ce(aq)}} \quad (4)$$

$$K_{Cekomp} = \frac{C_{Cekomp}}{(C_{Ce(org)})^\alpha} \quad (5)$$

$$K_{Cekomp} = K_{TBP}(C_{TBP})^\beta \quad (6)$$

Substitute equations (4), (5), and (6) into equation (3) to obtain the distribution equation for Ce in equilibrium, as shown in equation (7).

$$\left( \frac{C_{Ce,tot(org)}}{C_{Ce(aq)}} \right)_{data} = \left( K_{fCe} + K_{TBP}(C_{TBP})^\beta (K_{fCe})^\alpha (C_{Ce(aq)})^{\alpha-1} \right)_{model} \quad (7)$$

Which  $C_{Ce(aq)}$  is the concentration of free Ce in the aqueous phase (M),  $C_{Ce,tot(org)}$  is the total Ce concentration in the organic phase (M),  $C_{Ce(org)}$  is the concentration of free Ce in the organic phase (M),  $C_{Cekomp}$  is the concentration of Ce complex in the organic phase (M),  $C_{TBP}$  is the total TBP concentration (M),  $K_{fCe}$  is Ce phase equilibrium constant,  $K_{Cekomp}$  is equilibrium constant defined in equation (5),  $K_{TBP}$  is the equilibrium constant defined in equation (5),  $\alpha$  is the constant defined in equation (5), and  $\beta$  is the constant defined in equation (6).

The value of  $C_{Ce(aq)}$  and  $C_{TBP}$  are the measurement data in the study. Then the value of  $C_{Ce,tot(org)}$  is obtained from the mass balance calculation. Meanwhile, the value of  $K_{fCe}$  is obtained from a separate experiment, which extracts kerosene without TBP. While the value of  $K_{TBP}$ ,  $\alpha$ , and  $\beta$  are evaluated by minimizing the Sum of Squared Errors (SSE) according to equation (8). Furthermore, the deviation between the data and the modeling results is expressed in the average relative error, as stated in equation (9).

$$SSE_i = \sum \left[ \left( \frac{C_{Ce,tot(org)}}{C_{Ce(aq)}} \right)_{data} - \left( \frac{C_{Ce,tot(org)}}{C_{Ce(aq)}} \right)_{model} \right]^2 \quad (8)$$

$$\text{Average relative error} = \frac{\left| \frac{\left( \frac{C_{Ce,tot(org)}}{C_{Ce(aq)}} \right)_{data} - \left( \frac{C_{Ce,tot(org)}}{C_{Ce(aq)}} \right)_{model}}{\left( \frac{C_{Ce,tot(org)}}{C_{Ce(aq)}} \right)_{data}} \right|}{\text{number of data}} \times 100\% \quad (9)$$

### 3. Results and Discussion

#### 3.1. Extraction System Study

Cerium dominates the REE content in the Ce-hydroxide sample, as mentioned in Table 1. Other REE elements, such as Y, La, Ce, Nd, Pr, Nd, Pm, and Sm, are still in the sample at low concentrations. This phenomenon indicated that the leaching method was not selective enough for extracted Ce; therefore, other procedures, such as liquid-liquid extraction, were needed to purify Ce.

The Cerium from Ce-hydroxide was extracted by mixing an amount of feed solution from nitric acid media containing Ce solute with a solvent of TBP in kerosene diluent. The nitric acid was media to initiate the formation of the Ce complex based on the reaction shown in equation (2).

$$E_{Ce} = \frac{mass_{Ce,tot(org)}}{mass_{Ce(feed\ solution)}} \times 100\% \quad (10)$$

The successful indicator of the extraction process can be seen from the extraction efficiency. The extraction efficiency is expressed as the mass percentage of solute that moves to the organic phase, as shown in equation (10).

