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Simulation Solvent Extraction of Rare Earth Metal Source Origin from Marine Sediment

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Abstract. Ocean mining probably one of the world's largest untapped resources of rare earth elements. Specifically, the rare earth resources from polymetallic nodule which receive less attention from industry due to the various challenges. This article studied the simulation HDEHP-HCl system fractional cascade extraction strategy for extraction of rare earth elements from polymetallic nodule. HDEHP-HCl was capable of complete extract very high purity rare earth elements (99.9%). The fractional cascade extraction strategy simulation designed for the separation of rare earth elements could be momentous for practical application. The simulation data shows high purity of products at both outlets, aqueous and organic are obtainable. All these will provide the promising industrial applications of HDEHP-HCl system in extracting rare earth elements from polymetallic nodule with more fundamental data and guidance.

1. Introduction

Rare earth elements (REEs) are commonly extracted from primary ore via various techniques including selective oxidation, selective reduction, ion exchange, fractional crystallization, fractional precipitation and also solvent extraction (Gupta and Krishnamurthy 2005). The rare earth solvent extraction process is generally considered as the primary separation process, wherein REEs are separated from other elements by dissolving into solvent selectively. Nowadays most separation of REEs components from primary sources such as monazite, xenotime, and bastnaesite are done through solvent extraction.

The conventional method of acquiring the REEs is done through land mining but due to certain issues such as geopolitics, scarcity, etc, it is important to consider non-conventional mining which is one of them is ocean mining. Ocean mining is predicted will be the future trend of mining replacing depleted source from land mining. Seafloor could be the largest hidden untapped source of REEs on earth. Reported by (Takaya et al. 2018), deep-sea mud contains extremely rich rare earth elements including yttrium are found at the Pacific Ocean near Minamitorishima Island, Japan. The concentration of the REEs is estimated at up to 8000 ppm and contains low concentration of thorium and uranium made them are preferred to be extracted and separated. According to the Korea Institute of Ocean Science and Technology (KIOST), the seabed deposit are categorized into the polymetallic nodule, ferromanganese crust, deep-sea sediment and



seafloor massive sulfides (Pak et al. 2019). In this paper, the focus will be only on polymetallic nodule. Polymetallic nodule is a hard-solid mass sized small golf, formed by the accumulation of matter within a mass of sediment. Polymetallic nodule can be found in a deep water about 4500 to 6500 m on the abyssal plain (van Wijk et al. 2019).

Solvent extraction, also called liquid-liquid extraction, is an extraction route by the application of a solvent to separate the REEs from another compound. Solvent extraction has become an important extraction method, particularly for REEs in the context of a multi-component system because it is easily adaptable for continuous production while the mass transfer from phase to phase is readily accomplished (Suli et al. 2017). The basic principle underlying the solvent extraction is the concentration differences between solid and liquid that leads to diffusion of molecules diffuse from one another (Ahrens 2016). There are three components of the solvent extraction process: solid solute, insoluble solids, and solvent. The diffusion of the intra-particle soluble component controls the extraction rate. This method operates based on the solubility of REEs in water or solvent. The first step of solvent extraction is the separation of REEs from other elements through the leaching process. The REEs are dissolved in the aqueous solution or reagent, and a suitable extractant is used to extract the REEs from the reagent.

Solvent extraction basically comprised of three steps which are extraction, scrubbing or washing, and stripping. The basic principle of extraction through hydrometallurgy is to utilize the characteristic of metal ions where they distribute themselves between aqueous and organic solution, then extract the desired metal from organic solution and left the unwanted metal in the aqueous solution (Quinn, Soldenhoff, and Stevens 2017). Stripping or washing step is used to remove any impurities presence in the organic solution and improve purity of the desired element. Scrubbing solution is recycled back to the extraction and mixed with feed aqueous solution due to the scrubbing solution may contain valuable metals. Stripping step is the reverse to the extraction and it is used to transfer desired metal from pregnant organic solution to the stripping solution. In an extraction system, the feed is an aqueous solution and the extractant and modifier are organic solutions (Gupta and Krishnamurthy 2005).

The solvent extraction method is the main industrial process for REEs which involves two main steps – starting with the leaching process and followed by individual extraction of the targeted REEs. This method is simple, fast, wide-scoped and often applied for the processing of rare earth because it enables large volume processing. Due to this reason, the method is favourable at the industrial scale (Gupta and Krishnamurthy, 2005). In the solvent extraction process, an aqueous solution containing REEs will be in contact with the organic extractant.

Cascade solvent extraction is solvent extraction comprised of multi-stages of extraction in order to achieve the intended separation result (Wichterlová and Rod 1999). Cascade solvent extraction are categorized into few strategies which are cross-current extraction, counter-current extraction, fraction extraction and recirculating extraction (Zhang, Zhao, and Schreiner 2016). Counter-current and cross-current strategy extraction strategies are classic strategies of solvent extractions. Counter-current strategy is widely used compare to cross-current strategy. Counter-current extraction strategy limitation is the its inability to achieve high purity and high recovery simultaneously (Yang et al. 2015). Xu and co-worker had developed fractional solvent extraction strategy for REEs in early 1980. The strategy is very effective since it can achieve high purity and recovery at the same time.

