



# The evolution of mineral processing in extraction of rare earth elements using liquid-liquid extraction: A review

Nur Nadiatul Hidayah<sup>a</sup>, Sumaiya Zainal Abidin<sup>a,b,\*</sup>

<sup>a</sup> Faculty of Chemical & Natural Resources Engineering, Universiti Malaysia Pahang, 26300 Gambang, Pahang, Malaysia

<sup>b</sup> Centre of Excellence for Advanced Research in Fluid Flow (CARIFF), Universiti Malaysia Pahang, 26300 Gambang, Pahang, Malaysia



## ARTICLE INFO

### Keywords:

Rare earth elements  
Liquid-liquid extraction  
Ionic liquid  
Synergist  
Conventional extractant

## ABSTRACT

The attempt to extract rare earth elements (REE) has started over a century ago using activated carbon and continues until today with various methods involved to improve the extraction yield. Instead of solid-liquid extraction, the use of liquid-liquid extraction (LLE) has been more common due to the convenient arrangement of the process. Solvent extraction is the main process applied in LLE of REE and along the way, various kind of solvent extractants have evolved. The use of traditional extractants (e.g., benzene, heptane, and kerosene) in LLE has been diverted to the application of conventional extractants (e.g., tributyl phosphate (TBP), di-(2-ethylhexyl) phosphoric acid (D2EHPA), and Cyanex 923 to increase the extraction efficiency. Apparently, the disadvantages of conventional extractants have led to the application of ionic liquid (IL) in the evolution of extraction of REE. IL was found as a potential extractant for REE due to its ability to extract certain metals, green solvent, and has the flexibility to create different combination of cation and anion. However, conventional extractants appear to be more effective in the extraction of REE compared to IL. Therefore, the complex solvents are then compromised and synergised to create better extractant with both advantages between conventional extractants and IL. Most synergistic extractants (SE) appear to be more effective in the extraction of REE and able to reduce the use of chemicals. These advantages make SE more desirable in solvent extraction. This paper highlights the evolution of REE extraction using various kind of extractants with advantages and disadvantages discoveries based on various literatures.

## 1. Introduction to rare earth elements

Rare earth elements (REE) are comprised of scandium (Sc), yttrium (Y), and a group of lanthanide. Lanthanide is a group of 15 elements located in periodic table under the 4f block and very close to radioactive elements (Singh, 2007). At the early stage of REE separation, REE were divided into two groups (Greenwood and Earnshaw, 1997). The first group is the light rare earth (LRE) or also known as cerium (Ce) group where Sc is considered as a part of LRE. The second group is the heavy rare earth (HRE) or also known as Y group. Greenwood and Earnshaw (Greenwood and Earnshaw, 1997) classified the REE into two divisions based on the solubility of REE in sodium sulphate (Greenwood and Earnshaw, 1997) where HRE is soluble in sodium sulphate but LRE is insoluble in sulphate solution.

Hatch Gareth (2012), however, convinced that REE should be

divided into three categories of light, medium, and heavy REE. Relatively few sources had acknowledged medium rare earth (MRE) as a new level that contains of samarium (Sm), europium (Eu), and Gadolinium (Gd) (Kabay et al., 2010; Walters et al., 2011; Hatch, 2012). The new division of MRE was caused by promethium (Pm), a scarce element exists in between neodymium (Nd) and samarium (Sm). The concentration of Pm in mineral is too little making it not feasible for commercial wise. This had formed a gap in between Neodymium (Nd) and Sm, creating a clear division of LRE and MRE. Apart from the scarcity of Pm MRE has moderate solubility in sodium phosphate compared to LRE and HRE. Therefore, Hatch (2012) and Haque et al. (2014) stated that the precise classification of REE is LRE (Lanthanum (La) to Nd), MRE (Sm to Gd), and HRE (Terbium (Tb) to Lutetium (Lu) and Y). Regardless, based on V. Zepf (Zepf, 2013), a lot of arguments had been made in deciding the grouping of REE into LRE, MRE, and