This research studied Ce extraction, in which the distribution in the aqueous phase and the organic phase was predicted to have reached an equilibrium condition. An equilibrium condition is achieved when there is no mass transfer from the aqueous phase to the organic phase, and instead, the amount of solute in the aqueous and organic phases remains constant. The REE extraction using neutral organophosphorus such as TBP, takes 15 minutes to reach equilibrium (Kuang *et al.*, 2017). Thus, if the extraction time is selected for more than 15 minutes, the amount of Ce extracted into the organic phase tends to be constant, so it is ineffective.

The stirring speed is regulated so that the contact between the feed solution and the organic solvent takes place optimally. A faster stirring speed would result in better extraction efficiency. However, it should also be noted that a quicker stirring speed could cause an emulsion to form. The emulsion makes the aqueous phase and organic phase hard to separate (Basuki *et al.*, 2020). Therefore, a stirring speed of 150 rpm was used in this research.

##### 3.1.1. The effect of HNO<sub>3</sub> concentration

The feed solution is the aqueous phase in the extraction process which consists of a dissolved component (solute) and diluent. In this study, Ce concentrate was the solute, while HNO<sub>3</sub> was the diluent. Extraction of Ce on HNO<sub>3</sub> media using TBP solvent will follow the solvation reaction mechanism. This mechanism is based on the solvent type and the acid concentration used. The reaction steps that occur in the extraction of Ce are shown in equations (1) and (2).

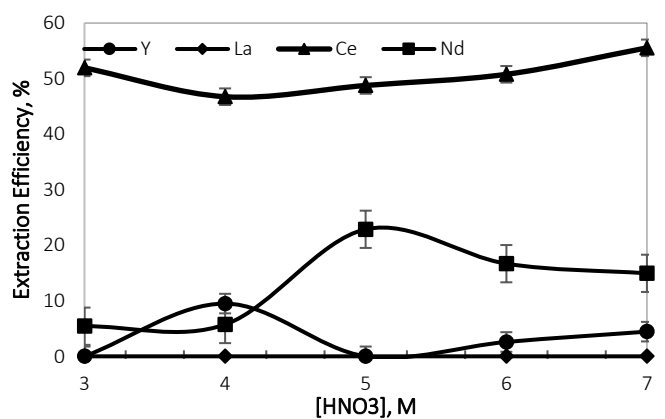
Nitric acid is used as an intermediate in forming complexes between solvents and metals, as shown in equation (2). On the other hand, the acid concentration influences the extraction process. Previous studies have stated that acidic conditions can cause phosphate ester solvents such as TBP to be degraded. The mechanism of TBP degradation occurs through acid hydrolysis and dealkylation. Acid hydrolysis of TBP only occurs at low acid concentrations (<2 M), and dealkylation occurs at high acid concentrations, resulting in bond breaking (Gillens and Powell, 2013). Tri Butyl Phosphate is degraded to form Di Butyl Phosphate (DBP) and, to a lesser extent Mono Butyl Phosphate (MBP). The presence of this product affects the performance of TBP as an extraction solvent. Di Butyl Phosphate (DBP) and Mono Butyl Phosphate (MBP) react with the extracted metal to form complexes or

precipitates which remain soluble in the aqueous phase of the nitrate. This phenomenon will reduce the effectiveness of extraction (Lamouroux *et al.*, 2000).

This research has studied the effect of HNO<sub>3</sub> on various concentrations of 3M to 7M on the effectiveness of the extraction of Ce and other REE using 15% TBP solvent, the ratio of the volume of feed solution and the solvent is 1, the extraction time is 15 minutes, and the stirring speed is 150 rpm. The effect of variations in HNO<sub>3</sub> concentration on the extraction efficiency of Y, La, Ce, and Nd can be seen in Figure 1.

The extraction efficiency of Ce at 3M to 7M HNO<sub>3</sub> concentrations tends to be stable even though at 4M HNO<sub>3</sub> concentrations, the Ce extraction efficiency is at its lowest point of 46.74%. However, in these circumstances, a sizable quantity of Y and Nd were removed to the organic phase. That was 9.49% for Y and 5.73% for Nd. The extraction efficiency of Nd tends to increase along with the high concentration of HNO<sub>3</sub>, but La in various conditions is not extracted.

