

RESEARCH ARTICLE | JANUARY 20 2017

## Rare earth element enrichment using membrane based solvent extraction **FREE**

I. G. B. N. Makertiharta; P. T. Dharmawijaya; M. Zunita; I. G. Wenten



*AIP Conf. Proc.* 1805, 070001 (2017)

<https://doi.org/10.1063/1.4974442>



View  
Online



Export  
Citation

CrossMark

### AIP Advances

Why Publish With Us?

- 25 DAYS**  
average time to 1st decision
- 740+ DOWNLOADS**  
average per article
- INCLUSIVE**  
scope

[Learn More](#)

# Rare Earth Element Enrichment Using Membrane Based Solvent Extraction

I.G.B.N. Makertiharta, P.T. Dharmawijaya, M. Zunita and I G. Wenten\*

*Department of Chemical Engineering, Faculty of Industrial Technologi, Institut Teknologi Bandung, Jl. Ganesha 10, Bandung, 40132, Indonesia*

\*Corresponding author: igw@che.itb.ac.id

**Abstract.** The chemical, catalytic, electrical, magnetic, and optical properties of rare earth elements are required in broad applications. Rare earth elements have similar physical and chemical properties thus it is difficult to separate one from each other. Rare earth element is relatively abundant in earth's crust but rarely occur in high concentrated deposits. Traditionally, ion-exchange and solvent extraction techniques have been developed to separate and purify single rare earth solutions or compounds. Recently, membrane starts to gain attention for rare earth separation by combining membrane and proven technologies such as solvent extraction. Membrane-based process offers selective, reliable, energy efficient and easy to scale up separation. During membrane-based separation process, one phase passes through membrane pores while the other phase is rejected. There is no direct mixing of two phases thus the solvent loss is very low. Membrane can also lower solvent physical properties requirement (viscosity, density) and backmixing, eliminate flooding phenomenon and provide large interfacial area for mass transfer. This paper will summarize research efforts in developing membrane technology for rare earth element separation. Special attention will be given to solvent extraction related process as the commonly used method for rare earth element separation. Furthermore, membrane configuration and its potentials will also be discussed.

**Keywords:** rare earth, membrane, solvent extraction, hydrometallurgy, purification

## INTRODUCTION

Rare earth elements (REE) are a group of fifteen elements belonging to the lanthanide series with unique properties that are useful for the development of green and energy efficient technologies<sup>1</sup>. REE can be classified into light rare earths (LRE) (e.g. lanthanum, cerium, praseodymium, neodymium, promethium, and samarium) and heavy rare earths (HRE) (europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium) according to International Union of Applied and Pure Chemistry (IUPAC)<sup>2</sup>. Despite of their name, REE are not so rare in terms of crustal abundance. However, they are deposited in low concentration (about 200 known minerals with less than 0.01%) and difficult to be separated from one another make them considered rare<sup>3</sup>. Most RRE are obtained from rare earth minerals like banastite, monazite, and xenotime<sup>4</sup>. REE is widely used for various applications such as catalyst, glassmaking, metallurgy, ceramics, and permanent magnets<sup>5,6</sup>.

Separation and purification of single REE from their minerals is difficult and often determines the economic and environmental aspect of the process. Solvent extraction is a common separation process for metal ion usually used because of its simplicity, speed and wide scope. Moreover, it can be used for trace metal separation from their minerals. On the other hand, there have been increasing concerns for the environmental impact of solvents used for solvent extraction<sup>1</sup>.

Membrane technology has rapid development primarily due to its advantages and potential to various applications in various sectors<sup>7-11</sup>. Membranes are a key element to increase the sustainability of chemical plant<sup>12,13</sup>. The interest of membrane usage is now widely varied starting from hydrogen production<sup>14,15</sup> up to petroleum refining and conversion, clean fuel production, and other applications<sup>16</sup>. Membrane materials are also varying from polymeric, inorganic, and liquid solvents.

