



Review on hydrometallurgical recovery of rare earth metals



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ABSTRACT

Rare earth metals are essential ingredients for the development of modern industry as well as designing and developing high technology products used in our daily lives. Consequently, the worldwide demand of rare earth metals is rising quickly and predicted to surpass the supply by 40,000 tons annually. However, their availability is declining, mainly due to the export quotas imposed by the Chinese government and actions taken against illegal mining operations. This has laid emphasis to exploit and expand technologies to meet the future necessities of rare earth metals. Bastnasite, monazite, and xenotime are their chief mercantile sources, which are generally beneficiated by flotation, gravity or magnetic separation processes to get concentrates that are processed using pyro/hydrometallurgical routes. To develop feasible and eco-friendly processes, R&D studies are being conducted for the extraction of rare earth metals from leached solutions (chloride, nitrate, sulfate, thiocyanate, etc.) using different cationic, anionic and solvating solvents or ions depending on material and media. Commercial extraction of rare earth metals has been carried out using different extractants viz. D2EHPA, Cyanex 272, PC 88A, Versatic 10, TBP, Aliquat 336, etc. The present paper reviews the methods used for the recovery of rare earth metals from primary as well as secondary resources, with special attention to the hydrometallurgical techniques, consisting of leaching with acids and alkalis followed by solvent extraction, ion exchange or precipitation. The piece of comparative and summarized review will be useful for the researchers to develop processes for rare earth recovery under various conditions.

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1. Introduction

Rare earth elements include the 15 elements of lanthanide group from lanthanum to lutetium, coupled with chemically similar yttrium and infrequently scandium. These elements are split into two sub-groups, the light rare earth elements (LREEs) from lanthanum to europium and the heavy rare earth elements (HREEs), which include the rest of lanthanide elements along with yttrium. Scandium is not included in either of these groups due to its much smaller ionic radius. Rare earth elements are comparatively abundant in the earth's crust than other commonly exploited elements but are not sufficiently concentrated to make them easily exploitable. This is due to the similarity in their ionic radii (Table 1) which makes them interchangeable in most minerals, and are very difficult to separate (Jordens et al., 2013; Gupta and Krishnamurthy, 2005). Rare earths are always found in varieties of minerals viz. silicates, halides, carbonates, phosphates, etc. (Table 2) but never found as pure metal (Jordens et al., 2013; Kumari et al., 2015). Nowadays, more than 250 rare earth minerals have been recognized but in most of them the concentration of rare earths is very low varying from 10 to 300 ppm (Zhang and Edwards, 2012).

The unique properties of rare earth metals is dominantly expanding its application and are needed to supply the required functionality in many high-tech components, green technologies and material industries of high-temperature superconductors, secondary batteries, hybrid cars, etc. The extensive use of rare earth elements is increasing their global demand and was estimated to be 136,000 tons per year, with a worldwide production of 133,600 tons in 2010 (Panayotova and Panayotov, 2012). Bloomberg News (2010) predicted that the demand would reach 210,000 tons per year by 2015, keeping in view the escalating demand of rare earths that is exceeding the industry's ability to produce as the commercial stocks are depleting. The forecast supply and demand of rare earths till 2014 is presented in Table 3 (Seaman, 2010). About, one hundred million tons of rare earth oxide reserves are presently accessible in the world, scattered in more than 30 countries (Chen, 2011). In 1950s, South Africa, India, and Brazil had rare earth mines in operation. Further, during 1960s to 1980s, the Mountain Pass in California became the largest global producer for the same up to 2002 till it closed. Thereafter, China began large scale production and exported rare earths at cheaper rate. Currently, it is the worldwide producer of rare earth elements producing ~97% of the total world supply. But their incessantly increasing requirement has aggravated the Chinese government to drastically limit the export of rare earths up to 35,000 tons while the yearly demand of other countries is estimated to reach 80,000 tons in 2015, thus, confronted with a rare earth supply

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Table 1

Ionic radii of rare earth elements (Jordens et al., 2013; Gupta and Krishnamurthy, 2005).

Rare earth elements	Ionic radius (nm)
La	1.061
Ce	1.034
Pr	1.013
Nd	0.995
Pm	0.979
Sm	0.964
Eu	0.95
Gd	0.938
Tb	0.923
Dy	0.908
Ho	0.894
Er	0.881
Tm	0.869
Yb	0.858
Lu	0.848
Se	0.66
Y	0.88

risk (Jordens et al., 2013; Panayotova and Panayotov, 2012). According to the U.S. Mineral Commodity Summaries of 2015, the global mine production of rare earth metals (Fig. 1) is 110,000 metric tons while the total reserves is found to be 130,000,000 metric tons. This restriction of supply is being met by the development of many new mining projects or reopening of old mines. Worldwide exploration for economically exploitable rare earth deposit as well as development of indigenous resources and technologies to meet the future requirements of rare earth metals is encouraged.

The objective of the present paper is to explore the current overview of rare earth recovery from various resources with regard to hydrometallurgical processes consisting of leaching, solvent extraction, ion-exchange and precipitation along with their selected environmental impacts and finally the research work further required in these fields.

2. Currently exploited primary and secondary resources

Minerals containing rare earth elements are differentiated into various groups depending upon the content of rare earths present in them. Bastnasite, monazite and xenotime are the three most frequently extracted rare earth minerals. However, ion-adsorbed clays are also very significant source in which 60% of the rare earth oxides comes from the group of HREEs. Rare earth elements are becoming progressively more important in transition to a green economy, due to their vital role in permanent magnets, lamp phosphors, catalysts, rechargeable batteries, etc.

2.1. Primary sources

2.1.1. Bastnasite

Bastnasite, a fluorocarbonate mineral containing approximately 70% rare earth oxide (mainly conquered by LREEs) became the principal source of most rare earth elements and are relatively straightforward to treat (Jordens et al., 2013; Ozbayoglu and Umit Atalay, 2000; Huang et al., 2005). It originates in vein deposits, metamorphic zones, igneous carbonatites deposits and are mainly obtained from the world's largest rare earth mines, the Mountain Pass, USA and the Bayan Obo mine in China (Gupta and Krishnamurthy, 2005). Some of the rare earth distribution present in major deposits of bastnasite minerals is illustrated in Fig. 2 with other metals present in trace amount (Long et al., 2010; Jordens et al., 2013; Chen, 2011). This ore is processed by numerous operations including gravity and magnetic separation to make intermediate rare earth concentrates and are further purified using solvent extraction as well as selective precipitation.

2.1.2. Monazite

A rare earth phosphate mineral, fairly similar to bastnasite as a LREE ore but with slightly more HREEs is known as monazite. Unlike bastnasite, monazite contains a high content of naturally occurring radioactive element, thorium (4–12 wt.%) and a variable amount of uranium which presents a negative aspect of mining and processing, thus eliminating all the monazite production except from southeast Asia and India. It is found throughout the world in placer deposits, beach sands, and is also a component of the Bayan Obo deposit. They are mainly mined as heavy mineral sand from beach deposits and recovered as a byproduct during processing of ilmenite, rutile and zircon (Gupta and Krishnamurthy, 2005; Kumar et al., 2014).

2.1.3. Xenotime

Xenotime is also a rare earth phosphate mineral, containing ~67% rare earth oxides which is rich in yttrium and HREEs, especially the even numbered lanthanides. In spite of its scarcity, xenotime is a vital mineral being a major source of HREEs and ion-adsorbed clays. It occurs in granites of Minas Geraes in Brazil, pegmatite veins at Hittero, Moss as well as in crystalline metamorphic rocks. Xenotime is recovered as a minor ore mineral during heavy sand recovery operations, primarily from monazite in Brazil, India, South Africa and Australia. Limited researches are only focused for the xenotime extraction from monazite using flotation and magnetic separation. Distribution of rare earths in monazite, xenotime and ion-adsorbed clays in some of their major deposits is presented in Table 4 (Long et al., 2010; Jordens et al., 2013; Chen, 2011).

To recover rare earth metals from these ores, various processing routes have been developed. Ores obtained after mining are beneficiated using flotation, magnetic or gravity separation methods. These beneficiated ores (a few successfully exploited minerals is mentioned in Table 2) are usually treated hydrometallurgically or at times by pyrometallurgical operations. However, the ion-adsorbed clays require little or no beneficiation and are directly processed using hydrometallurgical routes.

2.2. Secondary sources

The absence of cost-effective and operational primary deposits is forcing many countries to rely on the recycling of rare earth metals from pre-consumer scrap, industrial residues and end-of-life products. This can reduce the environmental challenges associated with rare earth mining and processing. Rare earth recovery from some of the end-of-life products is discussed in this paper.

2.2.1. Permanent magnets

Neodymium-iron-boron (NdFeB) alloys are the basis of rare earth magnets commonly known as Nd-Fe-B magnets, comprised an $\text{Nd}_2\text{Fe}_{14}\text{B}$ matrix phase surrounded by a neodymium-rich grain boundary with small admixtures of praseodymium, gadolinium, terbium, and especially dysprosium (increases temperature stability against demagnetization) along with other elements such as cobalt, vanadium, titanium, zirconium, molybdenum or niobium (Gutfleisch et al., 2011; Yu and Chen, 1995; Binnemans et al., 2013). This superfluous material is significantly found in hard disk drives (HDDs) along with other electronic goods such as loudspeakers, mobile phones, etc. On global scale, 600 million HDDs are manufactured consuming ~6000 to 12,000 tons of Nd-Fe-B alloys (Binnemans et al., 2013). Rare earth metals are generally recycled from three different magnet materials (1) swarf obtained during magnet manufacturing, (2) small magnets of end-of-life products and (3) large magnets in hybrid and electric vehicles or wind turbines. Direct recycling and re-use is applicable only for the large magnets while further processing is required for other rare earth magnets. A simplified flow sheet as described by Binnemans et al., 2013 for the recycling of rare earth metals from magnets is shown in Fig. 3.

Table 2

Minerals containing rare earth elements (Jordens et al., 2013; Long et al., 2010; Anthony et al., 2001; Kumari et al., 2015).

Phosphate REEs bearing minerals	Chemical formula	Weight percent		
		REOs	ThO ₂	UO ₂
Britholite (Ce)	(Ce,Ca) ₅ (SiO ₄ PO ₄) ₃ (OH,F)	56	1.5	–
Britholite (Y)	(Y,Ca) ₅ (SiO ₄ PO ₄) ₃ (OH,F)	56	1.5	–
Brockite	(Ca,Th,Ce)(PO ₄) ₂ ·H ₂ O	–	–	–
Chevkinite (Ce)	(Ca,Ce,Th) ₄ (Fe ²⁺ ,Mg) ₂ (Ti,Fe ³⁺) ₃ Si ₄ O ₂₂	–	–	–
Churchite (Y)	YPO ₄ ·H ₂ O	–	–	–
Crandallite	CaAl ₃ (PO ₄) ₂ (OH) ₅ ·H ₂ O	–	–	–
Florencite (Ce)	CeAl ₃ (PO ₄) ₂ (OH) ₆	–	1.4	–
Florencite (La)	(La,Ce)Al ₃ (PO ₄) ₂ (OH) ₆	–	1.4	–
Florencite (La)	(Nd,Ce)Al ₃ (PO ₄) ₂ (OH) ₆	–	1.4	–
Fluorapatite	(Ca,Ce) ₅ (PO ₄) ₃ F	–	–	–
Gorceixite	(Ba,REE)Al ₃ [(PO ₄) ₂ (OH) ₅]·H ₂ O	–	–	–
Goyazite	SrAl ₃ (PO ₄) ₂ (OH) ₅ ·H ₂ O	–	–	–
Monazite (Ce)	(Ce,La,Nd,Th)PO ₄	35–71	0–20	0–16
Monazite (La)	(La,Ce,Nd,Th)PO ₄	35–71	0–20	0–16
Monazite (Nd)	(Nd,Ce,La,Th)PO ₄	35–71	0–20	0–16
Rhabdophane (Ce)	(Ce,La)PO ₄ ·H ₂ O	–	–	–
Rhabdophane (La)	(La,Ce)PO ₄ ·H ₂ O	–	–	–
Rhabdophane (Nd)	(Nd,Ce,La)PO ₄ ·H ₂ O	–	–	–
Vitusite (Ce)	Na ₃ (Ce,La,Nd)(PO ₄) ₂	–	–	–
Xenotime (Y)	YPO ₄	52–67	–	0–5
Halide REEs bearing minerals	Chemical formula	Weight percent		
		REOs	ThO ₂	UO ₂
Fluocerite (Ce)	(Ce,La)F ₃	–	–	–
Fluocerite (La)	(La,Ce)F ₃	–	–	–
Fluorite	(Ca,REE)F ₂	–	–	–
Gagarinite (Y)	NaCaY(F,Cl) ₆	–	–	–
Pyrochlore	(Ca,Na,REE) ₂ Nb ₂ O ₆ (OH,F)	–	–	–
Yttrofluorite	(Ca,Y)F ₂	–	–	–
Carbonate REEs bearing minerals	Chemical formula	Weight percent		
		REOs	ThO ₂	UO ₂
Ancylite (Ce)	Sr(Ce,La)(CO ₃) ₂ OH·H ₂ O	46–53	0–0.4	0.1
Ancylite (La)	Sr(La,Ce)(CO ₃) ₂ OH·H ₂ O	46–53	0–0.4	0.1
Bastnasite (Ce)	(Ce,La)(CO ₃)F	70–74	0–0.3	0.09
Bastnasite (La)	(La,Ce)(CO ₃)F	70–74	0–0.3	0.09
Bastnasite (Y)	(Y)(CO ₃)F	70–74	0–0.3	0.09
Calcio-ancylite (Ce)	(Ca,Sr)Ce ₃ (CO ₃) ₄ (OH) ₃ ·H ₂ O	60	–	–
Calcio-ancylite (Nd)	Ca(Nd,Ce,Gd,Y) ₃ (CO ₃) ₄ (OH) ₃ ·H ₂ O	60	–	–
Doverite	YCaF(CO ₃) ₂	–	–	–
Parisite (Ce)	Ca(Ce,La) ₂ (CO ₃) ₃ F ₂	59	0–0.5	0–0.3
Parisite (Nd)	Ca(Nd,Ce) ₂ (CO ₃) ₃ F ₂	–	–	–
Synchysite (Ce)	Ca(Ce,La)(CO ₃) ₂ F	49–52	1.6	–
Synchysite (Nd)	Ca(Nd,La)(CO ₃) ₂ F	–	–	–
Oxide REEs bearing minerals	Chemical formula	Weight percent		
		REOs	ThO ₂	UO ₂
Anatase	(Ti,REE)O ₂	–	–	–
Brannerite	(U,Ca,Y,Ce)(Ti,Fe) ₂ O ₆	–	–	–
Cerianite (Ce)	(Ce ⁴⁺ ,Th)O ₂	–	–	–
Euxenite (Y)	(Y,Ca,Ce,U,Th)(Nb,Ta,Ti) ₂ O ₆	–	–	–
Fergusonite (Ce)	(Ce,La,Y)NbO ₄	–	–	–
Fergusonite (Nd)	(Nd,Ce)(Nb,Ti)O ₄	–	–	–
Fergusonite (Y)	YNbO ₄	–	–	–
Loparite (Ce)	(Ce,Na,Ca)(Ti,Nb)O ₃	–	–	–
Perovskite	(Ca,REE)TiO ₃	<37	0–2	0–0.05
Samarskite	(REE,Fe ²⁺ ,Fe ³⁺ ,U,Th,Ca)(Nb,Ta,Ti)O ₄	–	–	–
Uraninite	(U,Th,Ce)O ₂	–	–	–
Silicate REEs bearing minerals	Chemical formula	Weight percent		
		REOs	ThO ₂	UO ₂
Allanite (Ce)	(Ce,Ca,Y) ₂ (Al,Fe ²⁺ ,Fe ³⁺) ₃ (SiO ₄) ₃ (OH)	3–51	0–3	–
Allanite (Y)	(Y,Ce,Ca) ₂ (Al,Fe ³⁺) ₃ (SiO ₄) ₃ (OH)	3–51	0–3	–
Cerite (Ce)	Ce ₉ Fe ³⁺ (SiO ₂) ₆ [(SiO ₃)(OH)](OH) ₃	–	–	–
Cheralite (Ce)	(Ca,Ce,Th)(P,Si)O ₄	–	<30	–
Eudialyte	Na ₄ (Ca,Ce) ₂ (Fe ²⁺ ,Mn ²⁺ ,Y)ZrSi ₈ O ₂₂ (OH,Cl) ₂	1–10	–	–
Gadolinite (Ce)	(Ce,La,Nd,Y) ₂ Fe ²⁺ Be ₂ Si ₂ O ₁₀	–	–	–
Gadolinite (Y)	Y ₂ Fe ²⁺ Be ₂ Si ₂ O ₁₀	–	–	–
Geranite (Y)	(Ca,Na) ₂ (Y,REE) ₃ Si ₆ O ₁₈ ·2H ₂ O	–	–	–
Hingganite (Ce)	(Ce,Y) ₂ Be ₂ Si ₂ O ₈ (OH) ₂	–	–	–

Table 2 (continued)

Silicate REEs bearing minerals	Chemical formula	Weight percent		
		REOs	ThO ₂	UO ₂
Hingganite (Y)	(Y,Yb,Er) ₂ Be ₂ Si ₂ O ₈ (OH) ₂	–	–	–
Hingganite (Yb)	(Yb,Y) ₂ Be ₂ Si ₂ O ₈ (OH) ₂	–	–	–
limoriite (Y)	Y ₂ (SiO ₄)(CO ₃)	–	–	–
Kainosite (Y)	Ca ₂ (Y,Ce) ₂ Si ₄ O ₁₂ (CO ₃)H ₂ O	–	–	–
Rinkite (rinkolite)	(Ca,Ce) ₄ Na(Na,Ca) ₂ Ti(Si ₂ O ₇) ₂ F ₂ (O,F) ₂	–	–	–
Sphene (titanite)	(Ca,REE)TiSiO ₅	<3	–	–
Steenstrupine (Ce)	Na ₁₄ Ce ₆ Mn ₂ Fe ₂ (Zr,Th)(Si ₆ O ₁₈) ₂ (PO ₄) ₇ ·3H ₂ O	–	–	–
Thalenite (Y)	Y ₃ Si ₃ O ₁₀ (F,OH)	–	–	–
Thorite	(Th,U)SiO ₄	<3	–	10–16
Zircon	(Zr,REE)SiO ₄	–	0.1–0.8	–

2.2.2. Fluorescent lamps

Fluorescent lamps are gas discharge lamps comprising of a glass tube filled with an inert gas and coated with a thin layer of phosphor powder. Low energy consumption as well as longer life expectancy have greatly escalated the use of these lamps. A fluorescent lamp by weight consists of 88% glass, 5% metals, 4% plastic, 3% lamp phosphor powder and 0.005% mercury. The composition of phosphor powder obtained after crushing and sieving of the lamps generally contains halophosphate phosphor (45 wt.%), fine glass particles and silica (20 wt.%–30 wt.%), alumina (12 wt.%), rare-earth phosphors (10 wt.% to 20 wt.%) and a residual fractions (5 wt.%) (Binnemans and Jones, 2014). This phosphor powder is utilized either by re-using them directly in new lamps or by separating individual rare earth metals for further applications.