Jorjani and Shahbazi (2016) conducted a study that studied the effect of HNO<sub>3</sub> concentration on the extraction efficiency of REE using TBP dissolved in kerosene (Jorjani and Shahbazi, 2016). Extraction was carried out at various concentrations of HNO<sub>3</sub> from 0.5M to 6.3M using TBP 3.65M, FA: FO ratio of 1:1, and extraction time of 5 minutes. In this study, it can be studied that at the higher concentration of HNO<sub>3</sub>, the extraction efficiency of Y, La, Ce, and Nd will decrease. However, it is not significant and tends to be constant. The difference between the study's results and the research conducted by Jorjani and Shahbazi (2016) is possibly due to differences in the material (concentrate) used.



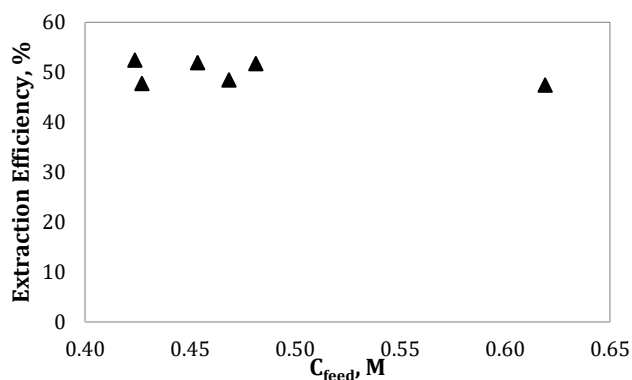
**Figure 1** The extraction efficiency of Y, La, Ce, and Nd at various concentrations of HNO<sub>3</sub> by using 15% of TBP-kerosene

Helaly *et al.* (2012) also conducted a similar study. Extraction was carried out at various concentrations of HNO<sub>3</sub>, namely 4M to 10M. The results showed that at concentrations of HNO<sub>3</sub> 4M to 5M, the extraction efficiency of Ce would increase, but at concentrations of HNO<sub>3</sub> above 5M, the extraction efficiency of Ce would decrease. The increase in the concentration of HNO<sub>3</sub> triggers a competition against TBP to form a complex so that the extraction efficiency of Ce decreases (Helaly *et al.*, 2012).

### 3.1.2. The effect of feed concentration

In the liquid-liquid extraction process, the solute in the aqueous phase will diffuse toward the organic phase. The high feed concentration will increase the value of the distribution coefficient because it provides a significant probability for solutes to be able to diffuse into the organic phase. This diffusivity value is directly proportional to the mass transfer rate; the more significant the diffusivity value, the greater the mass transfer rate. Fick's law can explain this phenomenon.

The effect of feed concentration on Ce extraction efficiency is presented in Figure 2. According to Fick's law, the higher the feed concentration, the higher the mass transfer rate from the aqueous phase to the organic phase, so that the extraction efficiency will increase. Under conditions of 15% solvent concentration, the effect of variations in Ce concentration in the feed from 0.42 M to 0.60 M on the extraction efficiency of Ce was studied. The highest Ce extraction efficiency occurred at a Ce feed concentration of 0.48 M, 52.62%. After the Ce concentration in the feed exceeds this value, the extraction efficiency decreases. This phenomenon is because TBP, which acts as an organic phase, has reached the limit for extracting elements in the aqueous phase.



**Figure 2** The cerium extraction efficiency at various feed concentrations and 15% of TBP-kerosene

Similar results were also expressed by Helaly *et al.* (2011), who, in their research, extracted cerium from the oxidized concentrate using TBP diluted in kerosene (Helaly *et al.*, 2012). The feed concentration is one of the variables studied, which varied from 20 g/L to 60 g/L in  $\text{HNO}_3$  media. The Ce extraction efficiency tends to increase along with the increase in feed concentration. However, after the feed concentration reached 40 g/L, the Ce extraction efficiency began to decrease.

