Journal of Cleaner Production 267 (2020) 122048

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

Review

Review of rare earth elements recovery from secondary resources for clean energy technologies: Grand opportunities to create wealth from waste

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ARTICLE INFO

Article history:
Received 30 November 2019
Received in revised form
23 April 2020
Accepted 2 May 2020
Available online 11 May 2020

Handling editor. Prof. Jiri Jaromir Klemeš

Keywords:
Rare earths
Extraction
Recovery
Secondary resources
Clean energy

ABSTRACT

Rare earth elements (REEs) are vital components of high-tech electrical and electronic based materials. In the global scenario, the deposits of natural rare earth elements (REEs) are limited except for countries such as China. This has led to a dependence on major secondary rare earth-bearing sources such as battery waste, scrap alloy, spent magnets, spent catalysts, waste light-emitting diodes (LEDs), and fly ash for a substantial recovery of REEs for their use. Recycling REEs from these secondary waste sources by hydrometallurgical routes appears to be a sustainable approach with low waste generation, few emissions, low energy consumption, economically feasible, and environmentally friendly. In most of the reported studies, secondary waste is subjected to chemical and or bioleaching followed by solvent extraction processes for clean separation of REEs. Subsequently, rare earth compound(s) are recovered through precipitation. Solvent extraction (liquid-liquid extraction) is one of the most vital stages in the overall process as REEs (light and heavy rare earths) exhibit a low separation tendency while being extracted with various solvent reagents from corresponding aqueous media. This review provides an in-depth discussion on the recycling strategies implemented to obtain REEs from numerous secondary wastes; extraction behavior of REEs; challenges, advantages, and disadvantages of the proposed methodologies; as well as proposed flowsheets for clean separation and recovery of REEs. In addition, the role of REEs in renewable and green energy technologies and the future aspects of the reprocessing technology of secondary REE sources are summarized and reported.

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https://doi.org/10.1016/j.jclepro.2020.122048
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1. Introduction of rare earth elements (REEs) and their applications

The new millennium is the most high-tech century with major utilization of rare earth elements (REEs). Day-by-day the consumption of natural resources increases due to rising population vis-a-vis their needs. As per the United Nations assumptions, the human population of the planet Earth will reach 8.5 billion by the year 2030 (Saleem et al., 2017), indicating that natural resources requirements will continue to be increase and that secondary-resource processing will become a necessity. Thus far, the occurrence of rare earth resources on this planet has been reported mainly in China. From 2010 onwards, China has controlled the rare earth ore/mineral exports to overseas (Mancheri et al., 2019).

Secondary resources such as manufacturing generated waste and used rare earth based materials becomes an eventual resource for REEs. Therefore, most countries depend on rare earth metal-bearing urban mines containing usually battery waste, spent magnets, scrap alloys, spent catalysts, waste light-emitting diodes (LEDs), and fly ash. In a case study, it was found that Asian countries like the Republic of Korea (South Korea) followed major advanced rare earth processing technology based on the above waste, as their natural resource deposits were very limited as in other countries. In consequence, key challenges e.g. post- and pre-consumer landfills, of these wastes are also being faced. On the other hand, advancements in technology are again becoming critical, as they are one of the root causes of environmental damage (Kiddee et al., 2013). Thus, the development of sustainable technology with minimum waste liberation and a low risk of environmental pollution is urgent to resolve such issues.

Rare earth metals have key roles in the contemporary lifestyle with a variety of uses in the electrical and electronic technology development. Hydrometallurgy technology, the metal ion extraction process in aqueous phase, is inexpensive and suitable for REE recovery from both primary ores/minerals and secondary sources such as waste from industries, electronic waste, and scrap (Yoon et al., 2016).

Countries such as South Korea are pioneers in the high −tech industries related to the manufacturing and supply of electronic and electrical goods based on the universal needs. However, the country faces two major difficulties: the generated manufacturing waste and after-usage scrap will create a landfill problem and that it is a nation possessing very limited natural resources.

The high population density is another important challenge to defy; per the 2018 Organization for Economic Cooperation and Development (OECD) data (data adapted from The World Bank website), the top ten nations of high population densities are South Korea (530), The Netherlands (511), Israel (411), Belgium (377), Japan (347), United Kingdom (275), Luxemburg (250), Germany (237), Switzerland (216), and Italy (205).

REEs have a variety of applications in fields, such as metallurgy, electronic appliances, chemistry, glass, alloys, and as catalysts in petroleum refining. They are also used to make permanent magnets (PMs). In addition, the worldwide REEs demand levels estimated for different uses are as follows: magnets, metal alloys, polishing, catalysts, glass/phosphors, and ceramics/others. The major player in the REE trade and production worldwide is China, followed by India, Australia, Malaysia, Brazil, the USA and Russia etc, which play relatively minor roles (Brudnick, 2011).

REEs are crucial in three major sectors: clean energies, lifestyle, and defense, (Table 1). The green energy sector deals with wind power, hybrid vehicles, lighting, and rechargeable batteries. Current lifestyles commonly include cellphones, iPads, compact discs

Table 1
Rare earths role in various sectors*.

Various sectors	Rare earth elements (REEs)
1) Green energy sector	
Lighting	Eu, Y
Rechargeable batteries	La, Ce
Wind power	Nd, Pr, Dy
Hybrid vehicles	Nd, Pr, Sm, Dy, Tb
2) Lifestyle sector	
LCD/PDP screens	Y, Ce, Eu, Tb
Magnetic resonance imaging	Nd, Gd
Cordless power tools	Nd, Pr, Sm, Dy, Tb
Cellphones, iPods, CDs-DVDs	Nd, Pr, Ce, La
3) Defense sector	
Optics	Eu, Y, Tb
Surveillance and protection	Nd, Y, La, Eu, others
Lasers	Dy, Tb
Aircraft materials	Y, others
Guidance and control	Nd, Pr, Sm, Dy, Tb
Power and communications	Nd, Pr, Sm, Dy, Tb
Microwave communications	Nd, Pr, Dy, Tb, Eu
Solar transducers	Nd, Y, La, Eu, others

*Source: UNCTAD Secretariat from Great Western Minerals Group Ltd, adapted from reference United Nations Conference on Trade and Development, 2014.

(CDs), digital versatile discs (DVDs), cordless power tools, liquid crystal display (LCD) screens, etc. The defense sector deals with various kinds of fields such as optics/lasers, aircraft materials, power/microwave communications, etc. (Table 1). All of these fields utilize REEs as a significant component of their parts (United Nations Conference on Trade and Development, 2014).

The United States of America Department of Energy (DoE) recognizes five REEs amongst all as critical (CREEs), namely, neodymium, yttrium, dysprosium, europium, and terbium, considering their reserve, and demand and supply levels (U.S. Department of Energy, 2010). Du and Graedel estimated the global rare earth in-use shares for Nd-Fe-B permanent magnets, which showed that neodymium, was estimated to have a big global in-use stock, followed by Tb and Pr/Dy (Du and Graedel, 2011).

Talking about recycling technology usually raises concerns regarding three major issues: limited raw materials, increasing energy costs for the processing of the primary resources, and landfilling problems. Countries like South Korea have very finite minerals and available ores are have low-grade metal values.

Concerning recycling, the most favorable option is always the prevention of the generation of as much waste as possible, followed by its minimization. The second option may be the reuse of minimized materials via recycling and energy recovery processing. The least favored option is the disposal in a proper place with appropriate treatment (Rao, 2006).

The generated waste rises several challenges including landfilling. Countries like South Korea, face the two major issues of fewer natural resources and limited landfilling space. Resources recycling can provide a solution to meet the certain national demand levels of REEs while resolving other environmental issues. From the data collected by Scopus on rare earths recycling, it was observed that in the new millennium, research efforts have been vigorously increased compared to the decades from 1951 to 2020 (Fig. 1).

The tendency toward recycling has affected the costs of particular metals. The present study addresses the future prospects as well as challenges of recycling strategies for rare-earth-based materials such as rare-earth-based electronic materials concerning their recycling.

The management of secondary waste including spent catalysts, spent batteries, e-waste, fly ash, and red mud (RM) is essentially warranted as this waste causes several environmental concerns due to the bearing of hazardous components upon direct disposal to the environment. At the same time, these are economically important sources due to the amount and variety of rare earth compounds they contain as well as other heavy metals. Therefore, to address these challenges, the development of sustainable recycling technologies for the recovery of metals while going towards a zero waste release to the environment is recommended (Barik et al., 2012).

Over time, several hydro-processing approaches have being employed to process the numerous secondary wastes for the extrication of REE values. Processes like adsorption (Awual et al., 2017; Awual et al., 2015; Awual et al., 2013a, 2013b and 2013c) have also been widely applied for rare earth separation alongside heavy metals using a variety of aqueous media, similar to solvent extraction (liquid-liquid extraction) phenomena. Of these methodologies, the adsorption process has the advantage of being an economical process, easy in operation, applicable in a wide pH range of the solution, and efficient for solutions bearing varying amounts of metal ion concentration (Awual et al., 2019a; Abbas et al., 2018; Shahat et al., 2015a, 2015b). The key feature of the sorption process include the effective as well as suitable adoption of low-cost materials such as clays, zeolites, activated carbons, agricultural waste, bio sorbents, and metal oxides, which have drawn attention to metal separation processes (Awual et al., 2019b; Awual et al., 2019c; Awual, 2016; Shahat et al., 2018).

Despite the number of advantages, the sorption method has some disadvantages, e.g. low selectivity, less loading capacity on multiple cycles of adoption, complex extraction behavior for various functional groups on the sorbent, the surface-less potential for its application in commercial/field level operations, and slow kinetics. The key limitations of the sorption process, namely, its low selectivity and minimal scope of industrial-scale operations, has led to choosing solvent extraction processes as an emerging separation technique in the hydrometallurgy domain while employing it for the separation of numerous metal ion(s) from the secondary waste solutions.

According to previously reported works for REEs extraction from

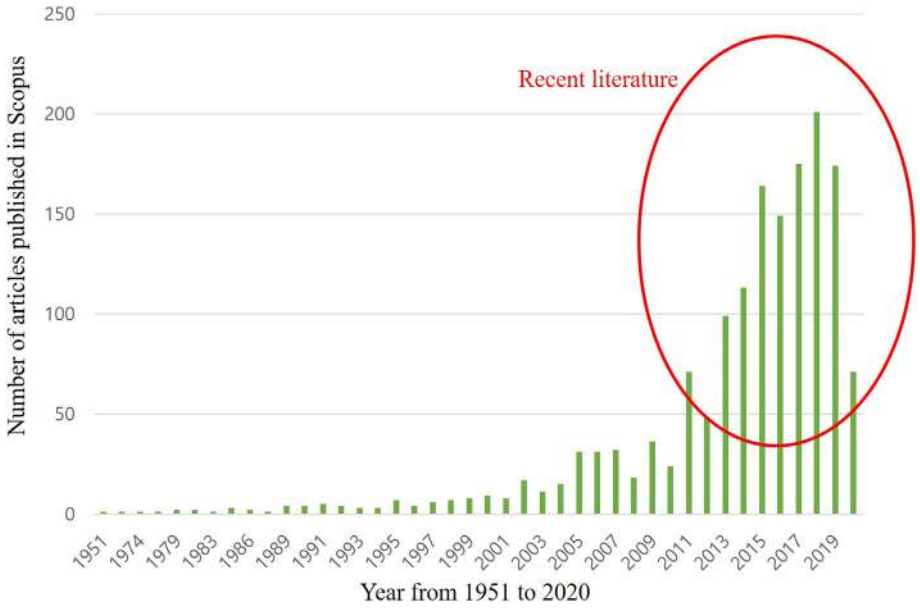

Fig. 1. Research papers published on the subject area of rare earths recycling 1951 to 2020 (Data from Scopus website, www.scopus.com, keywords are rare earths recycling).

secondary sources (Jyothi et al., 2020; Yoon et al., 2015a, 2015b) other methods such as the ion exchange (IX), supported liquid membrane process (SLM) and emulsion liquid membrane (ELM) are being used for the separation of various REEs (Parhi et al., 2017; Parhi et al., 2019; Das et al., 2018). In the former approach, either cation and/or anion based functionalized resins are applied for the separation of REEs with a similar operation mode as adsorption. While, the latter two approaches, the supporting material, mainly of the functionalized solvent reagent, with a good extractive ability nature is impregnated over the solid support membrane phase for the recovery of the targeted metal ion. Although these methods are successful up to laboratory-scale operations, there are still challenges in achieving a continuous mode as well as commercial-scale mode operations. Moreover, there are several other shortcomings to these processes including high time consumption, low recyclability, less selectivity, and low stability of the support phase. Therefore, to overcome such issues, the solvent extraction (liquid-liquid extraction) process is often considered the most promising option in which various commercial and green solvents are adopted for the clean REEs separation from several aqueous solutions.

In the periodic table, fifteen elements at atomic numbers of 57 (Lanthanum (La)) to 71 (Lutetium (Lu)) are recognized as rare earth elements (REEs) while two other elements, yttrium and scandium, with properties similar to those of the aforementioned elements are also included as REEs (Qi, 2018; United Nations Conference on Trade and Development, 2014).

Currently, electronic devices have been changing industrial processes alongside human lives, and the economic growth of several countries depends strongly on the export of electronics. Of the primary resources with limited REE concentrations, cerium is the highest at 60 mg/L and promethium is the lowest at 10^{-18} mg/L. REEs have a balancing problem (Koen et al., 2013b) due to their availability in nature. Lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), and promethium (Pm) belong to the light rare earth elements (LREEs) classification and are found in higher amounts in the earth crust, on the other hand, heavy rare earth elements (HREEs) with an atomic number greater than 62 (from samarium (Sm), to lutetium (Lu)), are scarcer in the earth crust (Qi, 2018; United Nations Conference on Trade and Development, 2014). Recycling could meet and ease the demand of a certain amount of these REEs.

Rare earth elements (REEs) have a variety of applications in industry among many high-tech and electronics industries. The distribution of rare earth elements according to their products are metallurgy, electronic parts, and other REE-based goods (Goodenough et al., 2018). Another sector is permanent magnets used as essential components in electrical and electronics products.

The amount of electronic waste generated all over the world reached 44.7 million metric tonnes in 2016, that is, 6.1 kg per person; furthermore, in the near future (by 2021), it is predicted that these figures will increase to 52.2 million metric tonnes and 6.8 kg per inhabitant (Awasthi et al., 2019; Balde et al., 2017). Electronic waste can create wealth when it is handled with suitable scientific methods; a recent report estimated 55 billion euros in 2016 profit of properly recycled electronic waste (Balde et al., 2017). These methods should have environmentally friendly approaches as well as economic feasibility. This can lead to a circular economy (Awasthi et al., 2019). Almost 40.7% of electronic waste was estimated from 49 Asian counties, approximately 4.2 kg per inhabitant (Balde et al., 2017).

Electrical and electronic products are usually discarded in landfills after usage becoming electronic waste (e-waste) (Balde et al., 2017). Fig. 2 shows the six categories in which electronic waste can be classified. According to the United Nations Organization (UNO) agenda for the near future year, of the 2030 Sustainable Development Goals, three are mostly affected by electronic waste; goal 3: good health and well-being, goal 6: clean water and sanitation, and goal 14: life below water (Balde et al., 2017). Research and development activities on electronic waste still need to improve and make it economically feasible and environmentally sound. Moreover, recycling policies should be implemented globally (Ogunseitan et al., 2009).

Electronic waste not only includes precious and rare earth metals but toxic elements such as arsenic, chromium, and mercury as well (Wang et al., 2016). These toxic metals are the main cause of damages to the environment as well as the ill effects on human health when electronic waste is not handled properly after usage.

Various reviews and reports reveal the necessity of new routes and economically as well as environmentally sound solutions for rare earth processing from ores and secondary resources (Cui and Forssberg, 2003; Jha et al., 2016; Reddy and Kumar, 2016; Kumari et al., 2015a, 2015b, 2019; Kumari et al., 2019a,b; Panda et al., 2014; Kim et al., 2013, 2015; Kumar et al., 2014; Koen et al., 2013a, 2013b, 2013c). The purpose of this review is to examine successful rare earth recycling processes developed until now for the comprehensive rare earth metals extraction routed through hydrometallurgical methods in light of environmental issues. The present review article also considers the role of REE in clean and green technologies alongside the opportunity they present to create wealth from waste.

2. Methodologies adopted for the processing of rare earth elements (REEs) from secondary waste

Hydrometallurgical approaches used to process secondary wastes bearing REEs have a number of advantages over other energy-intensive extraction processes like pyro-metallurgical methods. Hydro-processes include low production costs, low waste generation, less liberation of noxious gases (SOx, NOx, CO_2, and CO) to prevent environmental pollution. Moreover, the clean separation and recovery of a pure form of metal and/or metal compounds results in hydrometallurgical processing routes. In hydrometallurgical studies, initially, the secondary phases are subjected to chemical leaching and, later on in the second stage, the resulting leached solution is purified through several separation techniques such as solvent extraction (Das et al., 2018), liquid membrane separation (Parhi et al., 2019), adsorption (Iftekhar et al., 2018), ion exchange (Lopez et al., 2019), separation, and/or precipitation (Li et al., 2019).

For most rare earth elements, leaching processing operations followed by solvent extractions are commonly practiced. These methods have undergone extensive studies by researchers (Parhi et al., 2013, 2016; Tunsu et al., 2019; Innocenzi et al., 2018; Jyothi et al., 2020).

During leaching, operation parameters such as temperature, agitation speed, time, solid to liquid ratio (S/L), particle size, and lixiviant type (acids, alkalis, and salts) are varied to obtain a suitable optimum condition. In the solvent extraction process, factors, namely, the effect of pH (equilibrium), acidity/alkalinity of a solution, phase ratio, temperature, phase contact time, diluents effect, and salt effect, are varied to attain suitable conditions based on which extraction, as well as the stripping isotherm which was proved with counter-current simulation studies, are implemented and reported (Ritcey and Ashbrook, 1984).

Overall, through leaching followed by the solvent extraction route, the major concern in terms of metal extraction behavior, metal extraction yield, and effective separation perspective are essentially resolved. Some of the research and development mechanisms in this context are summarized in the following section.

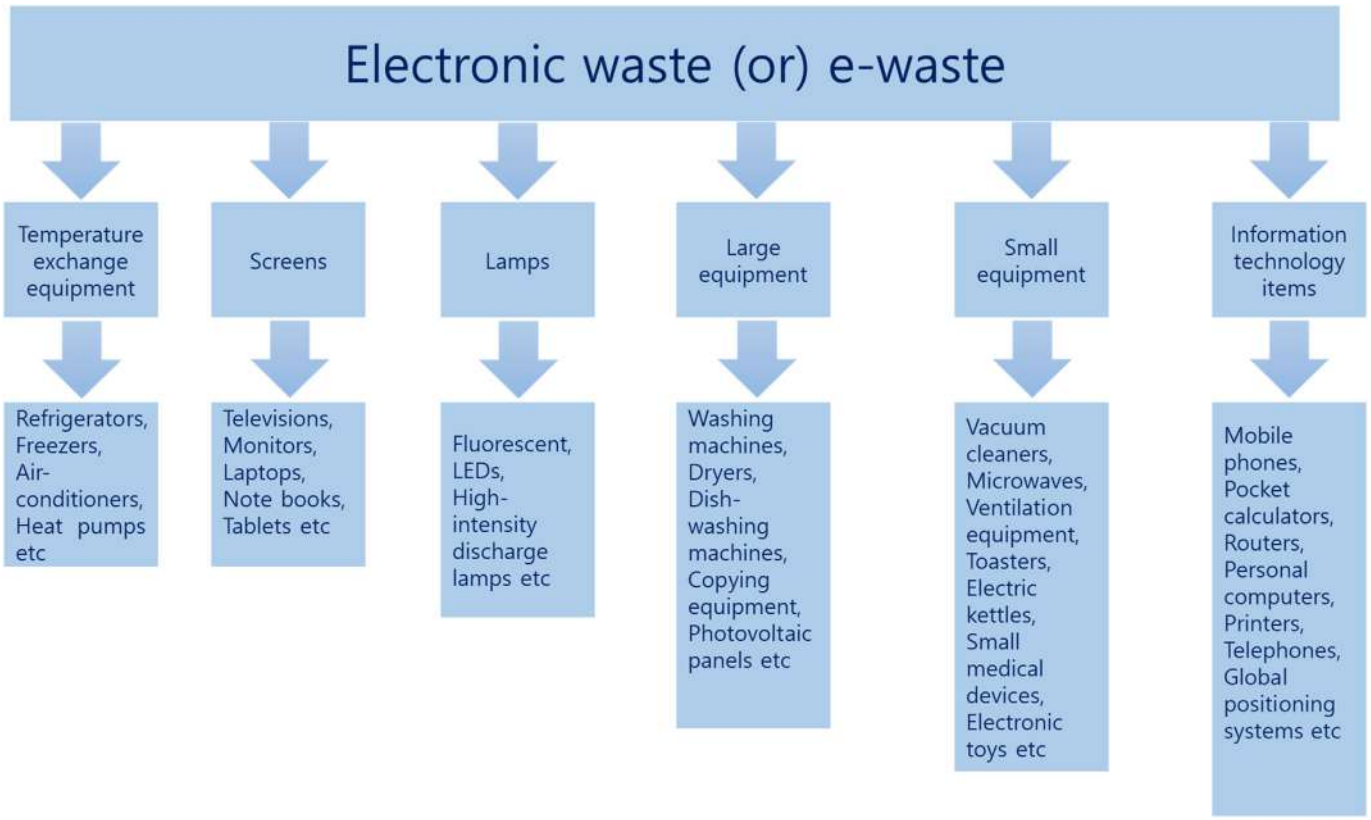

Fig. 2. Categories of the electronic waste (e-waste) as per The Global E-waste Monitor 2017 (Adapted, modified, and reproduced from reference Balde et al., 2017).