Solvent extraction has been used for mineral processing since the mid-1960s. Mixtures of two different solvents, namely synergistic extraction, can intensify the extraction of a metal compared to the normal effect obtained by using these solvents separately<sup>17</sup>. Many authors reported the synergistic solvent extraction system for extracting and separating rare earths using acidic, natural and solvating solvents<sup>18-25</sup>. Various alternatives to solvent extraction have been explored and advances in separation technologies have shown commercial establishment of membrane technology to substitute conventional solvent extraction for metal and other valuable materials recovery. Membrane process can be used to modify conventional solvent extraction by membrane contactor or liquid membrane. Membrane contactor provides interface between immiscible solvent so that only requires small system. Liquid membrane typically traps solvent in a module and pass the metal through the solvent with minimal loss of solvent. Ionic liquids have also been developed to substitute solvents for liquid membrane application<sup>26</sup>.

Despite of the successful application for rare earth separation, solvent extraction technology still needs modifications to achieve better performance and efficiency. Its sustainability and environmental benign should be increased. One possible way is through a modification of membrane process into the separation and purification process. This work will discuss about integration of membrane process into separation and purification of REE. Some key aspects to the development of membrane based REE separation will be discussed in detail.

## RARE EARTH METAL SEPARATION

Solvent extraction is a common technique to produce pure chemical compounds in various chemical industries such as pharmaceuticals, heavy organics and metals. Solvent extraction is based on fundamental physical chemistry of solvent-solute interaction, activity factors of the solutes in the pure phases, aqueous complexation and complex adduct interactions<sup>27</sup>. Most separation and purification process of REE use solvent extraction techniques using two immiscible liquids (solvents) to obtain two liquid phases with different metal ions concentration<sup>26,27</sup>.

Acid extractants follow a cation exchange extraction mechanism that involve displacement of a proton from extractant by the extracted metal and form a neutral complex that soluble in organic. The common acid extractants used are phosphoric, phosphonic, and carboxylic acids (C7-C15). In solvating extractants, the extractant removes some water molecules from hydrated metallic ion to boost their solubility in organic phase. The most common solvating extractants in REE separation is tri-butyl-phosphate (TBP). Basic extractants remove metallic ions from aqueous solutions as anionic complexes by anion exchange. Typical basic extractants are long chain amines<sup>26</sup>.

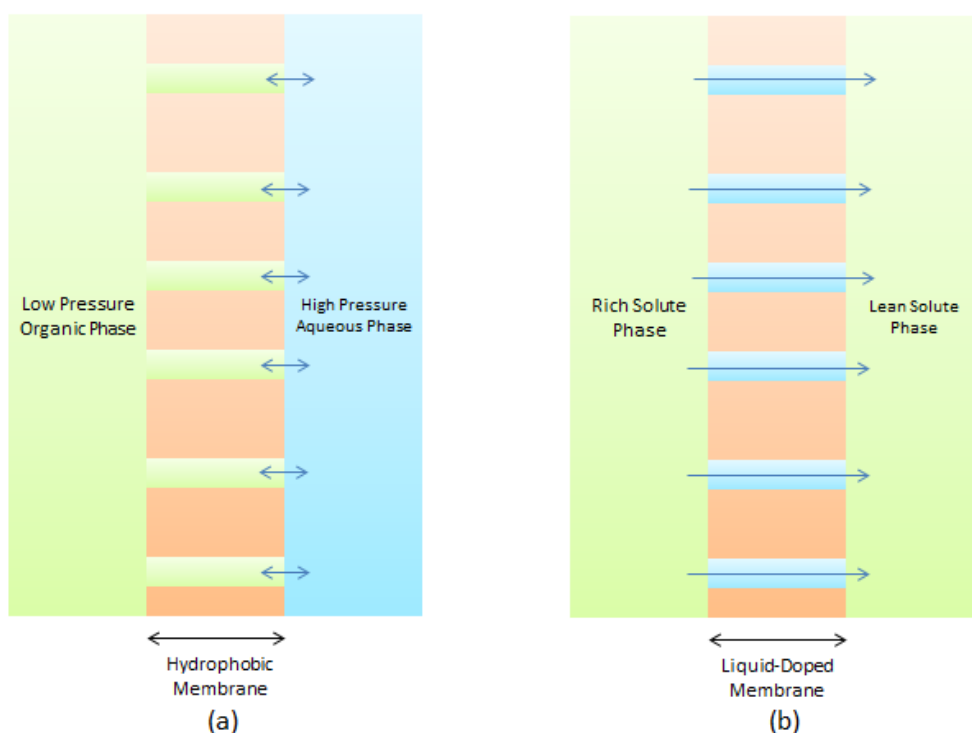
As stated before, bastnesite, monazite, and xenotime are the main rare earth mineral used for commercial purpose. Bastnesite concentrates are relatively straightforward to treat<sup>28</sup>. First, bastnesite concentrates are roasted to decompose carbonate minerals prior leaching with either hydrochloric or sulfuric acid. Cerium has the major composition in bastnesite. Hence, it should be removed first to reduce downstream equipment size. CeO<sub>2</sub> which is insoluble in acidic lixivants is formed during roasting. However, hydrochloric acid may promote reduction of Ce(IV) to Ce(III) making it hard to be separated from Ln(III). Other option is to oxidize cerium in aqueous phase after leaching all rare earths and recover it by filtration. For example, Ce(OH)<sub>4</sub> was precipitated at thorium plant using ammonium carbonate and ammonium persulfate<sup>28</sup>. Monazite and xenotime concentrates can be leached to decompose the orthophosphate lattice by either sodium hydroxide or sulfuric acid at elevated temperature. Sodium hydroxide is commonly chosen due to its better phosphate separation from the rare earths<sup>29</sup>. The ion-adsorption type rare earth ores are usually leached directly with inorganic acid, either in dumps or in situ, resulting in dissolution of most of rare earths in acidic solutions<sup>30-32</sup>.