Fractional solvent extraction strategy is carried out continuously and it is a multi-stage fractioning in a set of mixer settler known as batteries (Vázquez-Villegas, Aguilar, and Rito-Palomares 2015). First, REEs containing aqueous feed solution is mixed with an organic solvation agent to form complexes with REE ions. The solution then undergoes the stripping process where ions are extracted from the REE-enriched

organic phase by moving it into contact with an aqueous solution where the ions have higher solubility (Royen and Fortkamp 2016). Figure 1 shows the basic diagram for fractional solvent extraction where there are inlets and outlets for organic solution, feed solution, scrubbing stripping solution, and raffinate.

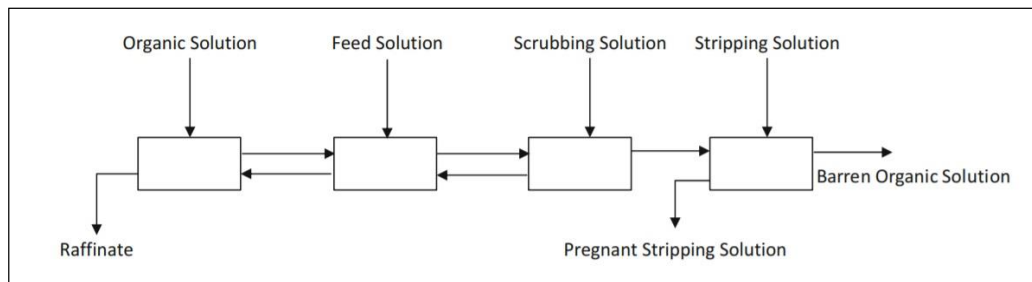


Figure 1. Basic Diagram for Fractional Solvent Extraction.
Source: (Zhang, Zhao, and Schreiner 2016).

2. Materials and Methods

2.1 Data

Data use in the development of the spreadsheet is acquired from Pak et al., 2019. As previously discussed there four types of marine cores which are polymetallic nodule, ferromanganese crust, deep-sea sediment and seafloor massive sulphides, but only data from polymetallic nodule was simulated and discussed in detail. The data for marine core type polymetallic nodule is as per table 1.

Table 1. Maximum rare earth elements in polymetallic nodule.

Rare earth element	Concentration (ppm)	Fraction (%)
La	248	9.65
Ce	1592	61.92
Pr	66	2.57
Nd	266	10.35
Sm	61	2.37
Eu	15	0.58
Gd	66	2.57
Tb	9	0.35
Dy	50	1.94
Ho	9	0.35
Y	133	5.17
Er	25	0.97
Tm	4	0.16
Yb	23	0.89
Lu	4	0.16

Source: (Pak et al. 2019).

2.2 Spreadsheet

The proposed method for simulation extraction of REEs from the polymetallic nodule through fractional extraction strategy as figure 2. The assumptions made during drafting the proposed method are;

- i) All the assumptions made during designing the proposed extraction processes are based on the Xu extraction principle (Zhang, Zhao, and Schreiner 2016).
- ii) The process was designed according to the fractional solvent extraction strategy.
- iii) All the calculations were done according to the work of Zhang, Zhao, and Schreiner 2016. Xu multi-stages cascade solvent extraction theory was used in designing the fractional extraction strategy of cascade solvent extraction. The fundamental of fractional extraction is illustrated by the Figure 3.

According to the theory, the purity of easily extractable and difficult solutes will be at organic and aqueous outlets respectively. The easily extractable and difficult solutes are denoted by A ($P_{An+m(o)}$) and B ($P_{B1(a)}$). A and B can be composed of several of REEs spectrum, for example A can be La-Nd while B is the rest remaining spectrum, Sm-Y. Notion a and b are representing the concentrating factor for solute A and B. Notion a is the ratio of A/B ratio in the organic outlet to the A/B ratio in the aqueous outlet. While notion b is representing the ratio of B/A in aqueous outlet to the ratio of B/A in feed. The purity of A and B at each outlet could be calculated through mass balance. Notions f'_A and f'_B are solutes fraction in the organic and aqueous outlets. $P_{An+m(o)}$ and $P_{B(n+m)(o)}$ are the purity of A and B at the organic outlets. While the extraction and scrubbing stages are denoted by n and m. Optimum equation method was applied to calculate the concentrating factor for A as major product as follow;

$$a = \frac{(P_{An+m(o)}) / (1 - (P_{An+m(o)}))}{(f_A / f_B)} \quad (1)$$

$$b = \frac{(a - Y_A)}{a(1 - Y_A)} \quad (2)$$

$$P_{A1(a)} = 1 - P_{B1(a)} \quad (3)$$

$$P_{B1(a)} = \frac{bf_B}{bf_B + f_a} \quad (4)$$

$$f'_A = \frac{f_A Y_A}{(P_{An+m(o)})} \quad (5)$$

$$f'_B = \frac{f_B Y_B}{P_{B1(a)}} \quad (6)$$

$$n = \log b / \log \beta E_M + 2.303 \log \frac{(P^*_{A(a)} - P_{A1(a)})}{(P^*_{A(a)} - P_{An(a)})} \quad (7)$$