For metal recovery, the most prominent process is hydrometallurgy (the aqueous processing of the metals from primary and secondary resources). The total areas and concepts related to hydrometallurgy were classified by the AJ Parker Cooperative Research Centre, Australia (Mooiman et al., 2005). Hydrometallurgy research areas and the total description were briefly described in Fig. 3 (Mooiman et al., 2005; Habashi, 1980).

The first step in hydrometallurgical processing is the leaching (dissolution) of concern acid/base reagents to rare earth based materials. Leaching of the REEs from various secondary sources was summarized and presented in Table 2. One study deeply, which examined the dissolution of rare earth oxides by using sulfuric acid and converted it to the focus rare earth sulfates, can be represented by the following equations (1) and (2) (Namil and Tetsuji, 2013):

$$RE_2O_3 + n\ H^+ = n\ RE^{3+} + n\ H_2O \quad (1)$$

$$nRE^{3+} + n\ SO_4^{2-} + n\ H_2O = RE_2(SO_4)_n.nH_2O \quad (2)$$

The other mineral acid, hydrochloric acid, also one of the most powerful reagents for REE leaching processes from primary (or) secondary resources; the reaction between HCl and rare earth oxides (REOs) are described by the follows equation (3) (Tom et al., 2014):

$$RE_2O_3 + n\ HCl = n\ RECl_3 + n\ H_2O \quad (3)$$

Recently, ionic liquids are also being utilized as leaching reagents; e.g. beta-inium-bis(trifluoromethylsulfonyl)imide [Hbet][Tf_2N] ionic liquid is used for NdFeB magnet leaching, proving to be fit for dissolved rare earth oxides by the following equation (4) (David and Koen, 2015a):

$$RE_2O_3 + n\ [Hbet][Tf_2N] = n\ [RE(bet)_n][Tf_2N] + n\ H_2O \quad (4)$$

RE = La (or) Nd (or) Pr, etc. n = numerical value in equations (1)–(3), or 4.

Various hydrometallurgical procedures (Fig. 4), including solvent extraction (liquid-liquid extraction); solid-liquid extraction, adsorption, supported liquid membrane, ion-exchange, super-critical extraction methods, etc., were utilized for rare earth recovery. Several types of extractants applied for REEs separation studies was summarized in Table 3. From permanent magnets (for example containing REEs such as Dy, Nd, Pr, and Tb); waste from electric arc furnaces (for example containing REEs such as Ce, La); residues from industries, namely red mud and phosphogypsum contain rare earths. Other end-of-life (EOL) products, in particular, fluorescent lamps (for example containing REEs such as Eu, Tb, or Y lamps), LEDs (for example containing REEs such as Ce or Y), LCD backlights (for example containing REEs such as Eu, Tb, or Y), plasma screens (e.g. Eu, Tb, or Y), and cathode-ray tubes (for example containing REEs such as Eu or Y) also have REEs (Koen et al., 2013a, 2013b, 2013c).

In addition, electrical and electronics-based equipment (EEE) such as computers, mobile phones, hard disks, wind turbine generators, and even electric bicycles contain mostly neodymium, dysprosium, terbium, and praseodymium REEs as permanent magnets. The aforementioned industrial production manufacturing generates certain types of waste at the time of manufacturing; after usage, rare-earth-based materials become scrap. Hydrometallurgical techniques are key processes, easy to handle and economically feasible methods for the recovery of the rare earths from this type of scrap or wastes.

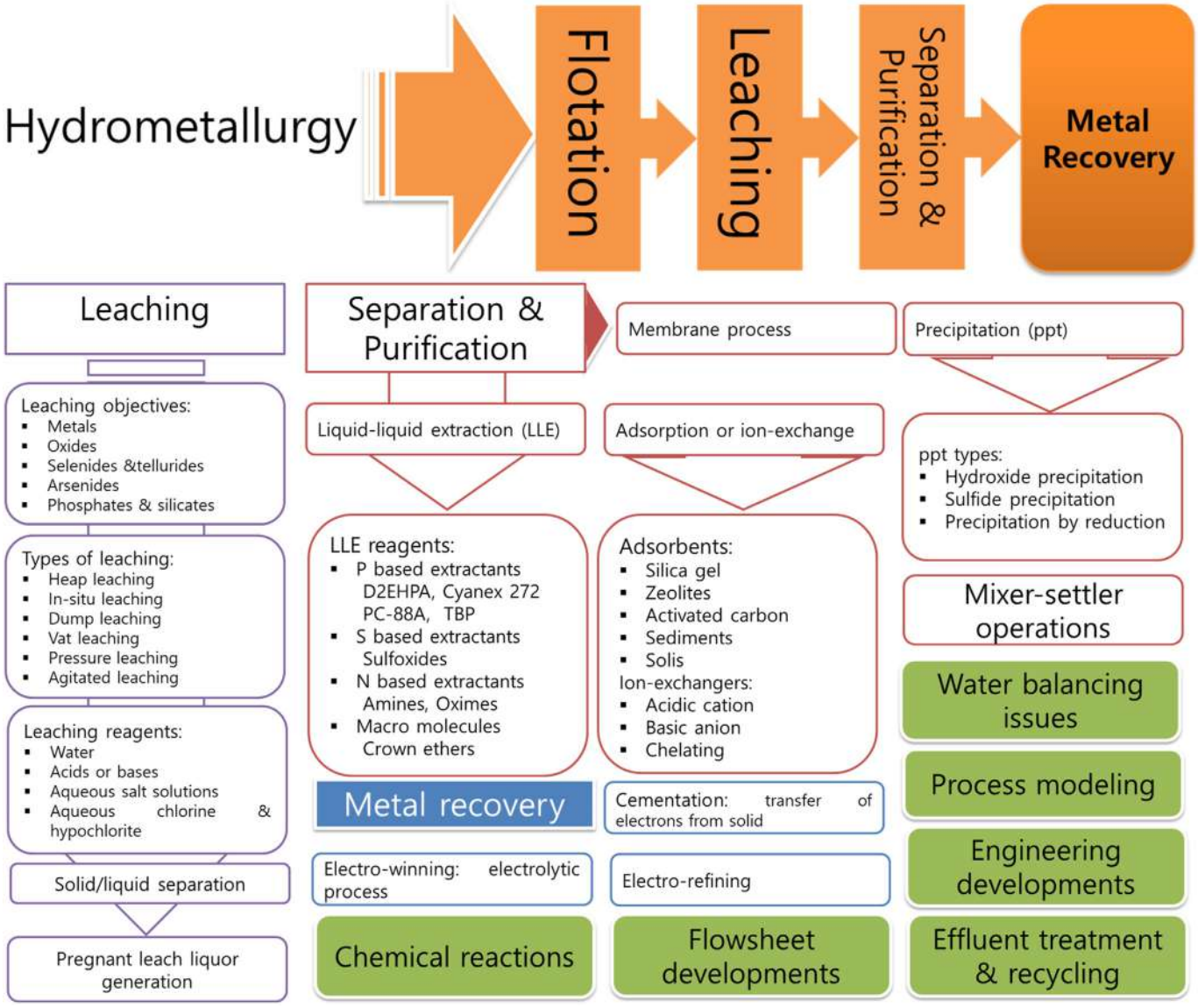

Fig. 3. Hydrometallurgy: aqueous processing of the metals, the role in REEs processing (Adapted, modified, and reproduced from reference Mooiman et al., 2005; Habashi, 1980).

3. Processes adopted for the treatment of secondary wastes

3.1. Spent NiMH battery processing for rare earth elements (REEs)

Spent nickel-metal-hydride batteries are processed using adsorbents (synthesized) for the recovery of REEs (Gasser and Aly, 2013). The detailed hydrometallurgical process is summarized in Fig. 5(a). In this process, researchers have used 2.25 g/L of $RECl_3$ (60% Nd and 40% La) for the substantial separation and recovery of Nd_2O_3 and $LaCl_3$. The key step adopted in this process is the usage of 0.1 g of LDH-Cyanex 272 for 10 mL of $RECl_3$ solution. Then, the resulted aliquot is processed for the separation of $LaCl_3$ using diluted HCl (0.01 mol/L). Subsequently, the filtrate solution is subjected to the recovery of Nd_2O_3 by oxalic acid.

The recovery of base metals (Ni, and Co) and REEs from spent NiMH batteries by hydrometallurgical methods is also reported (Fig. 5(b)). This investigation deals with a two-stage extraction, the first route for REE recovery after the sulfuric acid leaching process. During leaching, spent batteries are treated with NaOH followed by acid dissolution (1 mol/L HCl) to obtain $RECl_3$ concentrate. In the second stage, the leached solution is processed for base-metal separation using Cyanex 272. From the second stage operation, enriched strip rare-earth liquor is looped with the first stage to enrich the REE concentration (Li et al., 2009).

In another study, a similar type of NiMH batteries were leached using sulfuric acid (2 mol/L) with an S/L ratio of 1/10 at 20 °C and leaching time 2 h (Pietrelli et al., 2002). The leach solution containing 2.25 g/L of REEs and 12.4 g/L of nickel as well as minor quantities of Co, Fe, Mn, and Zn. Thus, from the mixture, total rare earth elements were precipitated with sodium hydroxide at a pH < 1.5.

Using H_2O_2 as a reductant in the leaching process with 1 mol/L sulfuric acid, spent NiMH batteries are leached with an S/L ratio of 1/20 and overall 2 days of leaching. The leached solution results contain 5.15 g/L REEs with a high content of nickel (19 g/L) and other elements such as iron (2 g/L) and cobalt (1.2 g/L). This solution was then processed by solvent extraction using N1923 (primary amine) as the extractant (Yun et al., 2015). The experimental study was optimized to attain a maximum extraction capacity using an extractant concentration of 10% N1923 + 4% ISD (iso-decanol),

Table 2
Summary of reported literature on leaching of rare earths from various secondary resources.

Rare earths	Source of material	Leaching reagent	Remarks	References
Y, Eu, Tb, Ce	Red rare earth phosphors	HCl	It's a dual dissolution by hydrochloric acid (DHA). The total REEs are leached up to 94.6%	Liu et al. (2014)
Y, Eu, La, Gd, Tb, Ce, Dy, Nd	End-of-life fluorescent lamps	Acetic acid (CH_3COOH), Glyconic acid ($C_6H_{12}O_7$), HNO_3, HCl	In a first stage of leaching process targeted to remove the calcium by using low acidic concentration (1 mol/L) and pure water. 1 mol/L of HCl can able to remove the ~100% of Ca within 10 min leaching time. With higher acid concentration (2 mol/L of HCl or HNO_3) utilized.	Pavon et al. (2019)
Tb, Eu, Y, Ce	Real waste trichromatic phosphors containing glass	HCl and NaOH	94% of the leaching of total REEs (Y-96%, Eu-99%, Ce-81%, and Tb-92%) done by this method.	Liu et al. (2019)
La, Ce, Sc, Y	Bauxite residue	HCl, HNO_3, H_2SO_4, H_3PO_4	Leaching efficiencies: Sc_2O_3-77% and Y_2O_3-35% with 4.0 mol/L of HNO_3 Sc_2O_3-55% and Y_2O_3-27% with 4.0 mol/L of H_3PO_4	Deng et al. (2019)
Nd	Magnets of hard disk drives	Malic and citric acids	Demagnetization did at 350 °C for 30 min time. 99% of Nd leached from unroasted sample with 1.0 mol/L malonic acid at 90 °C temperature S/L ratio was 1:20.	Reisdörfer et al. (2019)
Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	Middling's and coarse refuse material associated with a bituminous coal source	HCl	Calcination at 600 °C meaningfully and favorably improved rare earths recovery. REEs about 15–25% were leachable by ion exchange leaching using 0.1 mol/L ammonium sulfate at pH 5.0	Zhang and Honaker (2019)
Y, La, Ce, Eu, Tb, Gd	Lamp phosphor waste	HCl, H_2SO_4	First leaching done by H2SO4 and Y, Eu, Gd were effectively leached then followed by 2nd leaning with any mineral acid such as HCl or H2SO4, the leach liquor contained Ce, La and Tb were successfully leached.	Yurramendi et al. (2019)
La, Ce, Nd, Pr, Sm, Gd, Eu, Tb, Dy, Er, Ho, Yb, Lu, Sc, Y	Indian coal bottom ash	HCl, HNO_3, H_2SO_4, $FeCl_3$	4.0 mol/L of HCl was able to dissolve the REEs at 90 °C, within 2 h time of 50 g/L of pulp density	Kumari et al. (2019)
Y, Eu	Phosphorescent powders waste	HCl combines with H_2O_2	99% of Y and 61% of Eu were leached by using following experimental conditions: 1 mol/L of HCl, at 50 °C temperature, 4 h time, 2 mL of the H_2O_2	Wu et al. (2019)
Y, Eu, Sm, Ce	Waste cathode ray tube (CRT) phosphor	Sodium citrate, sodium pyrophosphate	Roasting process was done at 800 °C with concentrated NaOH, it will have ensued 79% of Zn was removed. After that, leaching experiment resulted high efficiency of REEs: Y-58%, Eu-90%, Sm-90% and Ce-87% with pyrophosphate solution	Alvarado-Hernández et al. (2019)
Sc, La, Ce	Bauxite residue (red mud)	H_2SO_4	Optimized leaching conditions: leaching time, 2 h, Solid: Liquid ratio is 1:10 and Acid: 2.0 mol of H_2SO_4	Singh et al. (2019)
Y, La, Ce, Pr, Nd	Coal fly ash (CFA)	HCl	The total amount of the REEs are in CFA was 494.76 mg/kg and 86.8% of the REEs are leached.	Tang et al. (2019)
La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y	Phosphogypsum (PG)	H_2SO_4 and HNO_3	By using H_2SO_4 leaching time in between 2 and 8 h maximum leached the 60–62% of Yb, Lu, Y whereas other REEs are leached 33–55%. On the other hand by using HNO_3 leaching time in between 2 and 8 h maximum leached the 81–90% of almost all REEs except Ce (61–65% leached)	Canovas et al. (2019)
Y, Nd, Dy	CFBC Bottom Ash	HCl	13.6 mg/kg of Y, 10.9 mg/kg of Nd, 2.07 of mg/kg of Dy was leached with 1–3 mol/L of HCl up to 62% of Y, 55.5% of Nd and 65.2% of Dy at high temperature 80 °C with 12 h leaching time	Tuan et al. (2019)
La and Ce	Spent asymmetric-capacitance power batteries	H_2SO_4, Citric acid, Acetic acid, Malic acid	With H_2SO_4 99% of La and Ce was leached at 90 °C temperature with 90 min leaching time for 20 g of solid sample. H_2O_2 (4 mL/L) was used as a reductant and liquid/solid ratio was 9:1.	Zhang et al. (2019)
Nd, Dy, Tb, Pr	Spent FeNdB Magnets	Acetic buffer	First step applied the buffer leaching to prevent the Fe precipitation: $Fe + n\ CH_3COOH = Fe(CH_3COO)_n + H_2$ $RE + n\ CH_3COOH = RE(CH_3COO)_n + n/2\ H_2$ $n\ Fe^{2+} + n\ RE = n\ Fe + n\ RE^{3+}$	Lorenz and Bertau (2019)
Y and Eu	Waste cathode ray tube phosphors	H_2SO_4	With the 3 mol/L of acid (H_2SO_4) concentration, in presence of 4 vol % of H_2O_2 at 55 °C temperature and 90 min leaching time was applied to leached 99% of the REEs such as Y and Eu.	Yin et al. (2018)

loading 7.41 g/L of REEs. For stripping 2.5 mol/L of hydrochloric acid was used to ensure a 99.5% stripping of REEs in a single stage (Yun et al., 2015). Based on this data, researchers have operated pilot plant test studies over 30 days and in which mixtures of 10% of N1923 and 4% of ISD showed a good combination for phase separation. The optimum conditions, namely, a phase ratio (A/O) of 1.5 and stripping reagent concentration of 2.0 mol/L HCl, yield good separation behavior. This study successfully operated and achieved a 99.9% rare earth extraction, >99.9% Ni (or) Co, and 95.5% of Fe removal from the LO phase. The final products resulted in rare earth-oxalates with ~99.7% (Yun et al., 2015).

3.2. Coal ash processing for rare earth elements (REEs)

Globally six nations are have major coal resources the USA possess the majority of resources (24.5%), Russian Federation (15.2%), Australia (14%), China (13.2%), India (9.6%), Indonesia (3.5%), Kazakhstan (2.4%), total middle East and Africa (1.4%), total South and Central America (1.3%), total Europe (12.8%) (BP Statistical Review of World Energy, 2019). Global statistics of coal reserves and consumptions from year 2018 (recent available data) was presented in Figs. 6 and 7 (BP Statistical Review of World Energy, 2019).

World electricity generation depends on various resources, coal being one of the main. From energy source predictions from year 2010 to year 2040, coal will be one of the highest depended-on resources for electricity in the near future (U.S. Energy Information Administration, 2013). The byproduct of these power plant sectors results in an abundant amount of coal ash, which is a very good secondary recourse for REEs. For example, Russian Far East deposits contain 300–1000 mg/L of REEs in coal (thickness 10 m) (Seredin, 1996).

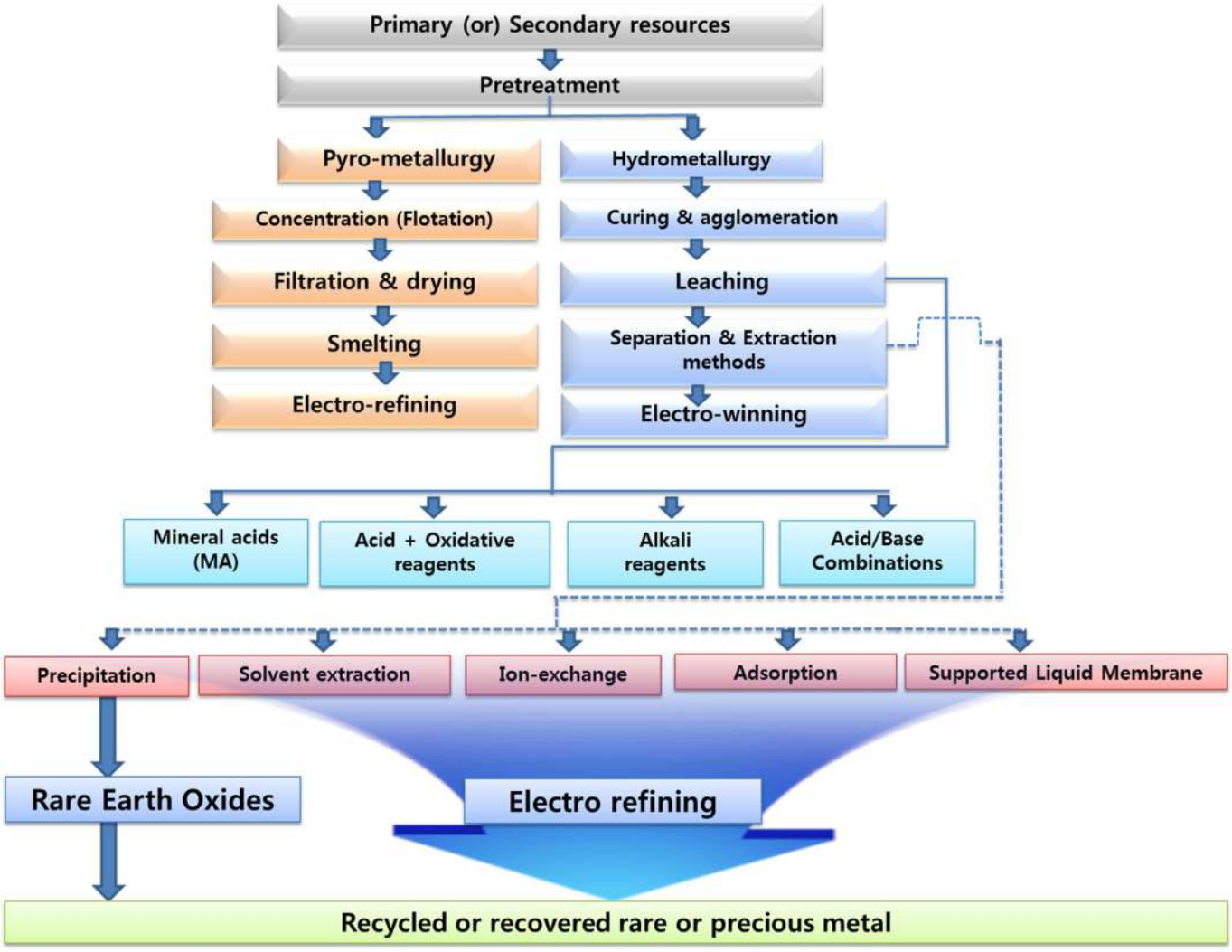

Fig. 4. The role of hydrometallurgical techniques for the processing of REEs (or) precious metals.

Table 3
Summary of reported literature of extractants used in REE extraction and separation studies.

Rare earths	Name of the extractant	References
Pr, Nd and Dy	Tri-ethyl-pentyl-phosphonium bis(trifluoromethyl-sulfonyl)amide ([P2225][TFSA]),	Matsumiya et al. (2014b)
Nd	Tri-hexyl(tetradecyl)phosphonium benzoate [T66614][BA] and trihexyl(tetradecyl) phosphoniumbis(trifluoromethylsulfonyl)imide [T66614][TFSA]	Panigrahi et al. (2016)
Sc, Y, La	$[(CH_2)_nCOOHmim][Tf_2N]$ (n = 3, 5, 7)	Chen et al. (2017)
Y (III)	HNO_3-Cyphos IL 104	Liu et al. (2010)
Sc, Al, Fe	Beta-inium-bis(trifluoromethylsulfonyl)imide, [Hbet][Tf2N]	Onghena et al. (2017)
Sc (III)	R_4ND	Parhi et al. (2019)
Sc (III)	D2EHPA, Cyanex 272	Das et al. (2018)
Nd and Pr	Na-D2EHPA	Parhi et al. (2016)
Total REEs (mostly 4f elements)	D2EHPA	Parhi et al. (2015)

Korean total primary energy consumption depends by ~31% on coal and coal imports from various countries like Australia, Canada, the USA, Russia, China, and Indonesia (Source: Korea Customs and Trade Development Institution and Korea Energy Economics Institute). The imported coal samples are utilized for power plants in South Korea.

