Recovery of Critical Rare Earth Elements for Green Energy Technologies

Jyothi Rajesh Kumar and Jin-Young Lee

Abstract 21st century is electronic revolution in human lives as well as energy is a one of the most significant task. Rare earth elements (REEs) occupies key role in our daily life as well as high-tech industrial applications. REEs are one of the energy critical elements, for sustainable growth, it depends on their utilization and re-use, reduce, recycling policy employments. The rapid growth of population and their needs will raise the demand of certain REEs. Global wide REE deposits mainly located at China, from 2010 onwards China made policy to control exports of REE's to foreign countries. REEs are utilized in many modern electrical and electronic devices such as smart phones, computers, LED lights etc. Recovery of the REEs from secondary resources is one of the best solution and alternative option, it needs co-ordination between nations as well as sustainable environmental regulations and implications and certain education to undeveloped countries. As per the Department of Energy (DoE), US the following rare earth elements (REEs) were under critical situation: Dy, Y, Nd, Tb, Eu, in another two namely Ce and Te under near to critical matrix. It shows that REEs scarcity for industry as well as sustainable developments is growing fast. As well as REEs are used in clean energy and defense technologies. As well as REEs predicted shortfall (million US $) are as follows: Y-85, Dy-22, Er-12 and Tb-7 etc. Green energy technologies should have high efficiency, clean and renewable and carbon-di-oxide emissions under control.

J. Rajesh Kumar · J.-Y. Lee (✉)
Convergence Research Center for Development of Mineral Resources (DMR),
Korea Institute of Geoscience and Mineral Resources (KIGAM),
Daejeon 305-350, Korea
e-mail: jinlee@kigam.re.kr

J. Rajesh Kumar
e-mail: rkumarphd@kigam.re.kr; rajeshkumarphd@rediffmail.com

H. Kim et al. (eds.), *Rare Metal Technology 2017*,
The Minerals, Metals & Materials Series,
DOI 10.1007/978-3-319-51085-9_2

Introduction

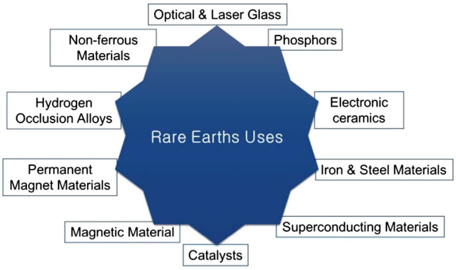
The fields of the rare earths recovery technologies are fascinating. Significant research and development work continues globally to explore and establish ways and means to put the rare earths to use, precious metals to recover and individually and collectively, in the service of civilization. The demand for rare-earths (REs) in the international markets increases with increasing developments in the advanced and high-tech technologies. The rare earths have an ever growing variety of applications in the modern technology. They provide many an industry with crucial materials and they provide many a customer with benefits. From these beginnings and over many years, industrial applications of rare earths have developed in metallurgy, magnets, ceramics and electronics, chemical, optical, medical and nuclear technologies.

A chronological account of the Chemistry and metallurgy especially hydrometallurgy (aqueous processing of the metal ions) of the REs arranges into three eras or ages. The period prior to 1950 may be called the Dark Age. The next two decades were the Age of Enlightenment. The period after early 1970s may be considered as Golden Age. In the first three decades of this golden era a number of remarkable advances and discoveries were made in the field of rare metals and these have left the future of the rare metals will be glorious and full of excitement, be it in Science, Technology, or in commercial utilization [1].

The REs have an ever growing variety of applications in the modern technology (Fig. 1). They provide many an industry with crucial materials and they provide many a customer with benefits. From these beginnings and over many years, industrial applications of rare metals have developed in metallurgy, magnets, ceramics and electronics, chemical, optical, medical and nuclear technologies. RE primary products are mainly used as raw materials for high-purity individual RE chemicals, and in making of petroleum and environment protection catalysts, misch metal and polishing powders.