2.2.3. Nickel-metal hydride batteries

A nickel-metal hydride battery, abbreviated NiMH is a type of rechargeable battery where nickel oxyhydroxide (NiOOH) is used at cathode while a hydrogen-absorbing alloy is used at anode. The energy density of these batteries can approach that of a lithium-ion battery and its capacity is 2–3 times greater than equivalent size NiCd batteries. To reduce the price, misch metal (mixture of LREEs) in metallic state is used instead of rare earth alloy. Spent batteries contain 36–42% nickel, 3–4% cobalt and 8–10% misch metal consisting of lanthanum, cerium, praseodymium and neodymium (Muller and Friedrich, 2006). Several researchers have developed methods for the recovery of rare earth metals from NiMH batteries (Lyman and Palmer, 1995; Li et al., 2009; Zhang et al., 1999; Luidold and Antrekowitsch, 2012; Kaindl et al., 2012).

2.2.4. Other secondary resources

In spite of rare earth content in these secondary resources mentioned above, they confronted poor recycling (less than 1%) due to inefficient collection, technological problems, and lack of incentives

(Tanaka et al., 2013). Thus, other resources are also encouraged and comparing to the phosphor recycling from spent fluorescent lamps, some effort has also been directed towards phosphor used in cathode ray tubes (CRTs) of color television sets and computer monitors. Rare earths have significant application in the use of cerium oxide as a glass polishing powder. For decades, cerium oxide in water is considered as best polishing agent for glasses (Niinisto, 1987). Fluid catalytic cracking (FCC) catalysts extensively used in the petrochemical industry are another source containing about 3.5 wt.% rare earth oxides, mainly lanthanum, and small amount of cerium, praseodymium as well as neodymium (Yu and Chen, 1995). Optical glasses, with total world production of ~20,000 tons/year, are suitable for lenses of cameras, microscopes, binoculars or microscopes having high refractive index and low dispersion. These lenses contains more than 40 wt.% of La₂O₃ along with Y₂O₃ and Gd₂O₃. Recycling of these spent optical glasses could yield about 1600 tons of rare earth oxides annually. Table 5 shows the present and future streams of rare earth metals available for recycling (Binnemans et al., 2013).

The rapid growth of rare earth mines can be controlled by rare earth recycling which is capable to offset a significant part of primary REE extraction in near future. The state of the art in processing these rare earth resources and their final recovery following hydrometallurgical routes is discussed in detail.

3. Processing of rare earth resources

As China tightens the noose on the rare earth export, worldwide investigation for their economically exploitable deposit or production as a byproduct is encouraged. But milling and processing of rare earth metals is an intricate and ore-specific operation that has probability for environmental contamination if not managed properly. The United States Environmental Protection Agency in 2012 declared that the waste streams generated during rare earth processing have been recognized, and their harmful waste potential has been assessed. However, adoption of new technologies shows potential to reduce the risk of environmental contamination.

Rare earth elements have strong affinity for oxygen and thus, their resources are principally present in oxidic form as rare earth oxides. Complex processing of these oxides to form utilizable products frequently varies between deposits. The major factors affecting the selection of treatment processes are the type and nature of deposit (e.g., beach sand, vein type, igneous and complex ores); its complexity as well as other valuable and gangue minerals (e.g., slimes, clay, soluble gangue) present with rare earth oxides (Ferron et al., 1991). Initial step for ore processing typically includes beneficiation process which does not alter the chemical composition of the ore; but helps in liberation of the mineral ore from host material. Differences in the physical properties such as gravity, magnetizability, and surface ionization potential enabled gravity separation, flotation, electrostatic and magnetic separation with dramatic percentage increase in rare earth oxides in the working material (Aplan, 1988). Subsequent steps aim to change the concentrated mineral into more valuable chemical forms through

Table 3

Estimated supply and demand of rare earth elements in 2014 (Seaman, 2010).

Elements	Supply (REO in tonnes)	Demand (REO in tonnes)	Surplus/Deficit (REO in tonnes)
Lanthanum	54,750	51,050	3700
Cerium	81,750	65,750	16,000
Praseodymium	10,000	7900	2100
Neodymium	33,000	34,900	–1900
Samarium	4000	1390	2610
Europium	850	840	10
Gadolinium	3000	2300	700
Terbium	350	590	–240
Dysprosium	1750	2040	–290
Erbium	1000	940	60
Yttrium	11,750	12,100	–350
Ho–Tm–Yb–Lu	1300	200	1100
Total	203,500	180,000	23,500

Data in italics with negative sign indicates the shortfall elements.

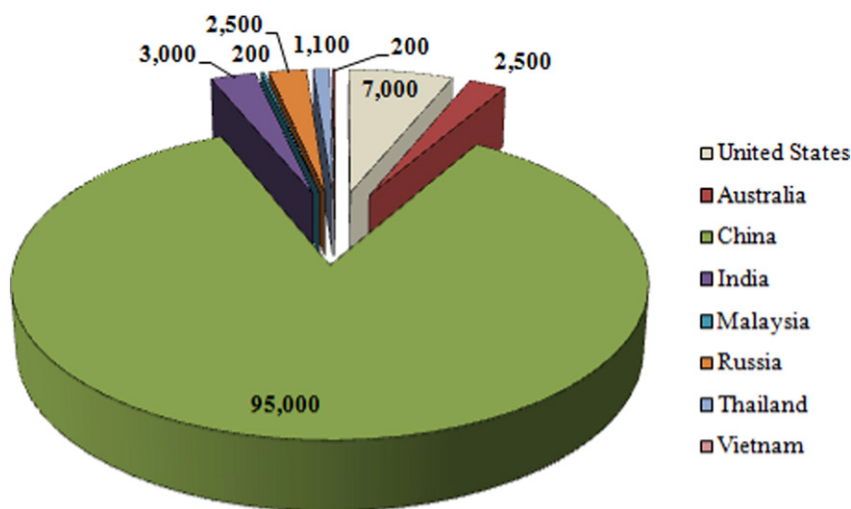


Fig. 1. Global mine production of rare earth metals in different countries (U.S. Mineral Commodity Summaries, 2015).

various thermal and chemical reactions, mainly utilizing hydrometallurgical techniques forming exploitable rare earth oxides. An outline of the major steps required for processing of beach sand mineral by physical beneficiation is shown in Fig. 4 (Gupta and Krishnamurthy, 2005). The solubility of rare earth salts, hydrolysis of ions and formation of their complex species are influenced by the basicity difference between various rare earths. Based on these properties, fractional crystallization and precipitation, ion exchange and solvent extraction leads to individual separation of rare earth metals (Gupta and Krishnamurthy, 2005). However, according to the United States Environmental Protection Agency (2012) rare earth recycling from the end-of-life products typically involves four key steps: (1) collection; (2) dismantling; (3) separation, and (4) processing.

4. Hydrometallurgical operations

Processed materials (primary/secondary) are hydrometallurgically treated using strongly acidic or basic solutions to selectively dissolve and precipitate metals of interest. The principle processes employed during hydrometallurgical treatment of rare earth resources mainly include leaching, solvent extraction, ion exchange and precipitation which varies, depending on the metals to be recovered. The basic processes used for rare earth recycling are similar to those utilized for raw ores and the same will be examined here as they have been applied to materials containing rare earth metals.

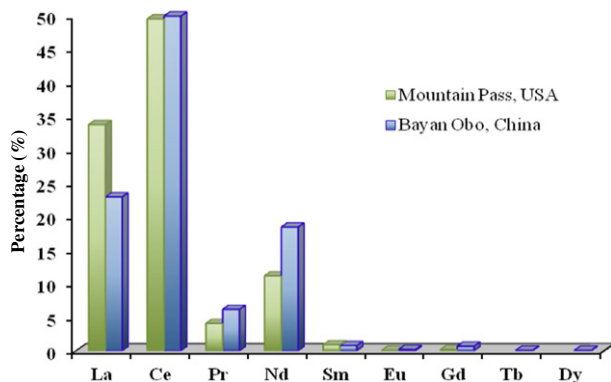


Fig. 2. Distribution of some rare earths present in major deposits of bastnasite minerals (Long et al., 2010; Jordens et al., 2013; Chen, 2011).

4.1. Leaching

Different existing technologies for leaching rare earth metals from primary and secondary resources is an important part of rare earth processing using hydrometallurgical route. Physically beneficiated concentrates are leached in suitable lixiviant directly or after heat treatment to dissolve the metallic values (Akkurt et al., 1993; Fatherly et al., 2008). The known processes range from acid leaching with H_2SO_4 , HCl , HNO_3 for primary ores, to leaching with $NaCl$ or $(NH_4)_2SO_4$ of ion adsorbed clays as well as combined base and acid leaching for End-of-Life products. Complete understanding of these processes is essential for applying them to develop more feasible methods for the recovery of rare earth metals. Studies carried out to recover rare earth metals from various resources available in different countries are described below.

4.1.1. Leaching technologies used for primary resources

The fluorocarbonate mineral, bastnasite is chemically susceptible to weathering which causes the rare earth oxides to dissolve and combine with available phosphates. They are comparatively easy to treat but in order to decrease acid consumption, bastnasite is roasted before leaching to decompose the carbonate present in the mineral. As half of rare earth content in bastnasite is Ce, so its removal before extraction considerably reduces the solvent extraction capacity to selectively separate individual rare earth metals. According to the United States Environmental Protection Agency (2012), the concentrates were initially calcined that convert Ce(III) to Ce(IV), leaving other rare earths in plus 3 state. Subsequent hydrochloric acid dissolution promotes Ce(IV) reduction and results in leaching of all rare earth metals leaving Ce in the residue. This insolubility of Ce by acid digestion is due to its oxidation from Ce(III) to Ce(IV). Leach liquor obtained was further processed using multistage solvent extraction methods to obtain pure rare earth compounds and Ce was oxidized in aqueous phase to precipitate it and obtained via filtration. However, to reduce the separation costs, Ce is oxidized to CeO_2 using roasting which avoids its dissolution in acidic medium (Xie et al., 2014). Bastnasite has also been roasted with ammonium chloride, which decomposes into gaseous HCl that forms rare earth chlorides, which are readily leached with hot water (Chi et al., 2004). Previous technologies used for bastnasite processing deals with the inability to extract rare earth fluorides which has been effectively resolved utilizing pre/post treatment with alkaline or sulfuric acid roasting using the reactions as discussed below (Gupta and Krishnamurthy, 2005):



Table 4

Rare earth elements distribution of monazite, xenotime and ion-adsorbed clay in some of their major deposits (Long et al., 2010; Jordens et al., 2013; Chen, 2011).

Major deposits	Rare Earth Elements (%)														
	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
Monazite Deposit (Green Cove Spring, USA)	17.5	43.7	5.0	17.5	4.9	0.2	6.0	0.3	0.9	0.1	T	T	0.1	T	2.5
Xenotime Deposit (Lehat, Malaysia)	1.2	3.1	0.5	1.6	1.1	T	3.5	0.9	8.3	2.0	6.4	1.1	6.8	1.0	61.0
High Y REE Clay (Longnan, China)	1.8	0.4	0.7	3.0	2.8	0.1	6.9	1.3	7.5	1.6	4.9	0.7	2.5	0.4	65.0
Low Y REE Clay (Xunwn, China)	43.3	2.4	7.1	30.2	3.9	0.5	4.2	T	T	T	T	T	0.3	0.1	8.0

T = Trace.

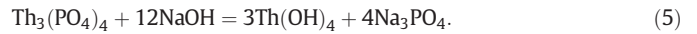


where 'RE' denotes rare earth.

Currently, at the Bayan Obo mine, China, sulfuric acid roasting of bastnasite is the main process used, in which the concentrate is heated with 98% H_2SO_4 solution to $\sim 500^\circ\text{C}$ for several hours. This process decomposes the fluorocarbonate matrix converting rare earths to their sulfates and releases CO_2 and HF gas. These rare earth sulfates are selectively precipitated as Na double sulfates by leaching the residue with NaCl containing water (Peelman et al., 2014). But the environmental threat caused by the emanation of fluorine gas during this process leads to the development and progress in bastnasite leaching technologies to prevent this hazardous emission. This is achieved by thermally treating the ore at 400°C for 3 h followed by its leaching with HCl which enables carbonate leaching up to 94.6% leaving fluorides unaffected with only 0.07% dissolution (Bian et al., 2011). Sulfuric acid is also used extensively in the U.S. for leaching rare earth concentrates. A schematic flow sheet for the leaching process used for Baotou rare earth concentrates in China is presented in Fig. 5 (Huang et al., 2006). Rare earth double sulfate mixture was prepared from Turkish bastnasite using sulfuric acid baking followed by water leaching which not only results in $\sim 90\%$ rare earth recovery but also produce hydrofluoric acid as a byproduct. Further precipitation using sodium sulfate at 50°C results in decontamination of these double sulfate salts from impurities (Kul et al., 2008; Kumar et al., 2014). However, the air roasting process which prevented Ce leaching together with other rare earths due to oxidation of Ce^{+3} to Ce^{+4} was improved by adding thiourea which keep Ce in its trivalent state after roasting and thus, leached together with other rare earth metals (Yorukoglu et al., 2003). Nitric acid digestion has also been used to recover 98% of rare earths from the crude bastnasite ore containing 7–10% rare earth oxides. Mechanochemical activation of bastnasite by milling it with NaOH followed by water washing and leaching in

HCl is also an effective effort resulting in 90% leaching efficiency (Zhang and Saito, 1998b).

Apart from bastnasite, monazite also requires suitable conditions to leach out the complex materials/metals present in it using acidic or alkaline solutions. The high content of thorium is of great concern during monazite processing and also get precipitated in the residue which cannot be recovered economically. However, in order to decompose orthophosphate lattice of monazite, sulfuric acid or sodium hydroxide leaching at high temperatures are preferred. Currently, sodium hydroxide is usually employed for leaching monazite at $140\text{--}150^\circ\text{C}$ and further the cake containing rare earth metals and thorium hydroxide was leached in acidic solution to produce leach liquor containing rare earth metals for their subsequent separation. This process not only recuperates rare earth metals but also the phosphate present in the minerals. The reactions during alkaline leaching are:



The residue left after digesting monazite in 60–70% NaOH at $140\text{--}150^\circ\text{C}$ for 4 h is treated in hot nitric acid and sulfuric acid. Further, solvent extraction studies were carried out using TBP for nitrate and amines of the solution for sulfate medium, respectively (Gupta and Krishnamurthy, 2005). But prior to this process, proper grinding of monazite is essential to extract $\sim 98\%$ even with relatively low grade ores. Moreover, it has been reported that the presence of Mn^{+4} oxidizes Ce to CeO_2 preventing its dissolution in HCl with other rare earth metals (Kuzmin et al., 2012). Different authors studied direct leaching of monazite using acidic or alkaline solutions under different experimental conditions to dissolve rare earths or undesired components to get the concentrate. But in order to improve rare earth recovery from monazite, the material is pre-treated before leaching in suitable lixiviant. Several literatures have been reported related to monazite pre-treatment for subsequent processing. These whole studies related to monazite

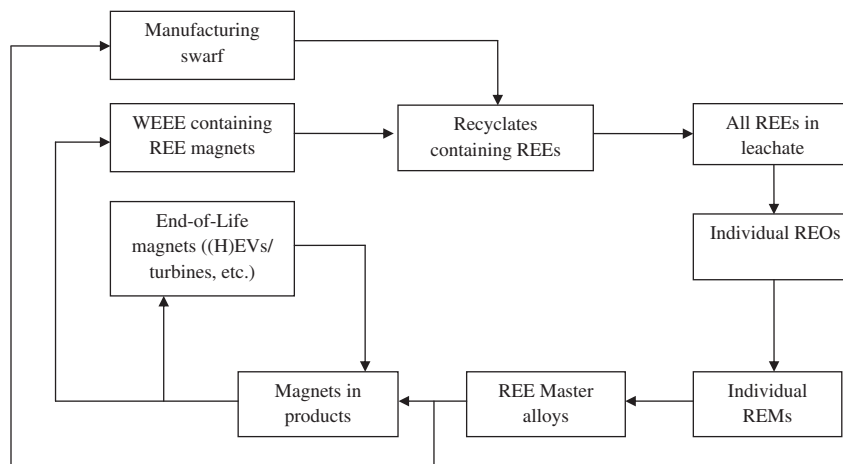
**Fig. 3.** Simplified recycling flow sheet for rare earth magnets (Binnemans et al., 2013).