REE recovery from coal power plant ash solutions was successfully achieved by leaching and biosorption. In a study, over three days of coal power fly samples (DK-TOP) were kept under 70 °C prior to a leaching investigation. The grained DK-TOP sample was reduced to a particle size of 315 μm then leached using HCl. The hydrochloric acid concentration was changed from 0.25 to 10 mol/L. It was observed that REEs such as Er, La, Pr, Ce, and Y were dissolved together with base metals (Li, Fe, Cu, and Al) (Ponou et al., 2016).

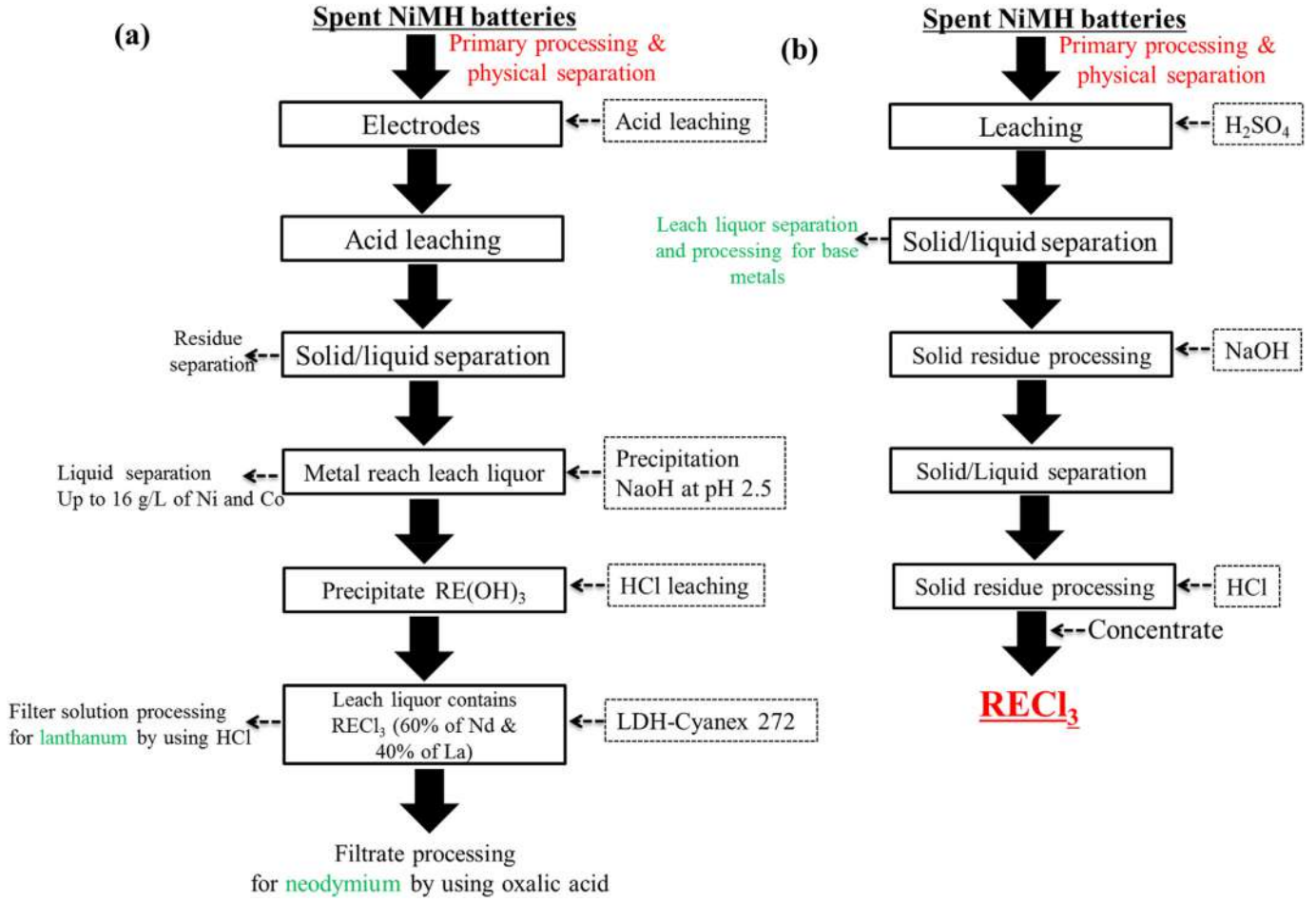

Fig. 5. Separation and recovery of the REEs from spent nickel-metal-hydride batteries (Adapted, modified, and reproduced from references (a) Gasser and Aly, 2013; (b) Li et al., 2009).

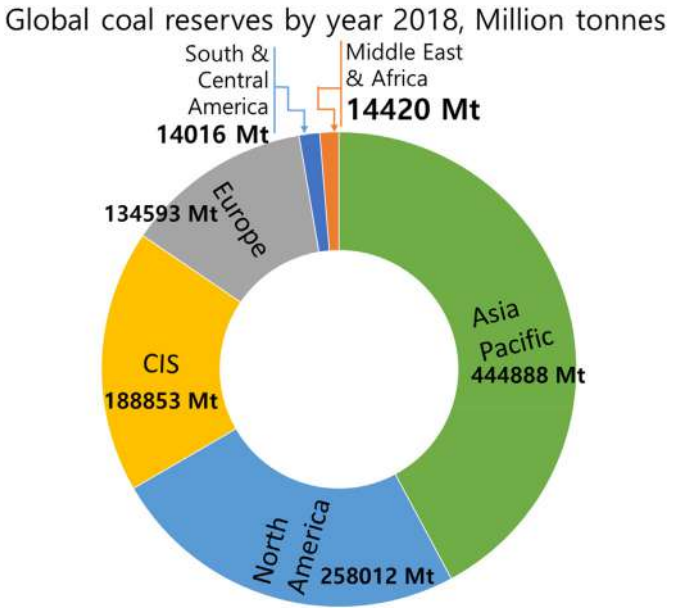

Fig. 6. Global coal reserves by year 2018, Million tonnes (Mt), (Data adapted from BP Statistical Review of World Energy, 2019).

The DK-TOP leached liquor was further treated with a bio-sorbent such as carbonized ginkgo leaves (GL450). Biosorption processes carried out at a pH range of 1–9 and optimized pH values found that 3 is advantageous for Er and 5 for La and Ce; whereas the entire study ranges of Y and Pr did not uptake. The co-adsorbed copper was removed by the desorption process with 1 mol/L HCl up to a 35.5% removal of Cu with zero loss of Ce and La (Ponou et al., 2016).

3.3. Spent fluorescent lamp processing for rare earth elements (REEs)

Five varieties of rare-earth-based phosphors are involved in fluorescent lamp manufacturing namely, red phosphor (Y_2O_3:Eu^{3+}), green phosphor ($LaPO_4$:Ce^{3+},Tb^{3+}, $GdMgB_5O_{10}$:Ce^{3+},Tb^{3+},(Ce, Tb)$MgAl_{11}O_{19}$), and blue phosphor ($BaMgAl_{10}O_{17}$:Eu^{2+}) (Ronda et al., 1998; Justel et al., 1998; Koen and Jones, 2014). Among the aforementioned phosphors Y_2O_3: Eu^{3+} has the highest intrinsic value.

Two light REEs, namely, europium and yttrium, can be recovered from spent fluorescent lamps by hydrometallurgical methods. The flowsheet developed as a part of this study is presented in Fig. 8(a). Spent fluorescent lamps (SFL) contain 1.65 wt% of yttrium oxide, 1.62 wt% of europium oxide, and other calcium products, with 61.52 wt% of orthophosphate and 34.48 wt% of calcium sulfate (Mahmoud, 2008). Two mineral acids, sulfuric acid, and nitric acid

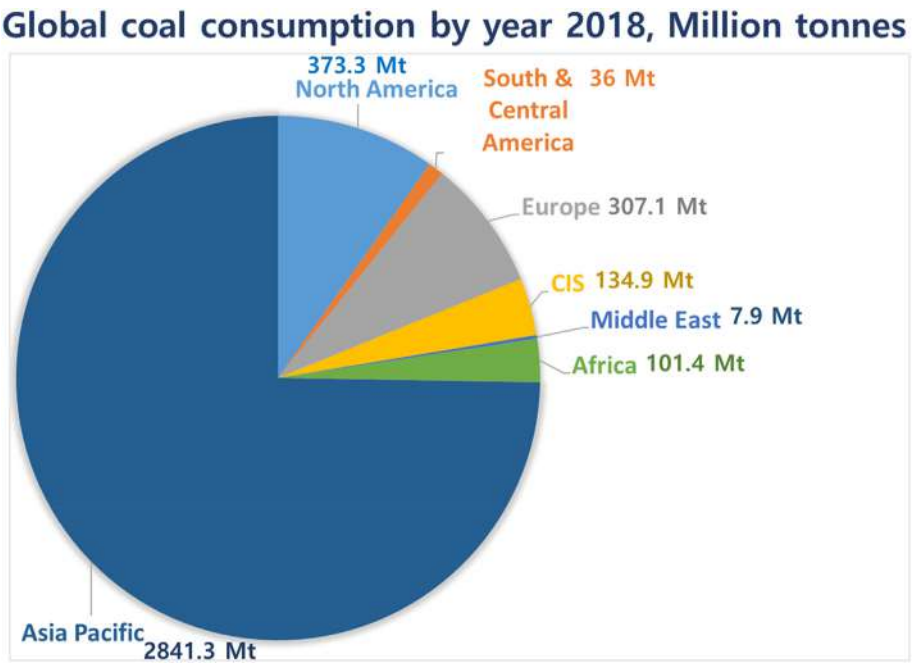

Fig. 7. Global coal consumption from year 2018, Million tonnes (Mt), (Data adapted from BP Statistical Review of World Energy, 2019).

are employed in an SFL leaching process with testing times of 0–12 h at 60 °C, with an acidity from 1 to 4 mol dm^{-3}. Less than 18.5% leaching efficiency was obtained, therefore, to improve the efficiency, 5 Mpa of pressure was applied with an increase in temperatures up to 125 °C. This led to an enhanced leaching efficiency exceeding 90% for both REEs (Y and Eu). Another method involved a pregnant leached liquor treatment with thiocyanate followed by solvent extraction using tri-methyl-benzyl-ammonium chloride. For stripping of the LO, nitric acid had a successful recovery rate of rare earths (Mahmoud, 2008).

Fluorescent lamp phosphor waste fractions having ~18% of REEs are processed for rare earth recovery using a hydrometallurgical process (Cristian et al., 2016). In this developed methodology, the first step is employed for a removal study consisting of two steps. Initially, this is a thermal treatment where ~99.99% impurities are removed and as much as 95% of mercury is separated. Furthermore, nitric acid was used to enable the leaching of REEs. In the first step, >90% of calcium was separated with a ~4% of REEs recovery. Again, a second leaching process was conducted for 24 h with 2 mol dm^{-3} using nitric acid to yield an enriched yttrium with europium concentrate. Finally, to separate yttrium and europium, a solvent extraction process was adopted as shown in Fig. 8(b) (Cristian et al., 2016).

To recycle rare earth metals from lamp phosphor waste a green solvent-based ionic liquid technology was developed and the authors reported the usefulness of the ionic liquid betainiumbis(trifluoro-methyl-sulfonyl) imide, [Hbet][Tf_2N] for rare earth recovery from various lamp phosphor waste types at 90 °C with a reaction time of 24 h. More than 80% of the REEs were recovered by this method (David and Koen, 2015b).

Another hydrometallurgical route was examined and reported for rare earth recovery from phosphor powders generated by fluorescent lamp waste (Fan et al., 2013). In that study, researchers applied two methods, a nitric acid and sulfuric acid leaching process, followed by liquid-liquid extraction mediated by an ionic liquid. From the sulfuric acid process, leach liquors of yttrium and europium were recovered, whereas the nitric acid leach liquor could recover lanthanum, cerium, terbium, and promethium in an acid stripping process (Fan et al., 2013).

REEs have been recovered from fluorescent lamp waste using a leaching process (Cristian et al., 2014). Three types of phosphors were tested, i.e. red, blue, and green, with a variety of REEs. In the first step, 25% (v/v) acetic acid was used for leaching and, thereafter, aqua regia was used to dissolve the obtained residue at 90 °C. In this methodology, researchers applied an ultrasound wave (UW) during the nitric acid leaching step to improve the leaching efficiency (Cristian et al., 2014).

Yttrium was leached from cathode ray tubes (CRTs) using 2 mol dm^{-3} of sulfuric acid for 3h at 70 °C, which was found as a suitable condition to achieve 99.99% metal leaching (Innocenzi et al., 2013). Substantial yttrium content was recovered by a precipitation method at a pH of 2.5; from these results, Y was precipitated up to 95% from CRTs (Innocenzi et al., 2013).

Bifunctional ionic liquid (Bif-IL) have been utilized for rare earth extraction using simulated fluorescent powder leach solutions. Chinese manufactured phosphorus-based extractants such as P204 (equivalent to D2EHPA) and P507 (equivalent to PC88A) interacted with Aliquat 336 to form Bif-ILs; these ILs were implemented for the extraction of 0.22 mol/L of REEs(III) from simulated waste fluorescent powder at a pH of 0.56. For the REE(III) loaded organic phase of Bif-ILs treated with >0.02 mol/L of nitric acid, complete rare earth back extraction was possible (Yang et al., 2012).

A two-step acid leaching process was developed for rare earth waste containing fluorescent powders. The developed flowsheet was presented (Zhang et al., 2013) in Fig. 9. Waste fluorescent powder containing various rare earth oxides (RE_nO_m, where RE = Y, Ce, Tb, Eu; n, m = numerical values) was associated with MgO, SO_3, ZnO, SiO_2, CaO, Fe_2O_3, and BaO. The first step of the two-step hydrochloric acid leaching resulted in a rich Y (95.6%) and Eu (96.3%) leach liquor with minor quantities of 8.1% of Ce and 9.8% of Tb. After first-stage acid leaching, the leach residue obtained was treated with alkali fusion at a high temperate (~800 °C) with NaOH for 2 h. After proper water washing was applied, 2nd stage acid leaching was performed to yield ~90.1% of Ce and ~88.3% of Tb leaching with ~1% of Eu and ~3.4% of Y (Zhang et al., 2013).

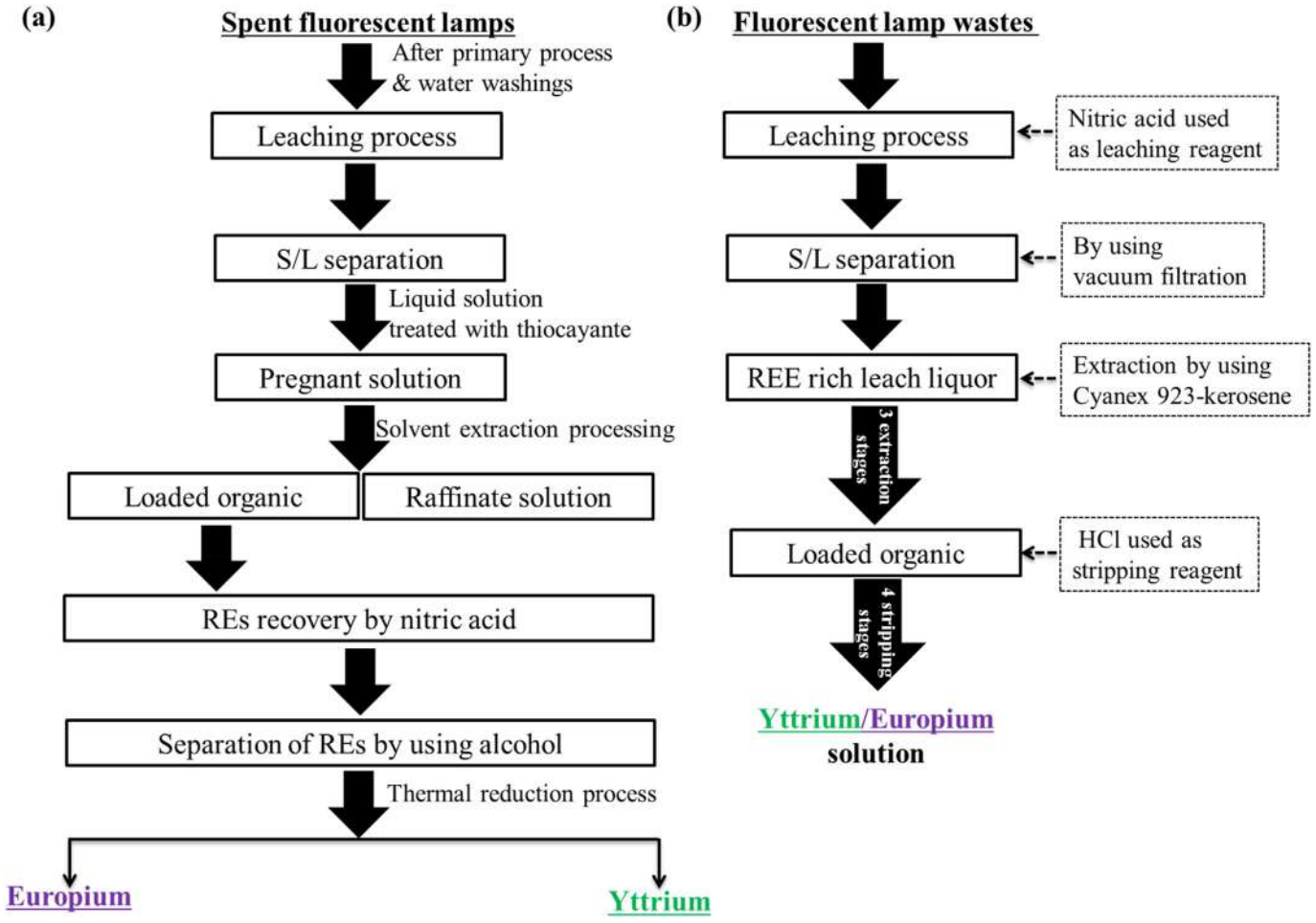

Fig. 8. Hydrometallurgical recovery of REEs fluorescent lamp wastes (Adapted, modified, and reproduced from references (a) Mahmoud, 2008; (b) Cristian et al., 2016).

3.4. Phosphogypsum processing for rare earth elements (REEs)

The recovery of REEs from phosphogypsum was reviewed. In a study, the usage of a high acid amount for the leaching of yttrium fluorite at a temperature of 100 °C and leaching time of 2 h was studied (Kinga et al., 2015). The leached liquor result contained REEs with other rare metals (Nb, Ta, Ti, Th, and U). This liquor was processed by a liquid-liquid extraction method using di-(2-ethylhexyl)phosphoric acid (DEHPA) using kerosene as solvent. Uranium and thorium were extracted and stripped by sodium carbonate and ammonium fluoride, after which, the extracted raffinate solutions were processed further by precipitation to prepare a rare earth oxide material (Kinga et al., 2015).

REEs were recovered from apatite phosphogypsum using two hydrometallurgical routes: leaching and solvent extraction (Jarosinski et al., 1993). In the 1st stage, sulfuric acid leaching was carried out by generating leached liquor to bear 1–2 kg/m^3 of RE_2O_3 and ~0.5% of P_2O_5. A solvent extraction investigation was then carried out using nonyl-phenyl-phosphoric acid (NPPA) and the re-extraction of REEs was reported using a high acid condition (8 mol dm^{-3} of H_2SO_4). After crystallization, the RE_2O_3 content was obtained at a rate of approximately 40% (Jarosinski et al., 1993).

3.5. Spent permanent magnet processing for rare earth elements (REEs)

Spent permanent magnets (PMs) are the most common secondary source type of REEs. Almost all electrical goods have PMs that are sources of the two key LREE elements dysprosium and neodymium. The membrane-assisted liquid-liquid extraction was established and the selective extraction of Nd, Dy, and Pr from PMs was reported (Daejin et al., 2015). Tetraoctyldiglycolamide (TODGA) and trialkyl phosphine oxide (Cyanex 923) (neutral extrantacts), were employed as solvent extractants. Other organic-phase solvents used in that study were tri-butyl phosphate (TBP) and Isopar L (used as a diluent system) for the selective extraction of REEs. In this study, further diluted nitric acid was applied for the back extraction of the loaded metals (Fig. 10) (Daejin et al., 2015).

The separation process was used for dysprosium (Dy) and neodymium (Nd) from a permanent-magnet scrap leached solution and reported (Yoon et al., 2015a, 2015b). Initially, pretreatment procedures such as an oxidation roasting process followed by acid leaching were applied to permanent-magnet scrap to obtain Dy-Nd-containing leached liquor. At the time of the leaching process, the researchers controlled the maximum iron. For each experiment, the desired pH levels were individually adjusted and dilution process was used to vary the metal concentration in the samples. The approximate metal concentration overall was ~1500–1700 ± 20 mg/L Dy and ~6900 to 7800 ± 30 mg/L Nd. All of the vital steps followed for this study are presented (Yoon et al., 2015a, 2015b) as a single flow chart (Fig. 11).