**Abbreviations:** ABC-BIL, bifunctional ionic liquid; CAPEX, capital expenditure; CHON, carbon, hydrogen, oxygen, and nitrogen; CMPO, octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide; CRE, critical rare earth; D2EHPA, di-(2-ethylhexyl)phosphoric acid; DHOA, N,N-di-n-hexyl octanamide; DODGAA, N,N-dioctyldiglycol amic acid; FIL, functionalised ionic liquid; HRE, heavy rare earth; HTTA, thenoyltrifluoro-acetone; IL, ionic liquid; LAMP, Lynas Advanced Material Plant; LLE, liquid-liquid extraction; LRE, light rare earth; MRE, medium rare earth; OPEX, operational expenditure; REE, rare earth elements; REO, rare earth oxides; SE, synergistic extractant; TBP, tributyl phosphate; TODGA, N,N,N',N'-tetraoctyldiglycolamide; VOC, volatile organic compound

\* Corresponding author at: Faculty of Chemical & Natural Resources Engineering, Universiti Malaysia Pahang, 26300 Gambang, Pahang, Malaysia.

E-mail address: [sumaiya@ump.edu.my](mailto:sumaiya@ump.edu.my) (S.Z. Abidin).

<https://doi.org/10.1016/j.mineng.2018.03.018>

Received 21 July 2017; Received in revised form 27 February 2018; Accepted 13 March 2018  
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HRE. The arguments are considered according to the characteristics, chemical data, ionic radius, and electron configuration of each REE (Zepf, 2013).

### 1.1. The resources of REE in minerals

Minerals bearing REE are available in mining reserves such as in mineral rocks mined from dry lands or placer deposit dug from watery reserves (Jordens et al., 2013; Rezaee Ebrahim Saraei et al., 2009; Sultan and Shazili, 2009). However, the concentration of REE in most of rock forming mineral is not economically efficient for commercial refining. The properties of minerals formed in different locations are varied in terms of its compositions. Apart from REE, other elements with similar properties are highly found in the same minerals as REE.

Based on geological survey, monazite, bastnasite, and xenotime are the three major minerals that enriched with REE and feasible for commercialisation. Mining and refining these minerals are practicable considering Ce, La, and Nd are enriched in bastnasite and monazite. While, xenotime bears mostly Y, Dy, Er, Yb, and Ho (Walters et al., 2011). Monazite is classified as phosphate minerals with a mixture composition of Ce, La, Pr, and Nd. In addition, monazite has a mix of radioactive elements such as thorium (Th) and uranium (U) at around 4–12% (Jordens et al., 2013). Bastnasite is a fluorocarbonate mineral and xenotime is an yttrium phosphate mineral (YPO<sub>4</sub>). Apart from bastnasite, monazite, and xenotime, ion-adsorbed clay is another source of REE that normally enriched with 60% of rare earth oxides (REO) (Haque et al., 2014).

Around 1988, Malaysia was the largest source of Y in the world that was extracted from xenotime quarried from the tin mining in Perak. Perak and Selangor were two known areas with xenotime and monazite. These minerals were actively excavated from tin placer deposits until the point where tin mining industry declined. Consequently, this situation affected the production and exportation of Y (Lee et al., 2011). REE industry on the other hand did not stop there in Malaysia. By 2010, Malaysia's direction in REE industry resumed when LYNAS invested in Lynas Advanced Material Plant (LAMP) to be built in Pahang, Malaysia. By 2013, this plant received continuous supply of raw REE ore from Lynas Australia for refining and production of REO (Haque et al., 2014).

REO reserves are abundance in around 30 countries. Though, China is well known to monopolise REE's market since 1990. China strongly holds the most power in the technology and the price of REE in the market. Baotou is a place in China that supplies approximately two third of REE from 95% of the world supply (Ryan, 2015). The REE market becomes tougher for other countries to compete with China despite the fact that the demand for REE increases yearly (Albrecht, 2015, 2016).