Table 5

Present and future rare earths containing materials available for recycling (Binnemans et al., 2013).

Pre-consumer production scrap and residues

1. Magnet swarf and rejected magnets (Nd, Dy, Tb, Pr)
2. REE containing residues arising during metal production/recycling
 - a) Postmelter & Electric Arc Furnace residues (Ce, La, critical rare earth metals)
 - b) Industrial residues like phosphogypsum, red mud, etc. (all rare earth metals)

End-of-life products

1. Phosphors (Eu, Tb, Y (Ce, Gd, La))
 - a) Fluorescent lamps
 - b) Compact fluorescent lamps
 - c) LEDs
 - d) LCD Backlights
 - e) Plasma Screens
 - f) Cathode-ray tubes (CRTs)
2. Permanent Nd–Fe–B magnets (Nd, Dy, Tb, Pr)
 - a) Automobiles
 - b) Mobile phones
 - c) Hard disk drives (HDDs)
 - d) Computers & peripherals
 - e) Consumer electric & electronic devices
 - f) Industrial applications
 - g) Electric bicycles
 - h) Electric vehicles & hybrid electric vehicle motors
 - i) Wind turbine generators
3. Nickel metal hydride batteries (La, Ce, Nd, Pr)
 - a) Rechargeable batteries
 - b) Electric vehicles & hybrid electric vehicle batteries

Land filled rare earth metals containing residues

1. Industrial residues like phosphogypsum, red mud, etc. (all rare earth metals)

leaching have been covered up by Kumari et al. (2015). Another process was also proposed where monazite was heated with CaCl_2 and CaCO_3 under reducing and sulphidizing atmosphere which converted rare earth phosphates to rare earth oxysulphides and oxychlorides and a stable oxide of thorium and chlorapatite were formed in 45 min. From this mixture, rare earth metals can be selectively leached in HCl (Merrett, 1990). Compared to the alkaline method, this process has many advantages viz. no requirement of fine grinding, less time required and Th is stabilized but the percentage recovery of rare earth metals is lower and sodium triphosphate is formed as a byproduct as in case of alkaline

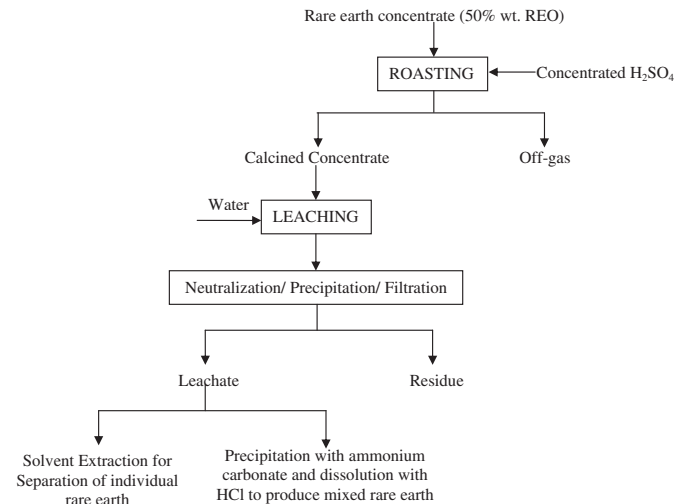


Fig. 5. Leaching process used for Baotou rare earth concentrates in China (Huang et al., 2006).

leaching. Thus, such drawbacks made alkaline treatment acceptable from industrial point of view.

Like monazite and bastnasite, experimental studies of alkali leaching and fusion for the recovery of rare earth oxide, intermediates grade xenotime concentrate was also investigated (Kumar et al., 2014). Either sulfuric acid leaching or alkali leaching methods are used for the extraction of rare earth metals from xenotime (Vickery, 1960; Gupta and Krishnamurthy, 1992). Different authors reported different methods using sulfuric and nitric acid, alkaline solution, water leaching after roasting with ammonium salt to leach out rare earth metals directly or after pre-treatment to improve dissolution behavior of the constituents. Low concentration acidic leaching of ion adsorbed clay containing 0.05–0.2 wt.% rare earth elements is also reported (Peelman et al., 2014). $(\text{NH}_4)_2\text{SO}_4$ and NaCl are the frequently used leachants for the ion adsorbed clay and the kinetics of this leaching process is very fast. No prior beneficiation processes are required for treating these clays (Moldoveanu and Papangelakis, 2013a). In China, ion clay containing 0.08 to 0.8 wt.% rare earth elements is being processed using 7% NaCl

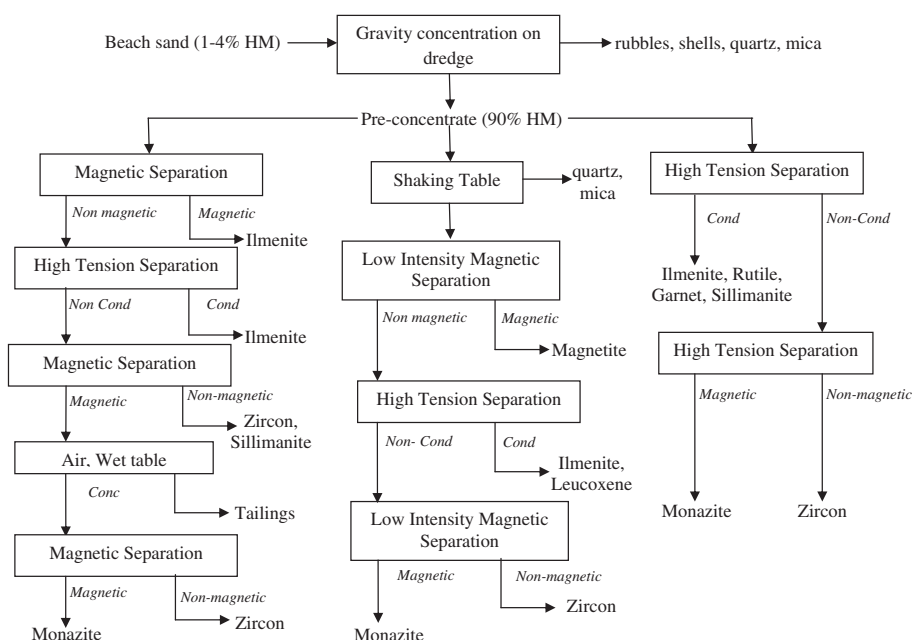


Fig. 4. Major steps required for processing of beach sand mineral by physical beneficiation (Gupta and Krishnamurthy, 2005).

and 1–2% $(\text{NH}_4)_2\text{SO}_4$ at a pH 4 achieving 95% rare earth recovery on commercial scale (Peelman et al., 2014). In Madagascar, seawater has been used as a leachant which results in 40% rare earth recovery, much less than that achieved with $(\text{NH}_4)_2\text{SO}_4$. R&D work in this segment is still going on (Moldoveanu and Papangelakis, 2013b). The detailed studies of these leaching processes will be helpful to resolve the difficulties faced during rare earth recycling from secondary resources.

4.1.2. Leaching technologies used for secondary resources

Mainly, two rare earth metals: Nd and Sm are to be recovered from the most common permanent magnets available. One is the Nd–Fe–B magnets and the other is based on samarium–cobalt alloys possessing high coercivity and good thermal stability. But these expensive SmCo magnets having low energy product as compared to Nd–Fe–B magnets and thus, proved unfavorable with the rise of Nd–Fe–B magnets. New rare earths magnets can be produced from recycled magnets either by its direct re-use via powder processing or its remelting (Binnemans et al., 2013). Today, HDDs are the largest user of Nd–Fe–B magnets and in order to recover rare earth metals, Hitachi developed a shredding process followed by magnetic and electrostatic processing, which is expected to provide ~60 tons rare earth annually (Hitachi, Ltd, 2010). Recently, use of hydrogen at atmospheric pressure was used to separate these permanent magnets from HDDs which results in the production of demagnetized hydride alloy powder of Nd–Fe–B. The powder extracted can be straight reprocessed from the alloy into new sintered magnets with magnetic properties of original magnets (Walton et al., 2012; Walton and Williams, 2011). However, apart from these techniques, the traditional hydrometallurgical processes have also been reported for the rare earth recovery from various types of permanent magnets as it selectively dissolves rare earths leaving behind iron (Walton and Williams, 2011). Leached solution obtained is injected into rare earths separation plant for their recovery (Binnemans et al., 2013). Total leaching as well as selective leaching of Nd–Fe–B magnets are the two preferred routes for rare earth recovery (Peelman et al., 2014). Nd extraction using selective leaching is achieved through roasting followed by leaching (Tanaka et al., 2013). An aqueous process have been also developed to separate Nd from scrap Nd–Fe–B magnets where 1 kg of the scrap required 10 L of 2 M H_2SO_4 solution. During the whole process the pH is maintained as low as possible (less than 2) to prevent the precipitation of iron. Double salt of Nd is formed by raising the pH to 1.5 is converted to neodymium fluoride by leaching in HF solution (Ellis et al., 1994; Lee et al., 2011). A process was also developed by Ames Laboratory, USA to recycle rare earths from $\text{Nd}_2\text{Fe}_{14}\text{B}$ on the basis of liquid solid reaction system (Xu, 1999; Xu et al., 2000). Nitric acid dissolution followed by precipitation with HF for the formation of neodymium–iron fluoride double salt is also investigated. But the use of HNO_3 is avoided as it produces nitrated waste water (Ellis et al., 1994; Lee et al., 2013). Ni-coated Nd–Fe–B sintered magnets are hydrothermally treated at 110 °C for 6 h using an aqueous solution of 3 M HCl and 0.2 N oxalic acid (Kumar et al., 2014). Although, the acid leaching process is effective, it is time consuming and large amount of non-recyclable reagents are utilized. This problem was solved by applying ultrasound technique during acid leaching at room temperature. However, this process works well with highly contaminated and oxidized swarf materials. (Tanaka et al., 2002). From overall studies, it must be noted that solubility of rare earth metals decreases with increase in temperature and in magnet recycling, leaching efficiency is more important than leaching rate. Thus, room temperature is preferred for its recycling (Lee et al., 2013; Peelman et al., 2014).

Like permanent magnets, fluorescent lamps are also rich source of La, Y, Tb, Eu, etc. which can be directly re-used in new lamps or chemically treated to get individual metals. Limited studies have been reported for the recovery of rare earth metals from large and compact fluorescent lamps but no research has been done for their recovery from small lamps used in LCD backlights or from phosphor used in white LEDs (Binnemans et al., 2013; Buchert et al., 2012; Kumar et al.,

2014). The lamp phosphors contain as high as 27.9 wt.% of rare earth oxide but out of which only 10 wt.% is actually recycled from phosphor fractions (Wang et al., 2011). Chemical treatment of the phosphor mixture dissolves rare earth metals into solution for their extraction via precipitation or solvent extraction, almost similar to the processing of rare earth ores. Different types of phosphors present in lamps show different behavior towards strong acids and other chemicals. The halophosphate phosphors and $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (YOX) easily dissolves in diluted acids (Yang et al., 2013) while the phosphate phosphor ($\text{LaPO}_4:\text{Ce}^{3+},\text{Tb}^{3+}$ (LAP)) and aluminate phosphors ($(\text{Ce},\text{Tb})\text{MgAl}_{11}\text{O}_{19}$ (CAT) and $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ (BAM)) show resistant towards acid attack. This is due to the presence of rare earths as oxides in YOX and much stronger chemical bonds in other phosphors (Peelman et al., 2014). Mechanical activation by ball milling creates disorder in the crystal structures of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor allowing dissolution under milder conditions (Mio et al., 2001). For dissolution of phosphate phosphor the same processes can be used as for the processing of monazite ore (Binnemans et al., 2013; Peelman et al., 2014). In 2011, Wang and his co-workers reported hydrochloric acid in combination with hydrogen peroxide to be a strong leachant for the phosphate phosphor dissolution. However, LAP, BAM and CAT phosphors can be chemically attacked by molten sodium carbonate at elevated temperature (Porob et al., 2012). A process was developed by OSRAM A.G. consisting of multistep leaching targeting specific compounds in the phosphor (Fig. 6) (Otto and Wojtalewicz-Kasprzac, 2012). Various leaching experiments were carried out on phosphor powders using different acids and ammonia solutions for the maximum recovery of rare earth metals, especially Y and Eu. Leaching behavior of phosphor powder with H_2SO_4 , HNO_3 , HCl and ammonia was studied. Ammonia leaching gives very low Y recovery while H_2SO_4 is preferred more as it leads to maximum recovery with less co-dissolution of other metals present (De Michelis et al., 2011). Large amount of Al_2O_3 present in the phosphor mixture forms $\text{Al}(\text{NO}_3)_3$ when dissolved in HNO_3 which acts as a salting-out agent and increases the efficiency of rare earth recovery by solvent extraction (Yang et al., 2012). A mixture of H_2SO_4 and HNO_3 under pressure was used to leach out Y and Eu from spent fluorescent tubes (Rabah, 2008). 96.4% of Y and 92.8% of Eu is leached out at 125 °C using acidic mixture for 4 h and maintaining autoclave pressure at 5 MPa (Binnemans et al., 2013). Dissolution of powder samples collected from computer monitors with H_2SO_4 at room temperature results in 96% Eu and Y recovery (Kumar et al., 2014). Tunsu and his co-workers reported that ultrasound also increases the efficiency regardless of the leachant (Tunsu et al., 2014). These studies would be helpful but to commercially recycle lamp phosphor more work is still required.

As far as NiMH batteries are concerned, their previous industrial recycling helps in stainless steel production as a cheap nickel source but rare earths were lost in the smelter slags (Muller and Friedrich, 2006). But several hydrometallurgical methods for the recovery of nickel, cobalt and rare earth metals from NiMH batteries were developed by various researchers using the process of leaching with HCl, H_2SO_4 and HNO_3 (Lyman and Palmer, 1995; Li et al., 2009; Kaindl et al., 2012; Nan et al., 2006; Zhang et al., 1998, 1999; Kanamori et al., 2009; Pietrelli et al., 2002) among which 4 M HCl was found to be most favorable for maximum dissolution of rare earth metals in leach liquor (Lyman and Palmer, 1995). Provazi and co-workers reported the recycling of different metals including Ce and La from a mixture of various types of household batteries which are initially grounded and heated for 4 h under inert atmosphere to eliminate the volatile metals present and then leached in H_2SO_4 (Provazi et al., 2011). A process was announced to be developed jointly by Umicore and Rhodia in 2011 for recycling rare earths from NiMH rechargeable batteries (Binnemans et al., 2013; Rhodia, 2011). Separation of nickel(II), cobalt(II) and lanthanides from spent Ni–MH batteries using HCl leaching was investigated (Fernandes et al., 2013). A hydrometallurgical process was developed for the separation and recovery of rare earth metals from spent Ni–MH rechargeable batteries using 2 M H_2SO_4

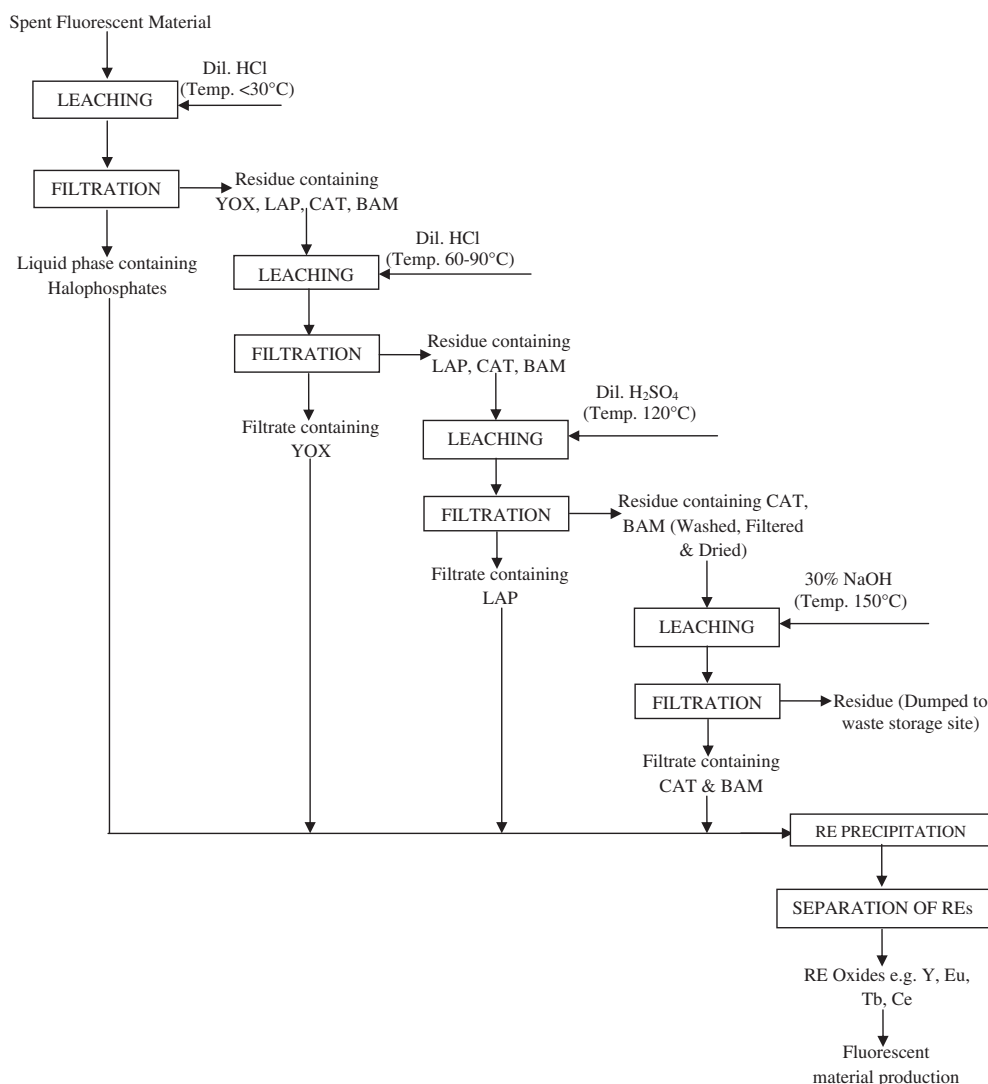


Fig. 6. A multistep leaching process developed by OSRAM to recover rare earth metals present in the phosphor powder (Otto and Wojtalewicz-Kasprzac, 2012).

solution at 95 °C followed by solvent extraction (Zhang et al., 1999). Battery waste were dissolved in 2 M HCl solution followed by the precipitation of metal ions using 2 M NaOH solution at room temperature (Kanamori et al., 2009). Mixture of three types of crystalline phases viz. NiO, CeO₂ and LaCoO₃ was identified by calcination at 1000 °C. This mixture was treated with NH₃ and the filtrate obtained was heated to precipitate out Ni(OH)₂, which is transformed into NiO by calcination. Residue containing rare earth metals was further leached in HCl (Binnemans et al., 2013). Various authors studied the leaching behavior of permanent magnets, phosphor powder and NiMH batteries at different condition which is summed up in Table 6.