Several primary steps were used for the dissolution of permanent magnet scrap, holding the iron interference level at approximately 55.9% for 60–70 mg/L (negligible amount). The additional solvent extraction process was carried out using two P-based extractants. This study involved the two organo-phosphorous

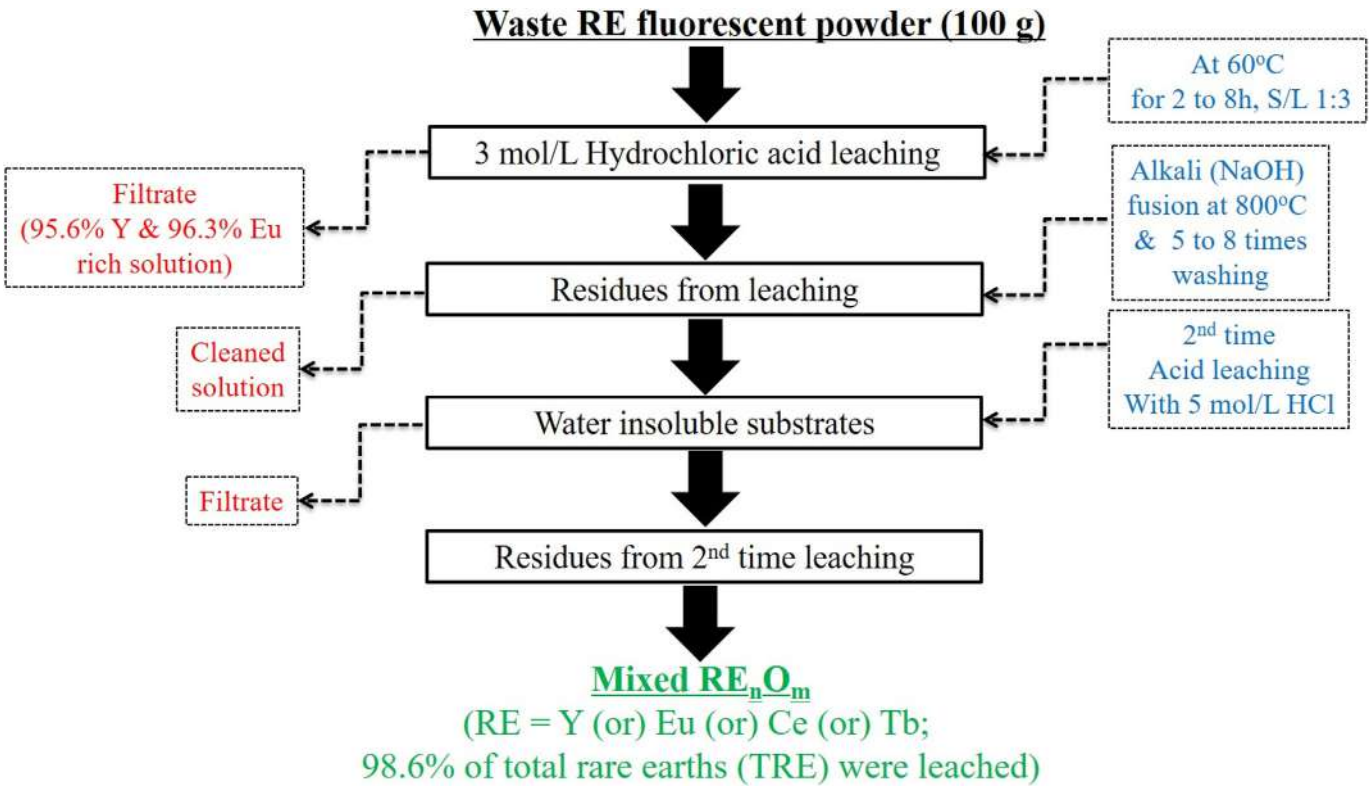

Fig. 9. Two steps acid leaching process for waste REEs containing waste fluorescent powders (Adapted, modified, and reproduced from reference Zhang et al., 2013).

extractants of D2EHPA and PC 88A. Both extractants were loaded onto dysprosium at a level of nearly ~2.3 g/L, however, D2EHPA co-extracted neodymium at a rate as high as 2.5 g/L. This may require extra processing steps such as scrubbing and selective stripping;

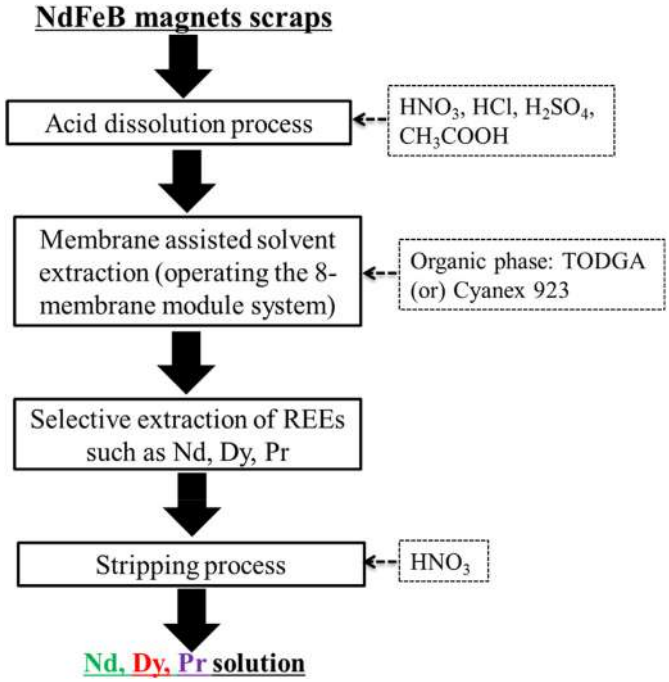

Fig. 10. Hydrometallurgical route for recovery of REEs from NdFeB magnet scraps (Adapted, modified, and reproduced from references Daejin et al., 2015).

whereas, in the case of PC 88A, the direct stripping of the loaded dysprosium with a very negligible loss of dysprosium metal is possible. As shown in Fig. 12, saturation loading of Dy was attained after four contacts resulting in a maximum loading of ~3473 mg dm^{-3}, requiring eight contacts to yield a maximum loading amount of 2481 mg dm^{-3} Nd with 0.1 mol/L D2EHPA. In another case, values above 4200 mg/L Dy and 1375 mg/L Nd with 0.1 mol/L PC 88A were reached (Yoon et al., 2015a, 2015b).

Generally, it is difficult to attain a very high separation factor for Dy and Nd because of their similar chemical properties. However, an attempt was made to improve the separation factor (SF) using D2EHPA and PC88A at varying pH levels of the solution. As can be seen from the results of Fig. 13, the SF value increased from 11 to 247 while changing the pH of the solution from more acidic to mildly acidic ranges (Yoon et al., 2015a, 2015b).

Cobalt-based magnet scraps were examined and established the process for REEs recovery through leaching followed by precipitation route (Tao et al., 2010). The high content of cobalt (49.8 wt %) magnetic scrap containing REEs such as 21.62 wt% of Sm, 4.34 wt% of Gd, as well as 16.04 wt% of iron was associated with the magnet phase. Sulfuric acid has been used as a suitable lixiviant for leaching. The results show that 88.5% of Sm, 95.4% of Co, 94.4% of Fe, and 85.2% of Gd extractions were obtained. The leached cobalt and iron were precipitated using $Na_2S_2O_8$ (sodium persulfate) at a pH of 4 and almost 9.44 g/L of cobalt and 3.018 g/L of iron were precipitated. A rare earth (RE) rich solution was further precipitated with oxalic acid (3.72 g of Sm and 0.7 g of Gd). A total REO concentration of 97.7% was obtained using the aforementioned leaching-precipitation methodologies.

The Nd-Fe-B type scrap magnet also contained a considerable amount of REEs like Nd (~30%) with a trace amount of Pr. However, the high content of Fe in the above magnet phase was an issue in obtaining high pure neodymium. Parhi, Behera and co-researchers

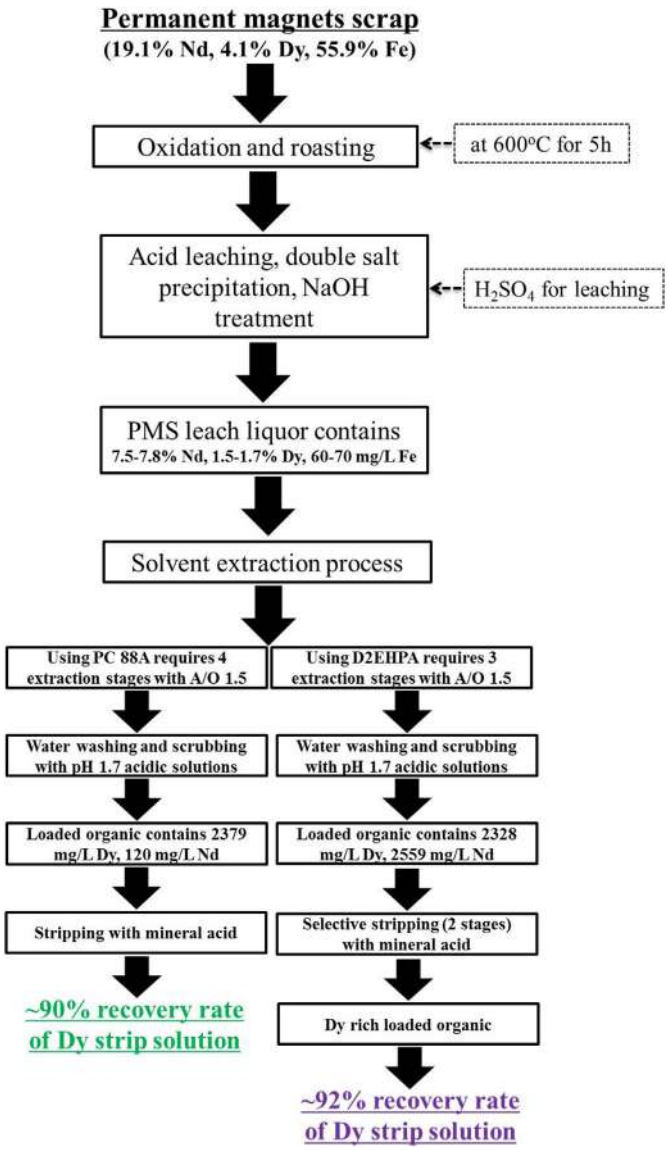

Fig. 11. Hydrometallurgical route for recovery of REEs from PMs (Adapted, modified, and reproduced from reference Yoon et al., 2015a; Yoon et al., 2015b).

were (Parhi et al., 2019; Behera el al., 2016; Parhi et al., 2016) investigated the recovery of neodymium and praseodymium through an integrated hydro-processing approach. Leaching with HCl as well as CH_3COOH was demonstrated resulting in a leached solution that bears a mixture of Nd, B, and a small content of Pr.

A promising solvent extraction of Nd and Pr was carried out using D2EHPA and Cyanex 272. It was apparent from the results that the loading efficiency was not significantly high even when increasing the extractant concentration and/or eq. pH up to 4.0. Therefore, saponified D2EHPA was employed and, as a result, the equilibrium pH and REE extraction efficiency was enhanced (Parhi et al., 2016, 2019).

The manufacturing of magnets generates a large amount of waste that is termed as scrap and contains a considerable amount of REEs. This REE-bearing scrap was processed for REE recovery by a chlorination process (with $FeCl_2$). After chlorination, 96.2% of the Nd and 94.2% of the Dy were extracted. This study proposes that the recycling process of REEs from sludge is possible to convert $RECl_3$ followed by RE_2O_3, according to the following equation (5) (Uda, 2010):

$$n\mathrm{REOCl} + \mathrm{H_2O} = \mathrm{RE_2O_3} + n\mathrm{HCl} \quad (5)$$

Here, RE = Nd, n = 1, 2, 3, … …. n number.

The other chlorination process using ammonium chloride Nd-Fe-B magnet scraps was presented and its recovery rate was maximized up to 90% (Masahiro et al., 2009). The reaction mechanism followed during the extraction is based on equations (6)–(8):

$$\mathrm{RE_2O_3} + n\mathrm{NH_4Cl} = n\mathrm{RECl_3} + n\mathrm{NH_3} + n\mathrm{H_2O} \quad (6)$$

$$\mathrm{RECl_3} + n\mathrm{H_2O} = \mathrm{RECl_3}.n\mathrm{H_2O}\ (n < 3) \quad (7)$$

$$\mathrm{RECl_3}.n\mathrm{H_2O} = \mathrm{REOCl} + n\mathrm{HCl} + (n\text{-}1)\ \mathrm{H_2O} \quad (8)$$

The carbo-chlorination process was successful for the selective recovery of REEs from NdFeB magnets; the overall process is expressed as the following reaction equations (9) and (10) (Yuuki et al., 2013):

$$\mathrm{RE_2O_3} + n\mathrm{C} + n\mathrm{Cl_2} = n\mathrm{RECl_3} + n\mathrm{CO}\ \text{at}\ >200\ ^\circ\mathrm{C} \quad (9)$$

Here RE = Nd

$$\mathrm{REBO_3} + n\mathrm{C} + n\mathrm{Cl_2} = n\mathrm{RECl_3} + n\mathrm{BCl_3} + n\mathrm{CO}\ \text{at}\ 200\text{–}900\ ^\circ\mathrm{C} \quad (10)$$

Here RE = Dy.

In the downstream solvent extraction process, organo-phosphorous reagents are mostly used for separation studies of Nd, Dy, and Pr. The extraction mechanism is based on the cation exchange phenomenon and, therefore, releasing H^+ ions is often observed as these reagents are used as acidic extractants (Fig. 14).

To establish the extraction mechanism, slope analysis methods are adopted, based on which, the association of a number of moles of H^+ ions as well as a number of extractant molecules, which participated during the complexation of REEs with solvent reagents, could be derived. The generalized equations proposed for these studies (Yoon et al., 2015a, 2015b) are based on equation (11):

$$\mathrm{M}^{n+}{}_{(aq)} + n(\mathrm{HA})_{2\ (org)} = \mathrm{MA_n(HA)_{n(org)}} + n\mathrm{H}^+{}_{(aq)} \quad (11)$$

Here, M = rare earth, $(HA)_2$ = PC 88 A, n = 1, 2, 3, 4, 5, 6, 7, 8, 9, ….n number, aq is the aqueous phase containing the metals, and org is the organic phase containing the extractant.

3.6. Processing of red mud for rare earth elements (REEs)

Other secondary resources like red mud (bauxite residue) have gained significant importance in bearing REEs and other base metals. REEs such as Ce (42%), La (14%), Sc (12%), Nd (11%), Y (10%), Pr (3%), Sm/Gd (2%), and Yb/Er (1%) were found and reported in Greek bauxite residue (Panagiotis et al., 2016).

An ionic liquid, betainiumbis(trifluoromethylsulfonyl)imide (HbetTf2N), was utilized during the leaching process, with the following optimized conditions: a temperature of 90 °C, time of 24 h, speed of 400 rpm, and pulp density of 40% for the extraction of REEs, represented in following equation:

$$n\mathrm{HbetTf2N_{IL}} + \mathrm{RE_2O_3} = n\ \mathrm{RE\ (bet)_3(Tf2N)_3} + m\ \mathrm{H_2O} \quad (12)$$

Here, 'n' denotes a numerical value, 'RE' is rare earth, and 'IL' denotes an ionic liquid at a temperature of 55 °C.

The leached metals were scrubbed by water followed by acid

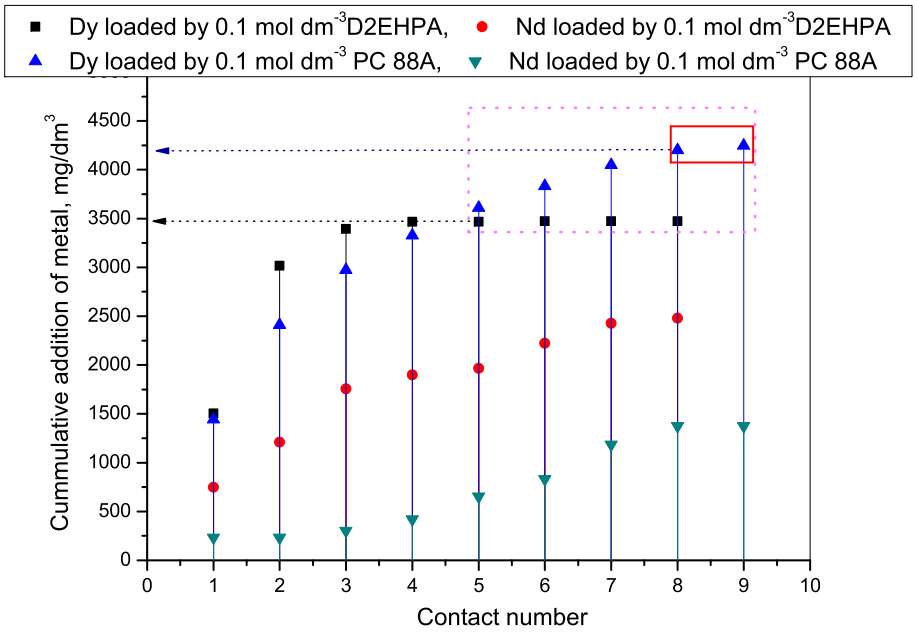

Fig. 12. Maximum loading capacity of the 0.1 mol/L of D2EHPA/PC 88A (Adapted, modified, and reproduced from reference Yoon et al., 2015a; Yoon et al., 2015b).

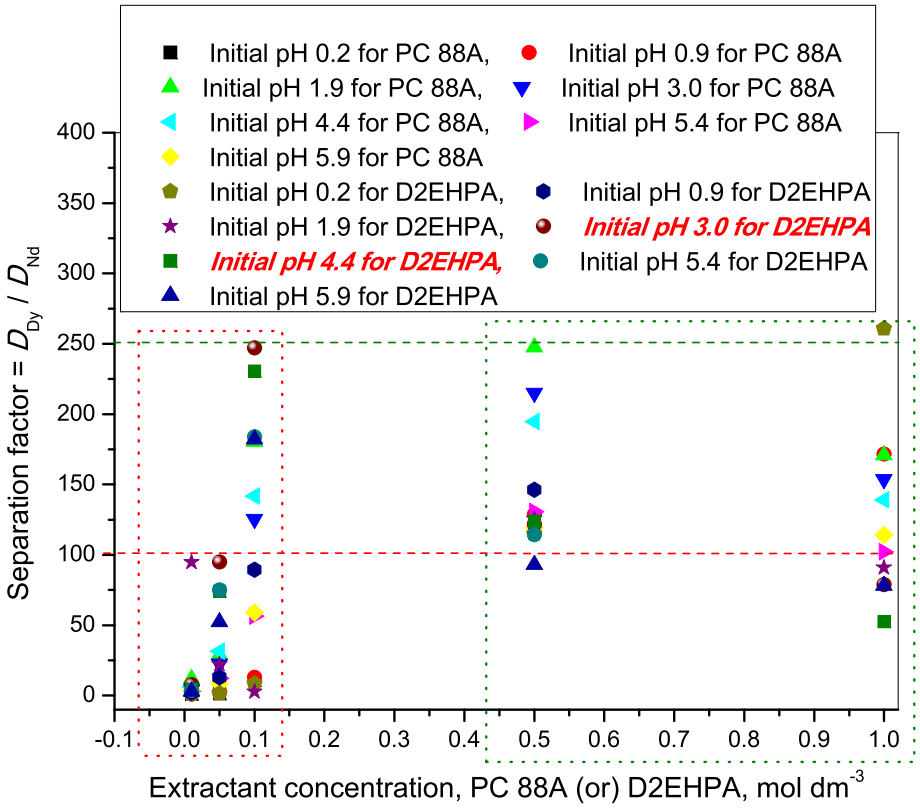

Fig. 13. Separation factors data in between rare earths such as dysprosium and medium extracted from waste permanent magnets leach liquors using D2EHPA and PC 88A (Adapted, modified, and reproduced from reference Yoon et al., 2015a; Yoon et al., 2015b).

(4 mol/L HCl) stripping. In another study, the reagents were replaced with sulfuric acid (4 N), which was used as a scrubbing reagent, followed by hydrochloric acid (12 N) used as a stripping reagent, showing ionic liquid losses of 5% (Panagiotis et al., 2016).

Three hydrometallurgical methodologies were established and applied for the recovery of REEs selectively from bauxite residue; these were sulfation, roasting, and leaching. Three different temperatures (ranging from 650 to 700 °C) were used and the roasting time was 1 h. It was found that Sc, Y, La, Ce, Nd, and Dy were leached at rates exceeding 50% with a recovery of less than 95%. Various

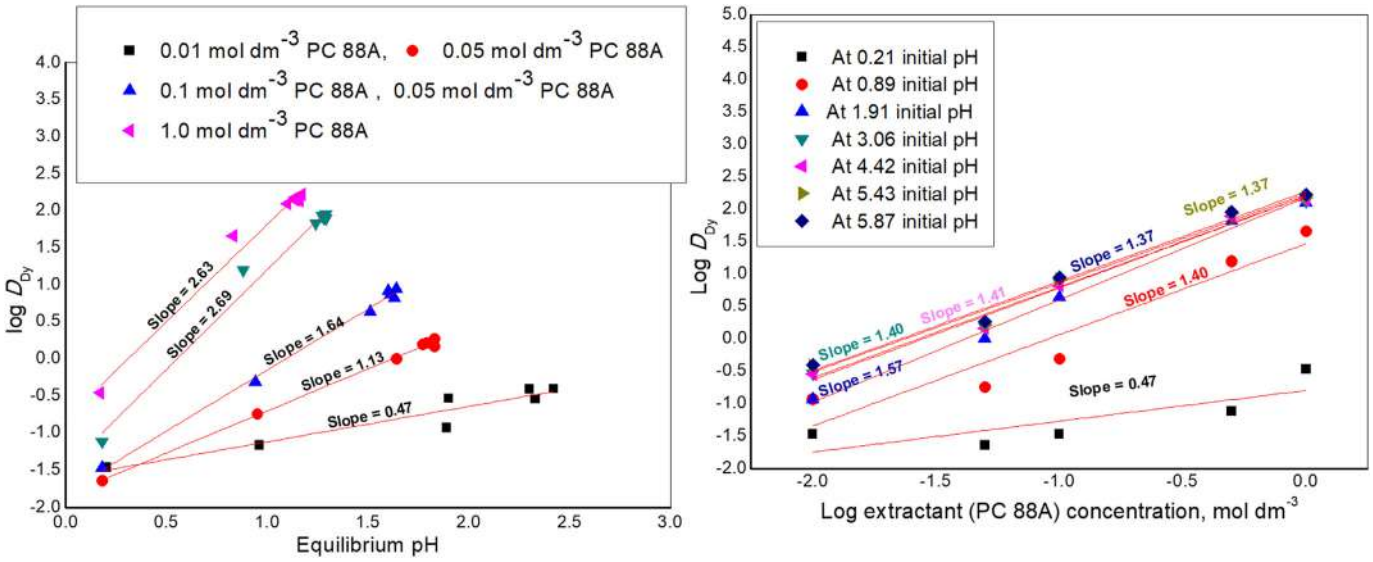

Fig. 14. Log D_{Dy} vs equilibrium pH/log extractant (PC 88A) concentration (Adapted, modified, and reproduced from reference Yoon et al., 2015b).

acids, such as nitric, hydrochloric, sulfuric, citric, acetic, and methanesulfonic acids, were implemented in the bauxite residue leaching process to recover the REEs. The acidic condition was optimized at 0.25 N; the initial acidity ensured neutralization (Chenna et al., 2016a, 2016b).