### 3.1.3. The effect of solvent concentration

Solvent concentration is one of the things that affect the extraction process. The higher the solvent concentration, the higher the viscosity. The high solvent's viscosity will reduce the diffusivity, resulting in the extraction process's difficulty. This phenomenon can be explained through the Stokes-Einstein Law.

Extraction was carried out at concentrations of TBP-kerosene from 5% to 25% at 3M  $\text{HNO}_3$  concentration, and Ce concentration in feed was 0.6191M. The effect of TBP concentration on the extraction efficiency of REE elements, namely Y, La, Ce, and Nd, can be seen graphically in Figure 3.

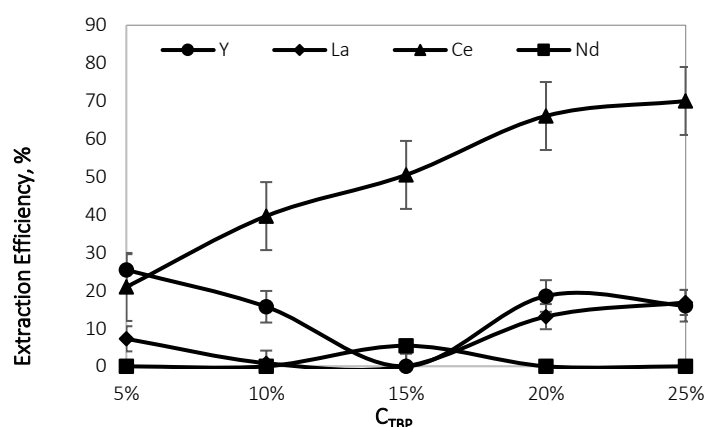
Figure 3 shows that a higher TBP concentration results in higher Ce extraction efficiency. The higher TBP concentrations cause the probability to form a complex increase. This phenomenon indicates that the solvent's ability to extract the elements is also increasing. The use of TBP concentrations over 25% or 0.92 M that provide maximum extraction efficiency is also limited by viscosity. The higher solvent viscosity will decrease the mass transfer from the aqueous phase to the organic phase. As a result, efficiency is reduced, as described in the Fick and Stokes-Einstein laws, as mentioned in other experiments (Jorjani and Shahbazi, 2016; Khan *et al.*, 2015; Helaly *et al.*, 2012).

The results are presented in Figure 1, and Figure 3 shows that the extraction efficiency of Ce is higher than the extraction efficiency of other REEs, namely Y, La, and Nd. This phenomenon indicates that the TBP is more selective in attracting Ce, which is in line with the research results of Li *et al.* (2019). It can be concluded that the best conditions for Ce

extraction from Ce-hydroxide concentrate are at a feed concentration of 0.62 M using 0.92 M or 25% of TBP concentration diluted in kerosene. In these conditions, the extraction efficiency of Ce has reached the highest value of 70.01%.

Table 2 shows that the methods used in this study are competitive enough to extract Ce compared to previous studies. The Ce extraction has also been done using other solvents, such as Cyanex 923 (Formiga and de Morais, 2016). The Ce extraction from Ce(III) concentrates in HNO<sub>3</sub> media using Cyanex 923 resulted in a Ce extraction efficiency of 100%. But the disadvantage of this solvent is the low selectivity to extract Ce only. In addition, this solvent also extracted La, Pr, and Nd with high extraction efficiency ranging from 98-99%.

The research data in Figure 1, Figure 2, and Figure 3 are further developed in the model of the equilibrium approach. The deviation of each model compared to the research data is expressed in relative errors as indicated in equation (8). While the overall deviation of model data to research data is described as a relatively average error, as shown in equation (9).



