

Selection of Extractant in Rare Earth Solvent Extraction System: A Review

Nurul Ain Ismail, Mohd Aizudin Abd Aziz, Mohd Yusri Mohd Yunus, Anwaruddin Hisyam

Abstract: *The process of separation, extraction, and purification in obtaining rare earth metals from the minerals is a tedious work due to the similarity of the rare earth metals in chemical and physical properties. Besides designing the rare earth extraction sequence and removing the impurities, the selection step for the type of extractant is also a crucial phase. There are numerous possible combinations of extractant – metal in rare earth separation, ranging from single extractant system to multiple extractant systems. This paper aimed to guide and suggest the best extractant, subject to the leaching condition and the targeted end product. Each type of extractant is revised separately in providing the mechanism and interaction of the rare earth metals. This paper also evaluate the past and current trends of these extractants besides identifying their strong point and the drawbacks.*

Index Terms: DEHPA, EHEHPA, extractant, rare earth, solvent extraction

I. INTRODUCTION

From a mobile phone to the most advanced instrument in medicine and defense, it would be impossible to uphold the current modernize life without rare earth (RE) metals. With the increasing demands from the industries, the extraction and separation of RE become more and more important. Despite the fact that they are not completely rare, United States Department of Energy [1] and European Commission [2] have labelled the supply of these REs as ‘critical’ for their limited resource. Due to the uncertain market of RE, the Europe researchers have been desperately introducing various measures such as trade policies, industrial adjustment, and budget allocations in the member states in securing the RE supply [3].

The RE comprises 15 elements from the lanthanide series, plus yttrium, and scandium. These REs can be categorized by a variety of physical properties depending on the applications of the RE as functional materials such as 1) the double-salt solubility (light rare earth [LRE] and heavy rare earth [HRE]); and 2) the extractability with acidic extractants

(LRE, medium rare earth [MRE], and HRE) (Table 1). For the characterization of RE based on double salt solubility, RE are converted to double sulfate salt precipitated, $(\text{NaRE}(\text{SO}_4)_2 \times \text{H}_2\text{O})$ and tested for their solubility in the water. The LRE from this category showed a very low solubility in water. In the classification based on the extractability with an acidic extractant, the lanthanide group, from lanthanum to neodymium, is known as LRE. MRE consists of samarium, europium, and gadolinium, while HRE is a group from terbium to lutetium. Yttrium usually belongs to the HRE group, whereas scandium does not belong to any group. Scandium has significantly different chemical properties compared to the rest of the RE, and it is rarely found in the minerals. The latter category is more common to be used in the literature.

Table 1: Classification of REMs

Double salt solubility	
Light Rare Earth	Lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm) and europium (Eu)
Heavy Rare Earth	Gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), lutetium (Lu) and yttrium (Y)
Extractability with acidic extractant	
Light Rare Earth	La, Ce, Pr, and Nd
Medium Rare Earth	Sm, Eu, and Gd
Heavy Rare Earth	Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y

Considering their similarity in the chemical and physical properties, RE usually exist in mineral form, which make the separation process more challenging and expensive. The separation of RE into individual RE is crucial before they could be introduced into various products. Therefore, RE metallurgy is considered critical, and it has consistently been studied by researchers since the 1970s. Their aim is to improve the purity of the end product, whilst reducing the cost, time, and waste at a minimum level. RE metallurgy is designated to the continuous line of unit operation, dealing with mining, physical beneficiation, chemical treatment, separation, and refining process (Fig. 1). Overall, the combination of the processes able to transform the ore to a combination or individual metal that is either a transition or an end product converting them into metal, alloy, or another compound. This paper focuses on exploring the key factor contributing to the selection of the extractant in the separation process, especially via solvent extraction.

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II. SEPARATION PROCESS IN RARE EARTH METALLURGY

The central point of RE separation process is to convert the RE concentrate to a RE mixture which is either the end or an intermediate product for the following production of the individual RE. Usually, the process requires one or more reagent to break down the ore and leach the RE into a

solution. Once all the metal is in the solution, the separation process could be done either by solvent extraction (SX), ion-exchange, fractional precipitation, fractional crystallization or chemical precipitation. Type of minerals, the concentration of the RE in the concentrate and targeted end product are the main aspects need to be considered before choosing the separation process.

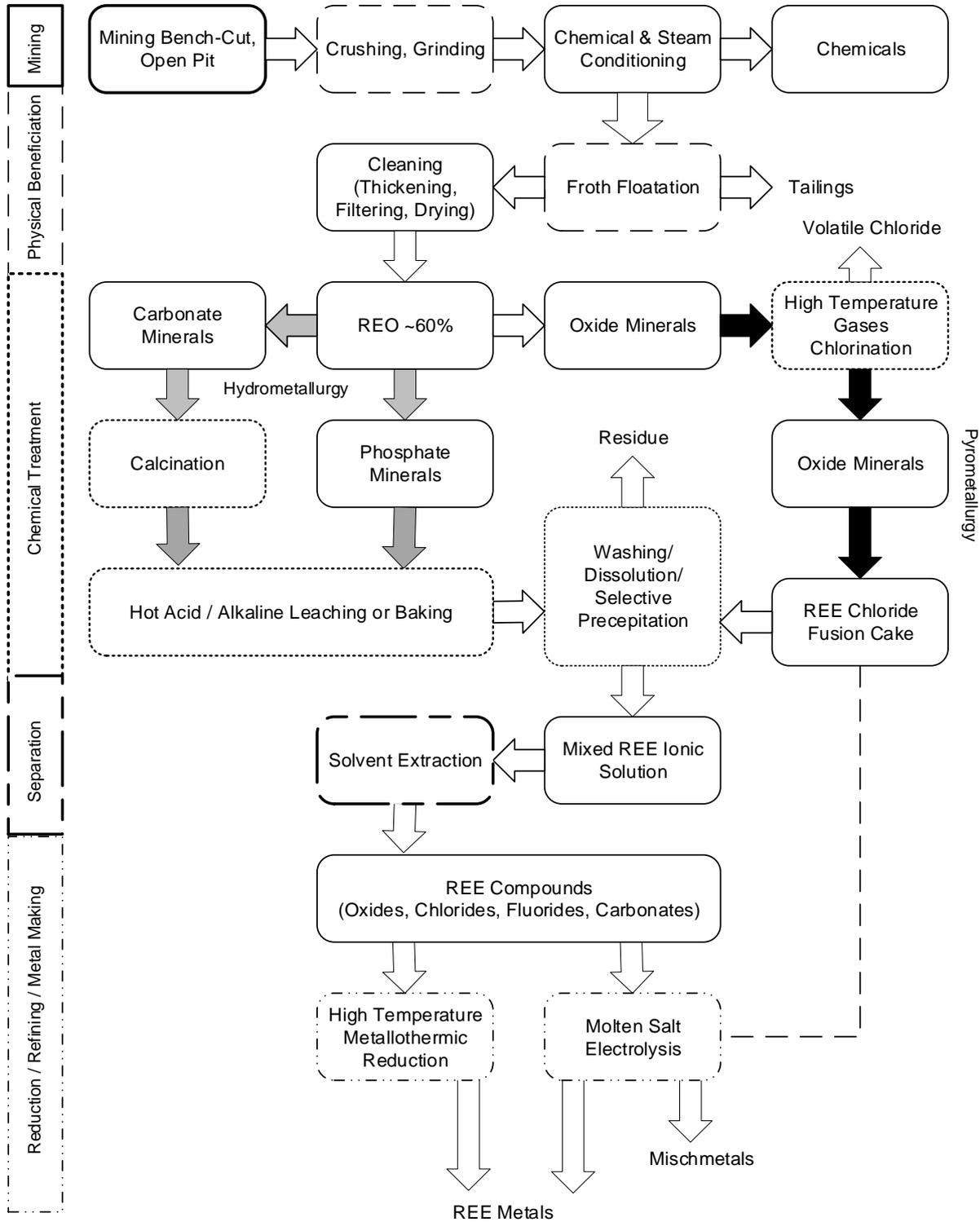


Fig. 1 Common rare earth metallurgy processing route

SX is the most commonly used technique in RE separation, especially in the industries due to its quick extraction process, large separation capability, and high extraction capacity. Apart from that, techniques such as fractional precipitation, ion exchange, and fractional crystallization were difficult to optimize due to the small difference in basicity [4]. Identical to ion exchange, SX incorporate the selective migration of a metal ion within two solutions. In the liquid-liquid extraction process, RE in the aqueous medium is attracted and captured by the extractant (in the organic phase) due to the chelating properties.