## MEMBRANE SOLVENT EXTRACTION RARE EARTH SEPARATION

Membranes are selective barriers than can transport particular species from one side to another. Membranes have been proven to be efficiently used for traditional equilibrium-based separation process such as solvent extraction. Nevertheless, solvent extraction requires well-dispersion of one phase in another for efficient contacting. Moreover, coalescence problem often arise with the disadvantages of loading, flooding and third phase formation<sup>1</sup>. The major advantages of membrane technique over conventional dispersion technique are: dispersion free operation, modular design for easier scale up, very high contact surface area per unit volume, independent control of process strain flow rates that eliminate loading and flooding limitation, easier handling of particulates<sup>2,3,33,34</sup>. Membrane operation that beneficial for REE separation and purification are membrane contactor and liquid membrane. The schematic difference of membrane contactor and liquid membrane is depicted in Fig. 1.

In membrane contactor (or extractor), an organic phase wets a microporous hydrophobic membrane and passes through one side while the other side of the membrane which is non-wetting aqueous phase with high enough pressure will hold the organic phase from getting out to aqueous phase. This way, aqueous-organic interface will be formed and kept at the pore mouth of the membrane. The solute transfer will be occurred through said interfaces. In this case, membrane does not function as a selective transport medium. It provides necessary interface and prevent the dispersion of both phases. It also influences the species extraction rate <sup>1</sup>.

On the other hand, liquid membrane acts as an immobilized solvent in which a transported solute related to its solubility in the liquid membrane used. One interesting case is when the transported solute actively reacts with the liquid and formed a solute-carrier complex. This transport mechanism is called facilitated or carrier-mediated transport <sup>5</sup>. There have been various separation objective for carrier-mediated transport using organic membrane <sup>35, 36</sup>. The separation for this method is controlled by the extraction/back-extraction equilibrium at the interfaces and reaction kinetics between solute and solvent under a non-equilibrium mass transfer process <sup>37</sup>. For the separation of metal ions, acidic ligands are commonly used for the extractant carriers <sup>38-41</sup>. One of the most important advantages of said system is the ability to tune the selectivity and efficiency of the transport via pH control of aqueous feed and/or receiving phases <sup>42</sup>.



**FIGURE 1.** Schematic difference between (a) membrane contactor and (b) liquid membrane

Goto et al. <sup>43</sup> develop a membrane separation process for Y, Ho and Er in a hollow fiber membrane extractor modified by plasma grafting polymerization. The result showed that plasma grafting enhance poly(acrylamide) adsorbance to REE under high influence of pH. It also provides a successful application of hollow fiber membrane module for REE separation.