$$P^*_{A(a)} = \frac{\beta E_M - 1}{\beta - 1} + \frac{(1 - E_M) \beta E_M P_{A1(a)}}{(\beta E_M - 1) + (1 - E_M)(\beta - 1) P_{A1(a)}} \quad (8)$$

$$m = \log a / \log \frac{\beta'}{E'_M} - 1 \quad (9)$$

To calculate the concentrating factor for B as major product as follow;

$$a = \frac{P_{B1(a)}/(1 - P_{B1(a)})}{(f_B/f_A)} \quad (10)$$

$$b = \frac{(b - Y_B)}{b(1 - Y_B)} \quad (11)$$

$$P_{B_{n+m}(o)} = 1 - P_{B1(a)} \quad (12)$$

$$(P_{A_{n+m}})_{(o)} = \frac{af_A}{af_A + f_B} \quad (13)$$

$$n = \log b / \log \beta E_M \quad (14)$$

$$m = \log a / \log \frac{\beta'}{E'_M} + 2.303 \log \frac{(P^*_{B(o)} - P_{B_{n+m}(o)})}{(P^*_{B(o)} - P_{B_{n(o)}})} \quad (15)$$

$$P^*_{B(o)} = \frac{\beta'/E'_M - 1}{\beta' - 1} + \frac{\beta'(1 - 1/E'_M)P_{B_{n+m}(o)}}{\beta' - E'_M + (E'_M - 1)(\beta' - 1)P_{B_{n+m}(o)}} \quad (16)$$

Type of feeding is important to understand because either the feeding is aqueous or organic will affect the whole extraction and scrubbing processes. Mixed average extraction factor for extraction (E_M) and scrubbing (E'_M), maximum extraction (S_o) and scrubbing (W_a) of solutes also could be determined through optimum equation method. Below is the formula to calculate the aqueous feeding variables.

$$\text{If } f'_B > \frac{\sqrt{\beta}}{\sqrt{\beta} + 1}, \text{ it is extraction control} \quad (17)$$

$$E_M = \frac{1}{\sqrt{\beta}} \quad (18)$$

$$E'_M = \frac{E_M f'_B}{E_M - f'_A} \quad (19)$$

$$S_o = \frac{E_M f'_B}{1 - E_M} \quad (20)$$

$$W_a = S_o - f'_A \quad (21)$$

$$\text{If } f'_B < \frac{\sqrt{\beta}}{\sqrt{\beta} + 1}, \text{ it is scrubbing control} \quad (22)$$

$$E'_M = \sqrt{\beta} \quad (23)$$

$$E_M = \frac{E'_M f'_A}{E'_M - f'_B}$$

Below is the formula to calculate the organic feeding variables.

$$\text{If } f'_B > \frac{1}{\sqrt{\beta} + 1}, \text{ it is extraction control} \quad (24)$$

$$E_M = \frac{1}{\sqrt{\beta}} \quad (25)$$

$$E'_M = \frac{1 - E_M f'_A}{f'_B} \quad (26)$$

$$S_o = \frac{E_M f'_B}{1 - E_M} \quad (27)$$

$$W_a = S_o + f'_B \quad (28)$$

$$\text{If } f'_B < \frac{1}{\sqrt{\beta} + 1}, \text{ it is scrubbing control} \quad (29)$$

$$E'_M = \sqrt{\beta} \quad (30)$$

$$E_M = \frac{1 - E'_M f'_B}{f'_A}$$

Task 1

The data collection and characterization are done by others since the data acquired from Pak et al., 2019.

Task 2

There are numerous solvent extraction systems available as discussed in the previous section, in this study HDEHP-HCl system was used in simulating the extraction of REEs spectrum from polymetallic nodule source.

Task 3

The separation factor of individual REE will be the crucial part in separating REES from each other. The larger the separation factor, the easier the REE to be separated and vice versa. Even though separation factor is very important, other factors such as rare earth distribution in the feed, feed mass flow rate, operation variables, process and equipment, the targeted REEs etc.

Task 4

At the Industrial separation facility, the REEs spectrum are not separated individually accordingly to the preferences but it is done by separating them into few fractions and commonly at initial step they are separated into HREE, MREE and LREE fractions (Yunus, Ismail, and Aziz 2018). Then each fraction is divided into sub-fractions according to the separation factor and finally separate individual REE. In this simulation, the whole separation process was divided into nine steps or circuit according to the rare earth elements extraction classification. The circuit proposed in this simulation is according to figure 5. Only Eu, Sm, Y, Dy, La, Ce, Pr, and Nd are extracted due to the amount of other REEs that are too small, make them are not economic viable.