Bauxite residue, namely, RM, also contains 30–50% aluminum oxide (Al_2O_3) with transition metals and trace REEs. Considering its high scale generation (RM global production every year is ~120 million t), there are serious issues due to its direct disposal in the environment. Thus, proper treatment for the recovery of REEs and extraction of other metal values from red mud is essentially required prior to its safe disposal. RM mainly has rich scandium, which is 95% of the economic value of the REEs in RM. Critical reported works in the context of RE extraction are reviewed and presented. RM leaching studies were reported with various mineral acids; nitric acid was observed as the most suitable reagent for the dissolution process. Results of 80% of Sc, 96% of Y, as well as 30–50% of light lanthanides were reported (Koen et al., 2013a, 2013c).

Various acids such as HCl, H_2SO_4, HNO_3, H_2SO_3, and H_3PO_4 were utilized for the direct leaching of RM to recover Sc and other REEs (Chenna et al., 2015). Acidity ranges from 0.5 to 6 mol dm^{-3} at temperatures ranging 25–90 °C were maintained during the experimentation. Some organic acids namely: methanesulfonic, acetic, citric, and oxalic were also employed for the RM leaching process. The alkali reagent sodium bicarbonate in the presence of CO_2 (6 atm), which was applied at a pH of 8 for the Russian bauxite residue leaching process, yielded 26% of Sc, 68% of Zr, and 6% of Ti metals (Chenna et al., 2016a).

Gallium and yttrium were also recovered from red mud by a liquid-liquid extraction, followed by a carbonation process (Thriveni et al., 2015).

3.7. Processing of waste phosphors for rare earth elements (REEs)

CRT phosphor was leached with hydrochloric acid solutions for the recovery of REEs (Fig. 15). The optimized leaching conditions were 5.0 mol/L of HCl at 80 °C after the leaching process oxalate precipitation was carried out. The precipitated REOs are calcined at 900 °C. The total recovery of REEs (Y_2O_3 and Eu_2O_3) was achieved by up to 99% (Xingmei et al., 2015).

Using sodium peroxide, waste phosphors (WPs) were processed for REE recovery (Wu et al., 2014), utilizing less energy. From this methodology, 99% of the REs were recovered at 650 °C. The X-ray diffraction (XRD) spectrum confirmed that the REE combination in the WPs was $(Ce_{0.67}Tb_{0.33})MgAl_{11}O_{19}$. Decomposition studies reported that 1 g of the WPs required 0.7 g of Na_2O_2. The chemical reaction associating (equation (13)) WPs with sodium peroxide was reported as follows:

$$(Ce_{0.67}Tb_{0.33})MgAl_{11}O_{19} + 6.5\ Na_2O_2 = MgO_2 + 0.67Na_2CeO_3 + 0.33Na_2TbO_3 + 11NaAlO_2 + 2.5O_2 \quad (13)$$

After a sodium peroxide treatment of the WPs, further extraction and dissolution was carried out using HCl. The reaction mechanism was reported as equation (14) (Wu et al., 2014):

$$Na_2REO_3 + (n+2)\ HCl = RECl_n + 2NaCl + 3H_2O \quad (14)$$

Here, RE = Ce (or) Tb and n = numerical value.

3.8. Other secondary source processing for rare earth elements (REEs)

REEs were recovered as by-products of an anhydrite-gypsum production process and the obtained REEs' overall recovery rate was 89.9%, resulting in a 96% pure form of the RE_2O_3 (Ibrahim and El-Hussaini, 2007). The detailed flowsheet is presented in Fig. 16

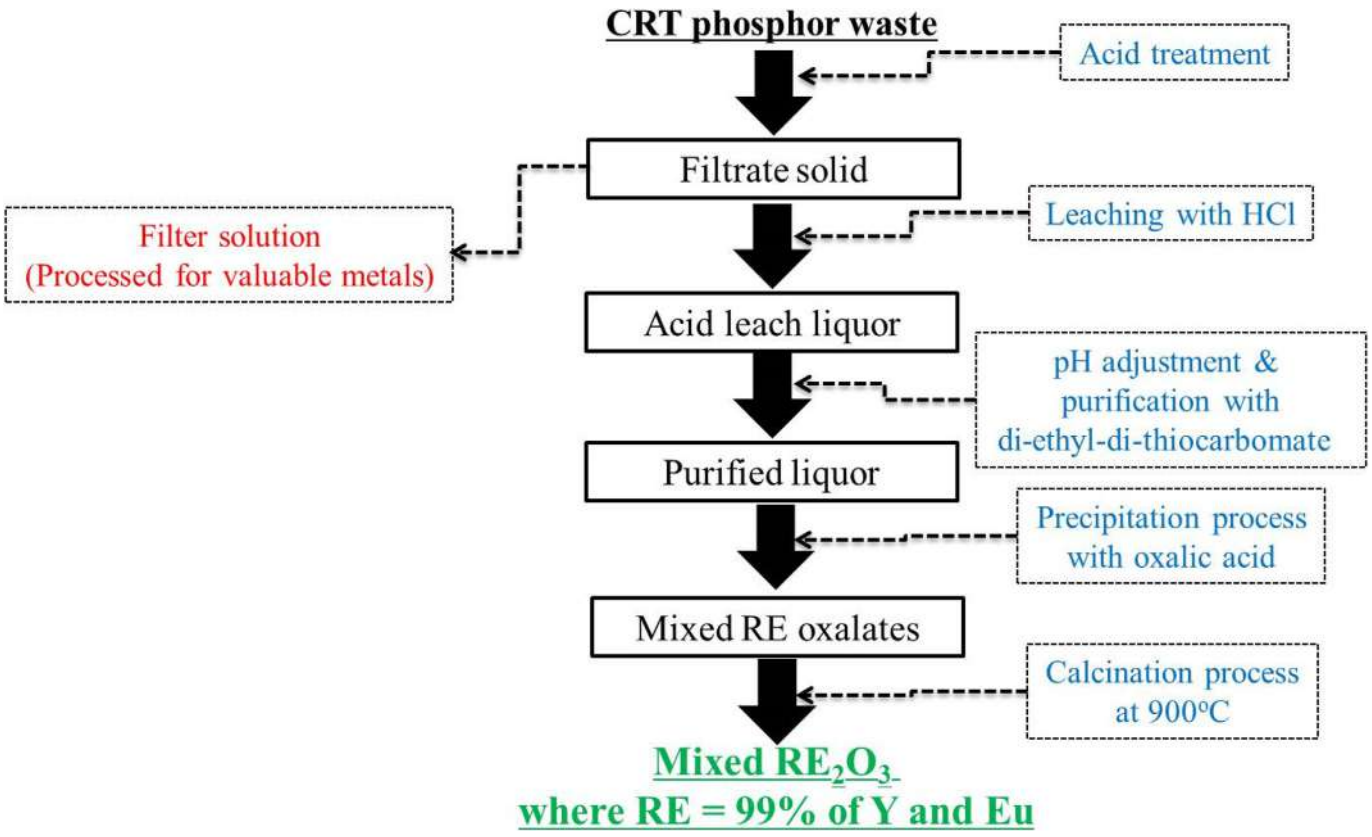

Fig. 15. A systematic flowsheet for REEs recovery from CRT phosphor waste (Adapted, modified, and reproduced from reference Xingmei et al., 2015).

(re-drawn from reference Ibrahim and El-Hussaini, 2007). In this study, Yttrium fluorite of El-Missikat was leached with a high concentration of sulfuric acid (9 mol/L) at 200 °C for 2 h and a two-step process was used to recover REE from the leached liquor. The first step was liquid-liquid processing using D2EHPA and TBP as extractants. After extraction, the loaded organic phase was subjected to a uranium and thorium separation study. In the second step, the obtained raffinate solutions were treated with oxalic acid to yield the precipitated respective rare earth oxalate. Finally, the filtrate was processed for the separation and precipitation of Nb, Ta, Ti, and REEs and then calcined at 950 °C to produce highly pure RE_2O_3 (Ibrahim and El-Hussaini, 2007).

REEs were recovered from spent nuclear fuel (SNF) using 30% TBP (Fedorov et al., 2016). Another source for rare earth elements is acid mine drainage (AMD) (Ayora et al., 2016). However, there were very small amounts of rare earth elements in those samples; 7.9 mg/L of REEs from the Monte Romero area and yttrium and 3.5 mg/L REEs from the Almagrera area. Such low concentrations of REEs were also recovered by various scientific methodologies by the aforementioned research groups.

Rare earth elements were recovered from Bayan Obo tailings through acid leaching and hydrolysis methodologies. In this process, a tentative flow-sheet diagram (Zhang et al., 2014) was developed and is presented in Fig. 17. In the first step, RE tailings were leaching with acid followed by hydrolysis at a pH of 2. The filtrate was processed for composite REOs by further hydrolysis at a pH of 7.15 and a saturated oxalate solution of 2% hydrogen peroxide. The precipitated product was calcined at 1000 °C for 1 h, generating the composite REOs (Zhang et al., 2014).

Ponou et al. reported the recovery of REE from clay minerals using biosoprtion and desorption (Ponou et al., 2014). The authors utilized parachlorella (Supplied by Panac. Co. Ltd) for biosorption studies concluding that beyond a pH of 7, the solution forms REE precipitate; therefore, a suitable pH range of 1–7 was maintained in the sorption study. Two biosorbents, dried parachlorella and carbonized parachlorella (at 250 °C) were introduced and maximum REE uptake values were noted at a pH of 7. Whereas in the case of carbonized parachlorella (at 350 °C), a pH of 4 was reported as the optimum condition for the best REE uptake. To recover the adsorbed REEs, three mineral acids, HCl, H_2SO_4, and HNO_3 concentration was modified from 0.1 to 1.0 mol/L at 30–70 °C.It was found that excepting Dy and Gd, the other REEs, La, Pr, Nd, and Sm could be easily desorbed (Ponou et al., 2014).

Other types of secondary REE source such as post-consumer hard-disc drives (HDD), were processed for REE extraction by metallurgical methods (Abrahami et al., 2015). This flowsheet (Fig. 18) demonstrated three extraction operation sequences; a physical separation of the HDDs followed by two metallurgical methods. After the physical processing of shredder preparation by thermal demagnetization followed by grinding/screening, Nd-Fe-B magnet concentrates were generated. These magnet concentrates were fed to be treated with pyro- and hydro-metallurgical processing methods (Fig. 18). The hydrometallurgical processing of HDDs followed several stages; the first stage was that of a selective leaching process with sulfuric acid followed by solution purification. After the removal of all solid residues, the solution was treated for double-salt precipitation (light pink color). By adding sodium hydroxide to this solution $NaNd(SO_4)_2.H_2O$ salt was produced. In the pyro-metallurgical route, a slag treatment was first conducted based on three major parameters: the composition of slag, ratio of slag:metal, and type of scrap. The process was followed by a metallo-thermic reduction; the results were studied and reported

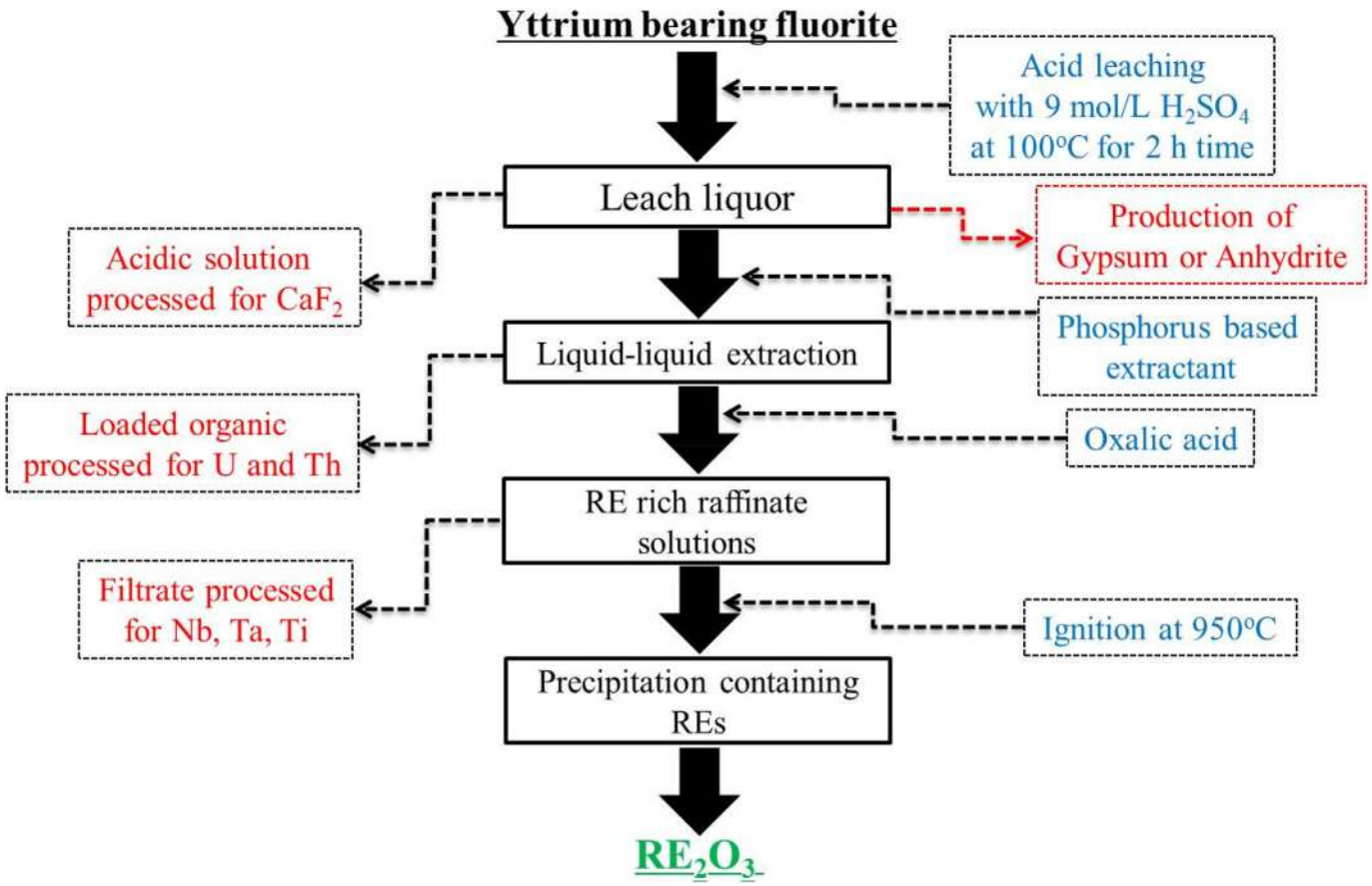

Fig. 16. Recovery of REEs (as by-products) from gypsum-anhydrite processing (Adapted, modified, and reproduced from reference Ibrahim and El-Hussaini, 2007).

(Abrahami et al., 2015).

REE recovery from computers monitor scraps (CMs) was also examined by an acid leaching process (Resende and Morais, 2010). CMs mainly contain REEs such as 17 wt% Y, 0.02 wt% Ce, 0.01 wt% Nd, and 0.76 wt% Eu among other elements. From these scraps, 96% of europium and yttrium were recovered. The following experimental conditions were optimized for REE leaching from SMS: 90 min leaching duration, ratio acid/solid sample of 1500 g/kg, and temperature of 25 °C. The final leach liquor contained 0.55 g/L of Eu and 16.5 g/L of Y with other transition elements (Resende and Morais, 2010).

REEs recovered from rare-earth mud (located in China, Mining REE deposit) by leaching processes and precipitation methods (Zhu et al., 2000). This rare-earth mud is rich in rare earth metal contents; 20% of the rare-earth mud contains 2–7% rare earth elements with 2–10% Mn and 2–8% Pb. Based on the Eh-pH diagram of various rare earth contents, the rare-earth mud was verified and a suitable reducing regent was selected. Four reducing reagents, sodium nitrate, sodium sulfite, oxalic acid, and ascorbic acid were utilized for this method. Out of the four reducing reagents, sodium sulfate had a better economic advantage. Therefore, a method was developed utilizing the reductant Na_2SO_3. The leaching efficiency was reported to be 74.6% Mn, 0.94% rare earth elements, and 0.55% Fe with Na_2SO_3. Impurities from the rare earth rich mud leaching solutions were removed by a $KMnO_4$ oxidation process. The purified rare earth rich mud was precipitated (Zhu et al., 2000) using ammonium-bicarbonate to produce crystal $RE(CO)_3$.

Other sources for REEs include spent optical glass (SOG), which was treated by the hydrometallurgical process to recover REEs (Jiang et al., 2004). The detailed flow diagram for REE recovery from SOG can be seen in Fig. 19. Using 6 mol/L HCl, REEs such as La, Y, and Gd were quantitatively leached out of SOG. Other parameters such as leaching time (40 min) and leaching temperature (368 K) were also optimized. The SOG leached liquor was processed for RE separation using 1.0 mol/L D2EHPA extractant at a pH of 3.9 with an O/A ratio of 1.25; almost all the Y (99%) and 9.5% Gd was extracted to a loaded organic medium (Loaded organic contained: 6.1 g/L of Y, 2.98 g/L of Gd, and 2.67 g/L of La). With the loss of 5% of the Gd, associated La was scrubbed using 0.4 mol/L HCl. Further stripping of the loaded RE Gd was successfully achieved with 1.3 mol/L HCl; up to 89% stripping was obtained (Jiang et al., 2004).

A novel recovery process was proposed for REE extraction from voice coil motors (VCM). This process proposed several operation steps; the initial step was the dismantling and demagnetization of the rare earth magnets, followed by oxidation/roasting, and acid leaching. Downstream, the leached liquor was processed for the precipitation of an iron group with a separation factor >90; followed by electrodeposition for Dy and Nd (Matsumiya et al., 2014a).

Clean technology for the recovery of scandium (Sc) from the scrap alloy phase has also been investigated (Das et al., 2018; Parhi et al., 2019). After obtaining the chloride mediated leached liquor, the separation of scandium was carried out using two organophosphorous reagents (D2EHPA and Cyanex 272). The extraction behavior, mechanism, stripping, and isotherm study were extensively investigated and reported. The co-permeation of other base metal impurities was observed in this study, ensuring the promising separation of scandium using either of the solvent reagents (D2EHPA/Cyanex 272) (Das et al., 2018) from the scrap liquor. In another study (Parhi et al., 2019) R_4ND, a bi-functional ionic liquid derived from D2EHPA and Aliquat 336, was adopted for the

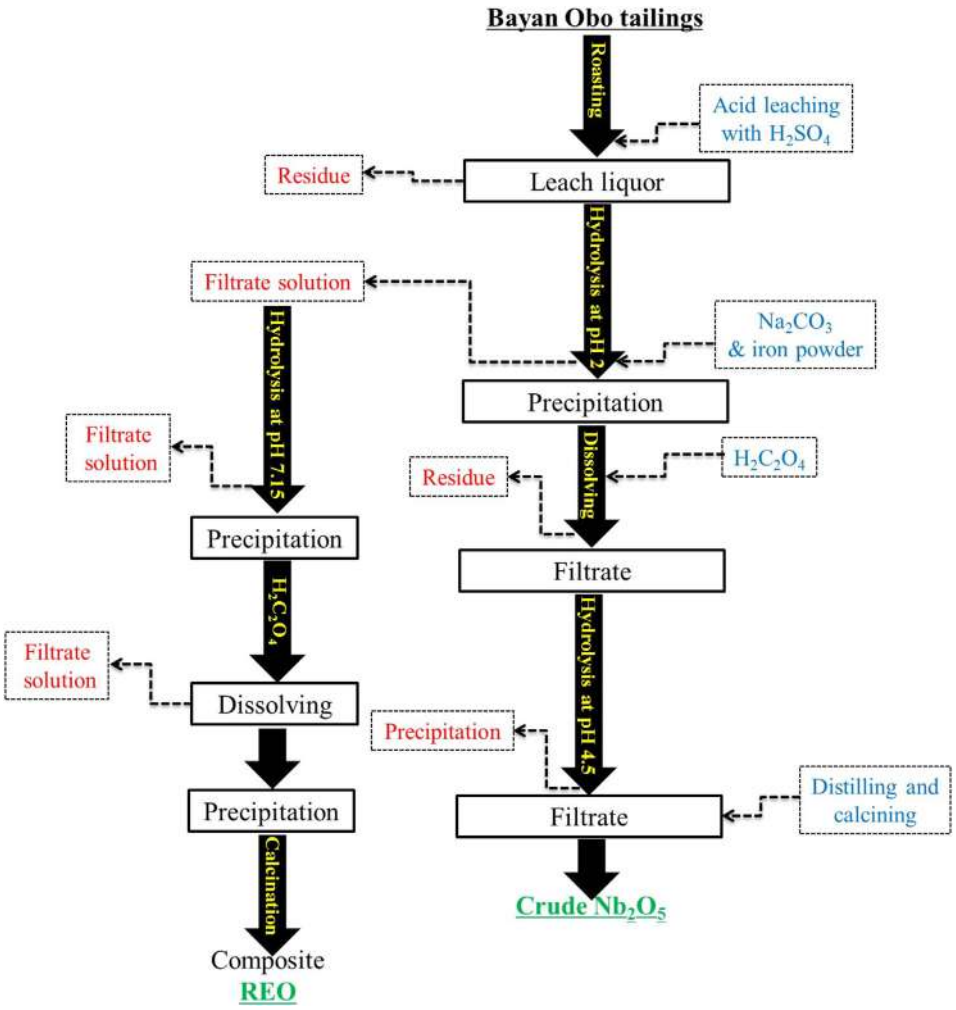

Fig. 17. Flow-sheet diagram for recovery of REEs from Bayan Obo tailings (Adapted, modified, and reproduced from reference Zhang et al., 2014).

effective extraction of scandium from the leached solution. The ionic liquids showed greater potential for the multifold enrichment of the rare earth metal (Sc) over other commercial solvent reagents.