As far as other secondary resources are concerned, acid or alkaline leaching is majorly used for rare earth recovery. Fluid catalytic cracking (FCC) catalysts consumes ~50% of the world's production of lanthanum but little interest has been shown towards its recycling where mostly acidic leaching is preferred (Yu and Chen, 1995; He and Meng, 2011). A process developed by Umicore recovers only precious metals while the rare earth contents are lost to the slag and no efforts have been made yet to recover them from the slag (Felix and Vanriet, 1994; Binnemans et al., 2013). A hydrometallurgical treatment of spent borosilicate optical glass was also investigated (Jiang et al., 2004, 2005; Kumar et al., 2014) in which rare earths are converted to their insoluble hydroxides by a hot concentrated NaOH solution (55 wt.%) at 413 K, followed by its leaching with hot 6 M HCl solution at a temperature

above 363 K. Recovery of rare earth metals from spent polishing powder was investigated (Kim et al., 2011). Cerium oxide polishing powders was dissolved in mixture of HNO₃/H₂O₂ followed by precipitation of the rare earths as carbonates and its transformation into oxides by calcination (Kumar et al., 2014). Removal of silica and alumina from spent cerium oxide polishing powder was carried out using sodium hydroxide at 50–60 °C for 1 h (Kato et al., 2000; Binnemans et al., 2013).

Leach liquors obtained through various leaching processes are put to different separation technique such as solvent extraction, ion exchange or precipitation, etc. to selectively extract rare earth metals from the liquor. The detailed description in the field of separation studies is presented below, which are further processed to produce value added products for various applications.

4.2. Solvent extraction (SX)

Solvent extraction is an important technique that is usually employed to separate and extract individual metals or to get their mixed solutions and compounds. To develop feasible and eco-friendly processes, R&D studies are being conducted for rare earth extraction from leached solutions using various solvents viz., anionic, cationic and solvating depending on material and media. The commercial extraction of rare earth metals from different leached solutions (chloride, nitrate, thiocyanate, etc.) using different cationic, anionic and solvating

extractants viz. D2EHPA, Cyanex 272, PC 88A, Versatic 10, TBP, Aliquat 336, etc. Rare earth metal recovery from different leached solutions such as chloride, nitrate, and thiocyanate is presented below. The piece of comparative and summarized review will be useful for researchers to develop processes for the recovery of rare earth metals under various conditions.

The similar physical and chemical properties as well as low separation factor of rare earth metals encounter difficulties in their separation. Their commercial value depends upon the purity and quality of the compound which is based on effective separation of the individual metals. Thus, for pure rare earth recovery from leached solutions, difference in their basicity and formation of species in the aqueous phase is employed for their selective oxidation/reduction, fractional precipitation, crystallization, ion exchange and SX processes. In SX process, rare earth separation and purification are made from the acidic/alkaline leached solution containing impurities such as Ca^{2+} , Fe^{3+} , Al^{3+} , and Pb^{2+} , which affects the quality of the products formed and can be removed using precipitation process. Different extractants, naphthenic acid, di-(2-ethyl-hexyl) phosphoric acid (D2EHPA), 2-ethylhexyl phosphonic acid mono 2-ethylhexyl ester (PC 88A, Ionquest 801), versatic acid, trialkyl-methyl ammonium chloride (Aliquat 336), bis (2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272), tributyl phosphate

(TBP), etc. are used as extractants for rare earth extraction in various industries (Gupta and Krishnamurthy, 2005; Thakur, 2000a). D2EHPA is the most widely studied extractant for rare earth separation from nitrate, sulfate, chloride and perchlorate solutions. Saponified PC 88A has been reported for their separation from chloride solutions while tributyl phosphate (TBP), a solvating extractant that extracts their nitrates from the aqueous solutions. Anionic complex from the aqueous solution is extracted using amine based extractants. Selective separation of some rare earth metals (Eu and Ce) are made based on their valence state in aqueous solution. The extractant, long chain quaternary ammonium salts has been used on commercial scale for the separation of high purity yttrium (Y).

The separation of trivalent lanthanides as a group from actinides as well as individual lanthanides from each other is a formidable challenge in the field of separation science. The lanthanides are usually separated using multistage extractions in counter-current mode in mixer settlers which are tedious and time consuming. Therefore, the development of new extraction systems for separation of lanthanides as a group or from one another using ion-specific compounds/solvents has also been reported. Several stages of mixer-settlers are employed for their separation on industrial scale. For leached solutions containing low concentration of rare earth metals, different ion exchange cationic or

Table 6

Summary of leaching behavior of permanent magnets, phosphor powder and NiMH batteries at different condition.

Permanent magnets		
Medium used	Relevant features of the process	References
Ammonium chloride	Extraction of rare earth metals from scrap Nd–Fe–B magnets through chlorination with NH_4Cl was studied. $\text{Nd}_2\text{Fe}_{14}\text{B}$ primary phase was selectively converted to NdCl_3 together with α -Fe and Fe–B solid residues by chlorinating at 573 K for 3 h.	Itoh et al. (2009)
Hydrochloric acid and oxalic acid	Ni-coated Nd–Fe–B sintered magnets were treated with an aqueous solution containing 3 M HCl and 0.2 N oxalic acid. 99% of the Nd present is recovered as neodymium oxalate.	Itakura et al. (2006)
Hydrochloric acid	Selective leaching of neodymium was carried out from roasted Nd–Fe–B magnets using 0.02 mol/L HCl solution in an autoclave at 180 °C leaching more than 80% of Nd along with Dy.	Koyama et al. (2009)
Nitric acid	Nd–Fe–B magnet scraps are dissolved in nitric acid followed by addition of HF which results in the formation of neodymium–iron fluoride double salt. This salt was dried and calciothermally reduced to the metallic state.	Ellis et al. (1994)
Sulfuric acid	A process was developed to separate rare earths from Nd–Fe–B magnets where 1 kg of magnetic scrap was dissolved in 10 L of 2 M H_2SO_4 . The pH of the leach liquor was increased to 1.5 at which double salt of Nd is formed, which is further leached in HF to form NdF_3 .	Lyman and Palmer (1992)
Nickel metal hydride batteries (NiMH batteries)		
Medium used	Relevant features of the process	References
Hydrochloric acid	Battery waste was dissolved in 2 M HCl solution and the dissolved metals were precipitated at pH 12 by addition of 2 M NaOH solution at room temperature.	Kanamori et al. (2009)
Hydrochloric acid	Leaching NiMH scraps with different mineral acids was investigated to dissolve rare earths. 4 M HCl was found to be best for rare earths dissolution which are further precipitated as phosphates by addition of phosphoric acid.	Lyman and Palmer (1995)
Sulfuric acid/hydrochloric acid	Leaching of Ni, Co and rare earths from spent NiMH batteries were investigated using 2 M H_2SO_4 /3 M HCl. Leach liquor was put to SX using 25% D2EHPA in kerosene, followed by stripping of rare earths from organic solution. Further, rare earths were precipitated using oxalic acid.	Zhang et al. (1998, 1999)
Sulfuric acid	A selective separation of rare earths by precipitation of sodium rare earth double sulfate was performed. Leaching using 2 M H_2SO_4 at 20 °C was performed. It recovers about 80% of the rare earths contained in spent NiMH batteries.	Pietrelli et al. (2002)
Hydrochloric acid	HCl was employed for the dissolution and separation of metals from NiMH batteries. At 95 °C, 99% rare earth metals were recovered in 3 h using 4 mol dm^{-3} HCl. Later, rare earth metals were extracted using 25% D2EHPA at pH 2.5.	Tzanetakis and Scott (2004).
Sulfuric acid	The positive and negative electrode materials of NiMH batteries were merged and leached with 3 M H_2SO_4 at 95 °C. About 94.8% of rare earths were separated from other metals at relatively high temperature. The remaining 5.2% rare earths were completely separated by SX with 20% P_2O_4 .	Li et al. (2009)
Fluorescent tubes		
Medium used	Relevant features of the process	References
Nitric acid and hydrochloric acid solution	Efficient leaching of Eu and Y was achieved in less than 24 h at 20 ± 1 °C, using weak nitric and hydrochloric acid solutions (0.5 M). Leaching of Ce, Gd and Tb did not reach equilibrium even after 96 h.	Tunsu et al. (2014)
Sulfuric acid	Recovery of Y from fluorescent powder using different acids (nitric, hydrochloric and sulfuric) and ammonia was investigated. Ammonia is not suitable to recover Y, whereas HNO_3 produces toxic vapors. The greatest extraction of Y is obtained by 20% w/v S/L ratio, 4 N H_2SO_4 at 90 °C. Y and Ca yields are nearly 85% and 5%, respectively.	De Michelis et al. (2011)
Sulfuric acid + nitric acid	Autoclave digestion of the fluorescent powder in the acid mixture for 4 h at 125 °C and 5 MPa dissolved 96.4% of the Y and 92.8% of the Eu. At low temperature sulfate salt of Eu and Y was converted to thiocyanate. Trimethyl-benzylammonium chloride solvent was used to selectively extract Eu and Y from the thiocyanate solution.	Rabah (2008)
Hydrochloric acid and sodium hydroxide	The effects of the acid leaching and alkali fusion on the leaching efficiency of Y, Eu, Ce, and Tb from the waste fluorescent powder were investigated. HCl is better than H_2SO_4 in acid leaching, and NaOH is better than Na_2CO_3 in the alkali fusion. The leaching rates of Y, Eu, Ce, and Tb are 99.06%, 97.38%, 98.22%, and 98.15%, respectively.	Zhang et al. (2013)

anionic resins are employed depending on the constituent of the aqueous solution using batch or continuous mode in column. The purified solution obtained after separation could be further processed to produce the value added products in the form of salt for industrial application.

Worldwide, extensive studies have been carried out for the extraction of various rare earth metals by solvent extraction process using different organic extractants in order to develop efficient process for their separation from different feed solutions. The corresponding salient features are presented in Tables 7 and 8, respectively. This is evident from the large number of literatures that appeared in different journals and proceedings. Rare earth extraction by SX including modeling of the process using different extractants has been reviewed (Thakur, 2000b). These studies have been classified based on the solution generated by the treatment of rare earths containing materials as chloride, nitrate, thiocyanate, phosphate, etc. The properties of their extraction and separation, formation of complex, separation factor, etc. have been highlighted in the present review paper by different research and academic institutions.

4.2.1. Chloride solution

Different authors studied the SX process for rare earths separation from the chloride solution using different organic extractants viz. anionic, cationic or solvating type depending on ions present in the solution as given below.

4.2.1.1. Cationic extractants. The cationic extractants are employed for the extraction and separation of rare earth metals as they form cationic species in the aqueous chloride solution. The overall extraction from aqueous media by cationic extractants in their acidic form can generally be expressed as (Peppard et al., 1958):



where Ln stands for any rare earth metal, A for the organic anion, and over scoring denotes that the species are present in the organic phase. However, rare earths extraction using cationic extractants are more intricate as the acidic extractants are usually aggregated as dimers in non-polar organic solutions, thus lowering their polarity. Thus, rare earth

Table 7
Different organic solvents used for the extraction of rare earth metals.

Extractants	Chemical Name	Structure	Producing company
Cyanex 272	Di-2,4,4-trimethylpentyl phosphinic acid		Cytec Limited, Canada
D2EHPA	Di-2-ethylhexyl phosphoric acid		Luoyang Aoda Chemical Ltd., China
PC 88A	2-Ethylhexyl phosphonic acid mono 2-ethylhexyl ester		Daihachi Chemical Industry, Japan
TBP	Tri-n-butyl phosphate		Luoyang Aoda Chemical Ltd., China
Kelex 100	7-(4-Ethyl-1-methyloctyl)-8-hydroxyquinoline		Sherex Chemicals, USA
LIX 84	2-Hydroxy-5-nonylacetophenoneoxime		BASF Corporation, USA
Versatic 10	Alkyl monocarboxylic acids		BASF Corporation, USA
Aliquat 336	Tri-octyl methylammonium chloride		BASF Corporation, USA

Table 8

Salient results on extraction of rare earth metals using various extractants from different solutions.