A. Fundamental of Solvent Extraction

Basic SX routine comprise extraction and stripping, and the process can be expanded to scrubbing, washing, and purification stages depending on the process requirement. An aqueous phase usually consists of an acid load with rare earth metals ($REM_a + REM_b$), which is mixed with an organic phase or “extractant” in the extraction stage. The REM of interest is denoted by REM_a , whereas the others are denoted by REM_b . Due to the REs’ abilities to separate themselves within aqueous and organic medium, some RE are carefully

moved into the organic phase. The extracted RE depends on the number of H^+ , and the highest number separates the lanthanide series further to the right part of the Periodic Table [5]. The extraction step is repeated over and over to enhance the separation of the REM_a towards REM_b . At the terminal stage, the remaining REM_b in the aqueous solution is channeled to raffinate and the extracted RE, that are mostly REM_a and some REM_b , are later sent to the scrubbing process. The scrubbing process is performed after the extraction process and carried out by adding water or diluted acid/base solution into the pregnant organic phase in removing any impurities or unwanted metals such as REM_b . This process could improve the purity of the desired metals. The organic phase contains only REM_a that are stripped by diluted acid or base, and then is recycled back to the extraction stage. The pregnant stripping solution leaves a stripping point with a high concentration of REM_a and it is recovered as REM_a oxide after a series of downstream processes. Fig. 2 shows the common process flow in a RE extraction circuit.

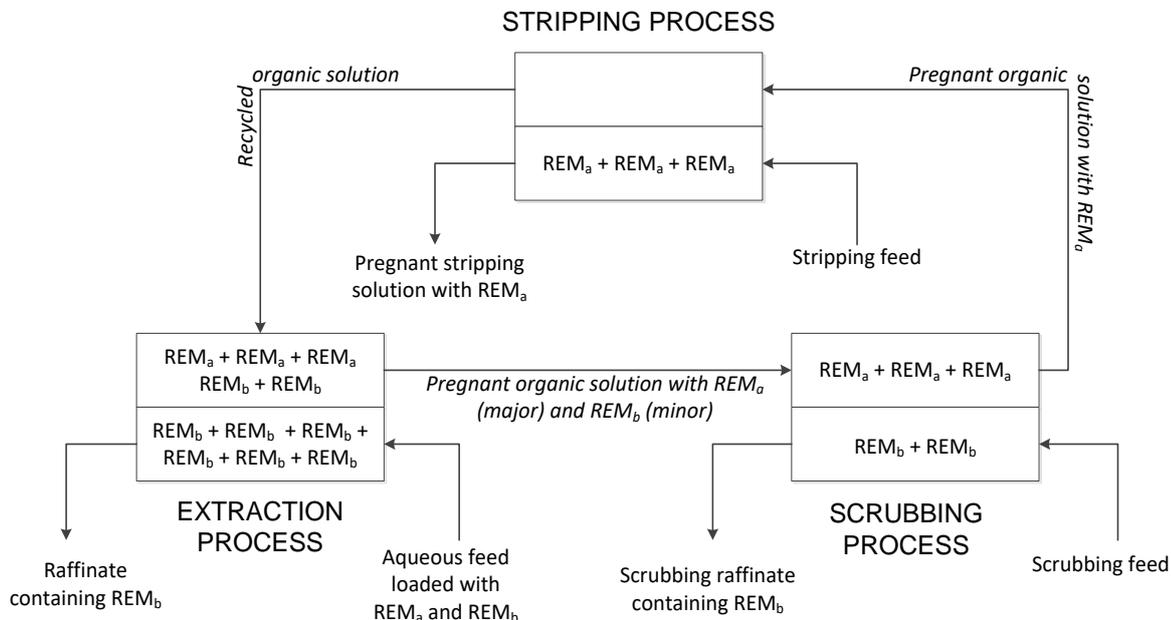


Fig. 2 Basic process flow in solvent extraction containing extraction, scrubbing and stripping process

For a complete cycle of rare earth solvent extraction (RE-SX), the process usually consists at least two out of three types of SX separation as described below:

- 1) Pre-concentration SX: This process is vital for feed with a low concentration of RE before separating the RE into RE mixture or individual metals. Usually, an extractant with high extraction capabilities is used [6].
- 2) Removal SX: For feed with a mixture of other elements or contaminants. This type of SX is commonly used as the first SX stage for extraction of RE from ores. In this case, a specific extractant need to be chosen which the distribution coefficient for the RE is far from the other elements or contaminants.
- 3) Individual SX: This process is applied to the high concentration of REM solution to separate them into individual metals.

Example on the type of SX system and the relationship with the selection choice of extractant will be discussed in

Subtopic IV.

B. Distribution Coefficient and Separation Factor in SX

SX was first observed by Hopkins and Quill in their investigation for the solubility of various RE nitrates and chlorides in different types of alcohol [7]. They succeeded in separating neodymium and praseodymium nitrate with the composition of 83:16 into 94:6 v/v after two stages of extraction. Eight years later in 1941, Appleton and Selwood introduced the concept of β in RE separation [8]. They conducted a simple liquid-liquid extraction and found that the β for the separation of La and neodymium thiocyanate is 1.06. They recommended that a continuous counter-current extraction might help in improving the separation process, compared to the traditional method that is fractional crystallization.



Better separation of 2.14 for three extraction stages was then achieved in separating lanthanum and neodymium nitrate in n-hexyl alcohol. In 1949, Warf proved that solvent extraction method which incorporates extraction and stripping stages could be applied in RE separation. Over 99.5% of Ce(IV) was extracted from Ce(III) with tributyl phosphate (TBP) in the presence of nitric acid, which was then stripped from its organic solution by the reduction to Ce(III) using hydrogen peroxide [9].

During extraction process, when the REMs distribution between the organic and aqueous solution achieved an equilibrium state, the distribution ratio (D) of the REMs is expressed as the following:

$$D_{REMa} = \frac{[REMa_{(org)}]}{[REMa_{(aq)}]} \quad \text{Eq. 1}$$

$[REMa_{(org)}]$ and $[REMa_{(aq)}]$ are the concentration of targeted REM or $REMa$ (Fig. 2) in the organic and aqueous phase, respectively. Sometimes, D is also denoted as distribution coefficient factor or distribution factor. The main point of extraction is to shift the targeted REM from the aqueous to the organic solution. The system that provides a higher value of D for REM is the most preferred choice for the process. If an extraction system comprises of various REM species, D is considered as the total concentration of REM in organic that is divided by the total concentration of REM in the aqueous as the following:

$$D = \frac{\sum[REMt_{total(org)}]}{\sum[REMt_{total(aq)}]} \quad \text{Eq. 2}$$

Another factor that has to be considered is the separation factor or β , which is the D of two REMs; $REMa$ and $REMb$ under the same system condition:

$$\beta_{REMa / REMb} = \frac{D_{REMa}}{D_{REMb}} \quad \text{Eq. 3}$$

The higher β indicates that the separation between $REMa$ and $REMb$ is easier. If the β is equal or close to one, the separation between those two metals is difficult. Even if it is possible, the system requires a large number of extraction stages to separate the metals completely.

Currently, there is no universal rule to evaluate or to rank the efficiency of an extraction system as it is a complex task. The efficiency does not only depend on the D or β , but it also comprises of other aspects, including physicochemical property, kinetics rate, and interfacial phenomenon. Besides that, it could become more perplex in industrial practice. Provisionally, it is sensible to evaluate the efficiency of one extractant by the value of D and β .

III. EXTRACTANTS IN THE RARE EARTH SOLVENT EXTRACTION SYSTEM

In the SX system, there are two inlet stream: organic feed and aqueous feed. An acid solution is commonly used as aqueous feed, and an aqueous feed is a mixture of organic solvent, extractant, and sometimes added with a modifier. The extractant is in charge in accumulating the desired REM into the organic phase for the the REM separation process. Most of the extractants are viscous in nature; thus, a diluent is required to dissolve the extractant as well as ensuring good

contact between the extractant and aqueous phase. The various types of diluent include kerosene, n-hexane, benzene, dichloromethane, and chloroform. Different diluent gives a different value of equilibrium constant depending on the extraction mechanism. Among the diluents, kerosene gives the largest number of the equilibrium constant, which makes it was a preferable diluent in RE extraction [10]. Sometimes, a modifier such as isopropanol [11], [12] and tributyl phosphate (TBP) [13] have to be included to increase the hydrodynamics of the system and to lower the possibility of the third phase formation.