In contrast, Cerium, recovered from polishing powder waste (PPW), separated other REEs such as lanthanum, praseodymium, and neodymium by calcination and an acid leaching process (Um and Hirato, 2013). The first stage dissolution process was carried out for REEs (each of a 0.08 mol/L concentration) dissolution using sulfuric acid 3 mol/L 90 °C and a reaction time less than 1 min. This precipitation reaction followed equation (15):

$$nRE^{3+} + nSO_4^{2-} + mH_2O = RE_n(SO_4)_n.mH_2O \quad (15)$$

Here, RE = La (or) Pr (or) Nd, m, n = Numerical values.

The two-step leaching process was illustrated by Yang et al. (2010). After the first stage leaching, except for Ce and Al oxides, other REEs were leached out. While in the second step leaching process, the remaining Al_2O_3 and CeO_2 were dissolved using sulfuric acid solutions. Second step leaching leads to the complete separation of cerium from aluminum (Yang et al., 2010). Another secondary resource for REEs is oil shale ash waste (Yang et al., 2010) from which REE recovery was also investigated through hydrometallurgical methods. A complete flowsheet is shown in Fig. 20. The total REs content in the Fe-OSA was reported as 0.14%; it had Pr, La, Tm, Yb, Nd, Tb, Sm, Ce, Eu, Gd, Dy, Ho, Er, Y and Lu. For the first stage, experimental iron was separated from the REEs using N235 as an extractant. The extraction of raffinate pH was adjusted to 6. Later on, second stage leaching was carried out by nitric acid and the obtained leach liquor was treated with TBP (solvent extraction process) to extract ~ 86.3% of the rare earth products with 94.2% purity (Yang et al., 2010).

4. Policy for the establishment of resources circulation society (RCS)

In the future, the recycling of RE-based materials will face five major challenges: 1) enlargement, 2) an ensured quality of recycling, 3) enhancing the efficiency collection, 4) energizing the process, and 5) improved public awareness. To meet the tenets outlined in Our Common Future proposed by the Brundtland Commission in 1987 (World Commission on Environment and Development, 1987), the following subject areas need to be established: the spread of extended producer responsibility (EPR) target products, eco-models, improved transportation, the development of recycling businesses, and cooperation between neighboring nations.

In South Korea, the waste management laws were first introduced in 1961 (waste clean-up law), and a waste management law was passed in 1986. A law related to resource saving and reutilization was introduced in 1992 and the new millennium

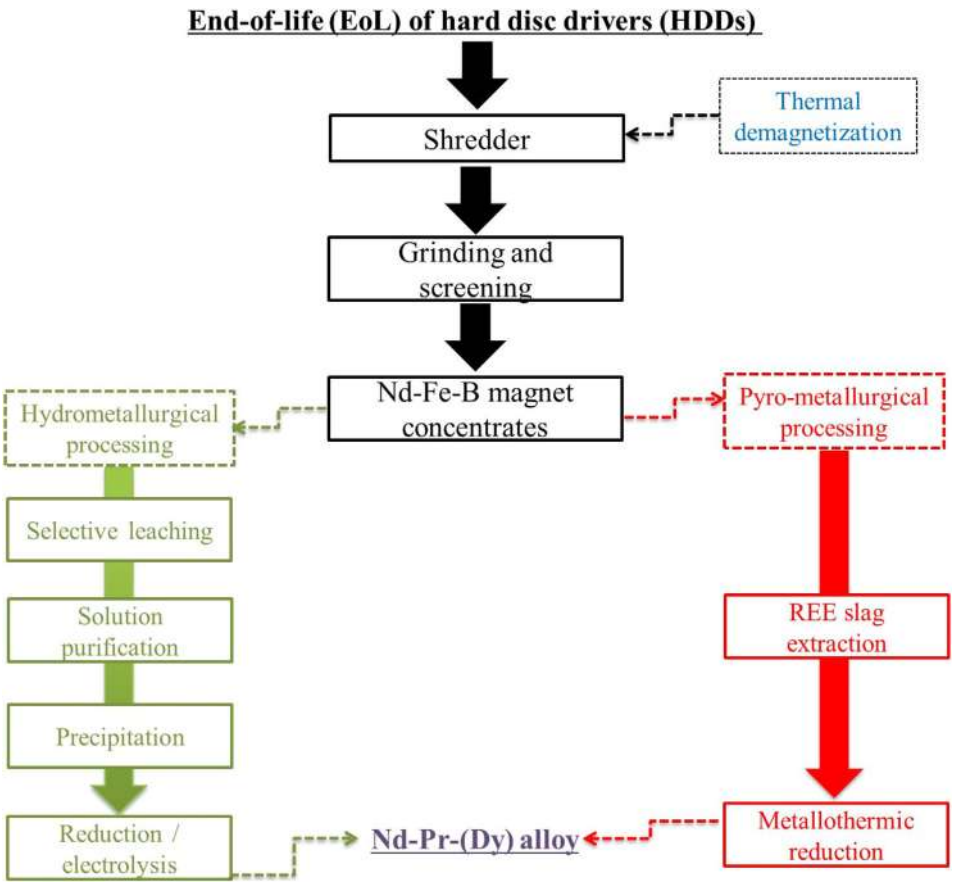

Fig. 18. REEs recovery processing from end-of-life (EoL) of hard disc drivers by pyro- and hydrometallurgical routs (Adapted, modified, and reproduced from reference Abrahami et al., 2015).

witnessed the introduction of the extended producer responsibility (EPR) system (Jaehyun, 2006). A policy for a resource circulation society (RCS) can be developed based on the following major pillars: a closed-loop resources society, measured circumstances for rare-earth-based waste generation, targets/strategies of the policy, directions for a mail recycling policy, the cultivation of recycling policies, and cultivation countermeasures for recycling industries. The main policy for the reuse of waste requires the following principles: the activation of a store of recycling goods, a guarantee system for the recovery of products, a proper eco-design to reduce the environmental load, and the remanufacturing of product parts. The reduction of waste includes the following principles: the introducing an EPR system, the regulation/restriction of oversized packaging, reducing the use of disposable goods, and reducing materials that generate industrial waste.

5. The role of rare earth elements (REEs) in green and clean energy technologies

Terbium, dysprosium, neodymium, and yttrium are the most important rare earth elements for green energy technologies. These are critical elements based on their supply and demand (U.S. Department of Energy, 2010). Currently, the planet needs clean and green energy to fulfill human needs. Clean energy technologies (CETs) include wind turbines, electric vehicles, fluorescent lightings, photovoltaic cells, etc. REEs (Dy, Nd, Tb, Eu, and Y) play a significant role in CETs that will likely grow day-by-day. As per the United States of America, Department of Energy (DOE) predictions, Ce and La are near critical and Dy, Nd, Tb, Eu, and Y are in a critical situation (U.S. Department of Energy, 2010). REEs play a significant role in low carbon technologies. The DOE (USA) has stated that some of the REEs are critical in supply due to various reasons (U.S. Department of Energy, 2010). At the same time, global REE reserves are mainly located in China followed by Brazil, Vietnam, Russia, India, Australia, Greenland, the USA, Tanzania, Canada and South Africa (USGS, 2020). Global rare earths reserves data was adapted and presented in Fig. 21. Their processing and economics depend on the tonnage, grade, and refining costs (U.S. Department of Energy, 2010).

Primary resource (PR) processing requires more energy consumption, more time, higher costs, and more human resources to handle mining projects. Mining projects are usually done in five steps: licensing (environmental plans, equipment, and transport), exploration, development, production, and marketing (Baolu et al., 2016; Zepf et al., 2014). PR processing for REEs can generate radioactive materials due to the association of uranium and thorium with REEs (Baolu et al., 2016). Whereas, secondary resource (SR) processing requires only a proper technology to recover the REEs from SRs. Secondary resource processing will solve three major problems, namely, environmental damage, landfills, and the increasing national demands for REEs. The global production of REEs is mainly from China (up to 97%) since 2010. However, the Chinese government decided to stop/regulate the export of primary resources (Baldi et al., 2014; Ting and Seaman, 2013; Zepf et al., 2014), which majorly influenced the clean energy technologies industry.

Modern renewables include solar power, hydropower, wind power, biofuels, etc. (REN21, 2012). Modern renewables are the

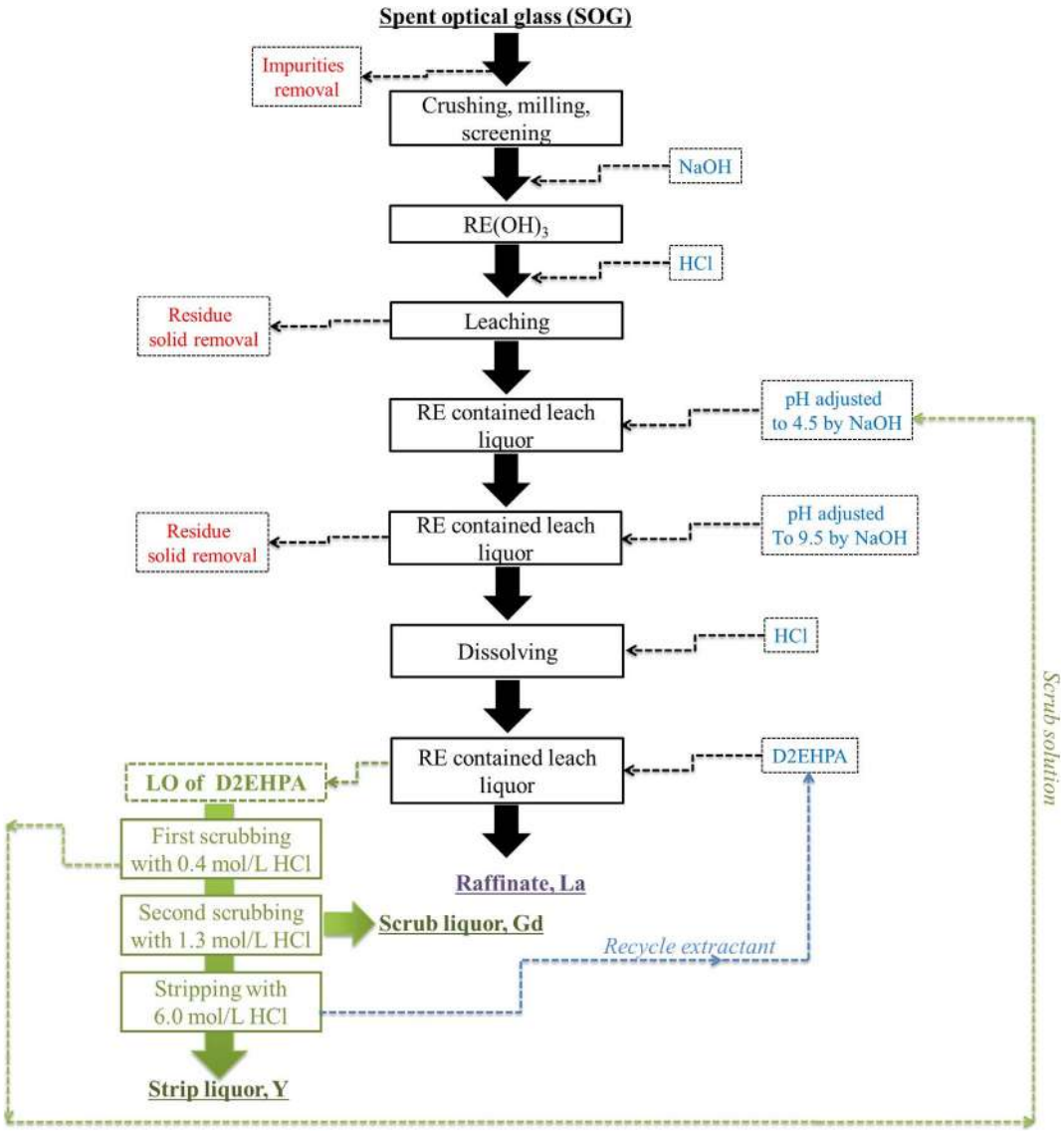

Fig. 19. REEs recovery processing of spent optical glass (SOG) by hydrometallurgical methods (Adapted, modified, and reproduced from reference Jiang et al., 2004).

fastest-growing energy source in the near future. Nations economies depend on industrial growth as well as the export and imports of goods, ultimately expanding the need for energy around the globe (International Energy Outlook, 2017). Electricity needs are also rapidly increasing in the industrial sector. Renewable energy shares are rising 2.8% per year, equaling that of coal by 2040 (expected to be 31% of the total global needs) (International Energy Outlook, 2017). The wind and solar energy sectors are the most important renewable energy sectors and are expected to dominate growing areas in modern renewable technologies in the near future across the world IEA, 2017). The global sales of electric vehicles (EVs) close 2 million in 2018 (International Energy Agency, 2019). Their sales growth in the top nations are as follows (year 2018 sales): China, Europe and the USA; in addition, electric buses run majorly in China (International Energy Agency, 2019).

Within the EVs, PMs are mainly used in motors. Ni-Metal-Hydride (NiMH) batteries cathode materials have a structure of AB_5, where A is the REE (La, Ce, Nd, or Pr) and B is the combination of Ni, Co, Mn, or Al (Kopera, 2004). Phosphors are used in fluorescent lighting (FL) and are manufactured using various REEs such as La, Ce, Eu, Tb, or Dy (U.S. Department of Energy, 2010). Lighting efficiency will lead to reducing energy demands (U.S. Department of Energy, 2010).

Global demands are growing dynamically and are inter linked with population growth and human needs. Currently, high-tech goods utilization is increasing day-by-day. To meet human needs and nations' demands for clean energy technology development as well as improving nations' economics, REE supplies will play a significant role. Secondary resources can potentially solve the global problems of environmental pollution, landfill problems, and the increasing demand for clean energy materials.

6. Life cycle assessment of rare earth elements (REEs) using secondary sources

Life cycle assessment (LCA) is the most significant process to evaluate the environmental impact of products over their complete life-cycle (Walter, 2014; Heijungs et al., 1996). LCA concerns the material (or) product processing, usage, and end-of-life (EoL) (Walter, 2014; Heijungs et al., 1996). LCA also takes into account the

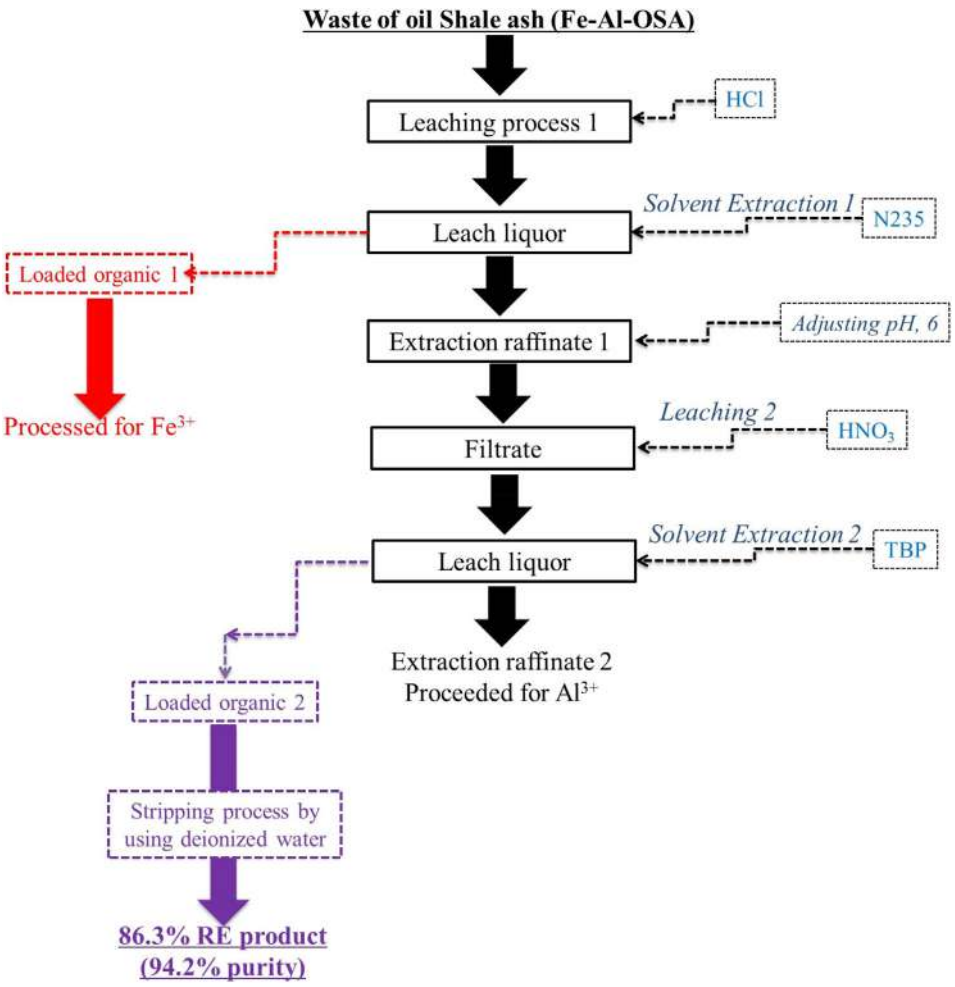

Fig. 20. REEs recovery from waste of oil shale ash (OSA) by using hydrometallurgical methods (Adapted, modified, and reproduced from reference Yang et al., 2010).

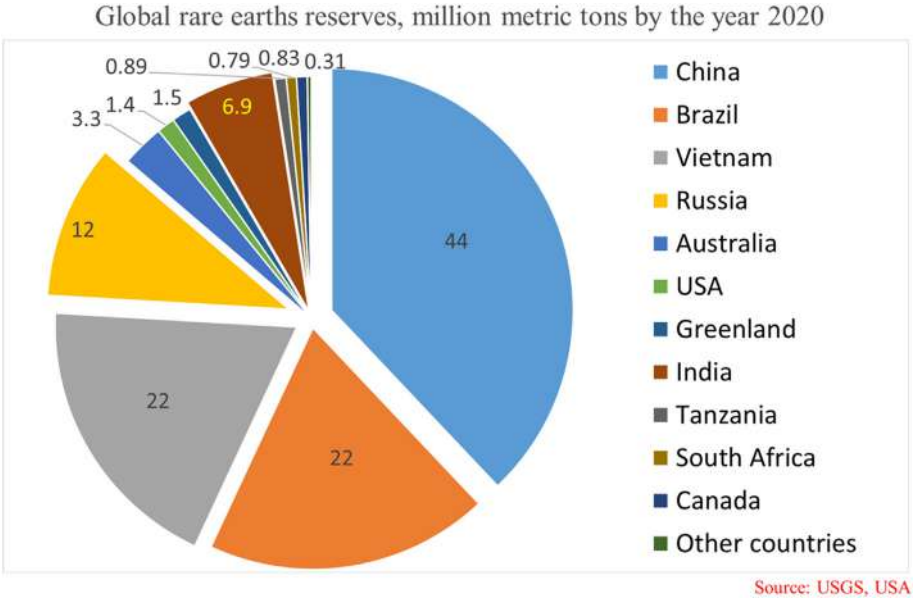

Fig. 21. Global rare earths reserves from various counties, million metric tons (data was adapted, modified, and reproduced from reference USGS, 2020).

environmental impacts of products and their removal/recycling strategies (Walter, 2014; Heijungs et al., 1996). As per the UNEP, France guidelines, LCA is composed of three steps: 1) recognizing the environmental loads such as energy and raw materials use, as well released emissions and generated waste; 2) evaluating the environmental impacts of step-one loads such as energy and raw materials; 3) finally, assessing the prospects available from waste to wealth creation as well as environmental protection (Walter, 2014; Heijungs et al., 1996). LCA will help solve two major problems such as environmental pollution and landfill problems. Countries South Korea has a high population density and contrasts producing rare-earth-based products such as electrical, electronic, and automobile products to global demand. Various stages are involved in the lifecycle of REE products, from the harvesting of primary/secondary resources to the manufacturing of the rare earth products (Fig. 22).

The LCA of PMs collected from computer hard disk drivers (HDDs) were calculated and reported. Comparing virgin PMs with recycled PMs, the two major environmental concerns were human toxicity (HT) and climate change (CC). Human toxicity value was 150 for virgin PMs; whereas, recycled samples were 3.6 (recycled via hand picking) and 28 (recycled via shredding) for unit kg 1,4-DCB-Eq; while the climate change values (kg, CO_2-Eq) were 27 (virgin PMs), 3.3 (recycled via hand picking) 10 (recycled via shredding), (Benjamin et al., 2014). These results were determined considering that recycled PMs are better for the environment compared with the primary production products of PMs due to less energy consumption (Benjamin et al., 2014).

UNEP presented an LCA interlink between six major areas including management (life-cycle based environmental policy and product strategy), distribution, sales/marketing, cleaner production, green procurement, and environmentally-conscious designs (UNEP metal recycling et al., 2013). Furthermore, LCA will influence the value chain management of different stakeholders. LCA implementation will provide advantages in two major biinfinite areas including environmental (reducing the utilization of materials up to >10% and improving fuel efficiency 5–10%) and economical (reducing production costs up to ~10%) (UNEP metal recycling et al., 2013).