Extractant	Aqueous feed	Salient features	References
2,6-Bis(5,6-dipropyl-1,2,4-triazin-3-yl) pyridine (n-Pr-BTP) in n-dodecane/1-octanol	A mixture of Am ³⁺ and Eu ³⁺ in nitrate solution	Almost 85% Am ³⁺ and 6% Eu ³⁺ extracted in 6 h with 0.03 M n-Pr-BTP in n-dodecane/1-octanol (7:3) diluent mixture from 1 M NaNO ₃ at pH 2.	Bhattacharyya et al. (2011)
4-Methyl-2-pentanone (MIBK) containing 3-phenyl-4-acetyl-5-isoxazolone (HPAI), 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP) and thenoyltrifluoroacetone (HTTA)	Aqueous solution containing La(III), Ce(III), Eu(III), Th(IV) and U(VI)	Extraction into MIBK containing HPAI found to be better extractant on comparing the extraction of the metals containing HPMBP and HTTA.	Jyothi and Rao (1989)
HPBI (3-phenyl-4-benzoyl-5-isoxazolone) in chloroform	La(III), Ce(III), Eu(III), Th(IV) and U(VI) in HCl	Extraction found to increase with pH and became almost quantitative near the pH at which the metal ion hydrolyses. Plots of log K _d vs. pH at constant ligand concentration gave straight lines with slopes of around two for U, three for La, Ce and Eu, and four for Th.	Jyothi and Rao (1990)
1-Phenyl-3-methyl-4-trifluoroacetyl pyrazolone-5 (HPMTFP) mixed with dicyclohexano-18-crown-6 (DCH18C6) and monobenzo-15-crown-5 (B15C5) in chloroform	Trivalent metals (Am, Cm, Cf and Eu) in 0.1 M NaClO ₄	With DCH18C6 the synergistic species extracted are M(PMTFP) ₃ ·(HPMTFP) (DCH18C6), (PMTFP) ₃ ·(DCH18C6), whereas with (B15C5) species are M(PMTFP) ₃ ·n(B15C5), n being 1 or 2 for all these metal ions.	Mathur and Khopkar (1988)
PC 88A in paraffinic kerosene	Dy and Tb from rare earths chloride solution from monazite	PC 88A extracted Dy and Tb from chloride solution. Dy and Tb were recovered with a purity of 97% and 83% respectively.	Mishra et al. (2000)
Cyanex 923 (TRPO) in xylene	Trivalent lanthanides (La, Nd, Eu, Tb, Ho, Tm, Lu) and yttrium (Y) in thiocyanate and nitrate solutions	Metal ions extracted from thiocyanate solution as M(SCN) ₃ ·nTRPO; [n = 3 and 4 for the lighter and heavier lanthanides respectively]. In nitrate solutions, metal ions are extracted as M(NO ₃) ₃ ·3TRPO.	Reddy et al. (1998)
Mixtures of Cyanex 301 and Cyanex 923 (TRPO) in xylene	Trivalent rare earths in nitrate solutions	Trivalent rare earth metal ions extracted as MX ₃ ·3HX with Cyanex 301. In presence of Cyanex 923, La and Nd are extracted as MX ₂ ·NO ₃ ·TRPO whereas Eu, Y and other HREMs extracted as MX ₃ ·HX·2TRPO.	Reddy et al. (1999)
4Sebacoylbis(1-phenyl-3-methyl-5-pyrazolone) (H ₂ SP) and 4-dodecandiolbis(1-phenyl-3-methyl-5-pyrazolone) (H ₂ DdP) in chloroform	Actinides [Th(IV), U(VI)] and Ln(III) (Nd, Eu, Lu) in nitrate solutions	Metal ions get extracted as Th(SP) ₂ , Th(DdP) ₂ , UO ₂ (HSP) ₂ , UO ₂ (HDdP) ₂ , Ln(SP)(HSP) and Ln(DdP)(HDdP) with H ₂ SP or H ₂ DdP. Th(IV) selectively separated from U(VI) and Ln(III) from 0.2 mol/L nitric acid using 4-acylbis(1-phenyl-3-methyl-5-pyrazolones).	Reddy et al. (2000)
1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP) in chloroform	All RE ions (except Pm) and Y in 0.1 M (Na, H) ⁺ ClO ₄ ⁻	Formation of Ln(PMBP) ₃ , two-phase stability constants (log β ₃ ·P _{Ln(PMBP)3}), pH for 50% extraction of metal chelates (pH ₅₀) and separation factors (S) between the adjacent elements have been evaluated using 5 × 10 ⁻² M HPMBP.	Roy and Nag (1978)
A mixture of phenyl-3-methyl-4-benzoyl-pyrazolone-5 (HPMBP) and bis-(2-ethylhexyl)sulphoxide (B ₂ EH ₂ SO) or octyl(phenyl)-N,N-diisobutylcarbamoyl methylphosphine oxide (CMPO) in xylene.	Metals (M = La, Eu, Lu and Am) in chloroacetate	HPMBP extracted metal ions as M(PMBP) ₃ ·HPMBP. With B ₂ EH ₂ SO as a neutral donor, the synergistic adduct species were M(PMBP) ₃ ·B ₂ EH ₂ SO and M(PMBP) ₃ ·2B ₂ EH ₂ SO, whereas with CMPO as a neutral donor the only complex extracted into the organic phase is M(PMBP) ₃ ·CMPO.	Santhi et al. (1994)
TOPS 99, PC-88A and Cyanex 272 in kerosene as diluent	Mixture of seven HREEs (Tb, Dy, Ho, Y, Er, Yb, Lu) and four LREEs (La, Ce, Pr, Nd) in phosphoric acid	Extraction efficiency of extractants towards lanthanides from H ₃ PO ₄ medium decreases in the series: TOPS 99 > PC 88A > Cyanex 272.	Radhika et al. (2010)
TOPS 99 in kerosene	LREEs La, Ce, Pr, Nd, and seven HREEs like Tb, Dy, Y, Ho, Er, Yb and Lu) in phosphoric acid solutions	The studies showed the separation of a mixture of rare earth metals into three concentrates, two heavy rare earth fractions (Yb + Lu and Tb, Dy, Ho, Y, Er) and one light rare earth fraction from 3 M acid using 1 M TOPS 99.	Radhika et al. (2011)

complexes formed may contain undissociated organic acid. So the equation is depicted more accurately as:



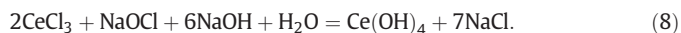
where H₂A₂ refers to the dimeric form of the organic acid. It is evident from Eqs. (6) and (7) that rare earths extraction with cation exchangers increases by increasing the pH of aqueous phase while the stripping process increases with the acidity of the aqueous stripping solution. Carboxylic acids, and organic derivatives of phosphorous acids are the cationic extractants generally used for the separation of rare earth metals.

4.2.1.1.1. Rare earths extraction using D2EHPA and HEHEHP. Di-(2-ethylhexyl) phosphoric acid (D2EHPA) and 2-ethylhexyl 2-ethylhexyl phosphonic acid (HEHEHP/PC 88A) are organophosphorous acids considered to be suitable extractants for the separation of rare earth metals (Murthy et al., 1986; Sundaram et al., 1992; Stroller and Richards, 1961; Lewis, 1972; Ritcey and Ashbrook, 1984; Nash, 1993). Their extraction mechanism with organophosphorous acids are reported (Sundaram et al., 1992; Lewis, 1972; Ritcey and Ashbrook, 1984; Nash, 1993) to

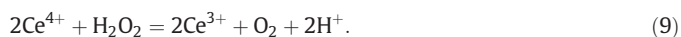
be the same as Eq. (7) due to low loading in the organic phase. Reddy et al. (1989) used D2EHPA diluted in kerosene for the extraction of Y, Er, Dy, Tb, Gd and Ho from aqueous chloride solution. The effect of HCl concentration on extraction of 0.1 M rare earth metal solution using 1 M DEHPA showed decrease in extraction with increase in HCl concentration and reaches a minimum value at higher acidities and the order was found to be Er > Y > Ho > Dy > Tb > Gd. A ten stage batch type counter current extraction studies carried out with 1 M D2EHPA and 0.2 M Y concentrate in 1.7 M HCl to produce Y of 85% purity from 55% Y concentrate. A process for the production of high purity (99.9%) Y₂O₃ using a dual solvent extraction system comprising of PC 88A and TBP from chloride and thiocyanate medium has been described (Deshpande et al., 1990). Lanthanide extraction using D2EHPA in toluene was similar for perchloric acid solutions (Piece and Peck, 1963), but poorer in nitrate media (Reddy et al., 1995). Distribution coefficients of rare earth ions between D2EHPA in toluene and aqueous chloride solution were found to have an inverse third-power dependency on the HCl concentration in the aqueous phase and a third-power dependency on the D2EHPA concentration in the organic phase, indicating that only one

of the acid groups of D2EHPA dimer dissociates and participates in extraction (Xie et al., 2014). The distribution coefficient of rare earths usually increases with atomic number but the separation factors/rare earth extraction depend on the acidity of the solution (as extractants are liquid cation exchangers) as well as on nature of the anion. The selectivity order for extraction was $\text{Lu} > \text{Yb} > \text{Tm} > \text{Tb} > \text{Eu} > \text{Pm} > \text{Pr} > \text{Ce} > \text{La}$ using 0.75 M D2EHPA in toluene from 0.5 M HCl solution and the average separation factor of two adjacent rare earth metals was 2.5 (Peppard and Wason, 1961). D2EHPA was utilized on large scale application in Molycorp for pre-concentrating Eu up to 15% from the chloride feed derived from bastnasite containing about 0.1% Eu_2O_3 (Kruesi and Schiff, 1968). Continuous SX process for separating middle and light rare earth fractions from the nitrate feed was also investigated (Preston et al., 1996a,b,c) where 8 counter-current stages were required by 15% v/v of D2EHPA in Shellsol AB to extract middle rare earths followed by scrubbing using 1 mol/L HNO_3 in 2–4 stages. 1 M D2EHPA separates 99.8% La_2O_3 product from feed containing 45% La_2O_3 , 35% Nd_2O_3 , 10% Pr_6O_{11} and 5% Sm_2O_3 (Nair and Smutz, 1967). Sm, Eu, and Gd can also be extracted from other lanthanides in a mixed nitrate-chloride leachate of monazite using D2EHPA (Rabie, 2007). The mathematical models for rare earths extraction behavior have been formulated to calculate the concentrations in organic and aqueous phases in any compartment of circuit. The flow sheets developed for the purification of Y from the concentrate using D2EHPA and PC 88A in a mini mixer settlers (100 mL capacity) are shown in Figs. 7 and 8, respectively (Thakur, 2000a). The compositions of the fractions obtained in the systems for both extractants are the same but the optimized process parameters are different.

SX has been used for the separation of light rare earths from chloride solution of monazite using D2EHPA on bench scale and validated on pilot extent. Subsequently, the versatile extractant, PC 88A (a weaker acid compared to D2EHPA, Daihachi Chemical Industry Co., Japan) diluted in kerosene was used for separating these elements due to higher separation factors (Table 9) (Maharana and Nair, 2005) and is amenable for rare earths separation at lower acidity and can be stripped off using lower concentration of acid compared to D2EHPA. At first, the light and heavy rare earth metals were separated from chloride medium of monazite using mixer settlers, which is operated in the continuous counter current mode by maintaining the required organic to aqueous (O/A) ratio and flow rates of both streams (Fig. 9) (Thakur, 2000b). In this process, mixed rare earths chloride is fractionated into 3 streams La–Ce–Pr–Nd fraction, Sm–Gd–Eu rich fraction and Y-heavy rich fraction using 30% saponified PC 88A via large number of stages in mixer settlers due to low separation factors of rare earth metals (Fig. 10) (Maharana and Nair, 2005). Rare earths analysis obtained by the above process is in (%) 23.9 La, 47.2 Ce, 6.4 Pr, 22.2 Nd and <0.3 Sm. The solution containing Sm–Gd–Eu is further treated with 30% saponified 1 M PC 88A and produced >95% pure Sm. The aqueous feed of the 1st step is processed with the same solvent to produce pure Nd. The raffinate containing Ce, La, and Pr from Nd separation is then processed to precipitate Ce by addition of sodium hypochlorite. The Ce is oxidized to tetravalent state and get precipitated as cerium hydroxide of 90% purity.



To produce pure Ce, the hydrated salt is dissolved in nitric acid followed by its extraction with 1 M PC 88A in 2 stages. The loaded organic is stripped with 2 M HNO_3 containing 6% H_2O_2 after scrubbing in 12 stages. Pure cerium oxide of 99.99% was produced on tonnage quantities.



The remaining solution after extraction of Ce contains La and Pr. The metals are precipitated as mixed carbonate and dissolved in HCl to increase the concentration. The solution containing 50% La is

purified by extracting HREEs leaving 99.9% La in the raffinate using 30% PC 88A. The process was implemented on plant scale which consists of 10 stages of extraction, 12 stages of scrubbing and 6 stages of stripping.

Various other acidic organophosphorus extractants like HEHEHP, marketed variously as PC-88A, lonquest 80, P-507 and SME 418 have gathered popularity for rare earth separation because their stripping is possible at lower acidities than from D2EHPA (Reddy et al., 1995). Moreover, D2EHPA extracts rare earths at low pH values but makes stripping of loaded metal difficult. A simple and effective process was also developed for the production of nuclear grade Dy_2O_3 from crude concentrate containing ($\text{Y}_2\text{O}_3 \sim 67\%$, $\text{Dy}_2\text{O}_3 \sim 22\%$, $\text{Gd}_2\text{O}_3 \sim 4\%$, $\text{Tb}_4\text{O}_7 \sim 4.0\%$, $\text{Ho}_2\text{O}_3 \sim 2.4\%$, $\text{Er}_2\text{O}_3 \sim 3.2\%$, $\text{Sm}_2\text{O}_3 \sim 1.06\%$) from the HCl leached solution using dual SX circuit with EHEHPA (similar to PC-88A) as extractant in mixer settlers (Singh et al., 2008). As the extraction order of rare earth metals with EHEHPA is $\text{La} < \text{Ce} < \text{Pr} < \text{Nd} < \text{Sm} < \text{Eu} < \text{Gd} < \text{Tb} < \text{Dy} < \text{Ho} < \text{Y} < \text{Er} < \text{Tm} < \text{Yb} < \text{Lu}$, Y and other HREEs are extracted in the first cycle leaving Dy, Gd, Tb, Sm, etc. in the raffinate, while Dy is extracted in the organic phase of the second cycle leaving LREEs, Tb and Gd in the raffinate. In the second cycle, Dy is purified to the extent of >99.5% with respect to other rare earth metals from the Dy concentrate obtained in the raffinate of the first cycle under the optimized condition of feed acidity, phase ratio and scrubbing. Y behaves as a HREE with EHEHPA/PC88A. Pure Dy_2O_3 of required specification has been produced in kilogram quantity of the nuclear grade with >98% recovery. The overall process also produces two concentrates as by-products namely Y (>93%, 1st cycle) and Tb (>54%, 2nd cycle) as source materials for further up gradation of these elements. The separation of Dy and Y from a concentrate (60% Y_2O_3) obtained from monazite is a difficult task due to the low separation factors, thus, a SX process was developed for the separation of Dy_2O_3 (~97% purity) and high grade concentrate of Y_2O_3 (93% purity) using extractants D2EHPA and PC 88A in the presence of Gd, Tb, Dy, Ho, Y, and Er (Thakur, 2000a,b). Before the onset of saturation effects, HEHEHP gets more heavily loaded with rare earth metals than D2EHPA which increases the extraction efficiency. HEHEHP is being used for the separation of rare earth metals in Baotou, China on commercial scale (Zhu, 1991) and from spent NiMH batteries (Fontana and Pietrilli, 2009).

At Bhabha Atomic Research Centre, Mumbai, India, monazite has been studied to produce rare earth chloride. The solution is processed by SX to produce Y concentrate (60% Y_2O_3) followed by further purification to 93% Y_2O_3 by another solvent extraction cycle. During this step, most of the Dy and Tb are separated to yield a concentrate assaying >50% Dy_2O_3 , 14% Tb_4O_7 , 10% Gd_2O_3 , 2.4% Ho_2O_3 , and 21% Y_2O_3 . An attempt has been made for simultaneous purification method to process a Dy-rich concentrate in order to obtain a high grade Dy_2O_3 by solvent extraction using PC 88A in paraffinic kerosene in C_{10} – C_{14} range as an extractant. The process is complicated and requires strict control of process variables (Mishra et al., 2000). The distribution ratio (D) of Dy was determined as a function of initial concentration of HCl for different initial concentrations of Dy. The separation factors, β were determined experimentally and found to be $\beta_{\text{Tb-Gd}} = 14.1$, $\beta_{\text{Dy-Tb}} = 2.7$, $\beta_{\text{Ho-Dy}} = 1.80$, $\beta_{\text{Y-Dy}} = 3.20$, $\beta_{\text{Er-Dy}} = 4.16$, practically constant under the experimental conditions used.

In order to improve the SX process, mathematical models have been used by different authors for rare earths separation and to predict the concentration of these metal ions in organic and aqueous phases at various initial acidities and metal concentrations (Thakur et al., 1993). The conditions have been optimized to obtain >97% purity of Dy during counter-current extraction and scrubbing using mixer settlers of 50 mL mixer capacity. The studies yielded four different products from its four exit points. The raffinate coming from the first exit was essentially Gd-rich solution containing other LREEs. The fourth and final exit point was for the stripped solution that contained 85% Y_2O_3 with 95% recovery. The remaining two exit points, involving scrubbing

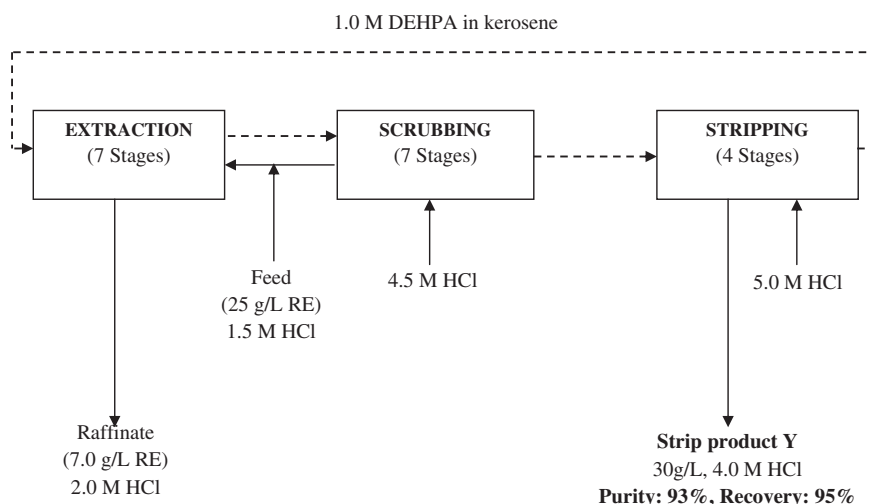


Fig. 7. Flow-sheet for the purification of yttrium from its concentrate (60% Y_2O_3) using DEHPA in kerosene (Thakur, 2000a).

stages, yielded an 83% pure Tb_4O_7 concentrate and a 97% pure Dy_2O_3 concentrate as shown in Fig. 11 (Mishra et al., 2000).

It should be noted that Cyanex 272 (bis(2,4,4-trimethylpentyl) phosphinic acid), is the only commercial extractant among some di-alkyl phosphinic acids being used. Dicyclohexylphosphinic acid (DCHPA) is another di-alkyl phosphinic acid which show inferior extraction selectivity for La, Pr, Eu, Ho and Yb because the cyclohexyl groups in DCHPA sterically hinder chelate formation (Cecconie and Frieser, 1989). Table 10 presents the extraction of some rare earth metals using Cyanex 272.