LEVEL 1	Step 1:	Separation of MREO+HREO from the raw mat				
Feed		Name	SF	Types	Priority	Feed Comp
Aqueous	Element 1	La-Nd	5.36	A	Major	84%
	Element 2	Sm-Lu	3.54	B	Minor	16%

Background Information					
Elements:	La-Y				
SP	S.36				
Extraction Difficulty:	Categories	Components	Sep. Factor		
	A	La-Nd	5.36		
	B	Sm-Lu	3.54		
Feed:	Categories	Components	Fraction, %		
	A	La-Nd	84.48%		
	B	Sm-Lu	15.52%		
Target:	Categories	Components	Purity, %		
	Major	Sm-Lu	99.99%		
	Minor	La-Nd	0.01%		
Recovery:	Categories	Components	Percentage, %		
	A	La-Nd	99.00%		
	B	Sm-Lu	1.00%		
Main Procedures	A as Major Product (B1)				
Procedure 1:	Concentrating Factors				
	Variable	AQ Ext Cont.	AQ Scrub Cont.	ORG Ext Cont.	ORG Scrub Cont.
	$\beta=\beta'$	5.36	5.36	5.36	5.36
	$f_a=$	0.8448	0.8448	0.8448	0.8448
	$f_b=$	0.1552	0.1552	0.1552	0.1552
	YA	0.9900	0.9900	0.9900	0.9900
	YB	0.0100	0.0100	0.0100	0.0100
	$P A n+m(O)$	0.9999	0.9999	0.9999	0.9999
	$PB1(a)=$	0.9483	0.9483	0.9483	0.9483
	$PA1(a)=$	0.0517	0.0517	0.0517	0.0517
	$a=$	1836.8329	1836.8329	1836.8329	1836.8329
	$b=$	99.95	99.95	99.95	99.95
	$f_a=$	0.84	0.84	0.84	0.84
	$f_b=$	0.16	0.16	0.16	0.16
	$P an(a)$	0.16	0.16	0.16	0.16
$P *A_{(a)}=$	0.35	0.88	0.35	0.70	
Procedure 2:	Optimum Process Parameters				
	FEED:	Aqueous	Opt Criteria* =	0.698440919	scrubbing control
	Feed: Aqueous *IF $f/b < ((\beta)^{0.5}/((\beta)^{0.5}-1))$, THEN it follows scrub cont.				
	Feed: Organic *IF $f/b < 1/((\beta)^{0.5}-1)$, THEN it follows scrub cont.				
	Aqueous Feeding	AQ Ext Cont.	AQ Scrub Cont.	ORG Ext Cont.	ORG Scrub Cont.
	$E M$	0.431760328	0.9000	0.431760328	0.742651595
	$E' M$	-0.174500679	2.3161	3.906021915	2.316099778
	S_o (Extraction)	0.124273984	1.471989864	0.124273984	0.471989864
	W_a (Washing)	-0.7122	0.6355	0.288	0.636
	Procedure 3:	Number of Stages			
No. of stages (ext), n		6	4	6	4
No. of stages (scrub), m		#NUM!	8	23	8
Total no. of stages, t		#NUM!	12	29	12
Total no. of stages, t (based on Feed and control)	FALSE				

Figure 2. Fractional extraction strategy spreadsheet.

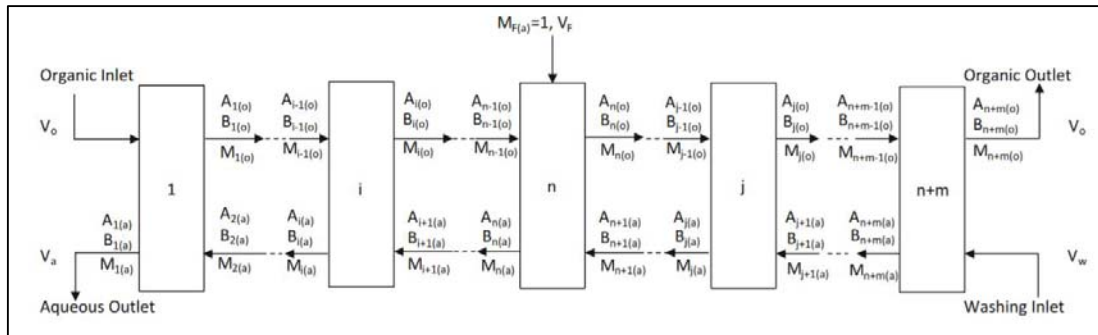


Figure 3. Concept of fractional extraction strategy.
Source: (Zhang, Zhao, and Schreiner 2016).