**Figure 3** The extraction efficiency of Y, La, Ce, and Nd at various TBP concentrations and 3M of HNO<sub>3</sub>

### 3.2. The Cerium Extraction Equilibrium Model

The equilibrium model is developed by applying the simplification that chemical equilibrium is an analogy to phase equilibrium. This model can estimate the distribution of Ce in the aqueous and organic phases. This model has also been used as an approximation for other similar equilibrium systems, thereby saving the research time. In the industrial field, this model is used to design a mixer settler.

The Ce distribution equilibrium model in various feed and solvent concentrations is solved using equation (7). The  $K_{fCe}$  value is obtained from the separate experiment without TBP. The depreciation of SSE resulted in the value of  $K_{TBP}$  is 13.3263,  $\alpha$  is 0.6963, and  $\beta$  is 1.1010.

$$\left(\frac{C_{Ce,tot(org)}}{C_{Ce(aq)}}\right) = 0.0317 + 1.2049(C_{TBP})^{1.1010}(C_{Ce(aq)})^{-0.3037} \quad (11)$$

The general equation describing the Ce distribution in this extraction system is shown in equation (11). The calculation results according to the data and model are presented in Table 2. Furthermore, the suitability between the model and data is graphically shown in Figure 4.

The equilibrium model that has been developed successfully represents the phenomenon of Ce extraction in the system. This phenomenon is measured by the average

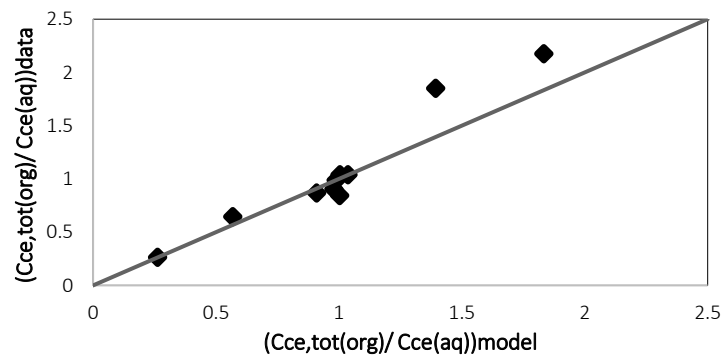


relative error value of the model compared to the data, which is still considered acceptable. Furthermore, it can be seen from the graphic visualization in Figure 4 that the data calculated using the model coincide with the diagonal line of the graph, which reflects the minimum deviation. The highest deviation occurred when the TBP concentration was 0.7352 M. This phenomenon is probably due to the higher system viscosity, so the non-ideality phenomenon needs to be considered when arranging the equilibrium model.

**Table 2** The calculation result and comparison of  $\left(\frac{C_{Ce,tot(org)}}{C_{Ce(aq)}}\right)_{data}$  and  $\left(\frac{C_{Ce,tot(org)}}{C_{Ce(aq)}}\right)_{model}$

$C_{TBP}$ (M)	$C_{Ce(feed\ solution)}$ (M)	$\left(\frac{C_{Ce,tot(org)}}{C_{Ce(aq)}}\right)_{data}$	$\left(\frac{C_{Ce,tot(org)}}{C_{Ce(aq)}}\right)_{model}$	Relative error (%)
0.1838	0.6191	0.2621	0.2621	0.00
0.3676	0.6191	0.6433	0.5682	11.68
0.5514	0.4536	1.0372	1.0043	3.17
0.5514	0.4685	0.9015	0.9799	8.69
0.5514	0.4813	0.9873	0.9880	0.08
0.5514	0.4271	0.8421	1.0028	19.09
0.5514	0.4237	1.0365	1.0365	0.00
0.5514	0.6191	0.8652	0.9088	5.04
0.7352	0.6191	1.8486	1.3936	24.61
0.9190	0.6191	2.1740	1.8341	15.64
Average Relative Error				8.80

The average relative error of the model to the data is 8.80%. This value is still relatively high, although still acceptable. The model simplifies the extraction equilibrium phenomenon so that non-ideality and interference from the environment are ruled out. The model is still helpful as an approach to existing phenomena.



