

Review

Recent Advances in Rare Earth Extraction: Where Do WEEE Stand?

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Abstract

The magnetic and optical properties of Rare Earths (REs) make these elements indispensable in green technology such as wind turbines and hybrid electric vehicles. Bastnesite, Monazite and Xenotime are the most common RE minerals. Various methods exist for extraction/separation of RE from their minerals. In general, the RE is concentrated by physical methods, then roasted with concentrated acid or alkali, leached with concentrated acids and the leachate is then extracted with various extractants. Studies on efficient RE extraction methods from the dissolved mineral leachates are increasingly popular due to projected supply issues. This threat to supply has prompted researchers to find methods which can not only extract virgin RE from its mineral but can also be applied to other sources of REs such as industrial RE scrap and waste electrical electronic equipment (WEEE or e-waste). Globally, an estimated 20-50 million metric tonnes of e-waste is generated annually and this contains a plethora of technologically relevant rare earth elements (REEs). This makes WEEE a rich source of RE as some metals have been estimated to be more concentrated in WEEE than in primary ores. Herein, we present a critical literature review on the past and current extraction methods of REs extraction from its minerals and e-waste.

Introduction

Rare earths (REs) include scandium, yttrium and the lanthanides (La – Lu, excluding Pm). Rare earth elements are extensively used in metallurgy, hard disc drives (HDDs), fluorescent light, flat screens, x-ray imaging, fibre optics, defence technology, hybrid cars and wind turbines.^{1,2} The wide range of RE applications is due to their unique catalytic, electrical, magnetic and optical properties. Nd, Pr, Dy and Tb have found application in high performance Neodymium Iron Boron (NdFeB) magnet used in hybrid electric cars, electric cars, wind turbines, HDDs of desktop personal computers and portable devices such as tablet, mobile phones, head phone speakers.^{3,4} Rare earth permanent magnets (REPMs) accounts for 38% of RE use in terms of volume. It is estimated that high performance NdFeBs magnets will continue to grow in demand with the highest growth rate at 10-15% which unambiguously points to potential supply issues⁵. Eu, Gd, Yb, Tb and Y have been used as phosphors in fluorescent light, flat screens, euro bank notes and imaging (MRI), while Er is used in erbium-doped fibre optics for signal amplification, (Table 1).^{2,6}

REs tend to exist as dispersed oxide and are rarely concentrated in mineral ores (hence the name) even though they are relatively abundant in the earth crust (Table 2). This uneven geographical distribution of the REs and preference of some REs over others have led to imbalance in demand and supply of some REs including neodymium, dysprosium, terbium, and erbium⁷. Currently, 95% of the world RE supply comes from China (Figure 1). The forecasted shortages led China to announce export quotas encouraged expansion of REs relevant industries in China. As a result of this threat to supply and clean sustainable technologies REs have been labelled as “critical” metals.^{3,7}

Table 1: Applications of Rare Earths

<i>light RE (more abundant)</i>	<i>Major End Use</i>	<i>Heavy RE (less abundant)</i>	<i>Major End Use</i>
Lanthanum	Hybrid engines, metal alloys, cheaper catalytic converter and other emission reducing technologies, energy storage in Ni Metal Hydride Batteries	Yttrium	Red colour, fluorescent lamps, ceramic, capacitors, metal alloy agent, wind and hydro power generation, medical imaging- MRI
Cerium	Auto catalyst, petroleum refining, metal alloys, cheaper catalytic converter and other emission reducing technologies, flat screen displays	Gadolinium	Magnets, phosphors for flat screen displays, medical imaging- MRI.
Praseodymium	Magnets, cordless power tools, medical imaging- MRI	Terbium	Phosphors, permanent magnets,
Neodymium	Auto catalyst, petroleum refining, hard drives in laptops, headphones, hybrid engines, cordless power tools	Dysprosium	Permanent magnet, hybrid engines, light weight and powerful motors,
Samarium	Magnets	Holmium	Glass colouring, lasers
Europium	Red colour for television and computer screens, medical imaging- MRI	Erbium	Phosphors, Erbium doped optical fibre for signal amplification
		Thulium	Medical x-ray units
		Ytterbium	Lasers, steel alloys, medical imaging- MRI
		Lutetium	Catalyst in petroleum refining

Source: DOI, U.S. Geological Survey, Circular 930-N⁶

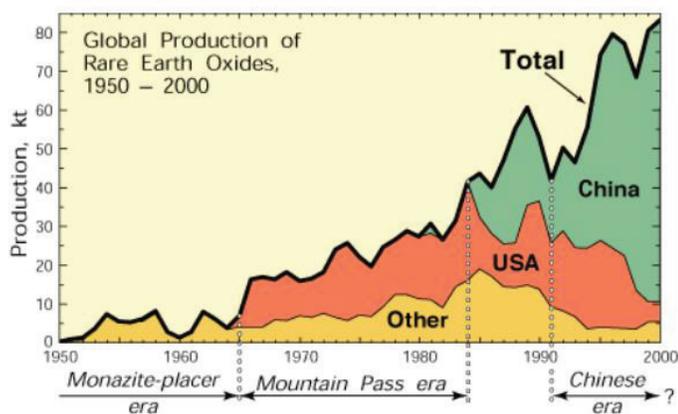


Figure 1: Global production of Rare Earth Oxides, 1950 - 2000⁸

Reduction in RE supply from China inevitably caused the prices of REs to upsurge to its all-time high in 2010 (Figure 2). Mountain Pass mine in California, USA was consequently reopened in 2012 to supply the much needed RE for green and defence technology. Although China had agreed to increase its export quotas in 2015, the recent shutdown of Mountain Pass mine in August, 2015 could be a major setback in the quest to relieve

China of its control over RE supply. There could be another huge rise in the prices of RE in the next few years if alternative source of REs is not devised. This kind of control over the resources necessary for clean and renewable technologies poses a huge threat to future development of such technology.

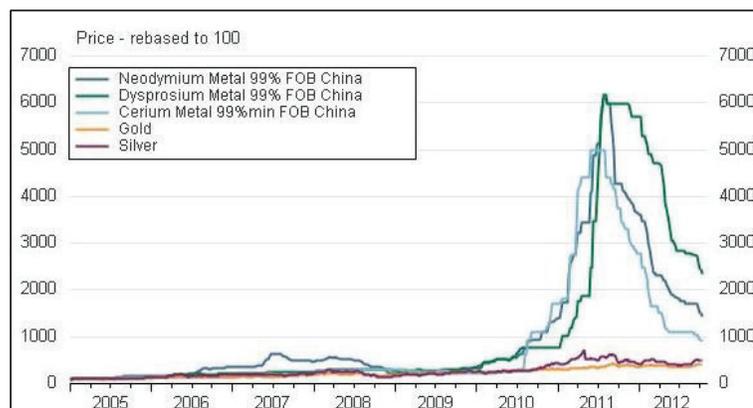


Figure 2: The Prices of Selected Rare Earths vs the Prices of Gold and Silver⁹

Rare Earth Minerals

Table 2: Rare earth abundance and contents (as a percentage of total mineral) in principal minerals

<i>RE Oxides</i>	<i>Crustal Abundance (ppm)</i>	<i>Bastnesite %</i>	<i>Monazite %</i>	<i>Xenotime %</i>
Light RE				
La₂O₃	35	32	23	0.5
CeO₃	66	49	45.5	5
Pr₆O₁₁	9.1	4.4	5	0.7
Nd₂O₃	40	13.5	18	2.2
Pm₂O₃	0			
Sm₂O₃	7	0.5	3.5	1.9
Eu₂O₃	2.1	0.1	0.1	0.2
Gd₂O₃	6.1	0.3	1.7	4
Heavy RE				
Tb₂O₃	1.2		0.16	1
Dy₂O₃	4.5		0.56	8.7
Ho₂O₃	1.3		0.09	2.1
Er₂O₃	3.5	0.1	0.13	5.4
Tm₂O₃	0.5		0.013	0.9
Yb₂O₃	3.1		0.016	6.2
Lu₂O₃	0.8		0.006	0.4
Y₂O₃	31	0.1	2.1	60.8
Total		100	100	100