To achieve a good separation, process of synthesizing or selecting the extractant must follow several criteria. Most importantly, the extractant must possess at least one functional group and a relatively long hydrocarbon chain or benzene/substituted ring element. The functional group such as P, N, O, or S acts as a metal complex with REM, and the carbon chain is used to intensify extractant solubility in the solvent of choice. On top of that, a good extractant must have positive selectivity towards the desired REM, excellent chemical stability, low density, and viscosity, as well as large surface tension. Some of these properties are crucial to prevent emulsion for the extraction and stripping process [10].

In the leaching stages (refer Fig. 1), dissolution of minerals into an aqueous solution usually occur in a very high concentration of acid. Wilson and his group explained in detailed the character of the anion that is formed in the aqueous which finally gives a significant hint on choosing the suitable extractant for the SX system [14]. If hydrochloric acid (HCl) is used in the leaching stage, neutrally charged extractant such as TBP and tri-n-octylphosphine oxide (TOPO) are preferred. Chloride anion from the HCl is an excellent inner-sphere ligand, and it could easily solvate the metal salt and form an extractable, neutral-charged complexes. However, the anion is more likely to exist as chloridometalates at a relatively high concentration of chloride. The most appropriate extractant to be used at a high concentration of chloride is cationic extractant as the metal salt can be extracted by the formation of outer-sphere assemblies or ion pairs. On the occasion that sulphuric acid (H_2SO_4) is used, anionic extractant is the best candidate. Compared to chloride, sulfate ion has a weak inner sphere ligand, and an anion is required to achieve a neutrally charged complex. Fig. 3 shows the simplified diagram of the selection of extractant based on criteria of acid in leaching system.

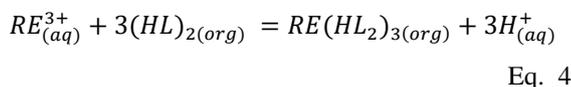
For the past 50 years, researchers have discovered the various type of extractants. However, only a small number of extractants are used in industrial practice. The extractant must act as a good separation agent between RE metals with a low operational cost to satisfy the industrial expectation. Di-2-ethyl-hexyl-phosphoric acid (DEHPA), 2-ethyl-hexyl-2-ethyl-hexyl-phosphonic acid (EHEHPA), versatic acid, versatic 10, and Aliquat 336 are selected and considered as practical for industrial application (Table 2) [4], [15]. However, some industries formulated their extractant and registered with a trade name, which makes it difficult to determine the active component. This study will discuss on these extractants regarding their chemistry properties, best metal-extractant combination and also their potential future development.

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A. Single Extractant System

1) Organophosphorus acid

The most commonly used RE extractants from the organophosphorus group are 2-ethylhexyl phosphoric acid mono 2-ethylhexyl ester or also known as EHEHPA / P507 and di-(2-ethylhexyl) phosphoric acid or also known as DEHPA / P204. Both extractants have colorless or yellowish transparent liquid with non-polar properties. Peppard et al. (1957) studied the properties and the application of DEHPA as an extractant in separating REMs. DEHPA was accepted as a feasible extractant with a high number of D, besides having the ability to lower the overall quantity of extraction stages needed in the RE separation. They also discovered the interaction of DEHPA, which majorly in dimer form towards RE^{3+} ions as shown in Eq. 4, indicating that pH value has a significant influence on the reaction [16]– [18]. Varying the pH of the aqueous solution could affect the amount of REM in the extraction, scrubbing, and stripping phase.



$(HL)_2$ refers to the dimeric species. (aq) is the aqueous phase, whereas (org) is the organic phases.

DEHPA and EHEHPA are categorized as cation-exchange extractants, which are similar to most of other organophosphorus acid. The metal replaces the hydrogen ion in the extractant and produces a soluble organic complex that has a neutral charge. In excess, the combination of RE and extractant complexes produce an 8-membered pseudo-chelate (Fig. 4) by holding one of the hydrogens in the dimer and releasing the other while replacing it with a metal cation [14].

Sato compared both DEHPA and EHEHPA in various condition. Based on the behavior of the REMs in HCl, the study concluded that REs follow the cation exchange mechanism in low acidity; and solvating mechanism in high acidity [19]. Both extractants displayed higher extraction efficiency for the metal with a larger atomic number in the lanthanide series; $La < Ce < Pr < Nd < Sm < Eu < Gd < Tb < Dy (< Y) < Ho < Er < Tm < Yb < Lu$. Table 3 and Table 4 show the β for these two extractants. The efficiency of the extraction process is parallel with the atomic number of RE for any given organophosphorus acid. The possible explanation for this is the attraction effect of the extractant anion, and the increase of the electrostatic force causes the size of the cation to become smaller [4].

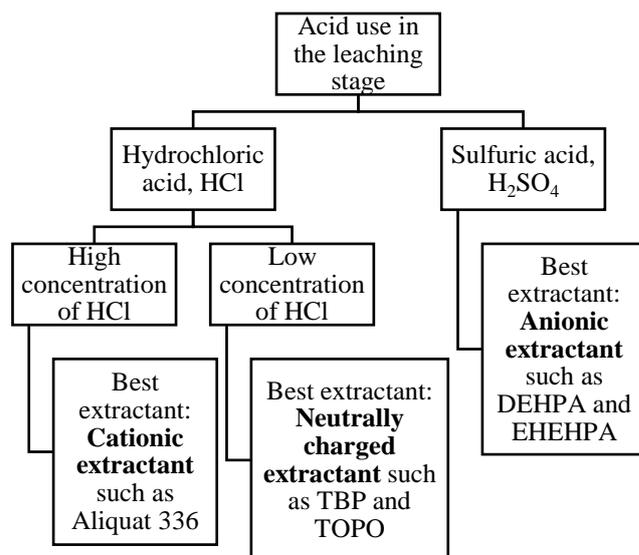


Fig. 3 Determination of extractant based on acid used in the leaching stage

Sato in his paper stated that DEHPA demonstrates a good separation ability for LRE compared to HRE due to the formation of complexes through the interaction between DEHPA towards HRE, especially for Tm, Yb, and Lu [19]. Based on the current relative accumulation of β for each REM, the Table 3 and Table 4 show an interesting pattern. $Eu > Gd > Sm$ and $Tb > Gd > Eu$ are the three most difficult elements to be separated in a mixture of REs for DEHPA and EHEHPA system, respectively. The central part of the lanthanides series has the highest difficulty for the separation process, and the difficulty level lessens towards the end. This might be the reason that samarium and europium could be easily separated only after they are reduced into a divalent state [4].

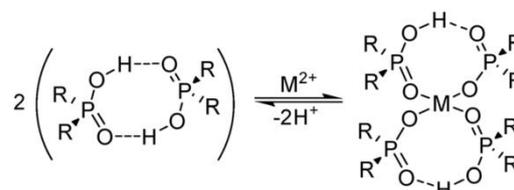


Fig. 5 Formation of 8-membered pseudo-chelate by involving phosphinic acids [14]

There are others few papers that evaluate the efficiency of DEHPA and EHEHPA as an extractant in the same environment [21]–[25]. Radhika et al. studied the separation possibilities of LRE; La, Ce, Pr, and Nd and HRE; Tb, Dy, Ho, Er, Yb, and Lu towards the three types of extractant, which are DEHPA, EHEHPA, and Cyanex 272. They found that the extraction efficiency is dependent on the pK_a for each extractant. $EHEHPA > DEHPA > Cyanex\ 272$ in H_3PO_4 medium [21]. The similar sequence of extraction is also obtained by Soo Kim et al. through the use of HCl medium; although in some condition, the β are higher in DEHPA compared to EHEHPA [23]. Contrary for La(III) in nitrate medium, DEHPA is proven to have higher extraction efficiency than EHEHPA under all experimental condition [22].



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In another study, almost all REs in the study, which are Sm, Gd, Dy, and Y, were extracted from the mixture by using 1 mol/L DEHPA, while 0.1 mol/L EHEHPA shows the capability of separating Dy-Y and Sm-Gd [24]. The 100% extraction indicates that there is no occurrence of separation for DEHPA.