**Figure 4** Deviation of  $\left(\frac{C_{Ce,tot(org)}}{C_{Ce(aq)}}\right)_{model}$  to  $\left(\frac{C_{Ce,tot(org)}}{C_{Ce(aq)}}\right)_{data}$

**3.3. Equilibrium Model Application**

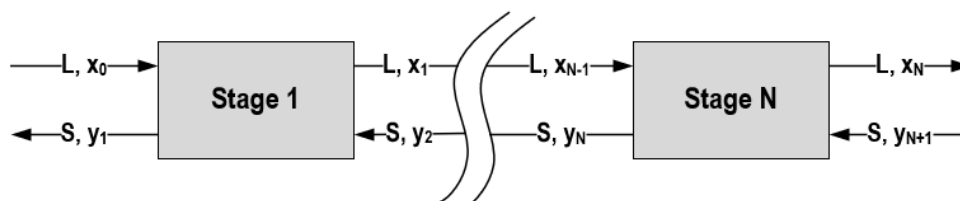
In this study, the feed solution used was conditioned as a dilute solution, so there was no interaction between Ce and other elements. The interaction that occurs is purely between each component and the TBP solvent. The resulting equilibrium model is pure Ce equilibrium. Thus, the equilibrium model can be used to predict the equilibrium phenomenon of Ce extraction with material such as Ce-hydroxide concentrates leached from REOH monazite.

$$(L \cdot x_{N-1} + S \cdot y_{N+1}) = (L \cdot x_N + S \cdot y_N) \tag{12}$$

$$y_N = 0.0317 + 1.2049(C_{TBP})^{1.1010}(C_{Ce(aq)})^{-0.3037} \tag{13}$$

Which  $L$  is the volumetric flow rate of the feed solution (L/hr),  $S$  is the volumetric flow rate of the solvent (L/hr),  $x$  is the Ce concentration in the aqueous phase (g/L),  $y$  is the Ce concentration in the organic phase (g/L), and  $N$  is the number of mixer settler stages.

As shown in equation (11), the equilibrium model can be widely used to predict the number of stages while designing the mixer settler. The equation is developed based on the mass balance for the multistage counter current mixer settler and the Ce equilibrium ( $y_N$ ) equation, as mentioned in equations (12) and (13), respectively. The equations (12) and (13) are then solved simultaneously to obtain the optimum mixer settler stages.



**Figure 5** Counter Current Extraction with Multistages Mixer Settler

The Ce extraction from Ce-hydroxide concentrate using TBP in a single stage can achieve extraction efficiency of up to 70%. Suppose the Ce concentration in the feed solution is 86.7540 g/L. In that case, the concentration of TBP is 20%, the volumetric ratio of feed solution to solvent is 1:1, and the extraction efficiency is desired to be 90% by entering these data and solving using equations (11) and (12) it is obtained that there are five stages of mixer settler needed. The Ce concentration in the aqueous and organic phase for each step of the mixer settler is presented in Table 3.

**Table 3** The Ce concentration for each stage of the mixer settler

No. Stage	$x$ , g/L	$y$ , g/L
1	72.1456	78.0860
2	53.7748	63.4702
3	33.0953	45.0994
4	13.8212	24.4199
5	1.4958	5.1458

#### 4. Conclusions

The Ce extraction from Ce-hydroxide concentrate leached from REOH monazite was successfully carried out using 0.92 M TBP in kerosene diluent so that the Ce extraction efficiency of 70.01% was obtained. The laboratory data is then used to develop the extraction equilibrium model to get a mathematical equation representing the Ce distribution phenomenon in the extraction system based on experimental laboratory data. The equilibrium model can describe the liquid-liquid equilibrium distribution in the extraction system, which is carried out with an average relative error of 8.53%. Five stages of mixer settler is needed to achieve 90% of separation efficiency.

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