Although the demand for REs will further increase in future, the problem of balancing between medium and heavy rare metals with light ones will continue to create trouble as before. The rare earth ore contains various metals of a nearly constant composition. Since RE cost level is likely to go up when, as a result of increasing demand for some specific rare metals the remaining ones are unutilized,

Fig. 1 Rare earths applications and uses in various sectors



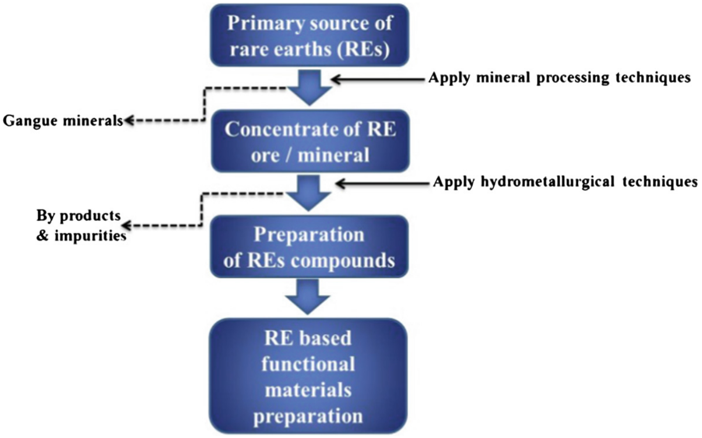


Fig. 2 Mineral processing and hydrometallurgical processing of the REs from primary sources to prepare functional materials

the rare earth manufactures will find it difficult to maintain stability in the supply of large quantities. There is a need to develop a demand for utilized rare metals or preferably a balanced demand for the available quantities of various rare metals.

There is yet another problem of distinguishing between the resources producing countries and resources consuming countries. Except America which possesses a vast reserve, major rare earth consuming countries like South Korea, Europe, Japan and others have to totally depend on imports, as mentioned earlier. As they don't have natural resources, it is difficult for them to ensure either a stable price or a stable volume of rare earth supply. Therefore, it might be necessary to promote mutual exchange of information and market exploration between the producing countries and to establish international collaboration at every stage from the starting material to final product. For REs processing from primary (or) secondary resources hydrometallurgy is one of the economical and environmentally friendly subject areas. The general flowsheet of the primary sources of REs processing was presented in Fig. 2.

Solvent extraction (liquid-liquid extraction) is widely used method for the separation of REs. In liquid-liquid extraction process, organophosphorus extractants have been commonly employed to achieve high separation efficiency between REs. The role of liquid-liquid extraction in metal recovery was presented as Fig. 3. The present paper deals the all possible area of hydrometallurgy to recover the REs. The general flowsheet of the LLE processing was presented as Fig. 4.

China having majority of the RE reserves about 36%, Russia other CIS (Common wealth of Independent States) nations having 19%, USA having 13% and Australia has 5% of the RE reserves. A global market receives the REs from various sources currently such as bastnasite, xenotime, RE laterite, ion adsorption

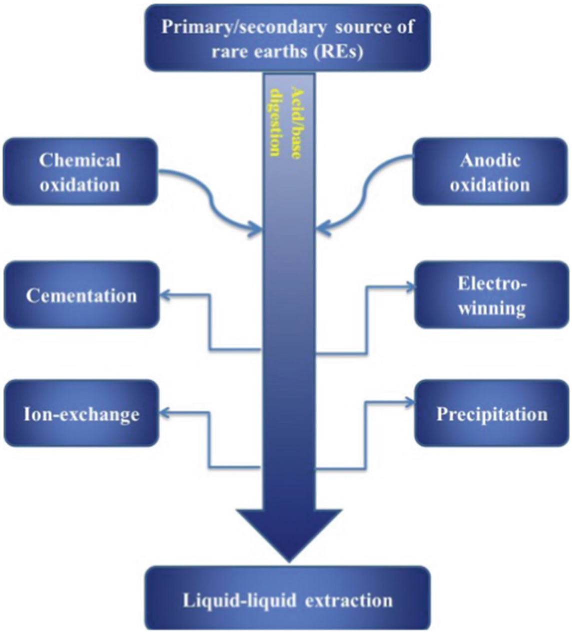


Fig. 3 The role of liquid-liquid extraction in metallurgical processing of REs from primary (or) secondary resources