For the separation of HRE, Abreu and Morais recommended the application of EHEHPA, rather than DEHPA. Throughout the study, EHEHPA excelled in all variables for both separation and stripping. EHEHPA showed

lesser interaction with REs, which makes the stripping process easier [26]. The increase of the β in EHEHPA causes the number of extraction stages to become lower. Contrarily, based on the reduction ionic radius and increment of coordination equilibrium constant, K_{ex} across the lanthanide group, Chen et al. summarized that the back extraction or stripping process was theoretically to be intricate due to lanthanide contraction [27].

Table 2: Structures and pK_a of the Common Industrial Extractant

Commercial Name	Full Name	Chemical Structure	pK_a
Organophosphorus Extractants			
P204 TOPS 99	Di-(2-ethylhexyl) phosphoric acid (DEHPA)		3.24
P507 PC 88A Ionquest 101	2-Ethylhexyl phosphoric acid mono 2-ethylhexyl ester (EHEHPA)		4.51
Carboxylic Acid Extractants			
Versatic 10	Neodecanoic acid		7.33
Versatic acid	Naphthenic acid		6.91
Amine Extractant			
Aliquat 336	Methyltriocetylamine chloride		

In the extraction process, lower D and extraction percentage commonly due to the increase of acidity in the aqueous phase. The high acidity comes from the additional H^+ that was produced from the cation-exchanging reaction. Researchers have found a solution by replacing the exchangeable H^+ of the extractant with sodium ion (Na^+) or ammonium (NH_4) through the saponification process. The most commonly used saponification agents are ammonium hydroxide (NH_4OH) and ammonium bicarbonate

(NH_4HCO_3). However, there are several drawbacks in saponification as the saponification agents are strong alkalis which could produce a significant amount of heat that can damage the equipment as well as affecting the overall extraction process. Saponification could also produce a large volume of wastewater containing ammonium.



Several researchers have studied the positive effects of saponification in elevating the D [12], [28], [29]. The acidic and saponified EHEHPA were used for the extraction of Nd from chloride medium; as a result, Lee and his group found that the saponified extractant could increase the D by 40% [28]. For industrial level, Thakur and his co-workers had developed a mathematical model for the production of neodymium oxide, Nd₂O₃ from the experimental data of 20% saponified EHEHPA, and the model had succeeded in obtaining over 5 kg of Nd₂O₃ (97%) with almost 85% recovery [12]. Besides that, an experimental quantitative co-extraction of Pr and Nd was done, and more than 99% of Nd purity was achieved by using 50% saponified 0.15M EHEHPA in the four stage of counter-counter extraction setup [30]. Currently, much effort has been dedicated to the search for an alternative to the saponification process. One of the solutions is to introduce complexing agent into the system, including ethylenediaminetetraacetic acid (EDTA) [31], pentetic acid (DTPA) [32], 2-ethyl-2-hydroxy butyric

acid [33], 8-hydroxyquinoline [34], lactic acid [35]–[38], and citric acid [35], [36], [38]. A group of researchers explored a system with the mixture of EHEHPA and 8-hydroxyquinoline in chloride medium to extract Pr(III), Nd(III) and La(III). They found that at pH 3.6, the largest synergistic enhancement factor occurred for Pr, Nd, and La(III) are 5.47, 3.37 and 2.86, respectively. These complexing agents were unable to work alone; however, the system could be improved and fit for industrial application as the mixture could reduce the acidity in the stripping process with the aid of the extractant [34]. The extraction of Ce(III) and Pr(III) in the chloride medium with the addition of lactic and citric acid was also performed and both metals showed decent outcome for both D and β [35]. Yin et al. described the effect of the complexing agent by showing that the system with DEHPA and lactic acid in chloride medium was able to double the extraction capacity up to 27.87 g/L, rather than 13.13 g/L in DEHPA-HCl system [37].

Table 3: Separation factor^u of Ln(III)-HCl-HDEHP in RE extraction

	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Ref.
La	2.14	2.28	2.43	11.8	26.3	44.6	71.1	101	125	212	319	414	425	[19]
Ce		1.07	1.14	5.2	12.3	20.9	33.3	47.2	58.4	99.1	149	193	199	[19]
Pr			1.06	5.16	11.5	19.5	31.1	41.1	54.7	92.7	139	181	186	[19]
Nd				4.86	10.8	18.3	29.2	41.5	51.3	87.1	131	170	175	[19]
Sm					2.23	3.75	6.02	8.55	10.6	17.9	27.0	35.1	36.0	[19]
Eu						1.69	2.70	3.83	4.74	8.04	12.0	15.7	16.2	[19]
Gd							1.60	2.26	2.80	4.75	7.15	9.30	9.55	[19]
Tb								1.42	1.76	2.98	4.48	5.83	5.90	[19]
Dy									1.24	2.10	3.16	4.11	4.22	[19]
Ho										1.70	2.55	3.31	3.41	[19]
Er											1.50	1.90	2.01	[19]
Tm												1.30	1.34	[20]
Yb													1.03	[19]

Table 4: Separation factor^a of Ln(III)-HCl-EHEHPA in RE extraction [19]

	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
La	1.30	1.42	1.67	3.33	6.52	9.52	22.5	36.4	93.9	117	156	175	199
Ce		1.09	1.28	2.57	5.02	7.36	17.3	18.0	72.3	90.5	120	135	152
Pr			1.17	2.35	4.59	6.72	15.8	64.2	66.0	82.7	110	123	140
Nd				2.00	3.94	5.74	13.5	21.8	56.3	70.5	93.7	105	119
Sm					1.96	2.87	6.74	10.9	28.2	35.3	46.8	52.6	59.5
Eu						1.46	3.45	6.39	14.4	18.0	24.0	26.9	30.4
Gd							2.35	3.81	9.82	12.3	16.3	18.3	20.7
Tb								1.62	4.18	5.23	6.95	7.81	8.83
Dy									2.58	3.23	4.29	4.82	5.45
Ho										1.25	1.66	1.87	2.11
Er											1.33	1.49	1.69
Tm												1.12	1.26
Yb													1.13

Since its discovery, DEHPA has become the most studied extractant, and the research is still ongoing. DEHPA has dominated the extraction process for the industry in China, and it was able to oust the prior extractant, TBP. For the current trend, the majority of the REs producers, especially in China, have switched to EHEHPA due to its replaceable role in the separation of the individual RE [27] as well as its ability to strip RE in relatively lower acidity compared to DEHPA [39]. DEHPA requires higher acidity level in the stripping process which could affect the operational cost

significantly as 10 kg of 33% HCl and 2 – 3 kg sodium hydroxide (NaOH) per kg are needed for the separation of every kilogram of RE oxide. Table 5 shows the pros and cons summary of these common extractants. In a single extractant system, it can be concluded that DEHPA is used to separate LRE and MRE, while EHEHPA is used to separate individual RE and HRE.

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However, the selection of the extractant is a complex process as there is the need to evaluate the extractant's effect on starting materials, composition, and target product.

Table 5: Summary of common extractants

	Advantages	Disadvantages
DEHPA	<ul style="list-style-type: none"> Poor solubility in aqueous solution Relatively high separation factor compared to EHEHPA Better separation in LRE and MRE as compared to EHEHPA 	<ul style="list-style-type: none"> Strong bonding capacity for HRE, which resulted in the difficulty to strip HRE from loaded organic Relatively higher acid and base consumption for stripping compared to EHEHPA Large amount of flammable diluent is usually used Requires saponification process
EHEHPA	<ul style="list-style-type: none"> Low consumption of chemical reagent and waste discharge Better separation of HRE Ability to separate individual RE 	<ul style="list-style-type: none"> High acidity is needed in stripping some of the HRE Large amount of flammable diluent is usually used Requires saponification process
HA	<ul style="list-style-type: none"> Low cost Easy preparation Able to extract high purity of yttrium 	<ul style="list-style-type: none"> Great solubility in aqueous solution resulting in extractant loss Y extraction process is done under high pH value, which leads to emulsification Composition of HA could be easily changed during the extraction process
Aliquat 336	<ul style="list-style-type: none"> Efficient for LRE extraction 	<ul style="list-style-type: none"> The extraction can only be carried out in high concentration of nitrate system

2) Carboxylic acid

The early phase of SX development uses carboxylic acids due to their attractive price, availability, and ease of use for the separation of RE. Various type of carboxylic acid extractants are currently available in the market. However, naphthenic acid (HA) and neodecenic acid (Versatic 10) acids are the leading extractants in RE separation, especially for yttrium. Preston conducted an extensive study on the extraction of more than 30 metal cations, including RE by using HA, Versatic 10, 2-bromodecanoic, and 3,

5-diisopropylsalicylic acids. The REMs of choice were from LRE (La^{3+} , Ce^{3+} , and Nd^{3+}), MRE (Gd^{3+}), and HRE (Ho^{3+} , Yb^{3+}) group [40]. These REs could be easily transformed into complexes, which are predominantly ionic in nature. HA and Versatic 10 able to extract REs in higher pH (~pH 4 -5) compared to the other two acids. The position of yttrium is also varied depending on the type of extractant in use. For Versatic 10 in xylene medium, the order is $\text{La} < \text{Ce} < \text{Nd} < \text{Gd} < \text{Y} < \text{Ho} < \text{Yb}$, whereas HA has the order of $\text{La} < \text{Ce} < \text{Y} < \text{Nd} < \text{Gd} \sim \text{Ho} \sim \text{Yb}$ [40].