Source: Mineral Facts and Problems, 1985¹⁰

REs are found in almost all mineral groups including silicates (e.g. eudialyte, allanite, zircon, steenstrupine etc.), fluoro-carbonates (e.g. bastnesite, synchisite, parasite and fluocerite), oxides (e.g. euxenite, fergusonite, pyrochlore, loparite and cheralite) and phosphates (e.g. xenotime, churchite, florencite, britholite and apatite). Bastnasite deposits in China and the USA constitute the largest percentage of the world's rare earth reserves, while monazite deposits in Australia, Brazil, China, India, Malaysia, South Africa, Sri Lanka, Thailand, constitute the second largest segment. Deposits with a high proportion of heavy rare earth elements (HREE) are very rare. Although the light rare earth elements (LREE) comprise 97-99% of resources, many of the HREE play a crucial role in emerging green energy and high tech applications together with the fast growing demand in the lighting industries (LED), thereby rendering HREE much more valuable than LREE.⁸

Potential Sources of Rare Earth Elements

Due to the growing technological application of RE, there is a huge amount of RE contained in waste electrical electronic equipment (WEEE) globally such that WEEE is considered an "urban mine". This has drawn considerable amount of interest with hopes of developing a technology that can efficiently extract RE from e-waste on an industrial scale in order to alleviate the heavy reliance on virgin RE – so called anthropogenic mining.

Rademaker et al. estimated that up to 100% of all hybrid electric vehicles, electric vehicles, desktop PCs, portable devices and 10% of wind turbines contain REPMs. The amount of REPMs in some of these devices reaches up to 700 kg. This "urban mine" was estimated to have the potential to cover up to 11-15% of REs demand. These estimates are predicted to continue growing over time as more wind and automotive technologies get to their end of life (EoL) stages.⁵ E-waste is therefore regarded as a potential source of REs that could alter the supply landscape which is currently heavily dominated by China.¹¹

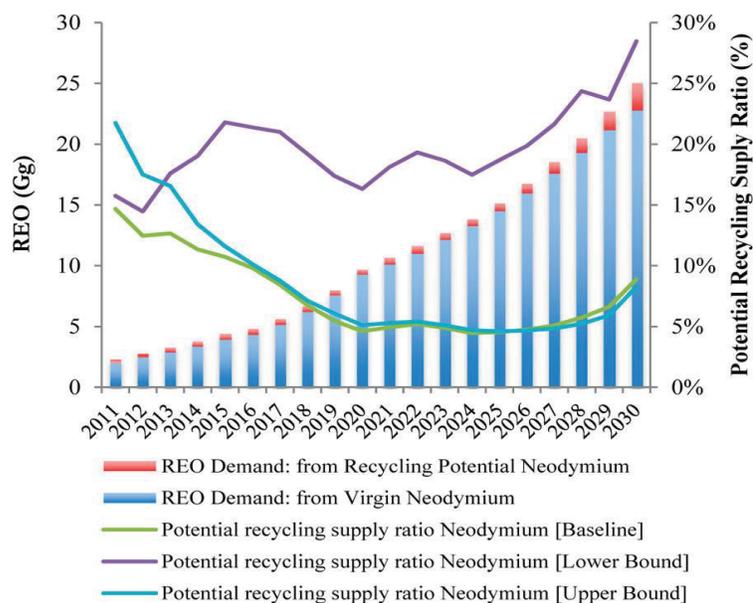


Figure 3: Potential recycling supply of Nd and predicted rise in demand of REs. [Reprinted with permission from: J. H. Rademaker, R. Kleijn and Y. Yang, *Env Sci & Tech.*, 2013, **47**, 10129-10136. © 2013, American Chemical Society].

The average life span of some of the technologies containing REs is quite long as in the case of wind turbines and electric cars. However the potential amount of REs present in EoL products with shorter life span is enough to substantially decrease dependency on virgin materials if the recovery and recycling chain is properly managed.⁵ Although RE recovery from manufacturing scrap and waste is done as industrial recycling, no commercial EoL NdFeB magnet recovery process exists for REs due to low prices of the REs in the past, dispersion of NdFeB in diversified scrap and very little or no incentive to recycling WEEE. However, the sharply rising prices for most REs, export quotas, current and forecast supply shortage and limited Chinese export have resulted in serious recycling considerations.¹²⁻¹⁴

Extraction of Rare Earths from Ores

After mining, crushing and grinding the minerals, RE is concentrated by floatation, magnetic or gravity methods which depends on the surface properties, magnetic susceptibility and specific gravity respectively. WEEE is similarly treated by crushing the electronic scrap containing RE into powder. This can be further concentrated using the physical methods listed above. The RE concentrates from mineral ores or WEEE is then subjected to hydrometallurgical treatment to obtain pure RE.

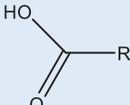
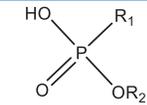
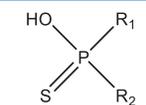
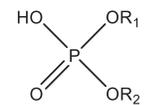
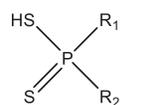
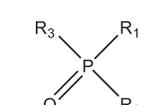
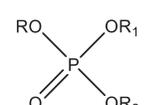
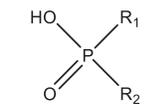
The minerals are roasted in the presence of acidic or caustic reagents. The residue is then leached with hydrochloric or sulfuric acid. The amount of acid required at this stage is minimised by the roasting at prior stage. The RE sulfates formed may be leached with water and neutralised with magnesium oxide. The leached solution is then converted to mixed rare earth chlorides by precipitation with ammonium carbonate, dissolution in HCl and crystallisation. Most commonly, the acid leached solution proceeds to one of the following extraction methods including solvent extraction or using ionic liquid, supercritical fluids; ion-exchange, membranes; microcapsules or functionalised resins and precipitation.

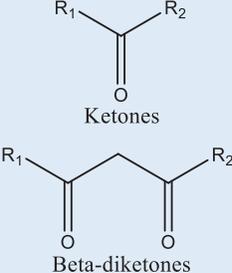
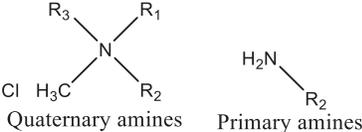
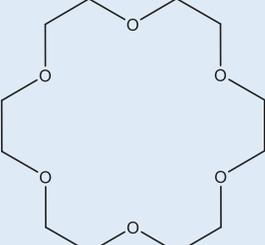
The ultimate goal is to develop a system that can efficiently extract RE from the acid leachate and easily stripped off the extractant for easy recovery of the extractants. This is why solid-liquid extraction system is more desirable as it can also solve the problem of loss of the organic extractants into the aqueous phase encountered in liquid-liquid separations.

Solvent Extraction

This technique involves the use of a biphasic system with the organic extractant dissolved in the organic layer and the RE dissolved in the aqueous phase. Ligands/extractants used in solvent extraction have been grouped by Ritcey and Ashbrook into cation exchanger, chelating exchanger, solvation extractants, and anion exchanger according to their type of interaction with the RE and the donor atoms they bear.¹⁵ Common extractants used in solvent extraction includes ligands of carboxylic acids, phosphoric acids, phosphonic acids, phosphinic acid, phosphorous ester, phosphine oxides, ketones, thiophosphates and amines.

Table 3: General Structure of Solvent Extractants.