4.2.1.1.2. Rare earth extraction using carboxylic acids. Different carboxylic acids, including naphthenic acids and versatic acids, for extracting rare earth ions has been reported (Bauer and Lindstrom, 1964; Korpusev et al., 1974). Much attention has been paid towards Y extraction and was investigated that the extraction behavior of Y (as middle REs or light REs) is associated either with the acidity of the extractant or steric hindrance caused by carboxylic acids' structure and the atomic number of rare earth ions (Zheng et al., 1991; Du Preez and Preston, 1992). Y resembles as light rare earth elements and middle rare earth elements with non-hindered and sterically hindered acids, respectively. Generally, Versatic 10 and naphthenic acid are used for Y extraction. But use of naphthenic acid changes the composition of the extractant and is also highly soluble in water which leads to significant loss of

the reagent. SX of trivalent lanthanides and Y from nitrate media using commercially available carboxylic acids such as Versatic 10 and naphthenic acids in xylene has been studied (Du Preez and Preston, 1992). Naphthenic acid and versatic acid along with D2EHPA in Shellsol 2016 at 15 °C was compared for extraction of Y from chloride solution containing La, Dy, Yb and Y. It was observed that Y has similar distribution co-efficient to the heavy rare earths in D2EHPA but it is similar to the LREEs in versatic and naphthenic acid (Zheng et al., 1991).

Two new carboxylic acid extractants viz. sec-nonylphenoxy acetic acid (CA-100) and sec-octylphenoxy acetic acid (CA-12) have been developed in China with relatively lower aqueous solubilities. Extraction of trivalent lanthanides (Sc, Y, Ln) from acidic chloride solutions using CA-100 in heptane has been reported. CA-100 extracts rare earths at lower pH values than Versatic 10 and Y with close similarity to HREEs (Wang et al., 2002; Li et al., 2007a,b). However, various extractants with lower solubility values like cecanoic, neo-heptanoic, and some 2-bromo alkanolic acids have also been investigated (Preston, 1994; Xu et al., 2003; Singh et al., 2006).

4.2.1.2. Chelating extractants. Chelating extractants extract metals by a mechanism similar to cation exchange as presented in Eq. (6). These extractants are generally examined for extracting Eu from nitrate solutions and Ce(III) and La(III) from chloride solutions. But their

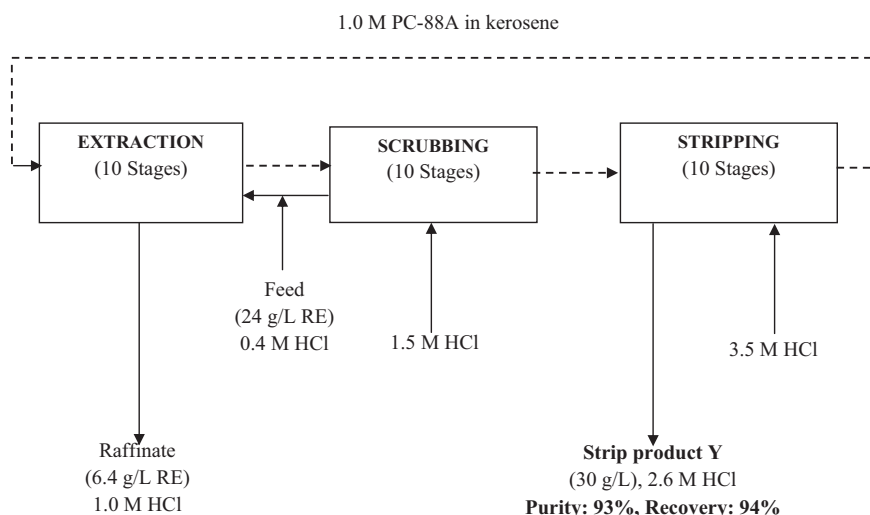


Fig. 8. Flow-sheet for the purification of yttrium from its concentrate (60% Y_2O_3) using PC 88A in kerosene (Thakur, 2000a).

Table 9

Separation factors for extraction of rare earths by DEHPA and PC 88A (Maharana and Nair, 2005).

Rare earth pair	DEHPA	PC 88A
Ce/La	2.98	6.83
Pr/Ce	2.05	2.03
Nd/Pr	1.38	1.55
Sm/Nd	6.58	10.60
Eu/Sm	1.90	2.30
Gd/Eu	1.43	1.50
Tb/Gd	0.93	5.80
Dy/Tb	2.40	2.82
Ho/Dy	1.90	2.00
Er/Ho	2.25	2.73
Er/Y	1.37	1.43
Tm/Er	2.90	3.34
Yb/Tm	3.09	3.56
Lu/Yb	1.86	1.78

performance is not as favorable as acidic extractants (Urbanski et al., 1996; Arichi et al., 2006). Different authors studied the extraction of rare earth metals from the chloride solution which forms a chelating complex with extractants. Acylpyrazolones have been found effective for the efficient extraction of lanthanides, actinides and other metals (Roy and Nag, 1978; Rao and Arora, 1977). Roy and Nag (1978) investigated the extraction behavior of all rare earth ions (except Pm) and Y using initial concentration of 0.05 M 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP) as the extractant in aqueous-chloroform medium at $25 \pm 1^\circ\text{C}$ maintaining the aqueous phase at constant ionic strength 0.1 M $(\text{Na}, \text{H})^+ \text{ClO}_4^-$. The Ln (PMBP)₃ complex was formed in the organic phase. The two-phase stability constants ($\log \beta_3 \cdot P_{\text{Ln(PMBP)}_3}$), pH for 50% extraction of metal chelates and separation factors (SF) between the adjacent elements have been also evaluated. A plot of $\log K$ (where K = extraction equilibrium constant) values against atomic number, Z show tetrad grouping.

As deposits of Th and U are generally associated with the rare earths metals, the SX studies have been made for extraction of lanthanides and actinides to develop an efficient procedure for their separation and purification. Jyothi and Rao (1989) studied the extraction of La(III), Ce(III),

Eu(III), Th(IV) and U(VI) from aqueous solutions into 4-methyl-2-pentanone (MIBK) containing 3-phenyl-4-acetyl-5-isoxazolone (HPAI). HPAI was found to be better extractant on comparing the extraction of metals with HPMBP and thenoyltrifluoroacetone (HTTA, diketone extractant). HPBI (3-phenyl-4-benzoyl-5-isoxazolone) in chloroform, a new chelating ligand in which the β -diketone moiety is fused to the heterocyclic ring, has been used for the extraction of La(III), Ce(III), Eu(III), Th(IV) and U(VI) (Jyothi and Rao, 1990). The solutions containing 30 ppm La, Ce, Eu, 20 ppm Th and 50 ppm U were used for studies in the pH range 1–3 by appropriate addition of 1 M HCl. The ionic strength was kept constant by addition of 1 M potassium chloride. For the pH range 3–6, acetic acid–sodium acetate buffers were used, with ionic strength maintained constant using potassium nitrate. The extraction of the metals with 0.01 M HPBI in chloroform as a function of pH showed that extraction was found to increase with pH and became almost quantitative near the pH at which the metal ion hydrolyses (Jyothi and Rao, 1990). Plots of $\log K_d$ vs. pH at constant ligand concentration gave straight lines with slopes of around two for U(VI), three for La(III), Ce(III) and Eu(III), and four for Th(IV), where K_d represents the distribution co-efficient of metals. Similar slopes were obtained for plots of $\log K_d$ vs $\log [\text{HPBI}]$ at constant pH. Hence the extraction systems can be represented as



Further, they reported the mechanism of extraction, the species extracted and extraction constants for each system (Jyothi and Rao, 1990). The system has been used to separate Th(IV) from U(VI) and from La(III), Ce(III) and Eu(III). A comparison of the extraction constants with those for the HPMBP and HTTA systems indicates that HPBI extracts these metal species better than HPMBP and HTTA do. Mathur and Khopkar (1987) reported the extraction of trivalent actinides Am, Cm and Cf and lanthanides Eu, Tb, Tm and Lu with 1-phenyl-3-methyl-4-trifluoroacetyl pyrazolone-5 (HPMTFP) in chloroform and benzene. The formation of a self-adduct species $\text{M}(\text{PMTFP})_3 \cdot \text{HPMTFP}$ has been observed with Am, Cm and Eu but only chelate species $\text{M}(\text{PMTFP})_3$ was observed with Cf, Tb, Tm and Lu. The reasons for the formation of a self-adduct species with lighter actinides and lanthanides and not with the heavier ones of the pyrazolones have been discussed.

As the crown ethers have been found with varied applications in the field of separation and purification, the mixtures of liquid cation exchanger and crown ethers have been found to synergistically enhance the extraction of some metal ions depending on the match of cavity size of the crown ethers with the diameter of the metal ions (Kinard and McDowell, 1981; Ensor et al., 1986). In 1988, Mathur and Khopkar reported the effect of dicyclohexano-18-crown-6 (DCH18C6) and monobenzo-15-crown-5 (B15C5) on the extraction of trivalent metals ($\text{M} = \text{Am, Cm, Cf}$ and Eu) by 1-phenyl-3-methyl-4-trifluoroacetyl pyrazolone-5 (HPMTFP) in chloroform from 0.1 M NaClO_4 ion in aqueous phase. With DCH18C6, the synergistic species extracted are $\text{M}(\text{PMTFP})_3 \cdot (\text{HPMTFP}) \cdot (\text{DCH18C6})$ and $(\text{PMTFP})_3 \cdot (\text{DCH18C6})$, whereas with (B15C5), the species are $\text{M}(\text{PMTFP})_3 \cdot n(\text{B15C5})$, n being 1 or 2 for all these metal ions. The synergistic effect on extraction of trivalent lanthanides (Nd, Eu, Tm) using mixtures of 3-phenyl-4-benzoyl-5-isoxazolone (HPBI) and 18-crown-6, 15-crown-5, benzo-15-crown-5, or dibenzo-18-crown-6 diluted in chloroform was found (Reddy et al., 1997). The extraction of Ln(III) from a 0.1 mol/L sodium perchlorate solution of pH 2.5 with HPBI concentration (0.001–0.02 mol/L) in chloroform showed a slope of 3.0 indicating the participation of three HPBI moieties in the respective extracted species. The Ln(III) was found to be extracted as $\text{Ln}(\text{PBI})_3$ with HPBI alone and as $\text{Ln}(\text{PBI})_3 \cdot \text{CE}$ complex

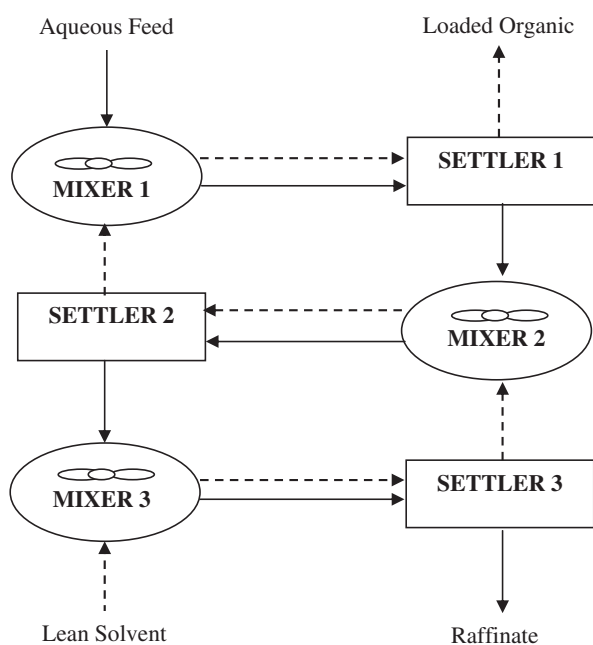


Fig. 9. Three stage counter current extraction in a mixer settler set up (Thakur, 2000b).

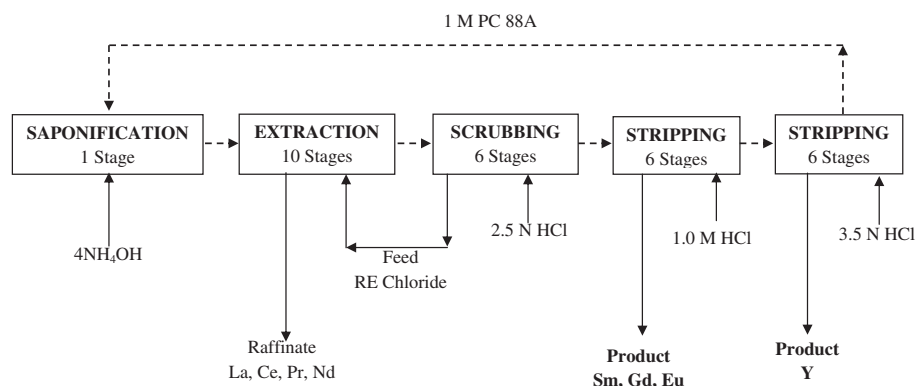


Fig. 10. Flow-sheet for the separation of LREEs from the HREEs from mixed rare earth chloride using SX (Maharana and Nair, 2005).

in the presence of crown ethers (CE). The equilibrium constants of the above species are found to increase monotonically with decreasing ionic radii of this Ln(III). The addition of CE to the metal chelate system significantly enhances the extractability of these trivalent metal ions. It also improves the selectivity among Nd–Eu pairs which has potential for extraction and separation of these trivalent lanthanides. Santhi et al. (1994) also reported the synergistic extraction of metals ($M = \text{La, Eu, Lu and Am}$) with a mixture of phenyl-3-methyl-4-benzoylpyrazalone-5 (HPMBP) and bis-(2-ethylhexyl) sulphoxide (B_2EHSO) or octyl (phenyl)-N,N-di-isobutylcarbamoyl methylphosphine oxide (CMPO) in xylene. With HPMBP alone, the metals extracted in the organic phase forming as $\text{M(PMBP)}_3 \cdot \text{HPMBP}$ type self adduct. With B_2EHSO as neutral donor, the synergistic adduct species are $\text{M(PMBP)}_3 \cdot \text{B}_2\text{EHSO}$ and M(PMBP)_3 , whereas with CMPO as a neutral donor, the only complex extracted into the organic phase is

$\text{M(PMBP)}_3 \cdot \text{CMPO}$. The synergistic extraction constants of the above species were deduced by non-linear regression analysis and found to increase monotonically with decreasing ionic radii of these metal ions.

4.2.1.3. Anionic extractants. Strong anionic ligands are required by the anion exchangers which extract metal ions as anionic complexes. It has been reported that the separation factors for contiguous rare earth metals with primary or tertiary amines were poor in chloride media but it shows potential in sulfate media (Rice and Stone, 1962; Bauer, 1966). Primene JMT (tri-alkyl methylamine) and Aliquat 336 (tri-octyl methylammonium nitrate) reagents are strong-base anion exchangers which require lower concentrations of salting out reagents than other amines. (Hsu et al., 1980; Huang et al., 1986; El-Yamani and Shabana, 1985).

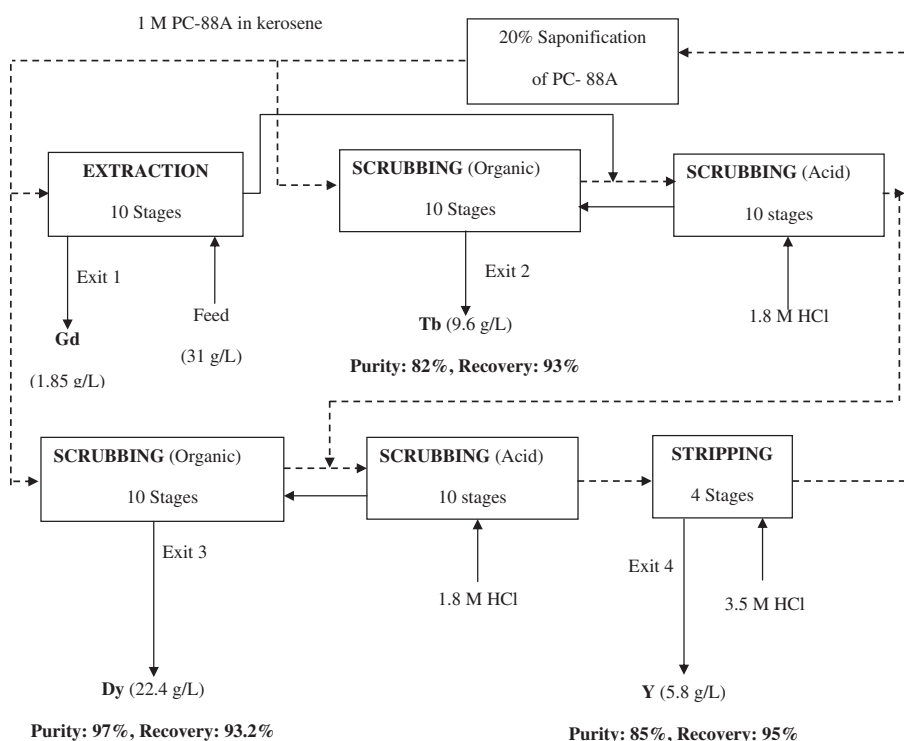
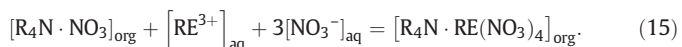


Fig. 11. Flow-sheet for simultaneous purification of Dy and Tb by PC 88A by a four-exit process (Mishra et al., 2000).

Table 10
Salient results on extraction of rare earth metals using Cyanex 272.