Preez and Preston continued the study for La, Gd, and Lu in nitrate, and some cases in sulfate system. They reported that the extraction of REs in carboxylic acid is depended on their atomic number [41]. This statement indicates that there is an explicit relationship in the steric bulk of the carboxylic acid molecule that is represented by the steric parameter (E_s) of the substituent alkyl group. In sterically hindered carboxylic acid like Versatic 10, the value of pH0.5 has resulted in the reduction from La to Lu and caused Y to behave like MRE. For straight-chain and less sterically hindered carboxylic acids, the value of pH0.5 is decreased from La until MRE, and it gradually rises at Lu, which caused Y to have similar behavior as LRE. Eq. 5, Eq. 6 and Eq. 7 show the equation for RE extraction in highly steric hindrance complex and low steric hindrance for LRE and HRE. Apart from Y, carboxylic acid extractants have poor selectivity towards other RE due to their large complex species that can coexist in the immiscible water phase. The carboxylic acid extractant is quite stable in a hydrocarbon solvent; however, in low polarity solvent, it has the tendency to associate and produce more complex speciation as shown in Fig. 6 [14].

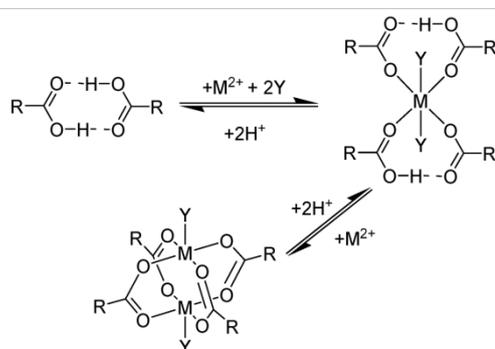
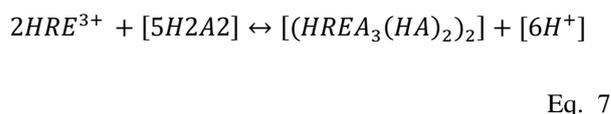
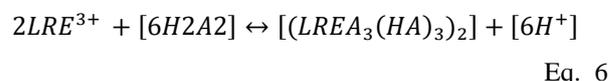
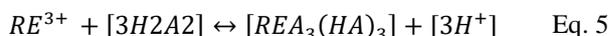


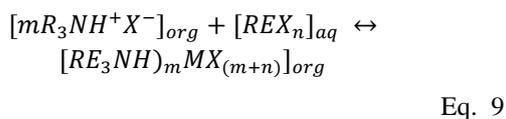
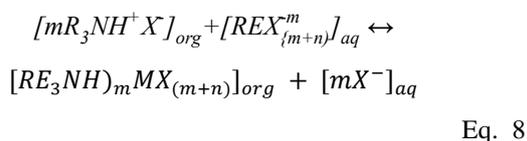
Fig. 3 Formation of neutral complexes during the extraction of M^{2+} cations by hydrophobic carboxylic acids ($\text{Y} = \text{H}_2\text{O}$ or RCO_2H) [14]

A study by Singh et al. discussed on the location of Y, specifically on the effect of the structural changes in carboxylic acid extractants [42], and the findings are similar to the observation by Preez and Preston in 1992 [41]. Both papers agreed on the usage of E_s for quantitative means in representing steric hinderance of carboxylic extractants. If the value of $E_s < 1$ is achieved, Y is inclined to behave more like LRE group, and it will be extracted along with the group. On the other hand, if $E_s > 2$, Y is positioned with MRE. These verdicts, however, with the assumption that RE in mixture behaves as the same as the individual.

Carboxylic acid extractant serves a practical use for RE processing as it is relatively cheap compared to the other common extractants besides being readily available. Besides that, carboxylic acid extractant has been used in a commercial process for various purposes, for instance, Thorium Ltd. In England and Molycorp processing plant in Colorado, they have been using HA to purify yttrium. In Thorium Ltd processing plant, a high purity of yttrium oxide (Y_2O_3), the percentage of 99.999% was achieved from the 47% Y_2O_3 concentrate [4].

3) Amine

Amine extractant consist of primary up to quaternary ammonium is very efficient in the separation of radioactive elements, non-ferrous metals, and REs [43]. For REs, amine extractant works well with LRE. When amine extractant is used with aqueous soluble amino carboxylic acid, HRE will be extracted the most. Therefore, this type of extractant has gained the attention of researchers. Coleman reported on the effect of solution acidity on molecular species in organic and aqueous phases for the separation and recovery of REM in the primary amine system. The suggested route for separation by amine extractant was either anion exchange mechanism or adduct formation as shown in Eq. 8 and Eq. 9, respectively [44].



R is an alkyl group and X is an inorganic anion.

As the potential of primary and tertiary amine in RE separation was revealed by the papers published by Bauer [45], [46], and in 1971 Baur and Lindstrom [47] extend the work to the Aliquat 336 in the presence of chelating agents such as DTPA, HEDTA and 1,2-diaminocyclohexanetetraacetic acid (DCTA). Aliquat 336 has the highest β with Socal 355L compared to other common water immiscible diluents such as toluene, xylene, and ethyl ether. It was verified that Aliquat 336 in nitrate system is a good extractant in the extraction of La-Pr, Pr-Nd, and Nd-Sm with the β of 93, 5.4, and 11.6, respectively. These values were higher in comparison to EHEHPA and DEHPA in chloride system [19]. The limitation of Aliquat 336 system is the dependency of the extraction efficiency on the amount of inorganic nitrate in the solution. The formation mechanism of the extractable complexes could only occur if the number

of nitrate ions in the solution is high. Cerna et al. in their paper mentioned that the high concentration of nitrate ion of 4 to 8M could reduce the β of the lanthanide series with increasing atomic number [48]. The high concentration of nitrate is necessary in the D of the system as it can provide the ease of penetration into the anion exchanger due to the decrease of net charge. Apart from that, ion dehydration from the partial stripping of the hydration sheath in the RE ions could also contribute to the rising number of extractable complexes. The hydration is higher in LRE, and it can be steadily reduced along the lanthanide series [49].

The application of these extractants is not limited to mineral hydrometallurgy. The same method could also extract and separate RE from electronic waste, in particular for the extraction of Pr and Nd from the permanent magnet. Preston stated that the separation of Nd from magnet could be achieved by using counter current solvent extraction process with Aliquat 336 extractant in the nitrate medium [50]. Besides Aliquat 336, multiple studies have proven the capabilities of other extractants such as Cyanex 272, DEHPA, EHEHPA, Cyanex 921, Cyanex 301, Cyanex 302, and Alamine 336 in extracting and separating Nd and Pr from pregnant leaching solution and synthetic solutions [28], [51]–[55]. Among these extractants, DEHPA and EHEHPA display better extraction efficiency due to their high selectivity when extracting REs (La, Ce, Nd, Pr, Y) from aqueous solutions.

B. Binary Extractant System

Currently, researchers are exploring new extractant, extraction system, or equipment in improving the separation process. Since the last decade, various extractant mixtures were introduced in the search of better extractant, including a combination of alkaline–acidic extractants [56]–[58], acidic–acidic extractants [39], [59], [60], and neutral organophosphorus–acidic extractants [61]. These binary extractant systems could improve the extraction capability and selectivity as well as enhance the solubility of the metal–extractant complexes in the organic solution, avoid probability of emulsification and formation of the third phases [61].