Extractants	General structures	Targets
Carboxylic acids		Y, Ce, Pr, LREE
Organophosphoric acids and esters	 Phosphonic acids	La, Ce, Pr, Eu, Tb, Tm, Yb, Lu, Nd, Ho, Gd, Sm, Dy, Er
	 Monothiophosphorus acids	
	 Phosphoric acids	
	 Dithiophosphorus acids	
	 Phosphine oxides	
 Phosphorus ester		
 Phosphinic acids		

Ketones and β-diketones	 <p style="text-align: center;">Ketones</p> <p style="text-align: center;">Beta-diketones</p>	Ln
Amines	 <p style="text-align: center;">Quaternary amines</p> <p style="text-align: center;">Primary amines</p>	Eu, Pr, Ce, Y, Tm
Crown ethers		Y, Sc, La, Ce, Pr, Eu, Tb, Tm, Yb, Nd, Gd, Sm, Er

Carboxylic Acids

Carboxylic acids have been well investigated in extraction studies. They are regarded as cation exchangers.¹⁵ High molecular weight carboxylic acids such as cecanoic (6-Methylheptanoic acid), naphthenic (cyclohex-3-ene-1-carboxylic acid), neo-heptanoic (4,4-Dimethylpentanoic acid) and versatic acids (neo-decanoic) have been investigated in the extraction of RE by Singh et al. and Zheng et al. with similar conclusions. Yttrium was found to have extraction behaviour of HREE with sterically hindered acids (neo-heptanoic and versatic acids) and also to that of LREE (Ce, Pr) with sterically less hindered acids (cecanoic, naphthenic).^{16, 17} Preston et al. have studied the extraction of RE with naphthenic acid and versatic acids from sulfate and chloride solutions. They found a dependence of the extraction properties of the carboxylic acids on the atomic number of the lanthanide and the steric hindrance caused by the structure of the carboxylic acids.¹⁸ Other carboxylic acids such as *sec*-nonylphenoxy acetic acid (CA-100) and *sec*-octylphenoxy acetic acid (CA-12) has also been employed in the extraction of RE. Results showed that *sec*-nonylphenoxy acetic acid (CA-100) shows better extraction of RE than neo-decanoic acid at lower Ph.¹⁹ The use of multi-dentate extractants including calix[n]arene with carboxylate systems have been shown to exhibit a better extraction efficiency than the monodentate analogs.^{20, 21}

Organophosphoric Acids and Esters

Phosphoryl containing extractant are very popular in extraction due to their donor ability.^{22, 23} This family of extractant includes phosphoric, phosphonic, phosphinic, monothiophosphorous, dithiophosphorous acids, phosphorous ester, and phosphine oxides.^{22, 24, 25} Zang *et al.* reported the extraction of La(III) from chloride solution using di-(2-ethylhexyl)phosphoric acid (P204 or D2EHPA or HDEHP) and a complexing agent, lactic acid. They found that the distribution ratios (a measure of how well extracted the metal is) increased with the increase in pH value in the feed and lactic acid concentration.²⁶ Peppard et al. also showed that the distribution ratio had an inverse power dependency on HCl concentration using the same extractants. The extraction order of Ln was found to be Lu > Yb > Tm > Tb > Eu > Pm > Pr > Ce > La while distribution coefficient increase with increase in atomic number.²⁷⁻²⁹ D2EHPA has also been applied on large scale extraction of RE from bastnesite by Molycorp in 1965.³⁰

Other phosphoryl containing podands have also been studied in the separation of Th(IV) and U(VI) from La(III), Nd(III), Ho(III) and Yb(III) in low nitric acid concentration with ethyl-, butyl-, and tert-butyl substituent on the aromatic ring found to exhibit the best results.³¹ Sato reported the extraction of lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium between hydrochloric acid solutions and solutions of di-(2-ethylhexyl)-phosphoric acid (DEHPA) or 2-ethylhexyl-2-ethylhexylphosphoric acid (EHEHPA marketed as PC-88A, P507, Lonquest 801) in kerosene. The extraction efficiency was found to increase with increasing atomic number and DEHPA was found to be a better extractant than EHEHPA in these conditions.²⁴ The extracted complexes have also been found to be more easily stripped.³² Commercial RE separation plant in Baotou, China uses a process which involves HEHEHP as an extractant.³³

Utilising 33 vol% dibutyl butylphosphonate in Shellsol 2325 (mixture of paraffins, cycloparaffins and aromatics) and tributylphosphate (TBP) in separate processes, Preston et al. was able to extract RE nitrates and oxides from leach liquor by the addition of 2.5 M ammonium nitrate.³⁴ The use of dialkylphosphinic acids (Cyanex 272) have been widely investigated.³⁵⁻³⁸ In a study by Talcher, the phosphorus solvent TOPS 99 (di-2-ethylhexyl phosphoric acid), 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC-88A), and bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272) were used in the extraction of lanthanum, cerium, praseodymium and neodymium. Terbium, dysprosium, holmium, yttrium, erbium, ytterbium, and lutetium has also been extracted from phosphoric acid solutions by Radhika et al. Results obtained indicated a decrease in extraction efficiency with increasing acid concentration and the general trend of the extractant efficiency was of the order TOPS 99 > PC 88A > Cyanex 272.³⁹ The extraction of single and binary La(III) and Nd(III) from nitrate solutions with PC88A in kerosene at 298 K has also been reported by Kao et al. A kinetic and thermodynamic study on the extraction of these RE showed higher extractability of Nd(III) over La(III). However, the stripping rate of Nd(III) was nearly two order of magnitude larger than that of La(III).⁴⁰

Ketones and β -diketones

β -diketonates are complexes of RE and β -diketones (1,3-diketones). These compounds and their derivatives were widely researched at the beginning of the 1960s at extractants.⁴¹ They have also been investigated in synergistic extractions and found to possess some extraction efficiency mostly as a mixture with other extractants.^{42, 43} β -diketones such as hexafluoroacetylacetone (HFAC) form hydrated chelate which are poorly extracted.⁴⁴ Butts and Banks concluded from their studies that hexafluoroacetylacetone in a mixture with tri-*n*-butylphosphate can effectively form solid extractable chelates. 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione have similarly been known to form chelates.^{45,46, 47}

Synergistic extraction of La(III) from chloride medium using triisobutylphosphine sulfide (TIBPS) and 1-phenyl-3-methyl-4-benzoyl-pyrazalone-5 (HPMBP) has been reported by Jia et al. Synergistic enhancement factor of HPMBP and TIBPS was calculated to be 2.40. They concluded that mixtures have no better separation abilities for rare earth elements than HPMBP.⁴⁵ HPMBP has been further investigated by Jordanov et al. as a sole extractant in the extraction of 13 lanthanides in aqueous-benzene media. The composition of the extracted species has been determined as $\text{LnP}_3 \cdot \text{HP}$ (where P is HPMBP).⁴⁸

Synergistic extraction of RE with a polyfluorinated β -diketone 1,1,1,2,2,6,6,7,7,7-deca-fluoro-3,5-heptanedione, (H(FHD)), as the ligand, and di-*n*-butylsulfoxide (DBSO) as neutral donor has been reported by Burgett and Fritz. Individual and mixed lanthanides were obtained with 97.5 and 97.1% recovery respectively.⁴⁹ Tri-*n*-octylmethylammonium nitrate (TOMAN) and β -diketone (α -acetyl-*m*-dodecylacetophenone: LIX54) in the presence of water-soluble complexing agent (ethylenediaminetetraacetic acid: EDTA) have been studied in RE extraction by Hirai and Komasaawa. They found that only free RE which is not complexed with EDTA could take part in the extraction.⁵⁰

Amines

A multitude of amines have been used in RE co-ordination chemistry and many researchers have now extended this to extraction of RE.⁵¹ Amines are regarded as anionic exchangers.¹⁵ They have been found to poorly extract RE in chloride media but better results in sulfate media.^{52, 53}

As early as in the 1950s, Coleman et al. conducted a screening of hundreds of amines and found that simple amines are best for extraction. They attributed this to organic phase insolubility at a high pH which is less severe in simple amines with molecular weight in the range of 200-600 Da. These amines are typically of the trialkyl-, tridecyl-, iso-octyl groups.⁵⁴

Triiso-octyl amine dissolved in xylene has been used to extract actinides and lanthanides by Moore. The study showed that under certain conditions, RE can be extracted using a similar system. The extraction efficiency was found to be in the order, thorium > europium, promethium > cerium > yttrium, thulium.⁵⁵

Trialkyl methylamine (Primene JMT) has been studied in the extraction of RE and found to extract La(III) and Y(III) from sulfate media.^{56, 57} Quaternary ammonium salt (Tricaprylmethylammonium chloride, Aliquat 336) have also been investigated in RE extraction.^{58, 59} Addition of EDTA to Aliquat 336 have been shown to improve LREE separation.⁶⁰ Aliquat 336 have been shown to extract Nd, Pr in 83 and 15% respectively and other RE in 2% from didymium (a mixture of praseodymium and neodymium) nitrate solution.^{61, 62}