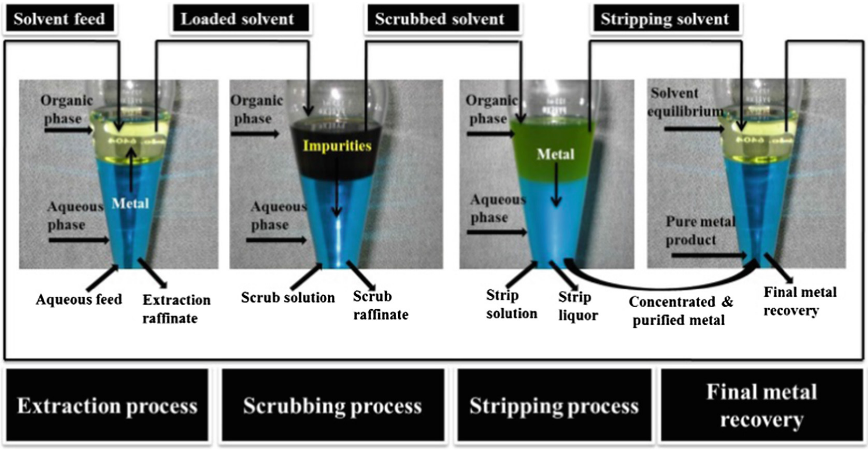


Fig. 4 General metal recovery flowsheet through liquid-liquid (solvent) extraction technique

clays and loparite etc. From year 2010 China reduces export quotas up to −40%, this is the main cause to elevation the criticality of demand REs. In new millennium, advanced and cleaner technologies were prime priorities in developed/ devolving nations. South Korean government made goal on this subject area of

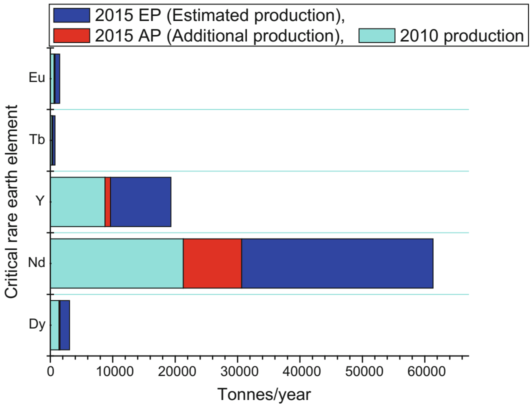


Fig. 5 Critical REEs supply and production comparisons in the years 2010 and 2015 [2]

research is make sure a reliable supply of materials critical to Korean mainstay industries. And develop the research and development policy for recycling of end-use products and designing for recyclability [2]. The critical rare earth elements supply and production was compared with year 2010 and 2015, the data was presented in Fig. 5.

Critical Rare Earths Processing by Hydrometallurgical Routes

Light rare earths processing by using tri-butyl-phosphate is well known route for single LREs separation and extraction (Fig. 6). The other organo-phosphorous based extractant such as TOPS 99 (equivalent to di-ethyl-hexyl-phosphoric acid). This process was developed by two stages, the beginning stage cerium was removed by precipitation methodology by using NaOCl mixed with NaOH, and purity of Ce is 78%. Cerium free raffinate solutions processed for other LREs (Fig. 7). Another organo-phosphorous based extractant such as PC-88A was saponified with NaOH then utilized for mixed rare earth chloride processing (Fig. 8).

The other critical REs such as Y, Dy and Tb were proceed by using various extractants through liquid-liquid extraction process. The first extraction cascade proceed by Versatic acid, the extraction raffinate solutions were generated LRE (light rare earths) rich concentration and loaded organic further processed by scrubbing and final LO contains HREs (Heavy rare earths). The scrubbed raffinate solutions were proceed for yttrium oxide by using TBP. The final extraction cascade was proceed for Tb and Dy by using saponified PC-88A (Fig. 9).

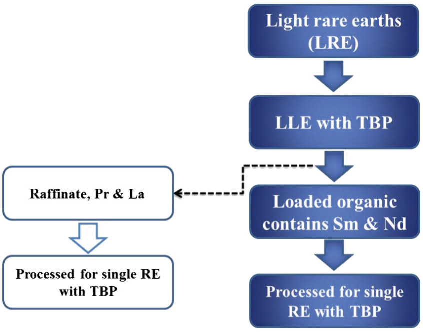


Fig. 6 Solvent extraction (liquid-liquid extraction (LLE)) of LREs from aqueous solutions by using TBP as an extractant system (this method developed by Indian Rare Earths Ltd (IREL, India)) [1]