In the acidic-acidic extractants system of RE separation, the synergistic interaction of EHEHPA with DEHPA are among the most discussed extractants [39], [62]–[68]. This system was introduced to overcome the limitations of both DEHPA and EHEHPA that are shown in Table 5 through the combination of extractant system which has low acidity in the stripping process and high extraction efficiency for the extraction of RE. This system demonstrates a very promising extractant as it has better β compared to their individual element (Table 6), besides exhibiting the highest extractability among other mixture of the system; EHEHPA/DEHPA > EHEHPA/Cyanex 301 > EHEHPA/HHEOIPP > EHEHPA/Cyanex 302 > EHEHPA/Cyanex 272 [62]. Although there were studies done in proving the synergistic effect of this system [39], [63], [64], [69], it is still nascent. In a study that investigated the extraction of Y, Nd, and Dy, Mohammadi and his co-workers found that pure extractants have better β , except for the extraction of Y from Dy [39]. Similarly, Zhang et al.



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found that the maximum β for Ce/La in the binary system without the addition of complexing agent is 3.35, which is lower than those in the EHEHPA with the value of 5.84 [70] and DEHPA with the values of (4.09, 3.92) [71].

Another important extractant that is commonly used in RE separation is bis-2,4,4-trimethylpentyl phosphinic acid or also known as Cyanex 272 that was developed by Cytech Industries Inc. Cyanex 272 has higher pK_a than DEHPA and EHEHPA with the values of 6.37, and it has larger steric hinderance because of the existence of methyl groups [72]. In the previous study, Cyanex 272 showed wonderful β and selectivity between adjacent RE and low extraction acidity, which makes the stripping process easier. However, Cyanex 272 is costly [73], and it could easily form an emulsion in a certain condition [73] as well as unable to separate few RE couples cogently [72]. The binary system of Cyanex 272 and EHEHPA was investigated by several researchers [15], [66], [74]. Xiong and his colleagues studied the extraction of Yb towards this mixture and verified that the occurrence of synergism even for the HRE pairs [74]. However, the data for HRE were insufficient as the paper only compared with the literature values, and the experimental condition was quite different. Zhang et al. found similar synergism outcome in the extraction of Y in chloride medium [65]. They proposed a theory for this system that no interaction with chloride ions occur as opposed to the single system due to the increase of steric hindrance, which resulted in the different complex structure, $RE(HA_2)_2(HB_2)$ (A and B refer to the conjugate base anion of EHEHPA and Cyanex272, respectively). Fig. 7 shows the transformation of the symmetry and stability of the binary system complex which could improve the metal selectivity and make the stripping process easier [27]. In conclusion, the synergistic effect can only be achieved at low acid concentration for the extraction of the selected LRE and HRE pairs in Cyanex 272-EHEHPA system; at higher acidic concentration, the synergism is concealed by the interaction of the extracted complexes which give rise to antagonism [15].

Table 6: Separation factor of some adjacent lanthanide in individual and mixture of DEHPA and EHEHPA

Element	DEHPA	EHEHPA	DEHPA +EHEHPA
Ho-Dy	1.24 [19]	2.58 [19]	1.72 [62]
Y-Ho	1.24[27]	1.7 [26]	1.84[62]
Y-Er	1.1 [26]	1.2 [26]	1.32[62]
Tm-Er	1.50 [19]	1.33 [19]	3.04[62]
Yb-Tm	1.30 [19]	1.12 [19]	3.11[62]
Lu-Yb	1.03 [19]	1.13 [19]	1.82[62]

Since the 1950s, various extractants have been introduced for the separation of RE. The weaknesses of these extractants are still obscure although they possess many advantages such as the attractiveness in the extraction efficiency and good β for the selected RE group. For example, EHEHPA, the most common organophosphorus acid extractant, encounters several difficulties regarding saponification issue, low β for HRE, and complicated extraction process. Although higher β can be achieved by using more advanced extractant such as Cyanex 272, there is the challenge of the increased cost and difficulty in controlling the extraction to avoid

emulsification. Apart from that, the RE processes require a large volume of non-polar solvent or diluent. Kerosene and n-heptane are widely used in the industrial process and standard for flammable and highly volatile solvent, which are strictly enforced. The public concern was raised after one of the RE processing factories in Mongolia stopped operating for several months due to a fire incident that burnt the factory. The source of the fire was believed to come from the kerosene in the processing plant [27]. In the effort to avoid such incident, researchers have tried to replace the current extractant and diluent with safer, non-volatile, and non-flammable materials.

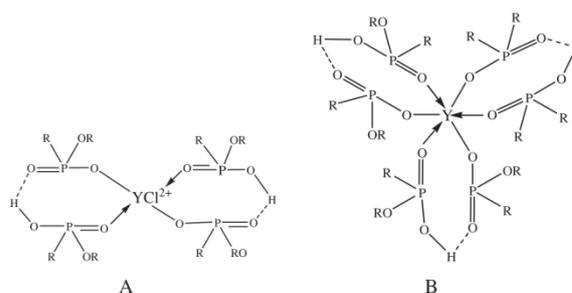


Fig. 4 The proposed structure of A) single system of Cl-EHEHPA/ Cl-Cyanex 272 and B) binary system of Cl-EHEHPA-Cyanex 272 [65]

Past few years has been filled with various research on the utilization of ionic liquid (IL) in the RE separation process. ILs are well-known for their fascinating properties, including low volatility and combustibility [75], high ionic conductivity as well as thermal stability [76]. Utilizing IL in the separation process of REs could provide a new perspective in the separation society as IL can be custom designed according to the requirement. There are at least a million binary ILs, and 1018 ternary ILs possible combinations through the various arrangements of cation, anion, and alkyl group that is attached to the cation head [77]. IL also has a unique attribute in the RE separation as it serves as both solvent [78] and extractant [79]. There is also a combination of two functional groups in one IL. In extraction, prevalent IL such as Cyphos 101 or Aliquat 336 is known as functionalized ionic liquid (FIL) or task specific ionic liquid (TSIL). This paper is interested in the recent trend of ILs, which focuses on bifunctional ionic liquid extractants (Bif-ILEs) by Aliquat 336, EHEHPA, and DEHPA. Aliquat 336 is a quaternary ammonium IL, and it is currently among the leading ILs with interesting properties of low cost [80] and contain the least toxicity [81], [82]. Sun and his team announced a new strategic approach in synthesizing ammonium type of IL and creating a new series of IL containing Aliquat 336 such as [A336][CA-12], [A336-CA100], [A336][P204], [A336][P507], [A336][Cyanex272], and [A336][Cyanex302]. These extractants are called Bif-ILEs due to the existence of the dual functional group, which are cation and anion that have a specific role in REMs extraction [83]. Sun also introduced the extraction process that involves both cation and anion, and it was given the term, "inner synergistic effect" [84]. The synergistic effect of the system is significantly enhanced with the involvement of both functional groups in the extraction process.

This unique inner synergistic effect offers greener separation as the saponification of the wastewater can be eliminated. It was reported that there were good efficiency capabilities and high β in the RE extraction by [A336][P507] and [A336][P204] [85]–[87]. The mechanism of Bif-ILE was based on the formation of an extractable complex by [A336]⁺ cation, as well as [P507]⁻ and [P204]⁻ anion with RE³⁺ (Fig. 8). Sun et al. found that the D in [A336][P204] was 70 times higher than their mixed precursor [84], A336+P204 due to

the strong interaction between Bif-ILEs and RE besides other interactions for instance electrostatic, van der Waals, and induction. [A336][P204] and [A336][P507] behave like a neutral organophosphorus extractants [80]. In comparison to EHEHPA and DEHPA as an extractant, the extraction of RE in the Bif-ILEs system can be done in low acidity with good separation efficiency as the H⁺ was not involved.