7. Environmental concerns with sustainable cleaner solutions

Usually, waste is generated after these secondary sources (magnets, catalysts, electrical and electronic gadgets, CRT lamps, LEDs, etc.) have fulfilled or ended their limited cycles of utilization in their respective industrial sectors. However, they can become a significant source of rare earth elements as they contain significant quantities. Therefore, the processing of this waste through proper processing methods for the recovery of REEs, yielding zero waste further establishes a waste-to-wealth technology is furthermost useful for society. The proposed integrated hydrometallurgical routes appeals to be a highly promising environmentally friendly approach while solving the two major problems of landfill issues and environmental protection. In-depth studies in the 21st century indicate a significant global environmental concern due to the generation of large quantities of industrial solid waste such as e-waste, spent catalysts, spent magnets, fly ash, and red mud. Most industrial waste is often disposed of without any treatment leading to an increase in the high levels of contamination (Kumar and Lee, 2017; Jyothi, 2020). The content of hazardous components including toxic heavy and rare metals are a key concern as they are a serious health threat to plant and animal life upon direct disposal. On the other hand, the content of valuable rare earth metals in these waste ensures potential alternate sources over primary REE-bearing resources. Maintaining their economic importance vis-à-vis environmental issues, recycling technology would be a most promising aspect to address both issues (Kumar and Lee, 2017; Jyothi, 2020). Green energy technologies have become significantly important in the new millennium 4th industrial revolution and rare earth elements are one of the key pieces in the development of green and clean technologies (Fig. 23).

Fig. 22. Stages of rare earths product life cycles from primary and secondary resources.

8. Future prospects

Insight into the development of a number of recycling technologies for the recovery of different REE from a wide variety of solid wastes addresses the key challenges and issues encountered during the processing of industrial solid wastes. As per the proposed studies (Yoon et al., 2015a, 2015b; Parhi et al., 2019; Das et al., 2018; Behera and Parhi, 2016; Parhi et al., 2015; Parhi et al., 2016; Parhi et al., 2017), the extraction of REEs is promising and effective over pyro-processing routes. However, several issues arise in both the upstream (leaching) and downstream stages (solvent extraction or liquid-liquid extraction) of operation for the recovery of REEs in the proposed technologies. As the existence of rare earth metals in secondary waste is diverse (some are found in oxide forms, whereas, others in sulfide/alloy forms), it is not convenient to solubilize some of the above complex matrices or indirect leaching stages even after using very high concentrations of acid and or alkali reagents. Thus, to overcome such issues, partial pretreatment like mechanical activation including milling, roasting, and baking at high temperatures followed by leaching is conducted. However, in these pretreatment processes, energy consumption is still higher. Therefore, the adoption of microwave- (MW) and UW assistance could be a promising alternative approach for attaining leaching efficacy in REEs from secondary solid wastes with short time lengths and low consumption of energy. The unique cavitation effect by the UW and heating irradiation mechanism of MW provides a significant impact on solubilizing metal values from complex solid waste matrices (Behera et al., 2019). In downstream operation, solvent extraction is preferentially adopted for REE-separation studies over others as it a proven technology from batch to commercial-scale operations with limited disadvantages. There is also the major concern over the separation of each of rare earth metal ions in pure form by the solvent extraction method. Ideally, close speciation behavior of individual rare earth metals in the aqueous phase results in poor separation affinity with the employed commercial reagents (D2EHPA, PC88A, Cyanex 272, Amines, TOPO, TBP). To improve the high separation factor synergistic extraction system, mixtures of TOPO/TBP reagents with organophosphorus reagents (Naeem et al., 2018; Banda et al., 2014; Wu et al., 2018) are employed. The results are impressive in terms of the enhancement of the separation factor up to a significant extent. The drawback of this synergistic system is that it has limited scope for continuous mode operation. Up to now, there has been limited success in attaining a high separation factor. The adoption of novel ionic liquids (R_4ND, R_4NCY, and TOGDA) (Parhi et al., 2019) could overcome such issues because of the salient feature unique complexation mechanism, unlike other studied extractants. Moreover, the stripping stage could be avoided while using the pure form of green ionic liquids solvent reagents. The adoption of green ionic liquids in solvent extraction (liquid-liquid) processing is an environmentally friendly approach with low waste generation, though further research work is in progress to explore how to achieve the high separation of either the REEs while separating them from corresponding mixed REE-based solutions. Overall, the above-proposed technologies not only ensure the development of clean technology/pure products but can also resolve environmental issues related to REE-based solid waste that are being generated in the daily progress of industrialization.

9. Conclusions

This general review study presents an overview of hydrometallurgical methods for REE processing from secondary resources such as permanent magnets, electric arc furnace residue, industrial residue types (phosphogypsum and red mud), plasma screens, LEDs, cathode-ray tubes, fluorescent lamps, and LCD backlights. The importance of REEs and their application to high-tech industries were presented. Waste recycling strategies, as well as policy steps for the establishment of a resource circulation society, have also been discussed. REEs play a key role in clean energy technologies. Some REEs are in a critical situation; it resulting in the necessity of technology development to process secondary resources to fulfill the national demands (certain levels) of rare-earth materials. Future energy sources are clean energy technologies including

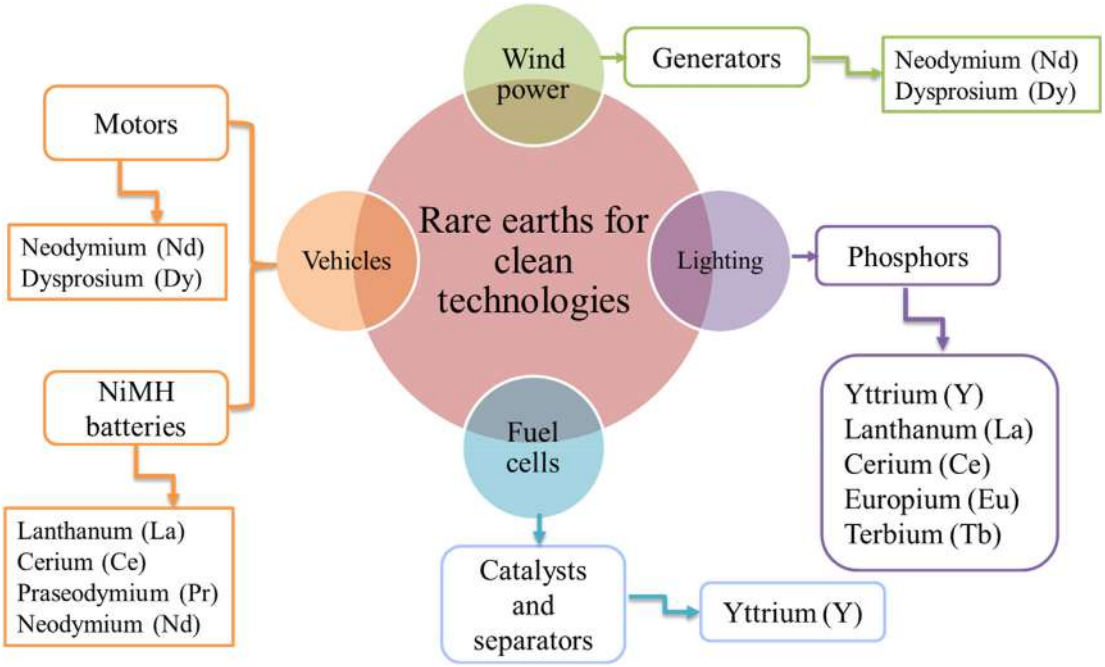

Fig. 23. Critical materials having **r**are earths for clean technologies (data was adapted, modified, and reproduced from reference Resnick Institute Report, 2011).

modern renewables as wind turbines, electric vehicles, and phosphors. In these modern tools, the usage of REEs is abundant, though life cycles are limited; generating more spent products. Unlike natural minerals, these spent products or waste are becoming a potential source of REEs (Nd, Pr, Sm, Dy, Ce, Eu, and Y) as their overall quantity is very high. The development of sustainable and clean technology for the recovery of numerous REEs vis-à-vis the generation of zero waste is warranted and is exclusively reported in this review. The proposed technology adopted for the recovery of REEs is mainly routed through an integrated hydrometallurgical operation that includes leaching-solvent extraction-precipitation, which has several advantages such as low toxic gas emission, zero waste generation, low operating costs, and clean extraction/separation yielding high purity rare-earth metal or metal compounds. In the proposed green approaches, the augmentation of ultrasound and use of green organic solvents in the leaching stage of upstream processes as well as the adoption of green ionic liquids reagents in a downstream stage are often more preferred over conventional pyro and/or hydro-processing routes for the substantial recovery of REEs from all these secondary sources. This article gives comprehensive information on REE processing from secondary resources and REEs utilization in clean energy technologies. LCA and end-of-life subjects are also briefly discussed. This review concludes with the potential adoption of the deliverable hydrometallurgical technologies from waste to wealth in the context of the quantum-amount recovery of the pure forms of numerous rare-earth metals. This has gained ample interest and scope for researchers to explore modern rare-earth research for fulfilling the day-by-day demand of pure rare earths.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by the National Research Council of Science & Technology (NST) grant by the Korean government (MSIT) (No.CRC-15-06-KIGAM). Co-author P.K. Parhi desires to acknowledge KIGAM, Korea for awarding him as a Research Advisor. Co-author Dr. Ji Whan Ahn is highly thankful to the Carbon Mineralization Flagship Center; Ministry of Science and ICT; Ministry of Trade, Industry, and Energy; and Ministry of Environment of Korea. Dr. Thriveni Thenepalli was likewise thankful and would like to acknowledge the Department of Science and Technology (DST), Ministry of Science and Technology, Govt. of India.

References

Abbas, K., Znad, H., Awual, M.R., 2018. A ligand anchored conjugate adsorbent for effective mercury(II) detection and removal from aqueous media. Chem. Eng. J. 334, 432–443.
Abrahami, S.T., Xiao, Y., Yang, Y., 2015. Rare-earth elements recovery from post-consumer hard-disc drives. Min. Proce. Extra. Meta. 124, 106–115.
Alvarado-Hernández, L., Lapidus, G.T., González, F., 2019. Recovery of rare earths from waste cathode ray tube (CRT) phosphor powder with organic and inorganic ligands. Waste Manag. 95, 53–58.
Awasthi, A.K., Li, J., Koh, L., Ogunseitan, O.A., 2019. Circular economy and electronic waste. Nature Electronics 2, 86–89.
Awual, M.R., 2016. Solid phase sensitive palladium(II) ions detection and recovery using ligand based efficient conjugate nanomaterials. Chem. Eng. J. 300, 264–272.
Awual, M.R., 2019a. Innovative composite material for efficient and highly selective Pb(II) ion capturing from wastewater. J. Mol. Liq. 284, 502–510.
Awual, M.R., Yaita, T., Shiwaku, H., 2013a. Design a novel optical adsorbent for simultaneous ultra-trace cerium (III) detection, sorption and recovery. Chem. Eng. J. 228, 327–335.
Awual, M.R., Kobayashi, T., Shiwaku, H., Miyazaki, Y., Motokawa, R., Suzuki, S., Okamoto, Y., Yaita, T., 2013b. Evaluation of lanthanide sorption and their co-ordination mechanism by EXAFS measurement using novel hybrid adsorbent. Chem. Eng. J. 225, 558–566.
Awual, M.R., Kobayashi, T., Miyazaki, Y., Motokawa, R., Shiwaku, H., Suzuki, S., Okamoto, Y., Yaita, T., 2013c. Selective lanthanide sorption and mechanism using novel hybrid Lewis base (N-methyl-N-phenyl-1,10-phenanthroline-2-carboxamide) ligand modified adsorbent. J. Hazard Mater. 252–253, 313–320.
Awual, M.R., Hasan, M.M., Shahat, A., Naushad, Mu, Shiwaku, H., 2015. Investigation of ligand immobilized nano-composite adsorbent for efficient cerium(III) detection and recovery. Chem. Eng. J. 265, 210–218.
Awual, M.R., Alharthi, N.H., Okamoto, Y., Karim, M.R., Halim, M.E., Hasan, M.M., Rahman, M.M., Islam, M.M., Khaleque, M.A., Sheikh, M.C., 2017. Ligand field effect for dysprosium (III) and Lutetium (III) adsorption and EXAFS coordination with novel composite nanomaterials. Chem. Eng. J. 320, 427–435.
Awual, M.R., Hasan, M.M., Asiri, A.M., Rahman, M.M., 2019b. Novel optical composite material for efficient vanadium(III) capturing from wastewater. J. Mol. Liq. 283, 704–712.
Awual, M.R., Hasan, M.M., Islam, A., Rahman, M.M., Asiri, A.M., Khaleque, M.A., Sheikh, M.C., 2019c. Introducing an amine functionalized novel conjugate material for toxic nitrite detection and adsorption from wastewater. J. Clean. Prod. 228, 778–785.
Ayora, C., Macías, F., Torres, E., Lozano, A., Carrero, S., Nieto, J.-M., Perez-Lopez, R., Fernandez-Martínez, A., Castillo-Michel, H., 2016. Recovery of rare earth elements and yttrium from passive remediation systems of acid mine drainage. Environ. Sci. Technol. 50, 8255–8262.
Balde, C.P., Forti, V., Gray, V., Kuehr, R., Stegmann, P., 2017. The Global E-Waste Monitor 2017. United Nations University (UNU), International Telecommunication Union (ITU) & International Solid Waste Association (ISWA), Bonn/Geneva/Vienna, ISBN 978-92-808-9053-2.
Baldi, L., Peri, M., Vandone, D., 2014. Clean energy industries and rare earth materials: economic and financial issues. Energy Pol. 66, 53–61.
Banda, R., Jeon, H.S., Lee, M.S., 2014. Separation of Ce and La from synthetic chloride leach solution of monazite sand by precipitation and solvent extraction. Metall. Mater. Trans. B Process Metall. Mater. Process. Sci. 45, 2009–2017.
Baolu, Z., Zhongxue, Li, Yiqing, Z., Cong, Z., Yixin, W., 2016. Rare Earth Elements supply vs. clean energy technologies: new problems to be solve. Min. Res. Mana. 32, 29–44.
Barik, S.P., Park, K.H., Parhi, P.K., Park, J.T., Nam, C.W., 2012. Extraction of metal values from waste spent petroleum catalyst using acidic solutions. Separ. Purif. Technol. 101, 85–90.
Behera, S.S., Parhi, P.K., 2016. Leaching kinetics study of neodymium from the scrap magnet using acetic acid. Separ. Purif. Technol. 160, 59–66.
Behera, S.S., Panda, S.K., Mandal, D., Parhi, P.K., 2019. Ultrasound and Microwave assisted leaching of neodymium from waste magnet using organic solvent. Hydrometallurgy 185, 61–70.
Benjamin, S., Yanping, X., Allan, W., John, S., Rex, H., Rene, K., Geert, V., Gert, J.K., 2014. Life cycle inventory of the production of rare earths and the subsequent production of NdFeB rare earth permanent magnets. Environ. Sci. Technol. 48, 3951–3958.
BP Statistical Review of World Energy, 2019.
Brudnick, I.A., 2011. The Congressional Research Service and the American Legislative Process, vols. 7–5700. R41347April 12.
Canovas, C.R., Chapron, S., Arrachart, G., Pellet-Rostaing, S., 2019. Leaching of rare earth elements (REEs) and impurities from phosphogypsam: a preliminary insight for further recovery of critical raw materials. J. Clean. Prod. 219, 225–235.
Chen, Y., Wang, H., Pei, Y., Wang, J., 2017. Selective separation of scandium (III) from rare earth metals by carboxyl-functionalized ionic liquids. Separ. Purif. Technol. 178, 261–268.
Chenna, R.B., Yiannis, P., Koen, B., Tom, V.,G., 2015. Leaching of rare earths from bauxite residue (red mud). Min. Eng. 76, 20–27.
Chenna, R.B., Bart, B., Yiannis, P., Koen, B., Tom, V.G., 2016a. Recovery of rare earths and other valuable metals from bauxite residue (Red Mud): a review. J. Sustain. Metall. 2, 365–386.
Chenna, R.B., Jasper, M., Bart, B., Yiannis, P., Koen, B., Tom, V.G., 2016b. Selective recovery of rare earths from bauxite residue by combination of sulfation, roasting, and leaching. Min. Eng. 92, 151–159.
Cristian, T., Christian, E., Teodora, R., 2014. Characterization and leaching of real fluorescent lamp waste for the recovery of rare earth metals and mercury. Hydrometallurgy 144–145, 91–98.
Cristian, T., Martina, P., Christian, E., Teodora, R., 2016. A hydrometallurgical process for the recovery of rare earth elements from fluorescent lamp waste fractions. Separ. Purif. Technol. 161, 172–186.
Cui, J., Forssberg, E., 2003. Mechanical recycling of waste electric and electronic equipment: a review. J. Hazard Mater. 99 (3), 243–263.
Daejin, K., Lawrence, E.P., Lætitia, H.D., Eric, S.P., Jim, H., Ramesh, R.B., 2015. Selective extraction of rare earth elements from permanent magnet scraps with membrane solvent extraction. Environ. Sci. Technol. 49, 9452–9459.
Das, S., Behera, S.S., Murmu, B.M., Mohapatra, R.K., Mandal, D., Samantray, R., Parhi, P.K., Senanayake, G., 2018. Extraction of scandium (III) from acidic solutions using organo-phosphoric acid reagents: a comparative study. Separ. Purif. Technol. 202, 248–258.
David, D., Koen, B., 2015a. Recycling of rare earths from NdFeB magnets using a combined leaching/extraction system based on the acidity and