Crown Ethers

Crown ethers and their derivatives are a group of macrocyclic ligands with ability to form interesting complexes with a variety of metal ions. Crown ethers of various sizes and substituents has been used in the extraction of RE.⁶³ 15-crown-5, 12-crown-4 and dibenzo-18-crown-6 have been employed in the extraction of Tb³⁺, Eu³⁺, Gd³⁺, Nd³⁺, Yb³⁺, Ce⁴⁺, Sm³⁺, Dy³⁺ and Lu³⁺ from aqueous solutions containing picrate into nitrobenzene solution. A 2:1 sandwich complex with 15-crown-5 was observed for europium but 1:1 complex with 12-crown-4 and dibenzo-18-crown-6.⁶⁴

Crown ethers have been used to extract La³⁺, Ce³⁺, Pr³⁺, Eu³⁺ and Er³⁺ from acidic solution in presence trichloroacetic acid from acidic solutions. The presence of trichloroacetic acid as counter ions was shown to improve the selectivity of 18-crown-6 derivatives.⁵⁴ Ensor et al. have shown that crown ethers can be used to synergistically enhance extraction of Ce³⁺, Pm³⁺, Eu³⁺ and Tm³⁺ along with a mixture of didodecyl naphthalenesulfonic acid. The selectivity and extraction efficiency of this extractants were improved by the addition of the crown ether.^{65, 66}

The use of azacrown ether for extraction has also been studied. 1,10-diaza-18-crown-6, 15-crown-5, benzo-15-crown-5, monoaza-, and tetraazacrown have been involved in extraction studies.⁶⁷⁻⁷¹ Mono-Aza dibenzo 18-crown-6 ether have been reported to extract La(III), Nd(III) and Sm(III) in synthetic solutions with a pre-concentration factor of 120 for La(III), 131 for Nd(III) and 151 for Sm(III) with efficient extraction results achieved.⁷² Selective extraction of Y³⁺ over Sr³⁺ has been demonstrated by Wood et al. They showed that by changing the carboxylic acid at the terminal end of the lariat to hydroxamic acid, the selectivity of the extractant for Y³⁺ over Sr²⁺ is greatly increased leaving a fraction of 99% pure Sr²⁺.⁷³

Ionic-Liquids (IL) Extraction

Recently, there has been an increased interest in the used of IL in RE extraction due to their unique properties such as non-volatility, non-flammability, and wide temperature range for liquid phase. This technique, like most of the techniques discuss in this paper, have been optimised and applied to RE recycling from e-waste.^{74, 75} They are usually composed of heterocyclic organic cations and various anions. The most attractive properties of ILs with respect to separation techniques is that their physicochemical properties can be easily

tuned by changing combinations of cations and anions and thereby changing the selectivity. They can be made to be water-immiscible salts by increasing the alkyl chain length of the cation incorporating hydrophobic anions. For example, increasing the alkyl chain length of 1-alkyl-3-methylimidazolium cations, from butyl to hexyl to octyl increased the hydrophobicity.⁷⁶⁻⁷⁹ Extraction of metal ions is more efficient in IL than in volatile organic solvents.⁸⁰⁻⁸⁴ They have also been known to overcome the stripping challenges encountered in typical solvent extractions.⁷⁵

Depending on solubility in the IL and extraction efficiency in the organic solvent, a wide range of extractants in combination with the IL have been investigated in RE extraction.⁸⁵ Turanov et al. has investigated the extraction of chlorides of (Ln = La, Ce, Pr, Nd, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y) into organic solutions of tetraphenylmethylenediphosphine dioxide, diphenyl(diethylcarbamoymethyl)phosphine oxide, and dibutyl(diethylcarbamoymethyl)phosphine oxide in the presence of ILs, 1-butyl-3-methylimidazolium hexafluorophosphate and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. The mixture was found to extract RE far more efficiently than when the IL was absent.⁸⁶

The use of eight imidazolium ILs ($[C_n\text{mim}][\text{NTf}_2]$ and $[C_n\text{mim}][\text{BETI}]$, $n = 4, 6, 8, 10$) and one pyrrolidinium IL ($[C_4\text{mPy}][\text{NTf}_2]$) as diluents using di(2-ethylhexyl)phosphoric acid (HDEHP) as an extractant for the separation of lanthanide ions from aqueous solutions of 50 mM glycolic acid or citric acid and 5 mM diethylenetriamine pentaacetic acid (DTPA) in a cation-exchange mechanism has been described by Sun et al. They reported excellent extraction efficiencies and selectivity which they attributed to the competition between the aqueous phase complexation by DTPA and the organic phase extraction by HDEHP.⁶³

Nakashima et al. reported the extraction of rare earth metals into ILs, $[\text{Bmim}][\text{PF}_6]$ from aqueous solutions using octyl(phenyl)-*N,N*-diisobutylcarbamoymethyl phosphine oxide (CMPO) as an extractant. The IL was found to increase the extraction efficiency in a cation-exchange mechanism.⁸² The extraction of Ce(IV) along with Th(IV) and Ce(III), Gd(III), Yb(III) nitrate by pure ionic liquid, $[\text{C}_8\text{mim}]\text{PF}_6$ has been investigated by Zuo et al. Ce(IV) was found to be extracted better than Th(IV) and the other REs through anion exchange mechanism in the $[\text{C}_8\text{mim}]\text{PF}_6$ alone.⁸⁷

Modification of the alkyl chain of the imidazolium IL to obtain 1-butyl, 1-octyl, and 1-dodecyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($[C_n\text{mim}][\text{Tf}_2\text{N}]$, $n = 4, 8, 12$) has been reported by Goto et al. Using this as the medium, they performed the extraction using a novel extractant, *N,N*-dioctyldiglycol amic acid (DODGAA) in extraction of Eu(III) and Y(III). The REs were extracted quantitatively in a proton exchange mechanism.⁸⁸ DODGAA is a much more soluble ligand than the CMPO⁸⁹ and has a higher selectivity.⁹⁰ Shorter alkyl-chain imidazolium IL, $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ was found to be a better extractant.⁹¹ Sc(III) has been separated from Y(III), La(III) and Yb(III) has also been extracted using similar IL, $[\text{C}_8\text{mim}][\text{PF}_6]$ containing Cyanex 925 as the extractant in a cation exchange mechanism by adding EDTA to the aqueous phase.⁹²

More recent ILs includes trihexyl(tetradecyl)phosphonium chloride which acts as both the organic phase and the extractant have been developed by Hoogerstraete et al. and have been tested in the separation of copper, cobalt, iron, manganese and zinc from rare earths resulting in purer RE fractions. The high affinity of iron(III) for the ionic liquid results in very high distribution ratios with percentage extraction reaching 99.98% although the extraction efficiency of other metals such as aluminium, magnesium, nickel, calcium and chromium was low.⁷⁹

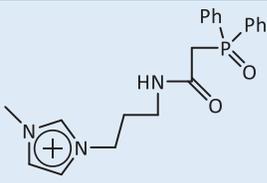
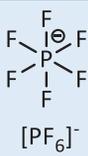
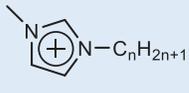
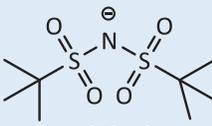
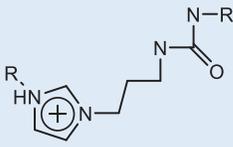
Xiaoqi et al. has further impregnated polarized XAD-7 resins with IL made up of [trialkylmethylammonium][sec-nonylphenoxy acetate] ($[\text{A336}][\text{CA-100}]$) and [tricaprylmethylammonium chloride][nitrate] ($[\text{A336}][\text{NO}_3]$). This type of ILs are considered to be cheaper and less toxic than the imidazolium type ILs.^{93, 94} The results of this study showed that, ($[\text{A336}][\text{NO}_3]$) was found to have higher adsorption properties due to the presence of the cation and anion. The impregnated resin was effective in separating Sc(III) from Ce(III), Eu(III) and Y(III) by adjusting the aqueous acidity. However, the marked viscosity could be a potential hindrance to the application of these systems.