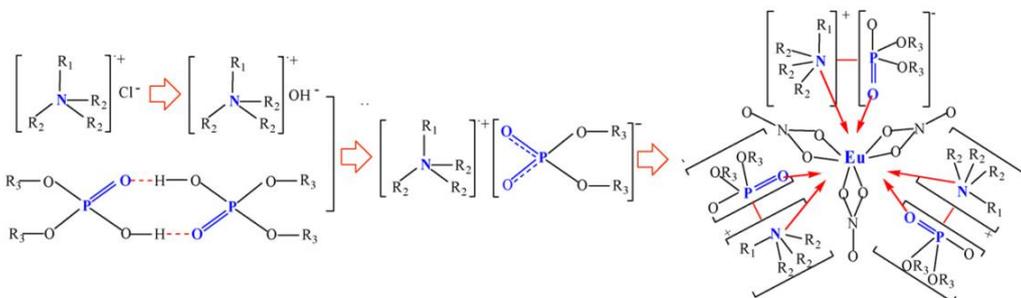


Fig. 5 Proposed structure and coordination of [A336][P204] with Eu³⁺[84]

Guo et al. found that [A336][P507] and [A336][P204] have better separation for LRE in chloride media, and the separation of HRE can be achieved in nitrate media [85]. The analyses in Table 3, Table 4, Table 7, and Table 8 demonstrate that [A336][P507] exhibits the highest β of LRE in chloride media, especially for Pr-Nd and Sm-Nd with the value of 9.52 and 4.70. There is a significant improvement in the β of this adjacent LRE compared to [A336][P204], EHEHPA, and DEHPA with the separation values of (5.61,4.14), (1.17,2.00) and (1.06, 4.86), respectively. In reality, the separation of Pr-Nd was among the toughest job in the industry, and the values of the maximum β obtained from other researchers were very low with $\beta = \sim 1.5$ [12], [19], [47], [88], [89]. In addition, [A336][P204] dominates the separation of HRE; from Er to Lu, followed by [A336][P507], and individual EHEHPA and DEHPA.

Although Bif-ILEs provide a better separation process than the traditional extractant for REs, there are still other emerging problems such as the formation of the third layer in the extraction system [11], [90], rise in viscosity of the organic phase [11], and cation deficit from shorter carbon chain [90]. The third layer in Bif-ILEs system existed due to the formation of macromolecules extractable complex that could hardly dissolve in the organic phase. The complex formed over the lone pair electron of P=O in the [P507]⁻ or [P204]⁻ and unshared nitrogen from [A336]⁺. This third layer has a higher viscosity than the organic phase, and its volume changed inversely with Bif-ILEs concentration [11]. However, Sun and Waters discovered an opposite phenomena involving the third layer phase that appears when the concentration of Bif-ILEs was maximum [90]. They assumed that the layer appeared because of the partitioning of the organic phase into two groups; high in metal-solvate (lower layer) and rich in diluent (upper layer) based on research published by Vasudeva dan Kolarik in 1996 [91]. Alternatively, the addition of isoctanol could eliminate the third layer and the reduce the viscosity of the organic phase. Isooctanol improves the solvating ability and quickly dissolved the complex in the organic solution [11].

IV. UNDERSTANDING SELECTION OF EXTRACTANT IN INDUSTRY

The selection of an extractant in RE-SX system is highly depended on the target product and feed mixture. The extractant chose in the primary SX separation affect the separation sequence and selection of the other extractant in the subsequent separation stage. Despite the number of the published materials available on the extraction characteristic of these organic extractants, the specific information of the SX processes in the industry is well hidden.

Table 7: Separation factor of a) [A336][P507] and b) [A336][P204] in chloride medium [85]

RE(III)	Ce	Pr	Nd	Sm
La	2.03	2.62	24.9	117
Ce		1.29	12.3	57.7
Pr			9.52	44.7
Nd				4.70

RE(III)	Ce	Pr	Nd	Sm
La	1.14	1.49	8.35	34.6
Ce		1.31	7.34	30.4
Pr			5.61	23.3
Nd				4.14

Table 8: Separation factor of a) [A336][P507] and b) [A336][P204] in nitrate medium [85]

RE(III)	Er	Tm	Yb	Lu
Ho	5.63	18.1	78.1	83.5
Er		3.22	13.9	14.8
Tm			4.31	4.61
Yb				1.07

RE(III)	Er	Tm	Yb	Lu
Ho	6.93	23.3	184	1577
Er		3.36	26.6	227
Tm			7.92	67.8
Yb				8.55

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Subtopic II discussed on the three types of SX system namely, preconcentration SX, removal SX and separation SX and their general relationship with the extractants. Incorporating that information with the characteristic of common extractants listed in Table 5, a good understanding of the RE processing in the industry is achievable. The preparation of pure yttrium oxide (Y_2O_3) from Mountain Pass bastnasite by Molycorp is one of the examples of utilization of all three SX separation systems (Fig. 9) [92]. The feed is a mixture of 50% Y_2O_3 /REO, and the targeted products are Y_2O_3 and a mixture of La-Er metals.

1) The SX1 is a preconcentration SX. The purpose of this extraction cycle is to increase the amount of the Y_2O_3 /REO in

the system from 50% to 95% using Aliquat – NO_3 in Cyclosol 53. Aliquat – NO_3 was chosen in this cycle probably due to the ability of the extractant to separate the LRE and MRE. In the SX1, the mixture of Y_2O_3 and HRE stayed in the aqueous system and carried to the SX2.

2) The SX2 is a removal type SX. Versatic acid has shown an excellent capability to extract the mixture with a high concentration of yttrium and left the unwanted metals /contaminants in the aqueous.

3) The SX3 is a separation SX, aimed to split the Y_2O_3 from La, Yb and Lu mixture.

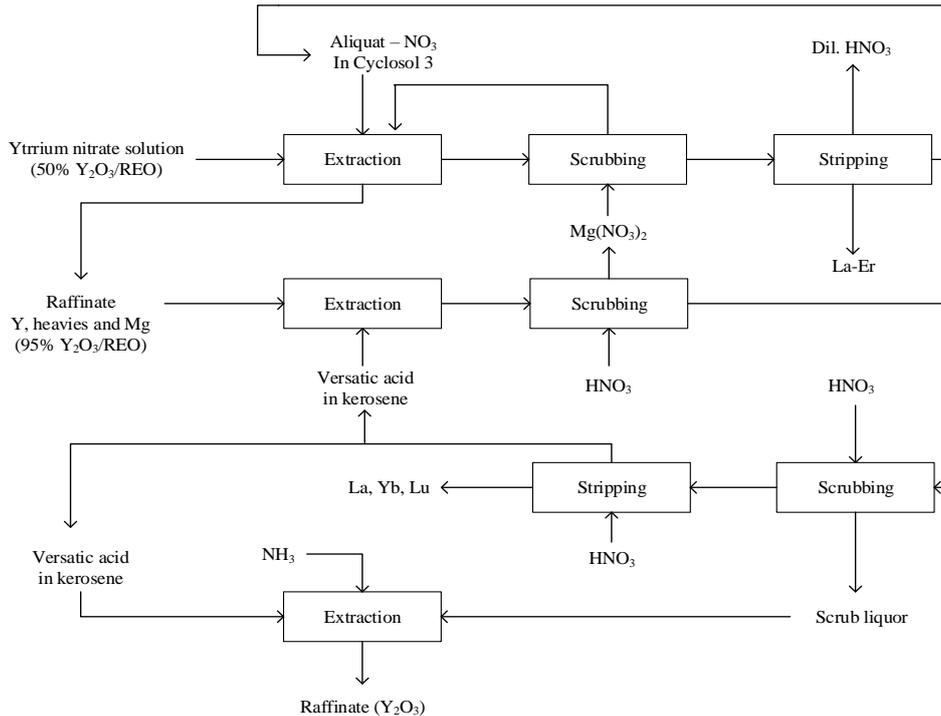


Fig. 6 Flow diagram of recovery of pure yttrium oxide at Molycorp[92]

Other examples are monazite processing from the Indian Rare Earth [4]. At the Alwaye plant, the operation to produce various individual RE concentrate such as Sm, Eu, Gd, and Y is divided into several production stages. Right after the chemical treatment, the mixed RE chloride solution undergoes pre-concentration SX stage to produce Sm-Eu-Gd concentrate from the scrubbing stage and Y concentrate from the stripping stage (Fig. 10). The second extraction stage aimed to separate the mixture of Sm-Eu-Gd concentrate into individual element. As both extraction stages dealing with the MRE, DEHPA is the best choice for the processes.

In the next stage, the RE chloride solution is extracted with partially saponified PC88A (EHEHPA) in kerosene for its ability to extract HRE. At the extraction stage, the MRE and HRE are kept in the organic phase and the LRE is leaving through the raffinate (Fig. 11). Afterward, the MRE is stripped selectively in the scrubbing cascade using 1 M HCl and leaving the HRE to be stripped in the stripping cascade by 3.5 M HCl. MRE in the strip solution is put through another separation SX process to produce individual Gd, Sm and LRE concentrate as shown in Fig. 12. The high concentration of Sm and Gd in the feed solution along with 1 M DEHPA in kerosene as the extractant efficiently separate them from the LRE mixture. The Sm concentrate is finally

stripped with 1.5 M HCl and 1 M DHEPA in two different stages, and the Gd concentrate is recovered from the stripping cascade with strong HCl solution. Overall, as expected, EHEHPA is employed in the process related to HRE and DEHPA is preferably used in the separation of LRE and MRE.