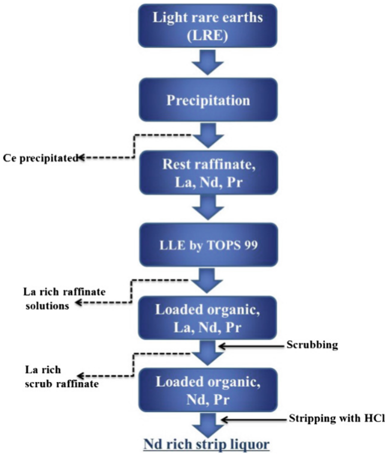


Fig. 7 LREs processed by hydrometallurgical methods [3]

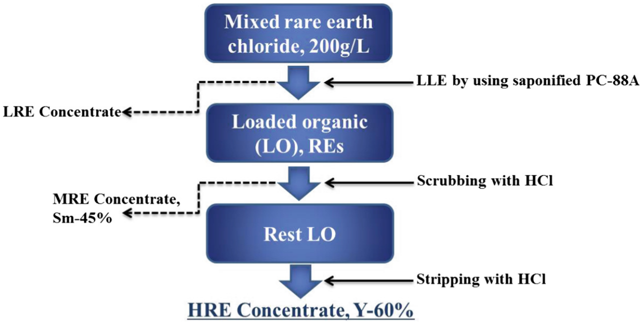


Fig. 8 REs processed by liquid-liquid extraction (LLE) by saponified PC-88A [1, 4]

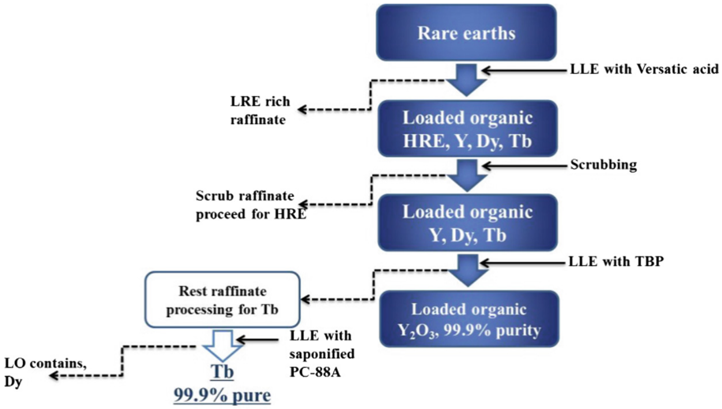


Fig. 9 Simultaneous extraction of Y, Tb and Dy by using various extractants [1, 4]

Critical Rare Earth Elements Processing by Iono-Metallurgical Routes

The media for metal recovery process is most important in metallurgy. Recent times, new class of solvents are applying in metal recovery, those are ionic liquids (molten (or) around ambient temperatures) [5, 6]. By using hydrometallurgical methods people were facing two major problems, one is waste water generation and further treatment, the other one is involving toxic chemicals such as cyanide, concentrated mineral acids, and caustic soda etc. [5]. Ionic liquids (ILs) were used in iono-metallurgy subject; these were involving low temperature processing for metals, this property will avoid the aqueous chemistry [5]. ILs was composed solely of ions, the liquid temperature below 100 °C. Various ionic liquids utilized for critical REs extraction processing, this summary data was presented in Table 1.

Rare Earths Processing by Using Organo-Phosphorus Extractants

Acidity ranged 0.5–5 mol/L was studied by using TOPS 99 (an equivalent to di-ethyl-hexyl-phosphoric acid) as an extractant system and H_3PO_4 solutions. The obtained data was presented as Fig. 10. Based on obtained data lower acidic conditions were more promising to critical REs such as Y, Dy, Tb and Nd. Concern separation factors data was also included in the Fig. 10. The other P based extractant PC 88A was utilized for REs separation at lower acidic ranges; the