Source	Metal	Salient features	References
Synthetic solution containing La, Nd and Pr	La, Nd and Pr	A process was developed to separate La from Pr and Nd from a synthetic chloride leach liquor of monazite. Saponified Cyanex 272 showed best extraction affinity towards Pr and Nd than La with extraction of La, Pr and Nd were 4.9%, 96.6% and 98.7%, respectively.	Banda et al. (2012)
Synthetic solution of La	La	Extraction of La(III) from acidic nitrate-acetate medium by Cyanex 272 in toluene either alone or in combination with trioctylphosphine oxide (TOPO) has been investigated. The loading capacity of Cyanex 272 is found to be 15.97 g La(III)/100 g Cyanex 272.	Saleh et al. (2002)
Aqueous in chloride medium containing Sm (III)	Sm	Kinetics and extraction of Sm(III) from chloride medium using a sodium salt of Cyanex 272 in kerosene was studied. Loaded organic was stripped with 1 M HCl in one stage at phase ratio 1:1.	El-Hefny et al. (2010)
Synthetic solution of Th, La, Ce, Y and Fe	Th, La, Ce, Y	Extraction of Th, some rare earth metals (including La, Ce, Y) and Fe was carried out using Cyanex272, Cyanex302 and TBP (HA) as extractants by Taguchi's method. Cyanex272 was found to separate Th and rare elements more efficiently compared to TBP.	Nasab et al. (2011)
Synthetic solution	La, Ce, Eu, Gd, Yb, and Lu	Separation of Yb(III) into the organic top phase, Eu(III), La(III), into PEG-rich middle phase and (NH ₄) ₂ SO ₄ in the bottom aqueous phase of Cyanex272/PEG/(NH ₄) ₂ SO ₄ -H ₂ O three-liquid-phase system was studied.	Sui et al. (2013)
Stock solution of ytterbium (Yb)	Yb (III)	Extraction of Yb(III) using Cyanex 272 in n-heptane using a constant interfacial cell with laminar flow has been studied.	Xiong et al. (2006)
Monazite leach solution	Nd	The synergistic extraction of Nd ³⁺ from monazite leach liquor was achieved by hollow fiber supported liquid membrane. 98% Nd was extracted at 0.1 M Cyanex 272 and 0.05 M TOPO and 4 M HNO ₃ was used as the stripping solution.	Wannachod et al. (2015)
Nitrate solution from monazite processing	Pr	Recovery of Pr via a hollow fiber supported liquid membrane using Cyanex 272 is studied. The extraction and stripping of Pr were 91.7 and 78%, respectively.	Wannachod et al. (2011)
Stock solution	Sm and Gd	A comparative study for the separation of two rare earths, Sm and Gd using SX was studied. Organic extractants D2EHPA, Ionquest 801 and Cyanex 272 were used for effective separation of Sm–Gd.	Benedetto et al. (1993)

Anionic solvents basically, amines have also been studied for the extraction of rare earth metals under different experimental conditions. The long chain quaternary ammonium salts, R₃CH₃N⁺X[−], in which R represents C₈–C₁₂ groups and X represents nitrate or thiocyanate, are effectively used for rare earths separation. The mechanism with such anion exchangers shows that during extraction a simple inorganic anion from an ion pair type extractant, such as a quaternary ammonium salt, is replaced by a complex metallic anion as represented below (Gupta and Krishnamurthy, 2005)



Extraction of some trivalent actinides and lanthanides from 11.9 M LiCl (pH 2.0) by some primary, secondary, tertiary and quaternary amines in xylene has been studied (Khopkar and Mathur, 1981). Negligible extraction of the metal ions was found with primary and secondary amines whereas they are appreciably extracted with tertiary and quaternary amines. The trivalent actinides were extracted to a greater extent from such solutions. The separation factors An(III)/Ln(III) for several trivalent actinides with respect to Eu(III) and Tm(III) are found to be much greater when tertiary amines are used as extractants compared to when quaternary amines are used, which has been ascribed to the extraction of higher chloro complexes of the metal ions by tertiary amines. Absorption spectra of Am(III) and Nd(III) extracted into the long chain amines from 11.0 M LiCl (pH 2.0) indicate that the octahedral hexachloro complexes are present in the tertiary amine extracts whereas lower complexes are predominantly extracted by the quaternary amines leading to the observed lower separation factors for the trivalent actinides with reference to the lanthanides. Possible role of hydrogen bonding in the stabilization of chloro complexes extracted by tertiary amines as well as the extraction of hydrated chloro complexes by the quaternary amines are discussed.

4.2.1.4. Solvation extractants. Various solvation extractants have been used for rare earths separations and it has been investigated that their extraction from chloride and nitrate medium using TBP (tributylphosphate) increases with increase in atomic number. However, the distribution coefficients were found to be much lower in chloride

compared to nitrate media. Concentrated nitrate systems proved to be more promising for separating rare earths lighter than Sm while the heavier could not be separated effectively. The synergistic SX behavior of Nd(III) with 1,1,1-trifluoro-4-(2-thienyl)-4-mercaptobut-3-en-2-one (HSTTA) and the neutral donors dipyriddy, tributyl phosphate (TBP) and tri-*n*-octylphosphine oxide (TOPO) (≡L) was investigated using benzene as the organic diluents. The extraction at ionic strength 0.1 (NaClO₄) has been found to follow the reaction (Nag and Chaudhury, 1977).



The extraction constants ($K_{3,n}$) and the adduct formation constants ($\beta_{3,n}$) have been evaluated. With dipyriddy, only mono adduct formation takes place, whereas, with TBP and TOPO, both mono and bis adducts are formed. The $\beta_{3,n}$ values for HSTTA systems are higher than for the corresponding HTTA systems.

The investigation for the extraction of Ce(IV) and Th (IV) from sulfate solutions using Cyanex 923 (mixture of four trialkyl-phosphine oxides i.e., trihexylphosphine oxide, dihexylmonooctyl-phosphine oxide, dioctylmonohexyl-phosphine oxide and trioctylphosphine oxide) in n-hexane reported that Ce(IV) extraction is insensitive to acidity while that of Th(IV) increased with the aqueous acidity (Lu et al., 1998). The extraction of rare earth metals from nitrate medium with Cyanex 925 (a mixture of branched chain alkylated phosphine oxides) in heptane is also reported. TBP used in 1960s to separate light rare earths in nitrate media was not economic, and thus not established on commercial scale although products of different composition were withdrawn from different stages (Sherrington, 1966). Later on, 15% TBP in Shellsol K selectively extracts Ce(IV) from nitrate feed containing rare earth metals, followed by stripping of organic phase by reducing the Ce(IV) with dilute hydrogen peroxide in two stages (Preston et al., 1996b).

4.2.2. Nitrate solution

As rare earths also form soluble complex in nitrate solutions, studies have been made by different authors for their separation using different extractants.

4.2.2.1. Extraction of trivalent rare earths. Gaikwad and Damodar (1993) studied the nature of extraction of holmium (Ho) with 2-ethylhexyl

phosphoric acid mono-2-ethylhexyl ester, naphthenic as well as versatic acids and the equilibrium constants of these systems from aqueous nitrate solution. The extraction mechanism and complexation models have also been proposed. The synergistic extraction of trivalent rare earths from nitrate solutions was reported using mixtures of Cyanex 301(HX) and Cyanex 923(TRPO) in xylene (Reddy et al., 1999). They also reported the formation of $\text{MX}_3 \cdot 3\text{HX}$ with Cyanex 301 alone. In the presence of Cyanex 923, La(III) and Nd(III) are found to be extracted as $\text{MX}_2 \cdot \text{NO}_3 \cdot \text{TRPO}$. On the other hand, Eu(III), Y(III) and heavier rare earths are found to be extracted as $\text{MX}_3 \cdot \text{HX} \cdot 2\text{TRPO}$. The addition of a trialkylphosphine oxide to the metal extraction system not only enhances the extraction efficiency of these metal ions but also improves the selectivity significantly, especially between Y(III) and heavier lanthanides.

Aliquat 336 extracts light rare earths more readily than the heavier ones from nitrate medium. Xenotime concentrate was leached with HNO_3 and lighter rare earths were extracted with Aliquat 336 in an aromatic diluent. SX process was also carried out for recovering neodymium oxide (95% Nd_2O_3) from light rare earth nitrate solution using 0.50 M solution of Aliquat 336 nitrate in Shellsol AB (Preston, 1996d).

4.2.2.2. Extraction of rare earths in the presence of actinides. As the actinides are present along with the lanthanides, the liquid–liquid extraction of Th(IV), U(VI) and trivalent lanthanides such as Nd(III), Eu(III) and Lu(III) from nitrate solutions using 4-sebacoylbis(1-phenyl-3-methyl-5-pyrazolone) (H_2SP) and 4-dodecandioylbis(1-phenyl-3-methyl-5-pyrazolone) (H_2DdP) in chloroform as extractants was studied (Reddy et al., 2000). The results demonstrate that these metal ions are extracted into chloroform as $\text{Th}(\text{SP})_2$, $\text{Th}(\text{DdP})_2$, $\text{UO}_2(\text{HSP})_2$, $\text{UO}_2(\text{HDdP})_2$, $\text{Ln}(\text{SP})(\text{HSP})$ and $\text{Ln}(\text{DdP})(\text{HDdP})$ with H_2SP or H_2DdP . The equilibrium constants of the above species were deduced by non-linear regression analysis. The results clearly highlight that Th(IV) can be selectively separated from U(VI) and trivalent lanthanoids when extracted from 0.2 mol/L nitric acid solutions using 4-acylbis (1-phenyl-3-methyl-5-pyrazolones). Th(IV), U(VI) and Lu(III) complexes of H_2SP were synthesized and characterized by IR and ^1H NMR spectral data to further clarify the nature of the complexes.

4.2.2.3. Comparative extraction of rare earths in chloride and nitrate solution. The relative extraction efficiency of N,N,N',N' -tetraoctyldiglycolamide (TODGA) towards Y^{3+} and Sr^{2+} compared from HNO_3 as well as HCl solutions showed much higher separation factor (SF) values in HCl medium as compared to those obtained from HNO_3 medium (Dutta et al., 2011). A separation scheme for ^{90}Y from ^{90}Sr has been developed. The purity of the separated ^{90}Y was ascertained from its decay profile and half-life measurements. The extracted species was found to be $\text{Y}(\text{X})_3 \cdot 3\text{TODGA}$ where X^- is the nitrate or the chloride anion. The thermodynamic parameters were also determined and the two phase extraction constants ($\log K_{\text{ex}}$) were calculated. The extraction of Y(III) was highly exothermic and entropy destabilized and was equally favorable for both HNO_3 medium as well as HCl medium.

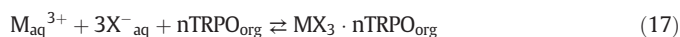
4.2.3. Thiocyanate solution

Different authors studied the extraction of rare earth metals from the thiocyanate solutions using various extractants. The extraction of Ce(III) from ammonium thiocyanate solutions by alkyl and aryl sulphoxides, tri-*n*-octyl phosphine oxide (TOPO), 2-thenoyltrifluoroacetone (TTA), and their solutions has been studied (Reddy and Reddy, 1977). The species extracted were found to be $\text{Ce}(\text{SCN})_3 \cdot 4\text{S}$, where S = di-*n*-pentyl sulphoxide (DPSO), di-*n*-octyl sulphoxide (DOSO), diphenyl sulphoxide (DPhSO), or TOPO. Synergic effects have been observed which are ascribed to the formation of mixed ligand metal complexes. The extraction of the metal is inversely dependent upon the initial metal concentration and temperature of the system.

4.2.3.1. La(III) extraction with TOPO and DBSO. Recently, the extraction behavior of La(III) from ammonium thiocyanate over concentration of 0.5–5 M using tri-*n*-octyl phosphine oxide (TOPO) and dibenzyl sulphoxide (DBSO) in carbon tetrachloride under different conditions was studied (Reddy et al., 2011). Both the solvents are potential extractants for La(III) and attain equilibria within 5 min. The thiocyanate forms zero-charged species with La as $\text{La}(\text{SCN})_3$ with TOPO and DBSO. The extraction is exothermic in nature with negative enthalpy represented as $\Delta H^\circ = -7.008 \text{ kJ/mol}$ (-1.675 kcal/mol). Thus, the increase in temperature could decrease in the extraction due to the decreased stability of the complex at higher temperature (Reddy et al., 2011).

4.2.3.2. Comparative extraction of Ln and Y in thiocyanate and nitrate solutions. As the anionic species also affect selective formation of rare earth complex in the organic phase, Reddy et al., 1998 compared the extraction of trivalent lanthanides (La, Nd, Eu, Tb, Ho, Tm, Lu) and Y in thiocyanate and nitrate solutions using Cyanex 923 (TRPO) in xylene. The metal ions are found to be extracted from thiocyanate solution as $\text{M}(\text{SCN})_3 \cdot n\text{TRPO}$; *n* is 4 and 3 for the lighter and heavier lanthanides, respectively. On the other hand, from the nitrate solutions these metal ions are extracted as $\text{M}(\text{NO}_3)_3 \cdot 3\text{TRPO}$. Similar solvation numbers have been reported elsewhere for the extraction of these trivalent lanthanides from thiocyanate solutions with neutral organophosphorus extractants such as trioctylphosphine oxide (TOPO) and tributylphosphine oxide (TBPO) (Khopkar and Narayanankutty, 1972) and also with dialkyl sulphoxides (Reddy et al., 1994).

According to Reddy et al. (1998), the lanthanides and Y in aqueous phase form a variety of complexes in the presence of thiocyanate or nitrate ions and the extraction reaction followed with Cyanex 923 (TRPO) is represented as



where $\text{X}^- = \text{SCN}^-$ or NO_3^- and *n* = 3 or 4. The equilibrium constants of extracted Y and the trivalent lanthanides viz. $\text{La}(\text{SCN})_3 \cdot 4\text{TRPO}$; $\text{Nd}(\text{SCN})_3 \cdot 4\text{TRPO}$; $\text{Eu}(\text{SCN})_3 \cdot 4\text{TRPO}$; $\text{Tm}(\text{SCN})_3 \cdot 3\text{TRPO}$; $\text{Lu}(\text{SCN})_3 \cdot 3\text{TRPO}$; and $\text{Y}(\text{SCN})_3 \cdot 3\text{TRPO}$ have been obtained by non-linear regression analysis. In both thiocyanate and nitrate systems, the distribution coefficient of lanthanides are found to increase with decreasing ionic radii and while that of Y lies along with those of middle lanthanides. The better selectivity and extraction efficiencies were obtained for trivalent ions when extracted from thiocyanate solutions as compared to the nitrate system.

The separation of Y is based on the different extraction behavior of rare earths in nitrate and thiocyanate systems (Sherrington, 1983). The position of Y in rare earth series is between Ho and Er based on its ionic radius. In nitrate system, Y behaves like HREE and in thiocyanate system it behaves like the lighter ones. Hence, it is possible to extract the LREE impurities up to Dy in nitrate system and subsequently to extract the heavy rare earths like Ho, Er, Tm and Yb in thiocyanate system. The flow-sheet for upgrading of Y from 60% to 99.9% is shown in Fig. 12 (Thakur, 2000b). Quaternary ammonium compounds have been used by MCI Megon in Norway for commercial production of 99.999% purity Y from the feed containing 60% Y_2O_3 produced from xenotime (Gaudernack et al., 1973).

The separation factor (SF) observed between Y and the heavy lanthanides ($\text{Lu}/\text{Y} = 56$; $\text{Tm}/\text{Y} = 9$) with Cyanex 923 in thiocyanate system were found to be significantly higher than the SF reported with D2EHPA (Ceccaroli and Alstad, 1981), which is commonly used in the separation of rare earth metals. Cyanex 923 may be useful for the separation and purification of Y especially from heavy lanthanides in fewer stages of counter current extraction as compared to the normally used extractants in the rare earths industry.

4.2.4. Phosphate solution

As the rock phosphate contains minor quantities of rare earth metals (<100 mg/kg of ore), their leaching produces solution containing these rare earths and U in phosphate media, which were reported to be extracted using SX process. However, a method has been developed for the recovery of mixed rare earth oxide from phosphoric acid as by-product using dibutyl butylphosphonate, trin-butyl phosphate, and D2EHPA (Preston et al., 1996a,b,c). The separation of eleven rare earths, seven HREEs (Tb, Dy, Ho, Y, Er, Yb and Lu) and mixture of four LREEs (La, Ce, Pr, Nd) from H_3PO_4 (0.5–5 M) medium using TOPS 99, (equivalent to di-2-ethylhexyl phosphoric acid), PC 88A and Cyanex 272 diluted in kerosene have been reported (Radhika et al., 2010). They reported the extraction and separation of HREEs and LREEs and also separation of HREEs as a group from LREEs in 3–5 M acid. The separation factors were evaluated based on the distribution coefficients for the separation of individual/pair of rare earths from others as well as the separation of HREEs from LREEs. Extraction efficiency of extractants towards lanthanides from H_3PO_4 medium decreases in the series: TOPS 99 > PC 88A > Cyanex 272. In 2011, Radhika et al., in further studies showed the separation of rare earths mixture into three concentrates at 3 M acid using 1 M TOPS 99 in kerosene. McCabe–Thiele extraction isotherm predicted the separation of Yb + Lu at an aqueous-to-organic (A/O) phase ratio of 2 in three stages using 0.1 M TOPS 99. Counter-current batch extraction simulation (CCES) of Yb and Lu at an A/O of 2 resulted in a raffinate containing 3.6 mg/L of Yb + Lu, corresponding to an extraction efficiency of 91.9%, whereas other five HREEs loss was about 6.7%. Stripping of Yb and Lu as per the predictions of McCabe–Thiele plot from loaded organic (LO) was selected at O/A phase ratio of 3 with 4 M HCl and counter-current stripping simulation studies resulted in 100% stripping efficiency. From the Yb + Lu raffinate, remaining five HREEs were extracted about 94% with 1 M TOPS 99 at an A/O ratio of 3 in three stages. The LREE (Pr and Nd) co-extraction is 9.8%. Quantitative stripping of HREEs from LO is achieved with 7 M HCl at an O/A ratio of 3 in two stages. Finally, a process flow sheet is presented (Fig. 13) (Radhika et al., 2011) for the separation of rare earths into three groups, two HREE fractions (Yb + Lu and Tb, Dy, Ho, Y, Er) and one LREE fraction from 3 M H_3PO_4 .