V. CONCLUSION AND FUTURE TREND

Undoubtedly, SX is the preferred technique in the past, present, and in the nearing future as SX offers economic advantages besides its ability to be easily adapted to a continuous process, especially on an industrial scale. Although multiple extractants have been proposed to be applied in the SX system, these new extractants are still hard to replace EHEHPA and DEHPA in the REMs hydrometallurgical industry due to insufficient research data. The current trend showed that the best option for extracting individual REM and HRE is by utilizing EHEHPA while DEHPA is best for separating LRE from MRE. For the minerals with a high concentration of Y, naphthenic acid is preferred.

Although this review could provide a guidelines in selection of extractant, this is a complex process as there is the need to evaluate another aspect such as starting materials, composition, and target product. More research on systematic structure-property studies should be conducted to understand the behavior of this extractant.

This study also has discovered the promising future candidate in REs extraction, which is Bif-ILEs, as it could perform the excellent separation. This extractant is a better choice for industrial application due to the affordable market

price of IL, its physicochemical properties, extraction capacity, selectivity, stripping and interfacial phenomenon. Bif-ILE could diminish the risk of explosion of flammable solvents in the traditional SX, and avoid saponified wastewater crisis. Although this extractant has some shortcomings as explained in the preceding section, it is believed that future research could find solutions in achieving more advantageous separation for the industrial application.

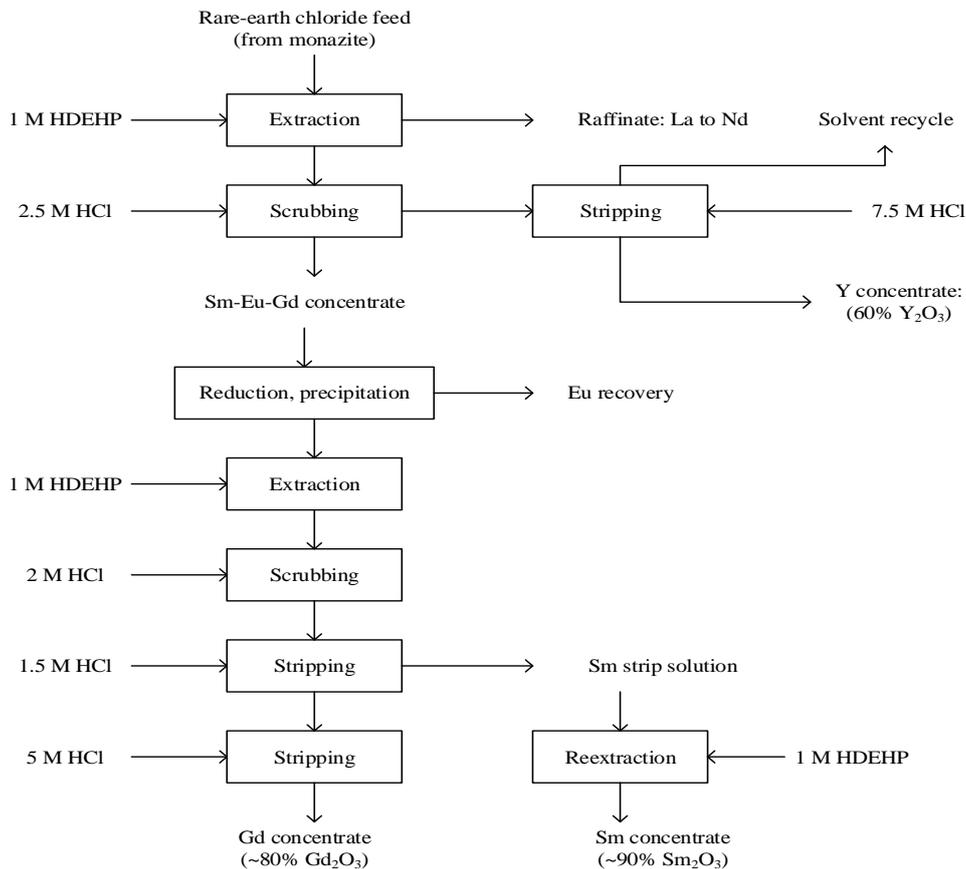


Fig. 7 Flow diagram of MRE separation at Indian Rare Earth I [4]

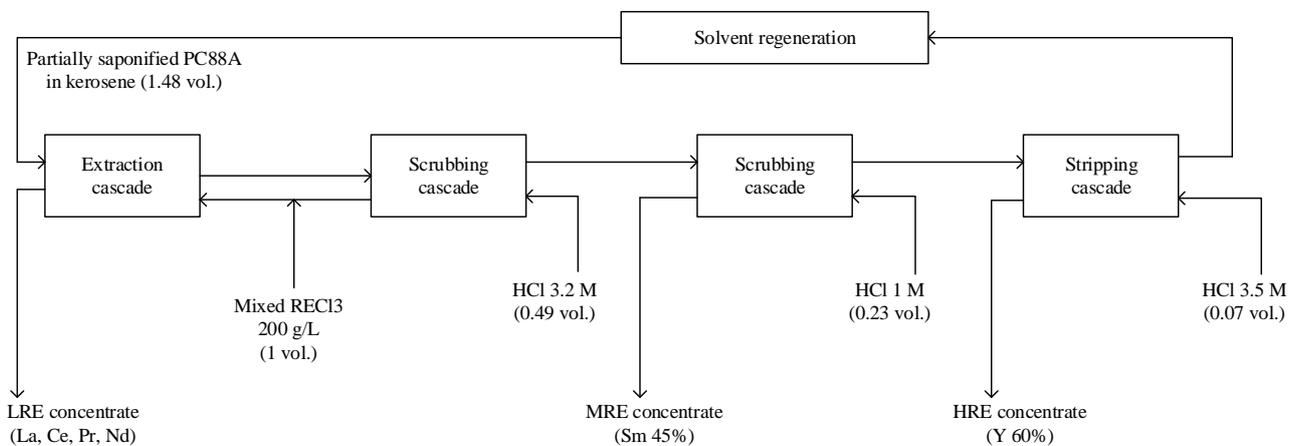


Fig. 8 Flow diagram for the separation of mixed RE into LRE, MRE and HRE concentrate [93]

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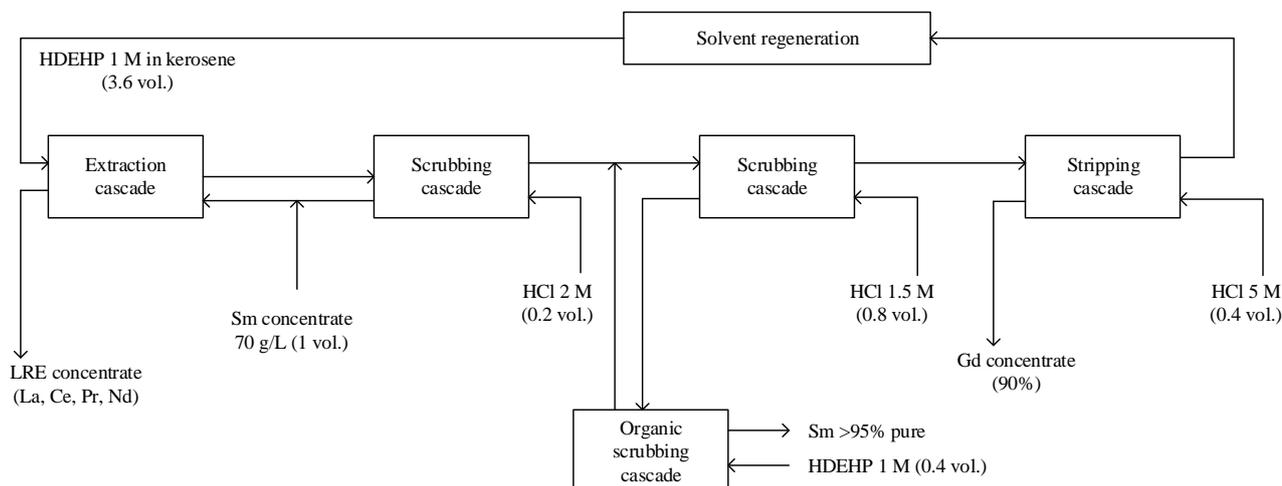


Fig. 9 Flow diagram for the Sm recovery from the MRE concentrate using DEHPA [93]

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