Table 1 Critical rare earths extraction processing by using ILs

Name of the IL	Media	Remarks	References
Neodymium extraction			
Tri-hexyl(tetradecyl)phosphonium benzoate [T66614][BA] Tri-hexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide [T66614][TFSA]	Chloride	The extraction efficiency was reported up to 98% for 2–52 g/L of feed Nd solutions The loaded Nd metal was back extracted (stripping) by using HCl (or) HNO_3	[7]
1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C6mim][NTf2]	pH 1–6 studied range	The possible extraction of neodymium was proposed as: $Nd(NO_3)_3 \cdot [Ph_3PC_3P(OEt)_2][PF_6]$ (IL)	[8]
Trihexyl(tetradecyl)phosphonium chloride (Cyphos® IL 101)	Nitrate	Nd and Dy were separated by using EDTA and 99.6% pure Nd_2O_3 was recovered by this method	[9]
Choline bis(trifluoromethylsulfonyl)imide, [Chol][Tf2N (IL) combined with choline hexafluoroacetylacetonate, [Chol][hfac] (extractant)	pH 2–6 studied range	The extracted neodymium compound was proposed as [Chol][Nd(hfac)4]. This compound crystal studies were examined	[10]
Trioctylmethylammonium dioctyl diglycolamate, [A336][DGA] (IL) mixed with trioctylmethylammonium nitrate, [A336][NO_3] (diluent)	pH 1–6.8 studied range	100% of Nd extraction was achieved by this IL, this extraction process was exothermic in nature was observed	[11]
1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [C_6mim][NTf_2], 1-hexyl-3-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, [C_6mpyr][NTf_2], and tributylmethylammonium bis(trifluoromethylsulfonyl)imide, [N_{1444}][NTf_2]	pH 0.5–6.0 studied range	Initial pH 2 is optimized condition for maximum Nd extraction. By using 1 mol/L nitric acid loaded Nd can recover by with four stages	[12]
Dysprosium extraction			
Tetraoctylphosphonium oleate [P8888][oleate]	pH 0.0–8.0 studied range	At pH 6.5 100% Dy extraction was reached. The trend of extraction efficiencies compare with other REs as follows: Yb > Er > Dy > Sm > Nd > La	[13]

(continued)

Table 1 (continued)

Name of the IL	Media	Remarks	References
TBP and triethyl-pentyl-phosphonium bis (trifluoromethyl-sulfonyl)amide ([P2225][TFSA])	–	The complex formed as $[\mathrm{RE(TBP)}_m^{3+}(\mathrm{TFSA}^-)_{x+y}]_{\mathrm{IL}}$ reported, here RE = Pr (or) Nd (or) Dy	[14]
Yttrium extraction			
[1-Alkyl-3-(1-carboxylpropyl)im][PF6]	Nitric acid	This IL was saponified then used for Y extraction. The stripping efficiency reported about 95%. The cation-exchange mechanism was proposed	[15]
Europium and terbium extraction			
Trifluoromethyl-1,3-diketonate-functionalised IL	Neutral pH	99% of the Eu and Tb were extracted	[16]

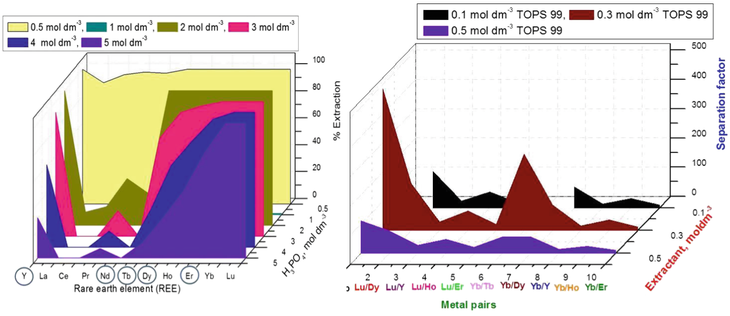


Fig. 10 Acid effect on rare earths using TOPS 99 as an extractant (adopted/reproduced from our own paper) [17]

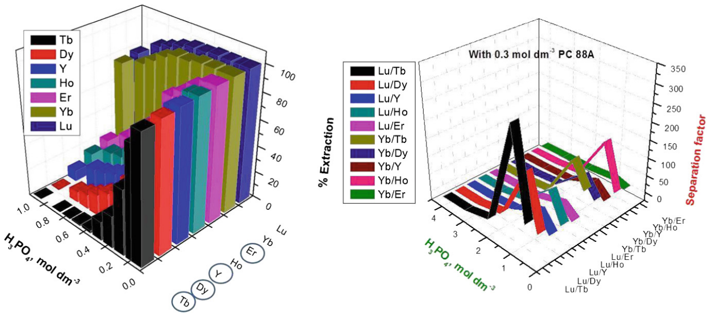


Fig. 11 Acid effect on rare earths using PC 88A as an extractant (adopted/reproduced from our own paper) [17]

obtained data was presented in Fig. 11. And it make known that, below 0.2 mol/L H3PO4 condition is better for critical REs.