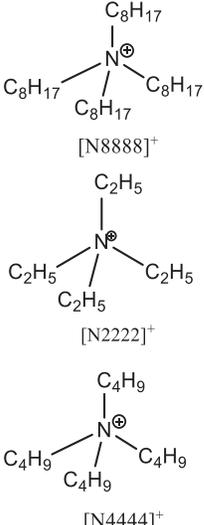
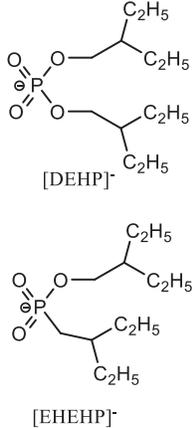
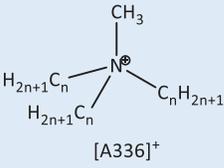
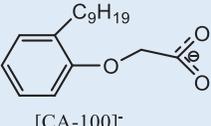
More recently, europium and other trivalent lanthanides were extracted with trihexyl(tetradecyl)phosphonium *N,N,N',N'*-tetra(2-ethylhexyl)malonate, [P₆₆₆₁₄][MA]. A good separation of the rare earths from the transition metals was achieved as the extraction efficiency increased over the lanthanide series.⁹⁵ Using tri-*n*-butylphosphate (TBP) and an electrolytic IL, triethyl-pentyl-phosphonium bis(trifluoromethyl-sulfonyl)amide ([P₂₂₂₅][TFSA]), Matsumiya et al. has shown that RE can be recovered through electrodeposition with better recovery than in a typical organic solvent.⁹⁶

Several other new ionic extractant (see Table 4), including tetrabutylammonium di(2-ethylhexyl)phosphate ([TBA][DEHP]), trioctylmethylammonium di(2-ethylhexyl)phosphate ([TOMA][DEHP]), trihexyl(tetradecyl)phosphonium di(2-ethylhexyl)phosphate ([THTP][DEHP]),⁹⁷ 1-Methylimidazole (1-MIM), 2-methylimidazole (2-MIM),⁹⁸ tetraethylammonium di(2-ethylhexyl)phosphate ([N₂₂₂₂][DEHP]), tetraethylammonium bis(2,4,4-trimethylpentyl)phosphinite ([N₂₂₂₂][BTMPP]), tetraethylammonium bis(2,4,4-trimethylpentyl)dithiophosphinite ([N₂₂₂₂][BTMPDTP]), tetrahexylammonium di(2-ethylhexyl)phosphate ([N₆₆₆₆][DEHP]), and tetraoctylammonium di(2-ethylhexyl)phosphate ([N₈₈₈₈][DEHP]) have been used as extractants with bis(trifluoromethanesulfonyl)imide/bis(perfluoroethanesulfonyl)imide ([C_{10mim}][NTf₂]/[BETI]) as the IL. The effect of various conditions on extraction efficiency was investigated by Sun et al.⁸⁵ They found that increase in the size of the cation can decrease the distribution ratio and selectivity of RE. Acidity and concentration of some of the ionic extractants were also shown to affect the extractability and selectivity of the IL systems. This anion and cation influence has also been more recently described by Rout and Binnemans.⁹⁹⁻¹⁰¹

Practical application of ILs in RE extraction from phosphor powders in waste fluorescent lamps have been studied by Yang et al. After a previous metal extraction studies with *N,N*-dioctyldiglycol amic acid (DODGAA) based IL^{90, 91} these phosphorus free extractants in IL ([C_{4mim}][Tf₂N]) system were used in the selective extraction of Y, Eu La and Ce from Fe, Al, Zn and other impurities in electronic scrap.^{75, 102}

Table 4: General Structure of the Cation and Ionic Parts of Commercial Ionic Liquids

Cation	Anion	Extractants	Targets
 <p>CMPO-modified IL</p>	 <p>[PF₆]⁻</p>	CMPO, TPEN, D2EHPA, Cyanex 272, Cyanex 925, Ph ₂ Et ₂ , Bu ₂ Et ₂ , TODGA, HYD, PC-88A,	Sc, Y, Ln
 <p>[C_nmim]⁺</p>	 <p>[Tf₂N]⁻</p>	Htta, CMPO-modified IL, DODGAA, HDEHP	
 <p>[TSIL]⁺</p>			

 <p>[N8888]⁺</p> <p>[N2222]⁺</p> <p>[N4444]⁺</p>	 <p>[DEHP]⁻</p> <p>[EHEHP]⁻</p> <p>[CA-100]⁻</p>	DTPA, Glyolic acid DEHP with THTP, TOMA, TBA; 1-MIM, 2-MIM, N2222 and BTMPP, BTMPDPT	Ln
 <p>[A336]⁺</p>	 <p>[CA-100]⁻</p>	[A336][CA-100], [A336][P204], [A336][P507]	Sc, Y, Ln (fluorescent powder)

Synergistic extraction

Synergistic effect with combinations of different extractants has been a subject of many studies in the area of RE extraction. Synergism occurs when the presence of a second extractant enhances the overall extraction efficiency.¹⁰³⁻¹⁰⁸ Extraction of uranium and lanthanides from phosphoric acid using DOPPA and TOPO has been studied.¹⁰⁹ Reddy et al. has also investigated the extraction of RE with bis(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301) and trialkyl phosphine oxide (Cyanex 923) in xylene. La(III) and Nd(III) were extracted as MX₂.NO₃.TRPO complex with Cyanex 923 while Eu(III), Y(III) and HREE extracted species were MX₃.HX.2TRPO (where X is Cyanex 923 and Cyanex 301). The extraction efficiency and the selectivity were enhanced by the addition of the trialkylphosphine oxide.¹¹⁰

The use of 1-phenyl-3-methyl-4-benzoyl-pyrazalone-5 (HPMBP, HA) and *sec*-octylphenoxyacetic (CA12, H₂B₂) as a synergetic system in the extraction of lanthanum and neodymium have been studied. The system was found to more effectively extract the LREE.¹¹¹ The synergistic extraction of Nd³⁺ or Sm³⁺ from a sulfuric acid medium, by mixtures of di-(2-ethylhexyl) phosphoric acid (HDEHP) and 2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester (HEH/EHP) were studied. Maximum synergistic enhancement coefficient was observed with a ratio of HEH/EHP to HDEHP was 3:2. The synergistic extracted species were Nd(HA₂)₂·HL₂ and Sm·(HA₂)₂·HL₂.¹¹²

The synergistic effect in the mixtures of 8-hydroxyquinoline (HQ) and 2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester (P507) in the extraction of Pr(III) and Nd(III) has been explored by Wu et al. they found a synergistic enhancement factor to be 5.47, 3.37 and 2.86 for Pr, Nd and La(III), respectively, when the concentration ratio of HQ to P507 is equal to 3:7 at pH 3.6.¹¹³

The use of 2-ethylhexylphosphonic acid mono-(2-ethylhexyl) ester (HEHEHP, P507) and organophosphorus acids [di-(2-ethylhexyl)phosphoric acid (HDEHP, P204), isopropylphosphonic acid 1-hexyl-4-ethyloctyl ester (HHEOIPP), bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272), bis(2,4,4-trimethylpentyl)monothiophosphinic acid (Cyanex 302), and bis(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301)] as mixtures of HEHEHP/HDEHP, HEHEHP/Cyanex 301, HEHEHP/HHEOIPP, HEHEHP/Cyanex 302 and HEHEHP/Cyanex 272 has been reported by Wang et al. The extraction efficiency

was found to be in the order of HEHEHP/HDEHP > HEHEHP/Cyanex 301 > HEHEHP/HHEOIPP > HEHEHP/Cyanex 302 > HEHEHP/Cyanex 272.¹¹⁴