For liquid membrane technique, synergistic extraction studied by several authors showed better performance compared with individual extractant <sup>44</sup>. Joshi et al. <sup>45</sup> studied the transport of uranium (VI) and europium (III) using supported liquid membrane using D<sub>2</sub>EHPA and some organo-phosphorous oxodonors (TBP, DBBP, TOPO, and Cyanex923). The study showed that supported liquid membrane that use TOPO and D<sub>2</sub>EHPA has good selectivity of U(VI) over Eu(III) from phosphoric acid feed. This combination is also reported to have good performance for separation of Nd from lanthanide series using hollow fiber supported liquid membrane <sup>46</sup>. Other synergistic effect was observed between Cyanex272 and TBP for the separation of yttrium ions from rare earths mixture in a microporous hydrophobic hollow fiber supported liquid membrane <sup>42</sup>. Zaheri et al. <sup>6</sup> studied the combination of

D2EHPA and Cyanex272 for separation of Eu from Dy. The paired extractant showed good selectivity for Eu and good long term stability.

## SUMMARY AND FUTURE OUTLOOK

The general trends of membrane based solvent extraction for REE separation and purification have been reviewed. Membrane-based process has the potential to push forward REE separation process to sustainable and environmentally benign process. The use of membrane contactor and liquid membrane can enhance the effectivity of solvent extraction in terms of chemicals and space used in a plant. The integration of membrane into solvent extraction is still open for modification in terms of membrane materials, process configuration, solvent used and combination of them.

## REFERENCES

1. A. Gaikwad, K. Chitra, G. Surender, and A. Damodaran, *Chemical and Biochemical Engineering Quarterly* **17** (3), 191-200 (2003).
2. C. Tompkins, A. Michaels, and S. Peretti, *Journal of Membrane Science* **75** (3), 277-292 (1992).
3. J. C. Hutter and G. Vandegrift, presented at *the ACS Symposium Series* 1992 (unpublished).
4. H. Ding, P. Carr, and E. Cussler, *AIChE Journal* **38** (10), 1493-1498 (1992).
5. C. Porter Mark, (New Jersey, Noyes publications, 1990).
6. P. Zaheri, H. Abolghasemi, M. G. Maraghe, and T. Mohammadi, *Chemical Engineering and Processing* **92**, 18-24 (2015).
7. E. Drioli, A. I. Stankiewicz and F. Macedonio, *Journal of Membrane Science* **380** (1), 1-8 (2011).
8. H. Strathmann, A. Grabowski, and G. Eigenberger, *Industrial and Engineering Chemistry Research* **52** (31), 10364-10379 (2013).
9. I. Wenten, *Desalination* **391**, 112-125 (2016).
10. N. F. Himma, S. Anisah, N. Prasetya, and I. G. Wenten, *Journal of Polymer Engineering* **36** (4), 329-362 (2016).
11. K. Khoiruddin, A. Hakim, and I. Wenten, *Membrane Water Treatment* **5** (2), 87-108 (2014).
12. M. De Falco, A. Salladini, E. Palo, and G. Iaquaniello, *Industrial and Engineering Chemistry Research* **54** (27), 6950-6958 (2015).
13. J. Catalano, F. Guazzone, I. P. Mardilovich, N. K. Kazantzis, and Y. H. Ma, *Industrial and Engineering Chemistry Research* **52** (3), 1042-1055 (2012).
14. H. Li, K. Haas-Santo, U. Schygulla, and R. Dittmeyer, *Chemical Engineering Science* **127**, 401-417 (2015).
15. S. Yun and S. T. Oyama, *Journal of Membrane Science* **375** (1), 28-45 (2011).
16. N. Kanellopoulos and M. Menéndez, in *Nanoporous Materials for Energy and the Environment* (Pan Stanford Publishing, Northwestern, 2011), pp. 283-297.
17. M. Aguilar and J. L. Cortina, *Solvent Extraction and Liquid Membranes: Fundamentals and Applications in New Materials*. (CRC Press, New York, 2008).
18. W. Xianglan, L. Wei, and L. Deqian, *Journal of Rare Earths* **29** (5), 413-415 (2011).
19. T. Miaomiao, J. Qiong, and L. Wuping, *Journal of Rare Earths* **31** (6), 604-608 (2013).
20. X. Sun, J. Zhao, S. Meng, and D. Li, *Analytica Chimica Acta* **533** (1), 83-88 (2005).
21. X. Huang, L. Jianning, L. Zhiqi, Y. Zhang, X. Xiangxin, and Z. Zhaowu, *Journal of Rare Earths* **26** (3), 410-413 (2008).
22. Y. Zhang, L. Jianning, X. Huang, W. Chunmei, Z. Zhaowu, and G. Zhang, *Journal of Rare Earths* **26** (5), 688-692 (2008).
23. X. Sun, J. Wang, D. Li, and H. Li, *Separation and Purification Technology* **50** (1), 30-34 (2006).
24. R. Banda, H. Jeon, and M. Lee, *Separation and Purification Technology* **98**, 481-487 (2012).
25. R. Torkaman, M. Moosavian, J. Safdari, and M. Torab-Mostaedi, *Annals of Nuclear Energy* **62**, 284-290 (2013).
26. T. Makanyire, S. Sanchez-Segado, and A. Jha, *Advances in Manufacturing* **4** (1), 33-46 (2016).
27. J. Rydberg, *Solvent Extraction Principles and Practice, Revised and Expanded*. (CRC Press, New York, 2004).