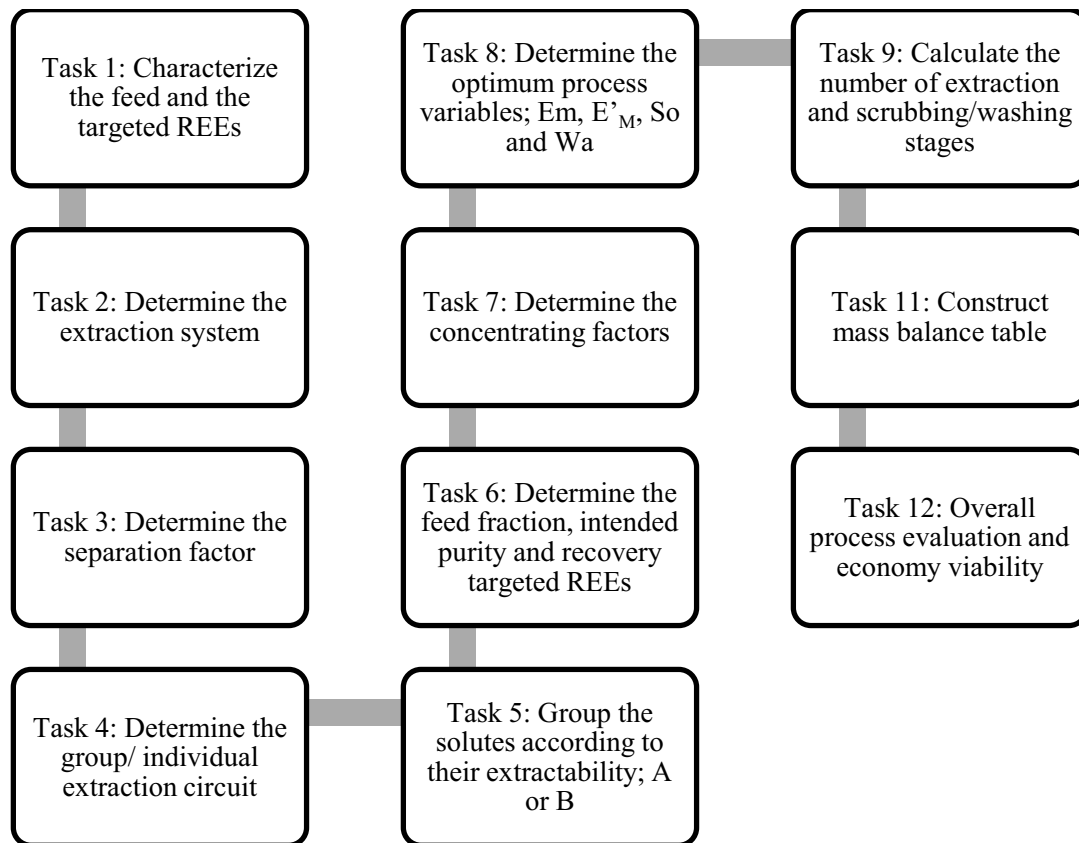


Figure 4. Principle Fraction Solvent Extraction Process.

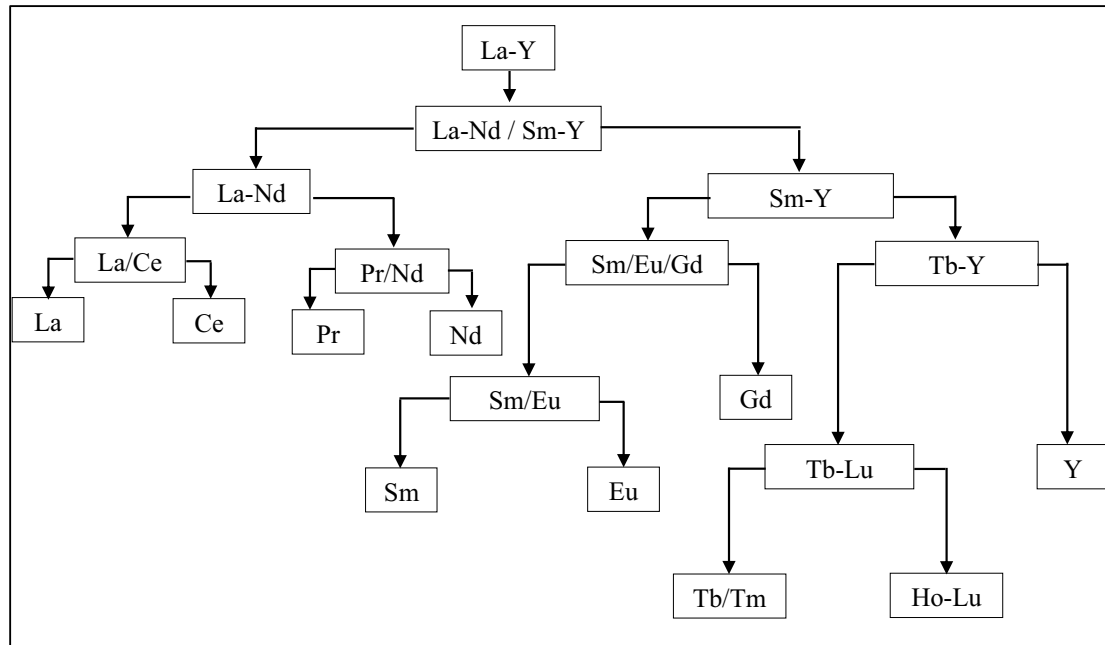


Figure 5. Fractional extraction circuit.
Source: (Zhang, Zhao, and Schreiner 2016)

Table 2 shows the fractional extraction strategy steps cover extraction of La, Ce, Pr, Nd, Dy, Y, Sm, and Eu. The first step LREE was separated from Ce-La-Pr-Nd from Sm-Eu-Gd-Tb-Dy-Ho-Er-Lu-Y. In the second step, MREE (Sm-Eu-Gd) was separated from HREE (Tb-Dy-Ho-Er-Lu-Y). Once step 2 completed, all the LREE, MREE and HREE were separated according to the separation factor. Step 2a onward was focusing on the sub-fractions of MREE by separating Gd from Sm-Eu. At step 2b, Eu separated from Sm. While at step 2c, Y separated from Tb-Lu. Step 2d, Dy separated from Tb-Lu. As mention earlier, other HREEs were left as residue due to the economic viability. Step 3 was intent to separate HREE into individual REE by separating them into La-Ce and Pr-Nd. Step 3a separated Pr from Nd, while step 3b separated Ce from La.