Mono- and dithiophosphinic acids in combination with ammonium salts have also been investigated in synergistic extraction systems by Belova et al. Salts of trioctylmethylammonium with dialkylphosphinic, dialkylmonothiophosphinic, and dialkyldithiophosphinic acids were employed in the extraction of RE. Extraction efficiency of binary extractants towards lanthanum chloride as well as lanthanum nitrate decreases in the series: dialkylphosphinate > dialkylmonothiophosphinate >> dialkyldithiophosphinate of quaternary ammonium base (QAB).¹⁰⁷

Supercritical Fluids

Supercritical fluids (SCF) have been adapted in the extraction of metal due to its unique properties. Above certain temperature and pressure (critical point), SCF is neither in its liquid or gas phase. It can diffuse like a gas and dissolve material like a liquid. Its extraction selectivity can be enhanced by tuning the temperature and pressure.¹¹⁵ These properties have been harnessed by a number of researchers to extract metals from industrial or electronic scraps. SCF can be modified by adding an appreciable amount of polar solvents such as methanol in order to improve the polarity of the organic phase and solubility of the extractants or the extractant-metal complex.¹¹⁶

Supercritical carbon dioxide (scCO₂) is an example of SCF which have received a lot of attention due to its low toxicity and is environmentally acceptable, cheap and low critical temperature and a moderate critical pressure. Unlike organic solvents, scCO₂ is inert to the extraction conditions; its solvency can be tuned to improve selectivity by small change in temperature and pressure. Residual contamination of aqueous phase by the organic phase is not an issue with scCO₂.¹¹⁷

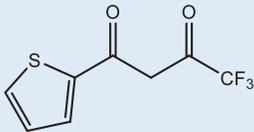
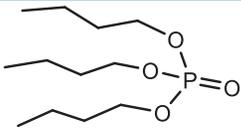
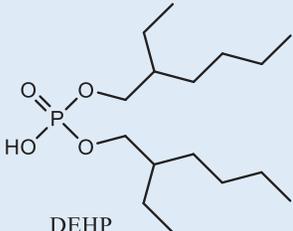
ScCO₂ containing various extractant have been investigated by a number of researchers.¹¹⁸ There exists a number of extractant including TTFA (Thenoyltrifluoroacetone), ACAC (Acetylacetonate), LiFDDC [Lithium bis(trifluoroethyl)-dithiocarbamate], TBA(tert-butyl alcohol), HFOD (1,1,1,2,2,3,3-Heptafluoro-7,7-dimethyl-4,6-octanedione), that have been widely used as various metal extractants in scCO₂.¹¹⁹⁻¹²⁶ Unfortunately, only a few of these extractants have made it to RE extraction. There is a general problem of solubility of these ligands and/or their metal complexes when using scCO₂. Although some ligands including CMPO, CMP, TBP, TOPO are more soluble in scCO₂¹¹⁵ only a handful of data on the solubility of CMPO, CMP, TBP, TOPO (Trioctylphosphine oxide) complexes exists in the literatures. However it has been shown that fluorinated ligands and their metal complexes are more soluble in SCF than non-fluorinated analogs. For example, fluorinated DCC and HFA and their metal complexes have been found to be very soluble in scCO₂.¹¹⁹

Lin and Wai studied the extraction of La³⁺, Eu³⁺ and Lu³⁺ from aqueous solution using TTFA as the chelating extractant in scCO₂. They obtained extraction efficiency of 30, 38 and 51% for La³⁺, Eu³⁺ and Lu³⁺ respectively. However, the use 50 mg of extractant in 40 ml of scCO₂ for the extraction of ≤50 % of 0.01 mg of lanthanide suggests very low efficiency of the system used in this study.¹²⁷ Laintz and Tachikawa has extended scCO₂-TBP extraction system to La³⁺, Ce³⁺, Sm³⁺, Eu³⁺, Gd³⁺, Dy³⁺, Yb³⁺ and Lu³⁺ and obtained extraction efficiency of 43.6 for La³⁺, 60.5 for Ce³⁺, 85.1 for Sm³⁺, 86.7 for Eu³⁺, 86.9 for Gd³⁺, 91.8 for Dy³⁺, 71.9 for Yb³⁺ and 69.2 for Lu³⁺ with 30% TBP.¹²⁸ This indicates significant improvement to scCO₂ extractions. Using the same extractant and DEHPA, in scCO₂, Dehgani et al. was able to extract Ce³⁺, Pr³⁺, Nd³⁺, Ho³⁺, Eu³⁺, Y³⁺ from aqueous phase comprised of 0.05 M Ln(NO₃)₃, 0.1 M HNO₃ and 3M NaNO₃ at 40 °C and 150 bar with 7 mole% TBP. The extraction efficiency for the LREE increased with increasing atomic number.¹²⁷

Laintz and Tachikawa have studied the effect of adding TTFA to TBP in a synergistic system and obtained slightly improved efficiency of RE extraction.¹²⁹ Dehgani has also investigated the use of TBP and DEHPA for Ln extraction. Most interestingly, they found that addition of 2.5 mole% DEHPA to 3 mole% (instead of 7 mole%) TBP significantly increased the extraction efficiency from 1 to 99% extraction of Yb³⁺.

Using TBP-HNO₃ complex has been adapted by Tomioka et al. for the extraction Nd from several oxides such as Nd₂O₃, ZrO₂, MoO₃, and RuO₂; and binary mixtures of the oxides such as Nd₂O₃-ZrO₂, Nd₂O₃MoO₃, and Nd₂O₃-RuO₂. Selective extraction of Nd from 0.01 mole Nd₂O₃ powder was obtained quantitatively using scCO₂ containing TBP-HNO₃ (TBP) at 313 K and 12 MPa, while Zr, Mo, and Ru were not extracted.¹³⁰ The application of scCO₂ containing tri-*n*-butyl phosphate (TBP) complexes with HNO₃ and H₂O in the extraction of Y, Eu, La, Ce and Tb from waste fluorescent lamp has also been investigated by Shimizu et al. Over 99% extraction efficiency was obtained for some of the metals from the fluorescent lamp.¹¹⁸

Table 5: General Structures of Extractants used in SCF

<i>Extractants</i>	<i>Structure of Extractants</i>	<i>Targets</i>
Thenoyltrifluoroacetone	 TTFA	La ³⁺ , Eu ³⁺ and Lu ³⁺
Tributyl phosphate	 TBP	Y, Eu, La, Ce and Tb, Nd oxides, La ³⁺ , Ce ³⁺ , Sm ³⁺ , Eu ³⁺ , Gd ³⁺ , Dy ³⁺ , Yb ³⁺ and Lu ³⁺
Di-(2-ethylhexyl)phosphoric acid	 DEHP	Ce, Pr, Nd, Ho, Eu, Y

Ion-Exchange Resin

Ion exchange was once the only practical to separate RE on large scale. As solvent extraction is now capable of large scale separation, ion-exchange is now only used to obtain high purity RE for analytics and electronics.¹³¹ The simplicity and convenience makes this method particularly attractive for separation and purification of RE.¹³²⁻¹³⁴ Commercial ion-exchange resins include amberlite, amberlyst, amberjet, dowex, and Duolite. They can be weak or strong cation, anion exchangers, mixed bed, chelating, or polymeric resins.¹³⁵

RE in red mud, the by-product of the alumina production, could be selectively separated from the main and minor elements, as well as from yttrium and the lanthanides using a combination of ion exchange-solvent extraction method. After a suitable borate/carbonate fusion of red mud, the sample solution was passed through the ion exchanger Dowex 50W-X8 and Fe, Al, Ca, Si, Ti, Na, Ni, Mn, Cr and V were removed by elution with 1.75 M HCl. Sc, Y and the lanthanides were quantitatively obtained by a subsequent elution with 6 M HCl. Scandium could then be selectively and near quantitatively extracted in the organic phase using di(2-ethylhexyl)phosphoric acid in hexane, while yttrium and the lanthanides remained in the aqueous phase.¹³⁶

The separation and analysis of RE using a mixed solvent ion-exchanger in a batch separation process has been described by Roelandts. After dissolving samples of RE containing Apatite in HNO₃, a basic anion-exchanger,