Bear Lodge Project is a new resource for REE located in North America. Bear Lodge Property has been claimed to contains 80% of the critical rare earth (CRE). As stated by the US Department of Energy in Critical Material Strategy Report, Nd, Eu, Tb, Dy, and Y are named as the critical rare earth elements within 5 to 15 years starting from 2011 (Bauer et al., 2010). These elements are classified as critical elements due to the scarcity of the elements. The aim of Bear Lodge Project is to compete with China in the production of CRE in terms of supply and price (Walters et al., 2011).

### 1.2. The values of REE

The significant values of REE are recognised on the ability to produce technologies with minimal emission release, boost in energy efficiency, and enhance digital technology. REE promises a future with advance green technology applications. Demand on REE has escalated as the world is aiming towards smaller, better, cleaner, and greener technology (Albrecht, 2015, 2013).

The use of REE in technologies nearly has no limits starting from the basic home appliances to aviation and space control. Nd for example, is well known as a high quality magnetic material and mostly used for

invention such as hybrid cars, wind turbines, and surgical robots. Other than that, the combination of Y, Pr, and Nd were used to improve glass shock resistance and lower the degree of expansion especially on high end welder's goggles (Greenwood and Earnshaw, 1997; Haque et al., 2014; Albrecht, 2015). Each of the elements offers a wide range of application regardless the similarity of their chemical and physical properties. Detailed researches on the application of REE are still ongoing as it leads to green innovation and invention.

### 1.3. The challenges in the production of REE

The production of high quality REE in large scale is complex due to its chemical properties. But, the complexity in the production of REE starts further before the breakdown of REE chemical properties. The challenges in the production of REE begins with the lack of REE resources, shortage in technical expertise, high capital expenditure (CAPEX) and operation expenditure (OPEX), unpredictable market price and demand, and the environmental, health, and safety concerns.

#### 1.3.1. The resources of REE

REO reserves are abundance in around 30 countries with approximately one hundred million tons of REO. Malaysia was reported as one of the world REE reserves with a total of 30,000 tons (0.03%) (Lee et al., 2011; Bauer et al., 2010). However, there is no general agreement on the information of legitimate plants that actually processes the excavated REE (Jordens et al., 2013). The formation of REE in minerals are varied and poorly understood by geological study (Walters et al., 2011). REE has never been found in equal or even predictable abundance. The continuous mining of REE might lead to declination of resources. This geological artefact is endlessly carved out from the earth crust until it is hardly left anything for the future.

The alternative to reduce the exploitation of REE reserves is done by recycling REE from the disposal of electronics waste. Certain countries took the initiative to recycle metals from old phone and spent batteries such as nickel-metal hydride (NiMH) battery (Xie et al., 2014). Y can be recovered from contaminated solutions, waste of electrical and electronic equipment (WEEE), and generic wastes (Innocenzi et al., 2014). REE can also be recovered from phosphor powder in fluorescent waste (Innocenzi et al., 2014). These are among the initiatives taken to reduce the continuous exploitation of REE reserves with the potential of reducing the cost for mining REE.

#### 1.3.2. Technical expertise

Technical expertise in REE industry mostly originates from China as this country gains the most profit from REE industry (Jordens et al., 2013). Technical understanding in the production of REE is essential to reduce the impact on the cost and quality of the final product. China is far ahead in REE technology since this country has become one of the major suppliers of REE in nearly four decades.

Regel-Rosocka and Alguacil (Regel-Rosocka and Alguacil, 2013) pointed out common complications encountered in the conventional production of REE. First, the loss of the organic phase into aqueous phase affected the volume of organic phase and reduced the extraction ability. Secondly, the risk of fire due to flammable diluents. Lastly, the formation of emulsion during extraction affects the quality of final recovery (Regel-Rosocka and Alguacil, 2013). These are the typical consequences of having poor understanding in technical aspects in the large scale production of REE.

Other than that, REE behaviour towards certain extractants makes the production more complex. For example, selectivity of Y can be anomalous as it can be similar to MRE when extracted by Versatic 10 (La < Ce < Nd < Gd < Y < Ho < Yb) and resembles to LRE when extracted by Napthenic acid (La < Ce < Y < Nd < Gd < Ho < Yb) (Xie et al., 2014). Lack of understanding in the behaviour of certain REE will lead to misperception of the best technical method or solution to be used.

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