Table 2. Proposed fractional solvent extraction cascade steps.

Steps	Description	REE Involvement
1	Separation of MREE and HREE from the raw material	Ce-La-Pr-Nd/Sm-Eu-Gd-Tb-Dy-Ho-Er-Lu-Y
2	Separation of MREO from HREO	Sm-Eu-Gd/Tb-Dy-Ho-Er-Lu-Y
2a	Extraction of Gd from Sm, Eu	Sm-Eu/Gd
2b	Extraction of Eu from Sm	Sm/Eu
2c	Extraction of Y from Tb-Lu	Y/Tb-Lu
2d	Extraction of Dy from Tb, Ho-Lu	Dy/Tb-Ho-Lu
3	Separation of Nd/Pr from La-Ce	La-Ce/Pr-Nd
3a	Extraction of Pr from Nd	Pr/Nd
3b	Extraction of Ce from La	Ce/La

Task 6, 7 and 8

Each extraction step is defined by the separation factor, the REEs spectrum, content, purity and recovery intended element. The first key is the separation factor, the higher separation factor, the easier the element is extractable and vice versa. During extraction, solute easily extracted denoted by A and solute (s) difficult to extract is denoted by B. The amount of A and B (feed fraction) will determine the extraction process outcome and this is important to stress out due to the feed with majority fraction will be either at the aqueous or organic outlet. Then the intended purity and recovery for REEs are determined. The purity and recovery yield will determine the number of separation stages. Then determine the concentrating factors for each solvent extraction process. The concentrating factor variable is differing to each other depending on either the process is A majority or B majority. To calculate the concentrating factors, fractional extraction strategy can be divided into eight conditions as shows in the table 3 below.

Table 3. Fractional extraction strategy condition.

Condition	Type of feed	Type of process control	Majority fraction
1	Aqueous	Extraction	A
2	Aqueous	Scrubbing	A
3	Aqueous	Extraction	B
4	Aqueous	Scrubbing	B
5	Organic	Extraction	A
6	Organic	Scrubbing	A
7	Organic	Extraction	B
8	Organic	Scrubbing	B

Source: (Zhang, Zhao, and Schreiner 2016).

At the beginning of the process, the feed is aqueous but after separation, there will be two products at the aqueous outlet and organic outlet. These product at each outlet will be feed to next separation process. Once all the detail variables acquire, the average extraction factor in extraction (E_M), average extraction factor in scrubbing (E'_M), maximum extraction of solutes A and B (S_o), and maximum scrubbing of solutes (W_a) were calculated. From these data, process nature can be determined process is extraction control or scrubbing control.

Task 9

Finally, the stage number for extraction and scrubbing are determined. A MS-Excel spreadsheet developed to calculate the number of extraction and scrubbing stages as discussed previously.

Task 10 and 11

Flow ratio for each separation pathway or circuit are determined. The flow ratio is determined based on the relationship between rare earths mass flow rate and concentration. Flow ratio is the ratio of feed flow rate (V_F), organic flow rate (V_O), and scrubbing solution flow rate (V_W) or $V_F/V_O/V_W$. After flow ratios are determined, the data will be used to constructed material distribution and balance table. The purpose of material distribution and balance table is to summarize all process parameters, material balances, total rare earth and concentration in the two phases of each stage, flow ratio, etc. All these data are useful for process optimization purpose. There are two type of material distribution and balance tables which are dedicated to

the aqueous and organic outlets. Figure 3 show example of constructed material distribution and balance table.

Stage	1	2	3	4	5	6	7	8	9	10	11	12
$S_{(o)}$	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.47
Wa	0.64	0.64	0.64	0.64	0.64	0.64	0.64	0.64	0.64	0.64	0.64	0.64
$V_{(o)}$	5.88	5.88	5.88	5.88	5.88	5.88	5.88	5.88	5.88	5.88	5.88	5.88
$[M_{O_{(o)}}]$	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
$M_{F(a)}$	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
$[M_{F(a)}]$	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
fA	0.84	0.84	0.84	0.84	0.84	0.84	0.84	0.84	0.84	0.84	0.84	0.84
fB	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16
V_f	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
HA	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
V_w	0.96	0.96	0.96	0.96	0.96	0.96	0.96	0.96	0.96	0.96	0.96	0.96
$M_{(o)}$	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.47	0.84
$M_{(a)}$	0.16	0.16	1.64	1.64	0.64	0.64	0.64	0.64	0.64	0.64	0.64	0.64
$[M_{(o)}]$	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.14
$[M_{(a)}]$	0.08	0.08	0.84	0.84	0.08	0.33	0.33	0.33	0.33	0.33	0.33	0.33

Figure 6. Material distribution and balance table.

Task 12

The purposes of process evaluation are to determine the optimum separation process, and to identify process limitation.