Dowex 1X8 100-200 mesh (nitrate form) RE mixed with the resin were then adhered to a cellulose support and analysed by X-ray fluorescence spectrometry.¹³⁷

Faris et al. has investigated the extraction of yttrium and scandium from methanol-nitric acid solution using a strongly basic anion-exchange resin in a column elution technique. The REs were eluted from the column in order of increasing atomic number with little individual separation for those higher than dysprosium. Large separation factor was found for those lighter than terbium. Scandium was not adsorbed in appreciable amount while yttrium behaved like lutetium. The extraction system has been extended to macro-scale process for fractionation of crude RE to obtain extremely pure RE.¹³⁸ Although with slightly different aim, Koopman and Witkamp were able to efficiently separate lanthanides from phosphoric acid processes using Dowex C-500 ion exchange resin functionalized with sulfonic acid functional groups.^{139, 140} Using AG50WX4 cation-exchange resin and CMPO, (16 wt.%) dissolved in TBP (24 wt.%) and supported on the inert porous polyacrylic substrate Amberchrom CG-71ms, lanthanides were quantitatively recovered.¹⁴¹ Lanthanum along with uranium and thorium were separated individually using Amberlite XAD-16 (AXAD-16)-*N,N*-dihexylcarbamoylmethyl phosphonic acid quantitatively in >99.8% efficiency from nuclear spent fuels as well as from geological and natural water resources.¹⁴²

Synthesised resins has also been used in extraction of RE. Draye et al. described the alkaline polycondensation of 8-hydroxyquinoline with formaldehyde to obtain a polymeric resins. The selective uptake of Eu^{3+} from aqueous solutions containing La^{3+} was found to be due to the incorporation of 8-hydroxyquinoline in the molecular matrix of the phenolic resins.¹⁴³

High pressure ion-exchange has been applied to separation of adjacent lanthanides by chromatographic elution from Dowex 50 resin showing that this system can be equally used to obtain pure lanthanides.¹⁴⁴

Microcapsules and functionalised resins

Microcapsules

The use of microcapsules to encapsulate extractants allows for easy recycling of the extractant¹⁴⁵, recovery of various metals,¹⁴⁵⁻¹⁴⁷ and ease of metal sorption unto microcapsule.¹⁴⁸⁻¹⁵⁰ This results in a solid-liquid system as opposed to the conventional liquid-liquid systems in hopes of overcoming the challenges posed by liquid-liquid system. Kondo et al. have shown the extraction process of lanthanum, cerium, neodymium, promethium and samarium in separate studies using encapsulated 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHPNA). Encapsulated EHPNA use in metal extraction is controlled by both the chelating complex formation reaction between the metal and extractant as well as the diffusion of the complex in the microcapsule pores.¹⁵¹⁻¹⁵³ They also reported the use of dibenzoylmethane encapsulated into MC by *in situ* radical polymerization of divinylbenzene. The results showed that the amount of metals adsorbed onto the MC increased as the pH increased. Also, the separation of dysprosium and gadolinium was achieved as only dysprosium was extracted at pH 6.0.¹⁵³

Extraction of RE using MC consisting of styrene (St)-divinylbenzene (DVB) copolymer and containing bis(2-ethylhexyl)phosphinic acid (PIA-226) has been studied by Nishihama et al. A mixture of Pr/Sm was efficiently separated using a column packed with these MC as Pr with high purity was obtained initially from the aqueous effluent solution, and Sm with high purity was obtained in the microcapsules.¹⁵⁴ After an earlier successful study with microcapsules containing 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHPNA),¹⁵⁵ Kamio et al. investigated the use of EHPNA in a microcapsule in the extraction of lanthanum, samarium and erbium. The initial extraction rates of lanthanides RE in the microcapsule system were found to be affected by the external aqueous conditions, such as the pH and metal concentration. It was found that the initial extraction rate for the microcapsule system varied in the same way with pH and metal concentration as it does in a liquid-liquid extraction system.¹⁵⁶ Selective extraction of neodymium using EHPNA encapsulated in magnetic alginate MC was reported by Zang et al.¹⁵⁷

Jing et al. reported the use of polysulfone microcapsules in RE extraction. The pierced polysulfone microcapsule was functionalised with EHPNA using ultrasonic method. Results revealed a high extraction of Sm^{3+} and Er^{3+} whilst La^{3+} extraction levelled off after 50%.¹⁵⁸ Wang et al. has investigated the optimisation of polysulfone MC preparation. The results EHPNA was imported at high loading ratio. The maximum uptakes of La^{3+} , Sm^{3+} and Er^{3+} were 3.02×10^{-4} mol/g, 8.05×10^{-4} mol/g and 5.58×10^{-4} mol/g, respectively.¹⁵⁹

Reagent impregnated resins (RIRs)

The use of RIRs in extraction of RE offers simplicity, coordination, a wide range of application and facile extractant recovery.¹⁶⁰⁻¹⁶⁸ Using 2-ethylhexyl hydrogen 2-ethylhexyl phosphonate (PC-88A) and Amberlite XAD-2, XAD-4, XAD-16 and XAD-7 as a polymeric support has been studied by Matsunaga et al. and results showed that the extraction rate is affected by amount of PC-88A impregnated into XAD-2, XAD-4 or XAD-16 resins with respect to their pore volume while the amount of PC-88A impregnated into XAD-7 had only little effect on the extraction rates.¹⁶⁹

Taking a step further, Sun et al. has reported the extraction of yttrium from other RE using IL impregnated resin. The IL was mixed with Cyanex923 and immobilised on a XAD-7 resin. Results showed a shorter equilibration time, 80% separation efficiency and yttrium was selectively extracted from Ho, Er, Yb and Sc by adding a water soluble complexing agent (EDTA) to the aqueous phase.¹⁷⁰

Merrifield chloromethylated (MCM) resin has been grafted with octyl(phenyl)-*N,N*-diisobutylcarbamoyl-methylphosphine oxide (CMPO) (MCM-CMPO) for the purpose of metal extraction. The resin showed very high sorption capacity values of $0.960 \text{ mmol g}^{-1}$ for U(VI), $0.984 \text{ mmol g}^{-1}$ for Th(IV), $0.488 \text{ mmol g}^{-1}$ for La(III) and $0.502 \text{ mmol g}^{-1}$ for Nd(III) under optimum HNO_3 medium.¹⁷¹ Ionic imprinted resin bearing diethylenetriamine pentaacetic acid (DTPA) and ethylenediaminetetraacetic acid (EDTA) derivatives have been reported in RE extraction with Gd(III)-imprinted polymers found to be more selective.⁵¹

Ion-imprinted polymer based on picolinic derivative have been shown by Chauvin et al. to be particularly well adapted for yttrium extraction, having a sizeable capacity ($8.9 \pm 0.2 \text{ mg g}^{-1}$ resin) and a fast rate of extraction ($t_{1/2} = 1.7 \text{ min}$). The group prepared the resin by copolymerization with styrene and divinylbenzene and subsequent acid treatment to remove the metal ion. The resin displayed high selectivity for yttrium and lanthanide cations against alkali and alkaline earth metals.¹⁷²

Liquid Membrane Extraction

This technique involves the use of *Liquid surfactant membrane* or *Supported liquid membrane*. It generally involves the selective permeation of metal ions through a very thin liquid membrane and a huge interfacial area for the separation of metal ions.¹⁷³ This technique generally utilised the concentration gradient in extraction of metal ions from the feed solution to the stripping solution. A thin liquid film made up of the extractant and a suitable solvent can be supported on a micro-porous hydrophobic hollow fibre and then used to transport the solute from the feed to the product side.¹⁷⁴

Using a liquid membrane system, the synergistic separation of yttrium ions from rare earths mixture using an acidic extractant, Cyanex 272, and a neutral extractant TBP mixed in kerosene has been investigated by Ramakul et al. The selective extraction of yttrium is thought to be due to the decrease in equilibrium constant with an increase in atomic number or decreases with the ionic radius of the lanthanides.¹⁷⁴ The use of other membranes including hinokitiol (4-Isopropyltropolone) and flavonol (3-hydroxy-2-phenylchromen-4-one)¹⁷⁵ and carriers including calix[4]arene,^{176,177} 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHPNA),^{88, 178, 179} crown ether carboxylic acids,⁶³ PC-88A,¹⁸⁰ di(2,4,4-trimethylpentyl)phosphinic acid,¹⁸¹ diethylenetriaminepentaacetic acid,¹⁸² *N,N,N',N'*-tetraoctyl diglycolamide (TODGA), *N,N*-di-*n*-hexyl

octanamide (DHOA),¹⁸³ Cyanex-301 (bis(2,4,4-trimethyl pentyl)dithiophosphinic acid)¹⁸⁴ for the transport and separation of RE have also been reported to exhibit remarkable RE extraction coefficients.