4.3. Ion exchange and precipitation processes

Before 1960, ion exchange method was the only way to separate rare earth metals but currently it is used only to extract small quantities of highly purified rare earth products (Xie et al., 2014). During ion exchange process, different ion exchange cationic or anionic resins are employed depending on the constituent of the aqueous solution using batch or continuous mode in column to extract rare earths from leached solutions with low rare earth concentration. The purified solution obtained after separation could be further processed to produce the value added products in the form of salt for industrial application. Application of ion exchange resins eliminates the requirement for a costly solid/liquid separation unit as in case of SX processes (Padayachee et al., 1996). Separation of rare earth metals by ion exchange process was initiated to separate fission products obtained from nuclear reactors (Spedding et al., 1956; Powell, 1961, 1964). Cation exchange was primarily used to obtain rare earths in which the polystyrenesulphonic cation exchangers are frequently used and rare earth cations are exchanged with H^+ , NH_4^+ or other cations derived from the ion exchange phase. The affinity of the exchanged ions for the cation exchanger depends majorly on the charge, size and degree of hydration of the exchanged ions while for ions with the same charge, the affinity depends on their size and degree of the hydration. As the atomic number of rare earth metals increases their ionic radius decreases and due to their similar values of ionic radius, there are no significant differences in their affinity for the polystyrene cation exchangers. As a result, individual rare earth metal could not be positively extracted from the solutions of mineral acids. However, solutions containing mineral acids with organic solvents can improve the rare earths separation as they are much harder sorbed on cation exchangers than using aqueous solutions of these acids (Starý, 1966). However, the mechanism of the processes involved in anion exchangers was much more complex and could not be explained clearly. Rare earth metals show little tendency to form anionic complexes with simple inorganic ligands and are poorly sorbed on the anion exchangers from aqueous solutions of hydrochloric and nitric(V) acids. They are also weakly sorbed from sulfuric(VI), phosphoric(V) and mixture of hydrochloric and hydrofluoric acid

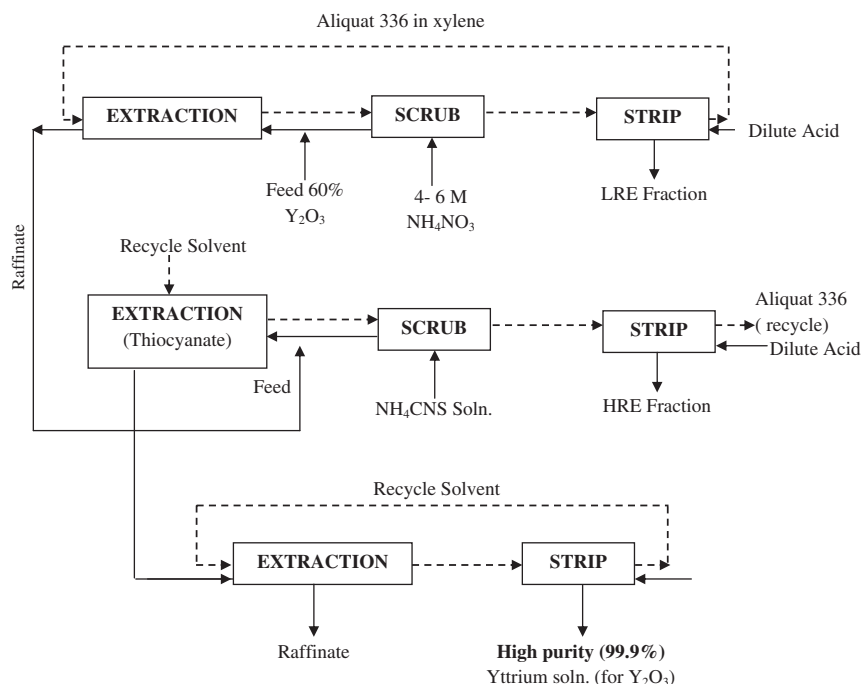


Fig. 12. Flow-sheet for the purification of yttrium (99.9% purity) using Aliquat 336 from the feed containing 60% yttrium oxide (Thakur, 2000b).

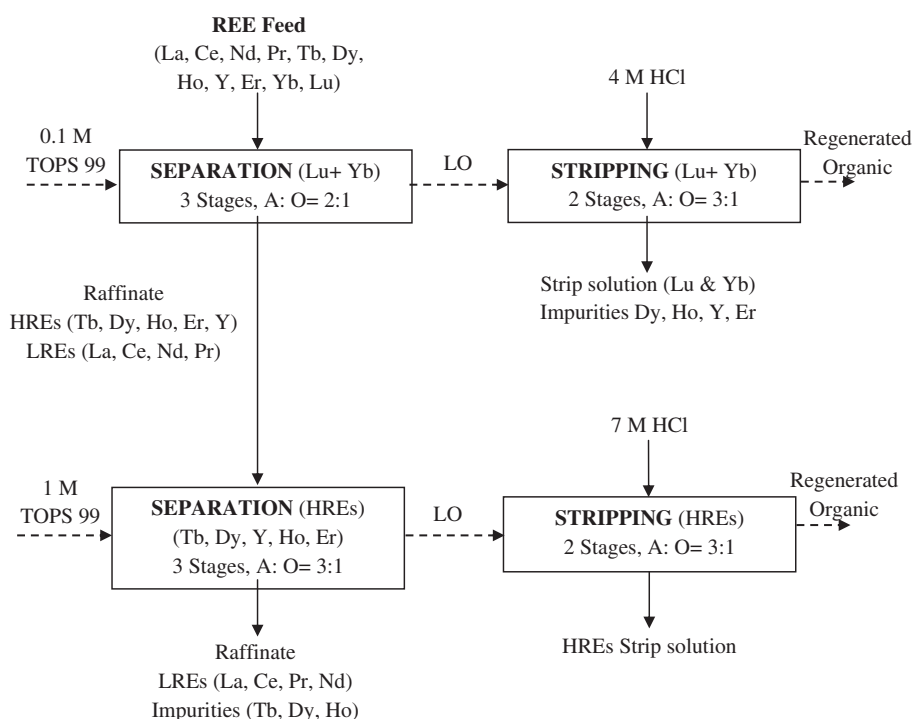


Fig. 13. Flow-sheet for the separation and recovery of rare earths from phosphoric acid solution (Radhika et al., 2011).

solutions (Jegorov and Makarova, 1971). Much better results of rare earths sorption were obtained from the solutions of chlorides, nitrites, nitrates, sulphites, sulfates, thiocyanates, thiosulphates and carbonates (Marcus and Nelson, 1959).

The chemical as well as spectrochemical analyses showed a natural fractionation of rare earth metals and the considerable variation in their proportion could show progressive differentiation. The study of fractional precipitation of adjacent pairs of rare earth metals provides information regarding their individual distribution and also, the possible mode of formation, and order of crystallization and deposition of the minerals. Solubility and fractional precipitation studies of the lanthanides in such systems as the oxalate, bromate, and sulfate are reported, indicating different orders of preferential precipitations. These studies were undertaken primarily for their possible application to the development of techniques for separating and purifying some of the lanthanides. Studies have been carried out by various researchers to extract rare earth metals using different types of ion exchange resins such as Tulsion CH-96, Tulsion CH-93, T-PAR, and IR-120P or by the process of precipitation using reagents viz. sodium sulfate, oxalic acid, ammonia, etc. and the detail study is presented in Table 11.

4.4. Environmental impact of rare earths processing

Processing of rare earth metals affects the environment directly or indirectly. Rare earth mining from their ores has the capacity to liberate toxic substances of radionuclides, acids, fluorides, etc. due to overtopping/collapsing of tailing dams. But to keep the environment free from these effects of rare earths mining, recycling of secondary resources is a great opportunity to secure these rare earths. The chemical processes used affect the whole ecosystem, thus the government enforces rules on companies. However, uncontrolled recycling of secondary resources also has the probability to create significant amount of hazardous emissions. Recovering metals through recycling processes is almost ten times more energy efficient than smelting metals from ores. Compared to primary processing, recycling of rare earth metals will provide noteworthy benefits with respect to air emissions,

groundwater protection, acidification, eutrophication, and climate protection. Moreover, rare earth metal recycling will not involve radioactive impurities as is the case with primary production. Recycling of secondary resources using pyrometallurgical routes should have proper gas treatment technologies in order to control the emission of dioxins and other gases formed during the processing. In hydrometallurgical treatments, special requirements are essential for the liquid and solid effluent generated to ensure environmentally sound operations without emission of any hazardous substance.

5. Conclusions

The present paper is based on extensive studies carried out globally for the efficient extraction and separation of rare earth metals from primary and secondary resources using hydrometallurgical routes of leaching, solvent extraction, ion exchange and precipitation. The results of the studies are given below:

- Variety of leaching technologies have been developed both for primary and secondary resources depending upon the mineralogy, rare earths occurrence and engineering feasibility. Both acid and alkaline leaching are interactively used for rare earths extraction from ores, among which alkaline treatment was found to be acceptable from industrial point of view.
- Rare earth metal recycling has the potential to counterbalance a major part of their primary extraction and most of the research has been directed towards the chemical processing of the collected rare earths recyclates. However, an efficient rare earths recycling requires the development of an environmental friendly, fully integrated and logistically sound flow sheets, including dismantling, sorting, pre-processing, and pyro-, hydro- and/or electrometallurgical processing steps to recover rare earths from magnets, batteries, lamp phosphors and other applications.
- The leach liquor generated is put to solvent extraction studies using different organic extractants such as cationic, anionic and solvating.

Table 11

Salient results on extraction of rare earth metals using the process of ion exchange and precipitation.

Ion exchange process		
Resin used	Salient features	References
Tulsion CH-96 and T-PAR	Solid-phase extraction of heavy rare-earths like Tb, Dy, Ho, Y, Er, Yb and Lu from phosphoric acid using Tulsion CH-96 and T-PAR resin has been reported.	Kumar et al. (2010)
IR-120P (cation-exchange polymeric resin)	Recovery of Y and rare earths using electroelution of a cation-exchange polymeric resin IR-120P Rohm & Haas-USA from chloride medium is reported.	Pinto and Martins (2001)
N-methylimidazolium functionalized anion exchange resin	N-methylimidazolium functionalized anion exchange resin was used for adsorption of Ce(IV) from nitric acid medium by reducing it to Ce(III).	Zhu and Chen (2011)
Tulsion CH-93	Solid-liquid extraction of Gd from phosphoric acid medium using amino phosphonic acid resin, Tulsion CH-93 is reported. The log D vs. equilibrium pH plot gave straight line with a slope of 1.8. The loading capacity of Tulsion CH-93 for Gd was 10.6 mg/g.	Radhika et al. (2012)
Dowex I-X8 anion-exchange resin	The distribution coefficients on Dowex I-X8 was determined for all rare earths at different proportions of nitric acid and acetone which is found to be sufficient for the separation of rare earths by ion-exchange chromatography.	Alstad and Brunfelt (1967)
D113-III resin	The adsorption and desorption behaviors of Er(III) ion using resin D113-III were investigated. The loading of Er(III) ion onto D113-III increased on increasing the initial concentration.	Xiong et al. (2009)
D72 (acid ion exchange resin)	The loading of Pr (III) ions was dependent on pH and adsorption kinetics of Pr (III) ions onto D72 resin followed pseudo-second-order model. The maximum adsorption capacity of D72 for Pr (III) was evaluated to be 294 mg g ⁻¹ for the Langmuir model at 298 K.	Xiong et al. (2012)
D151 resin	The adsorption and desorption behaviors of Ce(III) on D151 resin was achieved at pH 6.50 in HAC–NaAc medium. The maximum loading capacity of Ce(III) was 392 mg/g resin at 298 K.	Yao (2010)
Bio-Rad AG 50W-X2 cation-exchange resin	A new method for determining the stability constants for the mono- and difluoro-complexes of Y and rare earths, using a cation-exchange resin Bio-Rad AG 50W-X2 has been reported.	Schijf and Byrne (1999)
TODGA resin	A two-stage method to separate Lu and Hf from silicate rock and mineral samples digested by flux melting or HF–HNO ₃ dissolution using TODGA resin from Eichrom Industries is presented.	Connelly et al. (2006)
Amberlite XAD-4	The pre-concentration and separation of La(III), Nd(III) and Sm(III) in synthetic solution was achieved using Amberlite XAD-4 with monoaza dibenzo 18-crown-6 ether. The adsorbed rare earth elements were eluted by 2 M HCl.	Dave et al. (2010)
D152 resin	The sorption of rare earth ions from HAC–NaAc buffer solution using D152 resin containing –COOH function groups at 298 K are presented.	Xiong et al. (2008)
XAD-4 (crosslinked polystyrene resin)	A new chelating agent bis-2[(O-carbomethoxy)phenoxy]ethylamine has been synthesized using a facile microwave induced process. The ligand was appended on to XAD-4 resin and adsorption properties of La(III), Nd(III) and Sm(III) towards this resin were studied. The selectivity sequences of the resin for these metals were in agreement with their stability constants.	Kaur and Agrawal (2005)
Tertiary pyridine resin	The novel separation method of rare earths using tertiary pyridine type resin with methanol and nitric acid mixed solution was developed. The adsorption and separation behaviors of rare earths were investigated and found that it can be well separated mutually.	Suzuki et al. (2006).
Precipitation process		
Reagent used	Salient features	References
Sodium sulfate	A mixture of rare earths double sulfate was produced at 50 °C using 1.25 times the stoichiometric amount of Na ₂ SO ₄ . The total rare earths double sulfate content was >90% together with minor amount of other impurities.	Kul et al. (2008)
Oxalic acid	Leach liquor obtained from weathered black earth contains rare earth metals along with other impurities. Oxalic acid was used to precipitates them forming rare earths oxalates, which are further roasted at 900 °C for 1.5 h to form rare earth oxides.	Chi et al. (2000)
Hydroxide–oxalate mixture	The filtrate obtained by leaching the roasted pre-concentrate of bastnasite with a dissolution percentage of 89% for total rare earths was separated from the residue.93.6% of total rare earths present were precipitated using hydroxide–oxalate mixture with its subsequent ignition to oxides at 900 °C for 2 h.	Yorukoglu et al. (2003)
Ammonium hydroxide	Ammonium hydroxide was used to precipitate lanthanum as lanthanum hydroxide at pH ranging from 7.9 to 9.6. Precipitation was made for three times which results in recovery of 96% lanthanum oxide.	Soe et al. (2008)
Ammonia	Lanthanum hydroxide and oxide were prepared by the precipitation method at room temperature. Lanthanum nitrate was dissolved in water and 2 M ammonia was added drop wise to precipitate lanthanum until pH ~ 10 was reached.	Kim et al. (2008)
Sodium hydroxide, ammonium hydroxide and potassium hydroxide	Double salt of neodymium is formed using sodium hydroxide, ammonium hydroxide and potassium hydroxide, which is further leached with HF to form neodymium fluoride.	Lyman and Palmer (1993)
Sodium hydroxide	A total recovery of 99% rare earths was obtained after selective precipitation with sodium hydroxide at pH less than 2 after leaching the spent NiMH batteries by sequential sulfuric acid. A precipitate composed of lanthanum and cerium sulfates are produced.	Innocenzi and Vegliò (2012).

(a) The chloride solution has been most extensively studied for the separation of different light and heavy rare earth metals (Dy, Y, Gd, Er, Ho, etc.) using cationic, anionic and solvating organics from chloride medium. In case of cationic exchangers, the extraction of rare earths depends upon the acidity of the solutions. D2EHPA and PC 88A have been considered the most suitable extractants for separation of rare earths from chloride medium. Effective recovery of lanthanides has also been established using chelating extractant, acylpyrazolones. Appreciable extraction and separation of actinides and lanthanides metal ions was also achieved using tertiary and quaternary amines.

(b) It was also noticed that the extraction efficiency of metal ion is enhanced on addition of trialkylphosphine oxide especially between Y(III) and HREEs.

(c) Alkyl and aryl sulphoxides, TOPO, and TTA were considered suitable for the extraction of Ce from thiocyanate solution whereas La was extracted using TOPO and DBSO. The extraction of trivalent ions from thiocyanate solution showed better selectivity and efficiency compared to their extraction from nitrate solution.

(d) Solvent extraction studies for the separation of HREEs (Tb, Dy, Ho, Y, Er, Yb and Lu) and LREEs (La, Ce, Pr, Nd) using extractants

TOPS 99, PC-88A and Cyanex 272 from phosphoric acid solution showed the order of extraction efficiency as TOPS 99 > PC 88A > Cyanex 272.

- Apart from solvent extraction, ion exchange and precipitation are also studied for rare earths extraction. Different ionic resins and precipitating reagents were studied for rare earths extraction from solutions containing nitrate, chloride, sulfate, phosphate, etc.

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