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A Review of Rare Earth Mineral Processing Technology

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Abstract: The recent technological advancement has made the rare earth elements (REEs) more significant and they in turn have facilitated the culmination of more new technological applications owing to their unique physical and chemical properties. In this regard, renewable energy applications such as wind turbine and hybrid cars testify to the increasing demands on permanent magnet in the future. Considering such increasing demands on REEs, it is felt necessary to identify alternative producers of REEs outside of China as one of the measures to create a fair competition and control the price on the market. It is worth highlighting that the separation of rare earth can be both complex and challenging owing to similar properties which are shared by them. The purpose of this paper is to comprehensively review and summarize the rare earth processing routes, the mostly employed rare earth separation methods, supply and demand of rare earth around the world and some possible scenarios in rare earth market. This review has critically looked into a few authors' recent reviews on six major processes of rare earth processing steps and each step is considered as important to produce both high quality and better quantity of REEs.

Keywords: *Rare earth processing steps; Separation process; Application rare earth; Demand rare earth.*

Introduction

Rare earth overview

An increase in demand for rare earth elements (REEs) has been observed in recent years because of their unique properties and various applications. Presently, China has become the largest world supplier which reportedly produces more than 95% of total rare earth oxide (REO). In line with the recent drastic advancement in technology, REEs are becoming increasingly important sources of advanced science materials such as electronic, environmental, optical, magnetic and catalytic technologies. It has to be noted that these elements have now become more important for highly technological applications and most of the industries reportedly use REEs more than platinum group metals.[1] and they are notably used more than gold.[2] In the year of 2015, six major countries reportedly produced REEs, namely China, Australia, United States, Russia, Thailand, and Malaysia.[3]

REEs are defined as the seventeen elements in periodic table which include a group of lanthanide series, scandium and yttrium element.[4-6]Scandium and yttrium have the disposition to co-exist with similar chemical properties such as other REEs.[7-8] It has to be noted that most of the rare earth (RE) metals are reportedly discovered within the earth's crust which consists of mixtures of various REEs along with some non-metals. An estimated 200 different species of RE minerals which have been defined to date have indicated significant RE characteristics and the associated properties are defined as RE minerals.[9,10] Basically, REEs were originally discovered in compounds of carbonates, oxides, phosphates, halides, and silicates.[9] They are classified into 2 groups based on their atomic numbers: Light rare earth elements or LREEs and heavy rare earth elements or HREEs.[6]LREEs are also known as the 'ceries' which is within the atomic number ranging from 57-63 (La to Eu), whereas HREEs are known as 'yttrics' and it is within the atomic number ranging from 64-71 (Gd-Lu). In this regard, some scholars have classified both Scandium and yttrium into the heavy element category. [11-13] On the other hand, some others have highlighted that the third category RE can be classified as medium rare earth (MREEs) which refers to the elements of Sm, Eu, and Gd.[14-16]

It is noteworthy that there are six different ores mineral from industry productions which include bastnasite [$(Ce,La)(CO_3)F$], monazite [$(Ce,La)PO_4$)], xenotime (YPO_4), loparite[$(Ce,Na,Ca)(Ti,Nb)O_3$], apatite [$(Ca,REE,Sr,Na,K)_3Ca_2(PO_4)_3(F,OH)$], and ion-adsorption clays.[5] The first there minerals are known as the commercial REE mineral sources which contribute to almost 95% the world's reserves of REEs: bastnasite (70–75% REO), monazite (55–60% REO) and xenotime (55–60% REO).[17-23]Notably, most of xenotime minerals are discovered alongside with monazite with an estimated amount of 0.5–5.0% concentration of xenotime in monazite.[24-25] Besides, ion-adsorption clays (i.e., weather crust elution deposit rare earths) are also considered as one of the major

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types of REE ores.[5,26] These deposits have indicated relatively higher weathered REE-rich rocks which are developed from chemical weathering under particular climatic changes.[5] In contrast, the other two sources are loparite and apatite which are also considered as RE sources. Loparite is a titanate-niobatetantalate compound of RE which is mostly found in Russia which is indicated by most of the RE suppliers coming from Lovozerskoye deposit.[27] Besides, some authors had been reported that apatite minerals are also considered as the by-products of phosphate fertilizer production.[28]It is worth highlighting that LREEs are extracted from bastnasite and monazite, meanwhile HREEs are extracted from xenotime and ions-adsorption mineral. LREEs have reportedly which has large amount of REOs produced.[11] The productions of LREEs on a global scale are now dominated by bastnasite processing at Baotou, Inner Mongolia. The extraction of monazite and xenotime are derived from mineral sands and tin operation productions. Notably, the ionic absorption clay in southern China is mainly processed by means of yttrium and heavy RE.