3. Results and Discussions

The proposed cascade solvent extraction HDEHP-HCl system for polymetallic nodules case via fractional extraction strategy, which was applied to get high recovery and purity products at both aqueous and organic exit was demonstrated to evaluate the proposed method. Table 4 shows the result acquired by process simulation data from polymetallic nodule. To separate Pr, Nd, Ce, La, Sm, Eu, and Gd required total 406 stages comprising 231 and 175 stages of extraction and scrubbing respectively. At the beginning the process utilized the separation factor of LREE and mixture of HREE and MREE rather than individual REEs separation factor and two-outlet process to get LREE and mixture of heavy and middle two groups of rare earth concentrates. The process repeated to separate HREE and MREE. The LREE is further separated to get Pr/Nd and Ce/La, and finally acquired individual REEs spectrum. The result from table 3 shows that LREE and MREE are easier to be separated than HREE, this due to the number of REEs in the HREE are more than LREE and MREE. Also, the separation factor among the adjacent HREE members almost equal. In determine flow ratio, it is assumed $M_{F(a)} = 1 \text{ mol/min}$. Material distribution and balance table constructed for each separation circuit show that. In this article only case separation HREE and MREE from LREE is discussed due to the graph profile is almost similar to each circuit, only the values are different. All the parameter values are reflected by the table above.

Table 4. Process variables.

Step	Circuit	Number of stages			Flow ratio	
		Extraction	Scrubbing	Organic (mol/L)	Feed (mmol/min)	Scrubbing solution (mol/L)
1	Ce-La-Pr-Nd/Sm-Eu-Gd-Tb-Dy-Ho-Er-Lu-Y	4	8	5.88	1.00	0.96
2	Sm-Eu-Gd/Tb-Dy-Ho-Er-Lu-Y	31	13	7.68	1.00	2.34
2a	Sm-Eu/Gd	70	29	15.24	1.00	6.51
2b	Sm/Eu	56	20	21.35	1.00	9.20
2c	Y/Tb-Lu	13	39	13.46	1.00	4.07
2d	Dy/Tb-Ho-Lu	11	30	2.44	1.00	1.17
3	La-Ce/Pr-Nd	3	19	6.31	1.00	2.61
3a	Pr/Nd	24	9	8.15	1.00	2.75
3b	Ce/La	19	8	7.24	1.00	2.50

3.1 Case Separation HREE and MREE from LREE

The result of simulation using HDEHP-HCl system indicate potential for practical application of the system to extract the REEs spectrum. The main function of scrubbing is to increase the purity of the products at organic phase exit. The flowrate of scrubbing solution is usually low purposely to allow the REEs to get a complete exchange in the organic phase. LREE is considered as easier to be extracted as A, while mixture of HREE and MREE are more difficult to be extracted as B. The scrubbing acidity was settled at 2.0 mol/L. The purity of A group at organic exit of the last stage ($(P_{A_{n+m}})_o$) and B group at group at aqueous exit of the first stage $(P)_{B1(a)}$ are at 0.99 respectively. Through equations discussed above both extraction and scrubbing stages numbers were determined at four and eight stages respectively. The flow ratio of $V_F: V_O: V_W$ is resolved as 1:1.58:0.96. Specifically, 12 stages fractional extraction strategy simulation was done for the separation of LREE from mixture of HREE and MREE. As shows by figure 7, the final organic loading and mass flow rate of $[RE]_o$ reaches to 0.25 mol/L and 1.47 mmol/min throughout most of the stage only concentration of rare earth at aqueous increase from stage 1 to stage 3, this is extraction stage except for the last few ones because these stages are close to the scrubbing entrance at stage 12 with high acidity. The aqueous rare earth concentration $[RE]_{(a)}$ and mass flow rate $M_{(a)}$ are 0.84 mol/L and 1.64 mmol/min in extraction stages while 0.67 mol/L and 0.64 mmol/min in scrubbing stages.

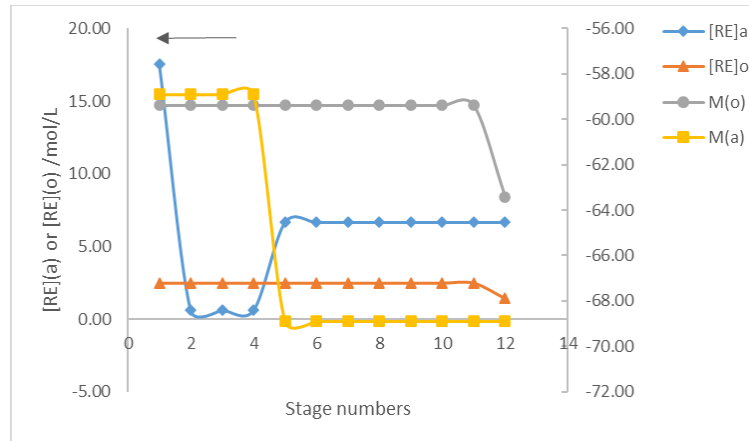


Figure 7. RE concentration at aqueous outlet and mass flow rate versus stages numbers.