thermomorphism of the ionic liquid [Hbet][Tf_2N]. Green Chem. 17, 2150–2163.
David, D., Koen, B., 2015b. Rare-earth recycling using a functionalized ionic liquid for the selective dissolution and revalorization of Y_2O_3: Eu^{3+} from lamp phosphor waste. Green Chem. 17, 856–868.
Deng, B., Li, G., Luo, J., Ye, Q., Liu, M., Rao, M., Jiang, T., 2019. Selectively leaching the iron-removed bauxite residues with phosphoric acid for the enrichment of rare earth elements. Separ. Purif. Technol. 227, 115714.
Du, X., Graedel, T.E., 2011. Global rare earth in-use stocks in NdFeB permanent magnets. J. Ind. Econ. 15, 836–843.
Fan, Y., Fukiko, K., Yuzo, B., Noriho, K., Masahiro, G., 2013. Selective extraction and recovery of rare earth metals from phosphor powders in waste fluorescent lamps using an ionic liquid system. J. Hazard Mater. 254–255, 79–88.
Fedorov, Yu S., Kulyako, Yu M., Blazheva, I.V., Goletskii, N.D., Zilberman, B. Ya, Metalidi, M.M., Petrov, Yu Yu, Ryabkova, N.V., Vinokurov, S.E., Trofimov, T.I., Myasoedov, B.F., 2016. Dissolution of WWER-1000 spent nuclear fuel in a weakly acidic solution of iron nitrate and recovery of actinides and rare earth elements with TBP solutions. Radiochemistry 58, 265–270.
Gasser, M.S., Aly, M.I., 2013. Separation and recovery of rare earth elements from spent nickel–metal-hydride batteries using synthetic adsorbent. Int. J. Min.-Proce. 121, 31–38.
Goodenough, K.,M., Wall, F., Merriman, D., 2018. The rare earth elements: demand, global resources, and challenges for resourcing future generations. Nat. Resour. Res. 27, 201–216.
Habashi, F., 1980. Extractive Metallurgy: Hydrometallurgy, vol. II. Gordon and Breach, Science Publishers, Inc., NY, USA, ISBN 0-677-01780-4.
Heijungs, R., Huppes, G., Udo de Haes, H.A., Van den Berg, N.W., Dutilh, C.E., 1996. Life Cycle Assessment: what it Is and How to Do it. UNEP, France, ISBN 92-807-1546-1.
Ibrahim, T.M.M., El-Hussaini, O.M., 2007. Production of anhydrite–gypsum and recovery of rare earths as a by-product. Hydrometallurgy 87, 11–17.
International Energy Agency (IEA), 2017. Global EV Outlook 2017: Two Million and Counting.
International Energy Agency (IEA), 2019. Global EV Outlook 2019: Scaling-Up the Transition to Electric Mobility.
Iftekhar, S., Srivastava, V., Casas, A., Sillanpaa, M., 2018. Synthesis of novel GA-g-PAM/SiO_2 nanocomposite for the recovery of rare earth elements (REE) ions from aqueous solution. J. Clean. Prod. 170, 251–259.
Innocenzi, V., De, M.I., Ferella, F., Veglio, F., 2013. Recovery of yttrium from cathode ray tubes and lamps' fluorescent powders: experimental results and economic simulation. Waste Manag. 33, 2390–2396.
Innocenzi, V., Ippolito, N.M., Pietrelli, L., Centofanti, M., Piga, L., Veglio, F., 2018. Application of solvent extraction operation to recover rare earths from fluorescent lamps. J. Clean. Prod. 172, 2840–2852.
International Energy Outlook, 2017. US Energy Information Administration (EIA), USA.
Jaehyun, O.H., 2006. Current status for resources recycling in Korea. In: Proceedings of the International Seminar on Mineral Processing Technology, Chennai, India, pp. 42–48.
Jarosinski, A., Kowalczyk, J., Mazanek, Cz, 1993. Development of the Polish wasteless technology of apatite phosphogypsum utilization with recovery of rare earths. J. Alloys Compd. 200, 147–150.
Jha, M.K., Kumari, A., Panda, R., Kumar, J.R., Yoo, K., Lee, J.Y., 2016. Review on hydrometallurgical recovery of rare earth metals. Hydrometallurgy 165, 2–26.
Jiang, Y., Shibayama, A., Liu, K., Fujita, T., 2004. Recovery of rare earths from the spent optical glass by hydrometallurgical process. Canadian Metal. Quar. 43, 431–438.
Justel, T., Nikol, H., Ronda, C., 1998. New developments in the field of luminescent materials for lighting and displays. Angew. Chem. Int. Ed. 37, 3084–3103.
Jyothi, R.K., 2020. Rare-Earth Metal Recovery for Green Technologies: Methods and Applications. Springer, Cham, Switzerland, ISBN 978-3-030-38105-9.
Jyothi, R.K., Chung, K.W., Kim, C.J., Yoon, H.S., 2020. Recovery of rare earth elements from waste permanent magnets leach liquors. Minerals, Metals and Materials Series 335–345 (ISBN: 978-3-030-36757-2).
Kiddee, P., Naidu, R., Wong, M.H., 2013. Metals and polybrominated diphenyl ethers leaching from electronic waste in simulated landfills. J. Hazard Mater. 252–253, 243–249.
Kim, J.S., Kumar, J.R., Lee, J.Y., 2013. Status and preparation technology of rare earth materials. In: The 8th Pacific Rim International Congress on Advanced Materials and Processing, TMS Meeting at Hawaii Island, USA, ISBN 978-0-470-94309-0, pp. 1765–1774.
Kim, J.S., Kim, H.S., Kim, M.J., Lee, J.Y., Kumar, J.R., 2015. Status of separation and purification of rare earth elements from Korean ore. TMS Annual Meeting 15–19, 117–126 (ISBN: 978-1-119-09730-2).
Kinga, P.-M., Katarzyna, G., Zbigniew, W., 2015. Potential management of waste phosphogypsum with particular focus on recovery of rare earth metals. Pol. J. Chem. Technol. 17, 55–61.
Koen, B., Jones, P.T., 2014. Perspectives for the recovery of rare earths from end-of-life fluorescent lamps. J. Rare Earths 32, 195–200.
Koen, B., Peter, T.J., Bart, B., Tom, V.G., Yongxiang, Y., Allan, W., Matthias, B., 2013a. Recycling of rare earths: a critical review. J. Clean. Prod. 51, 1–22.
Koen, B., Jones, P.T., Acker, K.V., Blanpain, B., Mishra, B., Apelian, D., 2013b. Rare-earth economics: the balance problem. JOM 65, 846–848.
Koen, B., Yiannis, P., Peter, T.J., Tom, V., G, Bart, B., 2013c. Recovery of rare earths from industrial waste residues: a concise review. In: Proceedings of the 3rd International Slag Valorization Symposium: the Transition to Sustainable Materials Management at Leuven Belgium, 19-20 March 2013, pp. 191–205.
Kopera, J.J.C., 2004. Inside the Nickel Metal Hydride Battery. COBASYS. June 2004.
Kumar, J.R., Lee, J.Y., 2017. Recovery of critical rare earth elements for green energy technologies. Minerals, Metals and Materials Series Volume Part F3, 19–29 (ISBN: 978-3-319-51084-2).
Kumar, V., Jha, M.K., Kumari, A., Panda, R., Kumar, J.R., Lee, J.Y., 2014. Recovery of Rare Earth Metals (REMs) from Primary and Secondary Resources: A Review. TMS Annual Meeting, San Diego, California USA, ISBN 978-1-118-88882-7, pp. 81–88.
Kumari, A., Panda, R., Jha, M.K., Kumar, J.R., Lee, J.Y., 2015a. Process development to recover rare earth metals from monazite mineral: a review. Miner. Eng. 79, 102–115.
Kumari, A., Panda, R., Jha, M.K., Lee, J.Y., Kumar, J.R., Kumar, V., 2015b. Thermal treatment for the separation of phosphate and recovery of rare earth metals (REMs) from Korean monazite. J. Ind. Eng. Chem. 21, 696–703.
Kumari, A., Parween, R., Chakravarty, S., Parmar, K., Pathak, D.D., Lee, J.C., Jha, M.K., 2019a. Novel approach to recover rare earth metals (REMs) from Indian coal bottom ash. Hydrometallurgy 187, 1–7.
Kumari, A., Jha, M.K., Yoo, K., Panda, R., Lee, J.Y., Kumar, J.R., Pathak, D.D., 2019b. Advanced process to dephosphorize monazite for effective leaching of rare earth metals (REMs). Hydrometallurgy 187, 203–211.
Li, L., Xu, S., Ju, Z., Wu, F., 2009. Recovery of Ni, Co and rare earths from spent Ni–metal hydride batteries and preparation of spherical $Ni(OH)_2$. Hydrometallurgy 100, 41–46.
Li, F., Wang, Y., Su, X., Sun, X., 2019. Towards zero-consumption of acid and alkali recycling rare earths from scraps: a precipitation-stripping-saponification extraction strategy using CYANEX®572. J. Clean. Prod. 228, 692–702.
Liu, Y., Zhu, L., Sun, X., Chen, J., 2010. Toward greener separations of rare earths: bifunctional ionic liquid extractants in biodiesel. AIChE J. 56 (9), 2338–2346.
Liu, H., Zhang, S.G., Pan, D.A., Tian, J.J., Yang, M., Wu, M.L., Volinsky, Alex A., 2014. Rare earth elements recycling from waste phosphor by dual hydrochloric acid dissolution. J. Hazard Mater. 272, 96–101.
Liu, H., Li, S., Wang, B., Wang, K., Wu, R., Ekberg, C., 2019. Multiscale recycling rare earth elements from real waste trichromatic phosphors containing glass. J. Clean. Prod. 238, 117998.
Lopez, J., Reig, M., Gibert, O., Cortina, J.L., 2019. Integration of nanofiltration membranes in recovery options of rare earth elements from acidic mine waters. J. Clean. Prod. 210, 1249–1260.
Lorenz, T., Bertau, M., 2019. Recycling of rareearthelements from FeNdB-Magnets via solid-state chlorination. J. Clean. Prod. 215, 131–143.
Mahmoud, A.R., 2008. Recyclables recovery of europium and yttrium metals and some salts from spent fluorescent lamps. Waste Manag. 28, 318–325.
Mancheri, N.A., Sprecher, B., Bailey, G., Ge, J., Arnold, T., 2019. Effect of Chinese polices on rare earth supply chain resilience. Resour. Conserv. Recycl. 142, 101–122.
Masahiro, I., Koji, M., Ken-ichi, M., 2009. Novel rare earth recovery process on Nd-Fe-B magnet scrap by selective chlorination using NH_4Cl. J. Alloys Compd. 477, 484–487.
Matsumiya, M., Ishioka, K., Yamada, T., Ishii, M., Kawakami, S., 2014a. Recovery of rare earth metals from voice coil motors using bis(trifluoromethylsulfonyl) amide melts by wet separation, and electrodeposition. Int. J. Miner. Process. 126, 62–69.
Matsumiya, M., Kikuchi, Y., Yamada, T., Kawakami, S., 2014b. Extraction of rare earth ions by tri-n-butyl-phosphate/phosphonium ionic liquids and the feasibility of recovery by direct electrodeposition. Separ. Purif. Technol. 130, 91–101.
Mooiman, M.B., Sole, K.C., Kinneberg, D.J., 2005. Challenging the traditional hydrometallurgy curriculum-an industry perspective. Hydrometallurgy 79, 80–88.
Naeem, A.T., Kashi, E., Salehi, M.A., Habibpour, R., 2018. Extraction and separation of La(III), Pr(III) and Nd(III) using binary mixture of D2EHPA with Cyanex272, TOPO and TBP extractants. Metall. Res. Technol. 115 (612), 1–8.
Namil, U., Tetsuji, H., 2013. Dissolution behavior of La_2O_3, Pr_2O_3, Nd_2O_3, CaO and Al_2O_3 in sulfuric acid solutions and study of cerium recovery from rare earth polishing powder waste via two-stage sulfuric acid leaching. Mater. Trans. 54, 713–719.
Ogunseitan, O.A., Schoenung, J.M., Saphores, M.J.-M., Shapiro, A.A., 2009. The electronics revolution: from E-wonderland to E-wasteland. Science 326, 670–671.
Onghena, B., Borra, C.R., Van Gerven, T., Binnemans, K., 2017. Recovery of scandium from sulfation-roasted leachates of bauxite residue by solvent extraction with the ionic liquid betainiumbis (tri-fluoro-methyl-sulfonyl) imide. Separ. Purif. Technol. 176, 208–219.
Panagiotis, D., Efthymios, B., Dimitrios, P., Ioannis, P., 2016. Selective leaching of rare earth elements from bauxite residue (red mud), using a functionalized hydrophobic ionic liquid. Hydrometallurgy 164, 125–135.
Panda, R., Kumari, A., Hait, J., Jha, M.K., Kumar, V., Kumar, J.R., Lee, J.Y., 2014. Leaching of rare earth metals (REMs) from Korean monazite concentrate. J. Ind. Eng. Chem. 20, 2035–2042.
Panigrahi, M., Grabda, M., Kozak, D., Dorai, A., Shibata, E., Kawamura, J., Nakamura, T., 2016. Liquid–liquid extraction of neodymium ions from aqueous solutions of NdCl3 by phosphonium-based ionic liquids. Separ. Purif. Technol. 171, 263–269.
Parhi, P.K., Park, K.H., Nam, C.W., Park, J.T., Barik, S.P., 2013. Extraction of rare earth metals from deep sea nodule using H_2SO_4 Solution. Int. J. Miner. Process. 119, 89–92.

Parhi, P.K., Park, K.H., Nam, C.W., Park, J.T., 2015. Liquid-liquid extraction and separation of total rare earth (RE) metals from polymetallic manganese nodule leaching solution. J. Rare Earths 33, 207–213.
Parhi, P.K., Sethy, T.R., Rout, P.C., Sarangi, K., 2016. Separation and recovery of neodymium and praseodymium from permanent magnet scrap through hydrometallurgical route. Separ. Sci. Technol. 51, 2232–2241.
Parhi, P.K., Behera, S.S., Das, S., Murmu, B.M., Samantaray, R., 2017. Hydrometallurgical processing technology for recovery of the light rare earth metals: scandium (III) and neodymium (III) from primary and secondary sources. In: Jyothi, J.R. (Ed.), Mineral Processing: Methods, Applications and Technology. NOVA Science, pp. 57–113. Book Edited by.
Parhi, P.K., Behera, S.S., Mohapatra, R.K., Sahoo, T.R., Das, D., Misra, P.K., 2019. Separation and recovery of Sc (III) from Mg–Sc alloy scrap solution through hollow fiber supported liquid membrane (HFLM) process supported by Bifunctional ionic liquid as carrier. Separ. Sci. Technol. 54 (9), 1478–1488.
Pavon, A., Fortuny, A., Coll, M.T., Sastre, A.M., 2019. Improved rare earth elements recovery fromfluorescent lamp wastesapplying supported liquid membranes to the leaching solutions. Separ. Purif. Technol. 224, 332–339.
Pietrelli, L., Bellomo, B., Fontana, D., Montereali, M.R., 2002. Rare earths recovery from NiMH spent batteries. Hydrometallurgy 66, 135–139.
Ponou, J., Wang, L.P., Dodbiba, G., Okaya, K., Fujita, T., Mitsuhashi, K., Atarashi, T., Satoh, G., Noda, M., 2014. Recovery of rare earth elements from aqueous solution obtained from Vietnamese clay minerals using dried and carbonized parachlorella. J. Envi. Chem. Eng. 2, 1070–1081.
Ponou, J., Dodbiba, G., Anh, J.W., Fujita, T., 2016. Selective recovery of rare earth elements from aqueous solution obtained from coal power plant ash. J Environ. Chem. Eng. 4, 3761–3766.
Qi, D., 2018. Hydrometallurgy of Rare Earths: Extraction and Separation. Elsevier, Amsterdam, The Netherlands, ISBN 978-0-12-813920-2.
Rao, S.R., 2006. Resource Recovery and Recycling from Metallurgical Wastes. Elsevier, Amsterdam, The Netherlands, ISBN 978-0-08-045131-2.
Reddy, B.R., Kumar, J.R., 2016. Rare earths extraction, separation and recovery from phosphoric acid media. Solvent Extr. Ion Exch. 34, 226–240.
Reisdörfer, G., Bertuol, D., Tanabe, E.H., 2019. Recovery of neodymium from the magnets of hard disk drives using organic acids. Min. Eng. 143, 105938.
REN21, 2012. Renewables 2012 Global Status Report. REN21 Secretariat, Paris.
Resende, L.V., Morais, C.A., 2010. Study of the recovery of rare earth elements from computer monitor scraps leaching experiments. Min. Eng. 23, 277–280.
Resnick Institute Report, 2011. Critical Materials for Sustainable Energy Applications. California Institute of Technology, USA.
Ritcey, G.M., Ashbrook, A.W., 1984. Solvent Extraction: Principles and Applications to Process Metallurgy. Elsevier, Amsterdam, The Netherlands.
Ronda, C.R., Justel, T., Nikol, H., 1998. Rare earth phosphors: fundamentals and applications. J. Alloys Compd. 275–277, 669–676.
Saleem, H.A., Damien, G., Nicholas, A., Edmund, N., Graham, B., Alecos, D., Ray, D., Maria, A.E., Judith, K., Anna, L., Lawrence, D.M., Roland, O., Janet, S., Richard, S., Gabi, S., Olivier, V., Natalia, Y., 2017. Mineral supply for sustainable development requires resource governance. Nature 543, 367–372.
Seredin, V.V., 1996. Rare earth element-bearing coals from the Russian far east deposits. Int. J. Coal Geol. 30, 101–129.
Shahat, A., Awual, M.R., Naushad, M., 2015a. Functional ligand anchored nanomaterial based facial adsorbent for cobalt(II) detection and removal from water samples. Chem. Eng. J. 271, 155–163.
Shahat, A., Awual, M.R., Khaleque, M.A., Alam, M.Z., Naushad, M., Chowdhury, A.M.S., 2015b. Large-pore diameter nano-adsorbent and its application for rapid lead(II) detection and removal from aqueous media. Chem. Eng. J. 273, 286–295.
Shahat, A., Hassan, H.M.A., Azzazy, H.M.E., El-Sharkawy, E.A., Abdou, H.M., Awual, M.R., 2018. Novel hierarchical composite adsorbent for selective lead(II) ions capturing from wastewater samples. Chem. Eng. J. 320, 377–386.
Singh, U., Thawrani, S.A., Ansari, M.S., Puttewar, S.P., Agnihotri, A., 2019. Studies on beneficiation and leaching characteristics of rare earth elements in Indian red mud. Russ. J. Non-Ferrous Metals 60, 335–340.
Tang, M., Zhou, C., Pan, J., Zhang, N., Liu, L., Cao, S., Hu, T., Ji, W., 2019. Study on extraction of rare earth elements from coal fly ash through alkali fusion – acid leaching. Min. Eng. 136, 36–42.
Tao, X., Xiaodong, Z., Zhong, L., Baoyi, L., Chunmei, M.A., Xiaoling, G., 2010. Recovery of rare earth and cobalt from Co-based magnetic scraps. J. Rare Earths 28, 485–488.
Thriveni, T., Kumar, J.R., Ramakrishna, C., Jegal, Y., Ahn, J.W., 2015. Rare Earth Elements Gallium and Yttrium Recovery from (Kc) Korean Red Mud Samples by Solvent Extraction and Heavy Metals Removal/Stabilization by Carbonation, vols. 15–19. TMS Annual Meeting, USA, pp. 157–168 (ISBN: 978-1-119-09730-2).
Ting, M.H., Seaman, J., 2013. Rare earths: future elements of conflict in Asia? Asian Stud. Rev. 37, 234–252.
Tom, V.H., Bart, B., Tom, V.G., Koen, B., 2014. From NdFeB magnets towards the rare-earth oxides: a recycling process consuming only oxalic acid. RSC Adv. 4, 64099–64111.
Tuan, L.Q., Thenepalli, T., Chilakala, R., Vu, H.H.T., Ahn, J.W., Kim, J., 2019. Leaching characteristics of low concentration rare earth elements in Korean (samcheok) CFBC bottom ash samples. Sustainability 11 (2562), 1–11.
Tunsu, C., Menard, Y., Eriksen, D.O., Ekberg, C., Petranikova, M., 2019. Recovery of critical materials from mine tailings: a comparative study of the solvent extraction of rare earths using acidic, solvating and mixed extractant systems. J. Clean. Prod. 218, 425–437.
Uda, T., 2010. Recovery of rare earths from magnet sludge by $FeCl_2$. Mater. Trans. 43, 55–62.
Um, N., Hirato, T., 2013. Dissolution behavior of La_2O_3, Pr_2O_3, Nd_2O_3, CaO and Al_2O_3 in sulfuric acid solutions and study of cerium recovery from rare earth polishing powder waste via two-stage sulfuric acid leaching. Mater. Trans. 54, 713–719.
Reuter, M.A., Hudson, C., van Schaik, A., Heiskanen, K., Meskers, C., Hagelüken, C., 2013. UNEP Metal Recycling: Opportunities, Limits, Infrastructure, A Report of the Working Group on the Global Metal Flows to the International Resource Panel. UNEP, ISBN 978-92-807-3267-2, 2013.
United Nations Conference on Trade and Development, 2014. (UNCTAD) Book on Commodities at A Glance-Special Issue on Rare Earths. Printed at United Nations, Geneva-GE, 14-50515 - May 2014-984-UNCTAD/SUC/2014/1.
U.S. Department of Energy, 2010. Critical Materials Strategy.
U.S. Energy Information Administration, 2013. International Energy Outlook. DOE/EIA-0484. July 2013.
USGS, 2020. Rare earths statistics and information. https://www.usgs.gov/centers/nmic/rare-earths-statistics-and-information.
Walter, K., 2014. Background and Future Prospects in Life Cycle Assessment. Springer, New York, USA, ISBN 978-94-017-8696-6, 2014.
Wang, Z., Zhang, B., Guan, D., 2016. Take responsibility for electronic-waste disposal. Nature 536, 23–25.
World Commission on Environment and Development, 1987. Our Common Future. Oxford University Press, Oxford, ISBN 019282080X.
Wu, Y., Wang, B., Zhang, Q., Li, R., Yu, J., 2014. A novel process for high efficiency recovery of rare earth metals from waste phosphors using a sodium peroxide system. RSC Adv. 4, 7927–7932.
Wu, S., Wang, L., Zhang, P., El-Shall, H., Moudgil, B., Huang, X., Zhao, L., Zhang, L., Feng, Z., 2018. Simultaneous recovery of rare earth uranium from wet process phosphoric acid using solvent extraction with D2EHPA. Hydrometallurgy 175, 109–116.
Wu, Y., Zhang, Q., Zuo, T., 2019. Selective recovery of Y and Eu from rare-earth tricolored phosphorescent powders waste via a combined acid-leaching and photo-reduction process. J. Clean. Prod. 226, 858–865.
Xingmei, S., Liaosha, L., Xingrong, W., Ping, W., Lianzhen, W., 2015. Recovery of rare earth from waste CRT phosphor. CIESC J. 66, 1498–1505.
Yang, H., Wang, W., Zhang, D., Deng, Y., Cui, H., Chen, J., Li, D., 2010. Recovery of trace rare earths from high-level Fe^{3+a}nd Al^{3+W}aste of oil shale ash (Fe-Al-OSA). Ind. Eng. Chem. Res. 49, 11645–11651.
Yang, H., Wang, W., Cui, H., Zhang, D., Liua, Y., Chen, J., 2012. Recovery of rare earth elements from simulated fluorescent powder using bi-functional ionic liquid extractants (Bif-ILEs). J. Chem. Technol. Biotechnol. 87, 198–205.
Yin, X., Tian, X., Wu, Zhang, Q., Wang, Q., Li, Bin, Gong, Y., Zuo, T., 2018. Recycling rareearth elements from waste cathode ray tube phosphors: experimental study and mechanism analysis. J. Clean. Prod. 205, 58–66.
Yoon, H.S., Kim, C.J., Chung, K.W., Kim, S.D., Kumar, J.R., 2015a. Recovery process development for the rare earths from permanent magnet scraps leach liquors. J. Braz. Chem. Soc. 26, 1143–1151.
Yoon, H.S., Kim, C.J., Chung, K.W., Kim, S.D., Kumar, J.R., 2015b. Process development for recovery of dysprosium from permanent magnet scraps leach liquor by hydrometallurgical techniques. Can. Metall. Q. 54, 318–327.
Yoon, H.S., Kim, C.J., Chung, K.W., Kim, S.D., Lee, J.Y., Kumar, J.R., 2016. Solvent extraction, separation and recovery of the dysprosium (Dy) and neodymium (Nd) from aqueous solutions: waste recycling strategies for permanent magnet processing. Hydrometallurgy 165, 27–43.
Yun, X., Liansheng, X., Jiying, T., Zhaoyang, L., Li, Z., 2015. Recovery of rare earths from acid leach solutions of spent nickel-metal-hydride batteries using solvent extraction. J. Rare Earths 33, 1348–1354.
Yurramendi, L., Gijsemans, L., Forte, F., Aldana, J.L., Rio, C.D., Binnemans, K., 2019. Enhancing rare-earth recovery from lamp phosphor waste. Hydrometallurgy 187, 38–44.
Yuuki, M., Naoto, T., Katsuyasu, S., 2013. Selective recovery of rare earth elements from Dy containing NdFeB magnets by chlorination. ACS Sustain. Chem. Eng. 1, 655–662.
Zepf, V., Reller, A., Rennie, C., Ashfield, M., Simmons, J., BP, 2014. Materials Critical to the Energy Industry: an Introduction, second ed. UK.
Zhang, W., Honaker, R., 2019. Calcination pretreatment effects on acid leaching characteristics of rare earth elements from middlings and coarse refuse material associated with a bituminous coal source. Fuel 249, 130–145.
Zhang, S.G., Yang, M., Liu, H., Pan, D.A., Tian, J.J., 2013. Recovery of waste rare earth fluorescent powders by two stepsacid leaching. Rare Met. 32, 609–615.
Zhang, B., Liu, C., Li, C., Jiang, M., 2014. A novel approach for recovery of rare earths and niobium from Bayan Obo tailing. Miner. Eng. 65, 17–23.
Zhang, Y., Chu, W., Chen, X., Wang, M., Cui, H., Wang, J., 2019. Recovery of rare earth metals and synthesis of Ni0.6Co0.2Mn0.2(OH)2 from spent asymmetric-capacitance power batteries. J. Clean. Prod. 235, 1295–1303.
Zhu, G., Chi, R., Xu, Y., 2000. Separation and recovery of RE and Mn from rare earth mud in China. Int. J. Miner. Process. 59, 163–174.