Acknowledgements This research was supported by the Convergence Research Project (CRC-15-06-KIGAM) funded by the National Research Council of Science and Technology (NST).

References

1. N. Krishnamurthy, C.K. Gupta, *Extractive Metallurgy of Rare Earths*, 2nd edn. (CRC Press, 2016)
2. Critical materials strategy, DOE, USA, 2010
3. S. Radhika, B.N. Kumar, M.L. Kantam, B.R. Reddy, Solvent extraction and separation of rare-earths from phosphoric acid solutions with TOPS 99. Hydrometallurgy **110**, 50–55 (2011)
4. N.V. Thakur, Mineral Process. Extractive Metal. Rev. **21**(1–5), 277–306 (2000)

5. A.J. Hunt, *Element recovery and sustainability* (RSC Publishing, 2013) (ISBN: 978-1-84973-616-9)
6. A.P. Abbott, G. Frisch, S.J. Gurman, A.R. Hillman, J. Hartley, F. Holyoak, K.S. Ryder, Ionometallurgy: designer redox properties for metal processing. Chem. Commun. **47**, 10031–10033 (2011)
7. M. Panigrahi, M. Grabda, D. Kozak, A. Dorai, E. Shibata, J. Kawamura, T. Nakamura, Liquid–liquid extraction of neodymium ions from aqueous solutions of $NdCl_3$ by phosphonium-based ionic liquids. Sep. Puri. Tech. **171**, 263–269 (2016)
8. W. Junping, Z. Jieying, F. Da, K. Xinchun, S. Yunyu, Z. Lingling, L. Hongze, J. Rare Earths **34**, 83–90 (2016)
9. S. Riano, K. Binnemans, Extraction and separation of neodymium and dysprosium from used NdFeB magnets: an application of ionic liquids in solvent extraction towards the recycling of magnets. Green Chem. **17**, 2931–2942 (2015)
10. B. Onghena, J. Jacobs, L.V. Meervelt, K. Binnemans, Homogeneous liquid–liquid extraction of neodymium(III) by choline hexa fluoroacetylacetonate in the ionic liquid choline bis (trifluoromethylsulfonyl)imide. Dalton Trans. **43**, 11566–11578 (2014)
11. A. Rout, K. Binnemans, Solvent extraction of neodymium(III) by functionalized ionic liquid trioctylmethylammonium dioctyl diglycolamate in fluorine-free ionic liquid diluent. Ind. Eng. Chem. Res. **53**, 6500–6508 (2014)
12. A. Rout, J. Kotlarska, W. Dehaen, K. Binnemans, Liquid–liquid extraction of neodymium(III) by dialkylphosphate ionic liquids from acidic medium: the importance of the ionic liquid cation. Phys. Chem. Chem. Phys. **15**, 16533 (2013)
13. D. Parmentier, T.V. Hoogerstraete, S.J. Metz, K. Binnemans, M.C. Kroon, Selective extraction of metals from chloride solutions with the tetraoctylphosphonium oleate ionic liquid. Ind. Eng. Chem. Res. **54**, 5149–5158 (2015)
14. M. Matsumiya, Y. Kikuchi, T. Yamada, S. Kawakami, Extraction of rare earth ions by tri-*n*-butylphosphate/phosphonium ionic liquids and the feasibility of recovery by direct electrodeposition. Sep. Puri. Tech. **130**, 91–101 (2014)
15. W. Wei, L. Yu, X. Aimei, Y. Hualing, C. Hongmin, C. Ji, Solvent extraction of yttrium by task-specific ionic liquids bearing carboxylic group. Chin. J. Chem. Eng. **20**(1), 40–46 (2012)
16. J.H. Olivier, F. Camerel, R. Ziessel, Lanthanide ion extraction by trifluoromethyl-1,3-diketonate-functionalised ionic liquids adsorbed on silica. Chem. Eur. J. **17**, 9113–9122 (2011)
17. B.R. Reddy, J.R. Kumar, Rare Earths Extraction, Separation, and Recovery from Phosphoric Acid Media. Sol. Ext. Ion Exch. **34**, 226–240 (2016)