3.2 Effect of scrubbing acid concentration

The simulation to evaluate the effect of acid concentration on the fractional extraction strategy on product collected at the aqueous outlet. The acid concentration at 1.0 mol/L, 2.0 mol/L, 4.0 mol/L, 8.0 mol/L and 10.0 mol/L were simulated as shows in the figure 8. The aqueous rare earth concentration [RE]a at acid concentration 1 mol L⁻¹ is 0.56 mol/L in extraction stage and 0.33 mol/L in scrubbing stage. As the acid concentration increased from 1.0 mol/L to 10.0 mol/L, the concentration of [RE]a also increased from 0.56 mol/L to 3.33 mol/L. The acid concentration is directly proportional to the concentration [RE]a. The simulation has limitation because at the certain point of acid concentration, the concentration of [RE]a will not change. To bear in mind, stripping acid will shorten the scrubbing stage numbers.

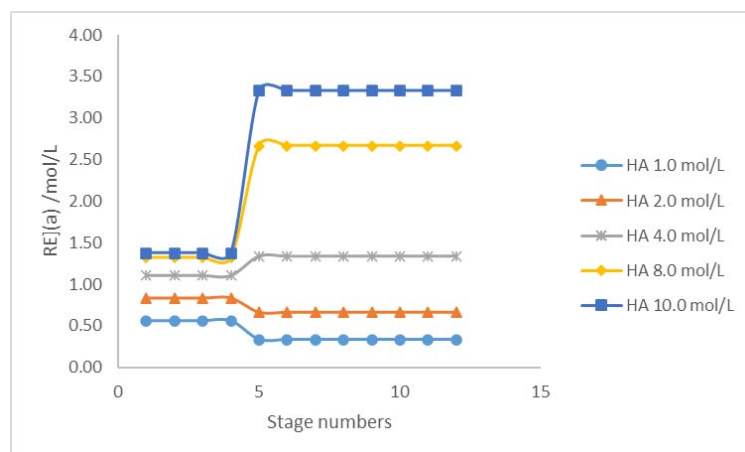


Figure 8. RE concentration at various acid concentrations.

3.3 Effect of feed mass flow

The graph Figure 9 show the relationship between feed mass flow (M_F), to the rare earth element concentration on the aqueous outlet, $[RE]_a$. It is observed that at all feed mass flow (M_F), the concentration rare earth concentration at extraction stages not much increase which is in between 0.56–1.38 mol/L. At the scrubbing stage, it was observed aqueous rare earth concentration $[RE]_a$ were significant increase which at 1.0 mmol/min, 2.0 mmol/min, 4.0 mmol /min, 8.0 mmol/min, and 10.0 mmol/min were 0.667 mol/L, 1.333 mol/L, 2.667 mol/L, 5.333 mol/L, and 6.667 mol/L, respectively. Feed mass flow (M_F) increase had significant effect on scrubbing stage than the extraction stage this due to the nature of the fractional extraction strategy. In the fractional extraction strategy, the feed is added at the n stage, at the end of extraction stage.

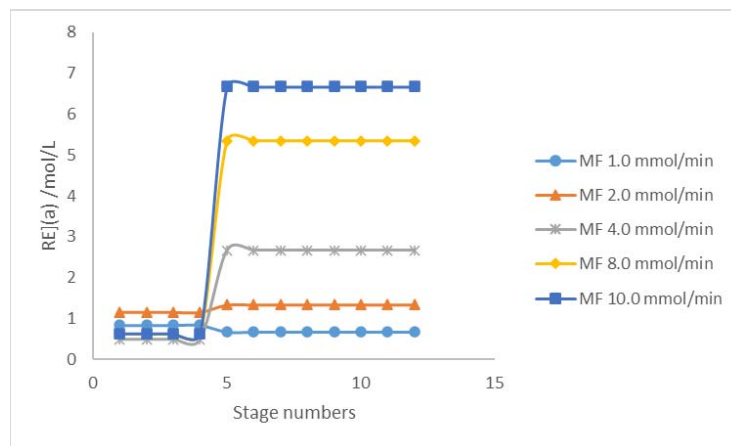


Figure 9. RE concentration at various feed mass flow rate concentrations.

4. Conclusions

From the test conducted, the range of kenaf fiber used has shown quite an improvement on the mechanical performance. On the abrasion test, 0.2% addition shows the lowest value on abrasion loss making it more durable to abrasion. While from the Marshall Stability test, the stability shows a significant value at 0.4% of Kenaf fibre addition, showing it has less air voids thus, increasing the pavement strength. Next, the stiffness of asphalt increases at 0.4% of Kenaf fibre presence showing that it improves the resistance and low temperature cracking of asphalt. For the density, 0.2% addition of fibre shows the highest density making it less exposed to premature pavement distresses. As for resilient modulus at 25 °C, it shows that the highest percentage of Kenaf fiber which is 0.6% gave the highest resilient modulus value. The higher the percentage of Kenaf, the higher the resilient modulus value. Based on the resilient modulus results that were obtained, it shows that the existence of natural fiber such as Kenaf fiber could influence the strength of pavement especially for low traffic. The same could be said for temperature of 40 °C. For dynamic creep test, at temperature of 40 °C, 0% of Kenaf fibre shows the lowest number of permanent strain while for 25°C, 0.60% addition of Kenaf fibre indicate lower permanent strain. This shows that, at lower temperature, the addition of Kenaf fibre in SMA could contribute in less permanent deformation. From the ranking table of each performance tests, Optimum fibre Content (OFC) is 0.3 %.

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