28. L. L. Rokhlin, *Magnesium Alloys Containing Rare Earth Metals: Structure and Properties*. (CRC Press, New York, 2003).
29. P. Alex, A. Suri, and C. Gupta, *Hydrometallurgy* **50** (3), 331-338 (1998).
30. Z. Heng, W. Yiming, J. Huaichun, and C. Xuesong, *Journal Chinese Rare Earth Society* **25** (1), 80 (2007).
31. Q. Tingsheng, F. Xihui, C. Lifeng, and F. Yanxi, *Journal of Rare Earths*, **26** (2), 274-278 (2008).
32. F. Xie, T. A. Zhang, D. Dreisinger, and F. Doyle, *Minerals Engineering* **56**, 10-28 (2014).
33. R. Prasad, S. Khare, A. Sengupta, and K. Sirkar, *AIChE Journal* **36** (10), 1592-1596 (1990).
34. C. Wang, R. Bajpai, and E. Iannotti, *Applied Biochemistry and Biotechnology* **28** (1), 589-603 (1991).
35. M. Azhin, T. Kaghazchi, and M. Rahmani, *Journal of Industrial and Engineering Chemistry* **14** (5), 622-638 (2008).
36. S. C. Lee, *Journal of Industrial and Engineering Chemistry* **14** (2), 207-212 (2008).
37. X.-J. Yang and A. G. Fane, *Separation Science and Technology* **34** (9), 1873-1890 (1999).
38. L. Bromberg, I. Lewin, and A. Warshawsky, *Journal of Membrane Science* **70** (1), 31-39 (1992).
39. R.-S. Juang, *Journal of Membrane Science* **85** (2), 157-166 (1993).
40. H. Kondo, M. Nishida, and I. Yoshida, *Analytical Sciences* **18** (2), 113-118 (2002).
41. Y. Yamini, M. Chaloosi, and H. Ebrahimzadeh, *Separation and Purification Technology* **28** (1), 43-51 (2002).
42. P. Ramakul, T. Supajaroen, T. Prapasawat, U. Pancharoen, and A. W. Lothongkum, *Journal of Industrial and Engineering Chemistry* **15** (2), 224-228 (2009).
43. M. Goto, T. Miyata, K. Uezu, T. Kajiyama, F. Nakashio, T. Haraguchi, K. Yamada, S. Ide, and C. Hatanaka, *Journal of Membrane Science* **96** (3), 299-307 (1994).
44. A. Gaikwad, *Talanta* **63** (4), 917-926 (2004).
45. J. Joshi, P. Pathak, A. Pandey, and V. Manchanda, *Hydrometallurgy* **96** (1), 117-122 (2009).
46. T. Wannachod, N. Leepipatpiboon, U. Pancharoen, and S. Phatanasri, *Journal of Industrial and Engineering Chemistry* **21**, 535-541 (2015).