Case Studies

Industrial RE extractions from host minerals

Molycorp is an American mining co-operation. Their process of europium extraction has been described by Gupta and Krishnamurthy. Calcination and leaching with HCl result in a RE chloride solution. 10% v/v D2EHPA in kerosene is used in the extraction at five different mixer and settler stages to obtain a raffinate of Nd with the LREE and Sm and the HREE in the organic phase. Further treatment of the raffinate with the extractant and precipitation with ammonium and hydrogen sulfide results in 98% extraction of europium. The extracted europium can then be stripped by addition of 4 mol/L HCl. Neutralisation to pH 3.5 precipitates the iron impurities. Further rounds of treatment of the europium solution with other HREE with 10% D2EHPA is required to separate the LREE. The europium is extracted along with other HREE while the remaining LREE remains in the raffinate. After stripping europium and the other RE, the europium(III) strip liquor is reduced to europium(II) which is then precipitated out as europium sulfate and calcined to europium oxide.¹⁸⁵

AS Megon is a mining company whose process for yttrium extraction has been described by Gaudernack.¹⁸⁶ Xenotime processing involves extraction of yttrium from concentrates of xenotime. Solvent extraction cycles with D2EHPA, scrubbing and stripping results in La, Ce, Pr and Nd and impurities which include Fe²⁺ in the raffinate. Selective washing results in the separation of the yttrium mixture into three groups. Tri-capryl methylamine is used as an extractant in the second yttrium extraction stage. The LREE contained therein are extracted while Y, Tm, Yb and Lu remains in the raffinate. A third stage involves the use of tri-capryl methylamine-NH₄SCN to produce high purity yttrium oxide.¹⁸⁶

A Monazite processing plant in Yue Long Chemical Plant in Shanghai, China uses an adaptation of the Rhône-Poûlenc (Rhodia Solvay Group) process. Monazites have high contents of HREE. Therefore acidic extractants are preferable as HREE have high affinity for acidic extractants. The monazite is digested in NaOH, filtered and leached with HCl. D2EHPA is used to extract the chloride solution. The extracted RE are split into three groups to produce carbonate, chlorides and oxides. Cation exchangers such as HEHHP and naphthenic acid are typically used in extraction of RE from the HCl or H₂SO₄ leachates. Controlled stripping results in individual RE oxides or chlorides.^{67, 68}

Industrial Recycling of Rare Earths

Opening/expansion of RE mines and recycling of REs from RE-containing EoL products, industrial pre-consumer scrap and industrial residues have been suggested as a ways of possibly mitigating the risk to REs supply. To this end, mining from old, new or reopened RE deposits including Mountain Pass Mine in California have been explored.¹⁸⁷ However, there is a question of whether these mines can compete with cheaper Chinese REs (one of the reasons some of these mines were shut down in the first place) and how long these mines will remain in operation as Mountain Pass Mine recently shut-down. Obviously, alleviating china's dominance over RE through opening of mines in other countries is not working as expected. Recycling of RE is therefore another viable alternative to Chinese REs that could be explored.

However, less than 1% of rare earths are being recycled commercially despite the vast amount of literature on (Lab scale) RE recycling.^{12, 13} Binnemans et al. has extensively reviewed the recycling of REs from RE permanent magnets, nickel metal-hydride batteries, lamp phosphors, glass polishing power, CRT phosphors, fluid cracking catalysts and optical glass in small and large scale.¹⁴ On a commercial scale, there is a lot of talk amongst manufacturers such as Honda, Mitsubishi Electric, Umicore, Japan Metals & Chemicals (JMC)

etc. to recycle REs from NiMH batteries, air conditioning units, waste lamps etc., although the exact recycling process is unreported in a lot of cases.

Umicore's NiMH batteries recycling operations include NiMH and Li-ion batteries. The batteries go in through a vertical shaft furnace, along with a small amount of coke and a slag former. Oxygen is injected at the bottom of the shaft furnace. The metals form alloys of Ni-Co-Cu-Fe and a slag which consists mainly of oxides of Ca, Al, Si, and Fe, and also contains Li and the rare earths.¹⁸⁸ Li as well as rare-earth concentrates can then be recovered from these oxide slags.^{189, 190}

Hitachi has developed a technology for commercial scale recycling of rare earth magnet from HDDs and air conditioner compressors.¹⁹¹ The HDD dismantler removes voice coil motors (VCMs) from the HDDs. The VCMs disassembled by the HDD dismantler are then demagnetized in an electric furnace, but the external yoke and rare-earth magnets that make up the VCM remain joined by a carbonized adhesive. The magnet recovery machine then separates the rare-earth magnets from the yoke, using a machine for performing the process. Recycling of RE magnet in air conditioners involves the use of a mechanical unit for cutting open the casing, a rotor removal machine that extracts the rotor from the motor, a demagnetizer that operates at room temperature using resonance damping demagnetization, and a magnet removal machine with a drop impact mechanism.

The actual separation RE from waste magnet is a much more complicated process. Ames Laboratory have developed and received commercial licensing for its RE magnet recycling technology. In principle, REs, particularly neodymium are very soluble in magnesium while the other components of magnets, like iron and boron are poorly soluble in magnesium¹⁹². The process involves melting and dissolving neodymium with molten magnesium leaving behind the other components of magnets, like iron and boron which are less soluble. Sintered, uncoated magnets that contain neodymium, praseodymium and dysprosium are broken up using an automated mortar and pestle until the pieces are 2-4 mm long. The tiny magnet pieces go into a mesh screen box, which is placed in a stainless-steel crucible. Technicians then add chunks of solid magnesium. A radio frequency furnace heats the material. The magnesium begins to melt, while the magnet chunks remain solid. Rare-earth magnet scraps are then melted in a furnace with magnesium. All three rare earths leave the magnetic material by diffusion and enter the molten magnesium. The iron and boron that made up the original magnet are left behind. The molten magnesium and rare-earth mixture is cast into an ingot and cooled. Then the magnesium is boiled off leaving just the rare earth materials behind.^{192, 193}

Conclusion

As innovation tends towards clean and renewable technology, it will become more imperative that sourcing of materials necessary for this purpose needs to be from green and efficient processes. More so, ease of access to RE is vital to sustain the growth of renewable technologies as the subject of future supply is met with a lot of uncertainty.

Efficient extraction of RE from their host minerals and e-wastes has been discussed. All of the methods discussed in this paper have seen major optimisation and some of which are now being applied on industrial scale in extraction facilities. Researchers seek to find a good balance between the environmentally friendly and efficiency in their extraction technique. However, the concentrated acids used in leaching can be environmentally expensive. An efficient recycling, neutralisation or disposal of the acid waste is vital. Solvent extraction has made significant advances but still retains its limitations such contamination of the aqueous phase by the extractants. Supercritical fluids, ionic liquids, ion exchange and membrane extractions hold promise of greener methods. A hybrid of techniques could be the future of extraction as it has been shown to be effective and environmentally benign. Extractant that have been proven in solvent extraction can be used in other techniques such as IL, scCO₂, and membrane in order to eliminate the need for organic solvent. Solvent extractants and IL can also be used in liquid membranes and resins thereby encouraging facile recover and reuse.

There is a need to translate the success of lab scale RE extraction to commercial scales RE extraction from RE containing e-wastes to meet the growing need for RE. Commercial scale RE extraction from mineral ores using proven extraction methods have been efficacious. Similar success can be expected if applied to RE recycling from e-waste.

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