Application of Rare Earth Element

It is considered almost impossible for today's world to move on without RE metals. Almost every recent technological product such as cell phones, computers, laptops, televisions, hybrid cars, wind turbines, solar cells, hard disks, and a range of other products of RE high-tech application in the world may testify to this statement. Humphries highlighted the ever increasing demand on REMs around the globe which was at an estimated 136,000 tons annually, and he predicted it to increase further to at least 185,000 metric tons by the year of 2015.[11] For instance, the Toyota Prius hybrid car is one of the cars in the manufacturing industry which have used REE. Hybrid engines are known to operate by means of both the combination of batteries and internal combustion engines. In this regard, the Toyota Prius model reportedly contains approximately 10 pounds of lanthanum element in its battery. It has to be noted that neodymium element is used to produce the magnets for hybrid motors. In addition, Terbium and dysprosium elements are added in hybrid cars to maintain neodymium's magnetic characteristics at relatively higher temperatures. There are more other applications are shown in Table 1 which includes defences technology, solar cells, computer chip, etc.[29] In this regard, the magnetic elements such as neodymium, terbium and dysprosium are major components of wind turbine and computer hard drive related applications. In addition, yttrium is an essential ingredient which is widely used for televisions' colour, fuel cells and fluorescent lamps. Cerium and lanthanum elements are mostly applied in catalytic converters. Europium element is a necessary component in compact fluorescent bulbs, televisions, and iPhone screens.

Table 1: Main application of REEs.

Element	Atomic No.	Application
La	57	• Electron microscopic tracer, studio lighting, laptop batteries, camera lenses and hybrid car batteries.
Ce	58	• Carbon-arc lighting, TV colour, screen, fluorescent lighting. catalytic converter
Pr	59	• Nickel metal hydride (NiMH) in hybrid cars, glass goggles for glass blowers and welders, high-intensity carbon arc lights
Nd	60	• NIB magnets (computers, hand phones, medical equipment, motors, wind turbines and audio systems), specialized goggles for glass blowers.
Pm	61	• atomic batteries for spacecraft and guided missiles.
Sm	62	• Magnets for headphones, small motors and pickups for some electric guitars, absorber in nuclear reactors, cancer treatment.
Eu	63	• anti-forgery marks on euro bank notes, nuclear reactor control rods, compact fluorescent bulbs
Gd	64	• Microwave, MRI, colour television picture tubes
Tb	65	• Magnet for wind turbine and hybrid car motor, speaker UV light for euro bank notes
Dy	66	• Speakers, compact discs and hard discs, medium source rare-earth lamps (MSRs) within the film industry
Ho	67	• Yellow or red colouring for glass, cubic zirconia, nuclear reactor control rods, solid-state lasers for non-invasive medical procedures treating cancers and kidney stones.
Er	68	• Nuclear reactor control rods, coloring agent in glazes and glasses. Laser for skin (remove tattoo)
Tm	69	• Laser, euro banknotes for its blue fluorescence under UV

		light to defeat counterfeiters.
Yb	70	• Stress gauges to monitor ground deformations caused by earthquakes or underground explosions, catalyst, fiber laser amplifiers
Lu	71	• Catalyst, detectors in positron emission tomography (PET)
Y	39	• Microwave filter, provide the red color in color television tubes, high-temperature superconductor YBCO
Sc	21	• Aerospace industry components and for sports equipment such as bicycle frames, fishing rods, golf iron shafts and baseball bats.

Rare Earth Ores Processing Steps

Most of the literature has been reviewed by several authors including beneficiation process [22] and solvent extraction.[23] However, there is still lack of reviewed on the overall RE processing. REEs processing consists of six main steps which include deposit exploration, mining, beneficiation, chemical treatment, separation, refining, and purification as it can be seen in Figure 1. It is worth highlighting that the industry takes the economic factors, potential impact on economy and environmental issues prior to mining. The pure REEs exist in complex rocks and they can be recovered by means of beneficiation process. The chemical treatment may take over to leach the REE concentration. Finally, individual element can be extracted by means of hydrometallurgy method and it is usually sold as either pure element or metal oxides to the consumers.

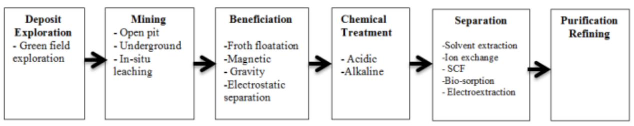

Figure 1: Schematic of REE processing steps.

Deposit Exploration

Most of REEs begin with the explorations and identifying the potential RE deposit locations to extract valuable minerals which are highly valued around the globe. It is worth highlighting that the relatively higher demand on valuable minerals such as gold, copper, RE minerals, platinum, etc. have increased the exploration on mining processes. Most of the companies usually begin with sampling and managing extensive studies by geochemical analysis. In this regard, they have to employ greenfield exploration activity as the preliminary stud.[30] However some authors stated that brownfield exploration is another kind of deposit exploration activity and this method has low risk than greenfield exploration activity.[31] Table 2 summarizes the description of greenfield exploration and brownfield exploration.

Table 2: Summary on greenfield exploration and brownfield exploration.

Category	Description
Greenfield Exploration	Greenfield exploration activity is more on predicting new area. Two types:- 1) Grassroot Exploration Project - Geologist has intention on mineral deposit located and spend cost on survey the mineral involving measuring gravity, magnetism, or radioactivity. The cost might be more than 10 million USD 2) Advanced Exploration Project - Geologist had comfirm the mineral deposit and proceeds to drilling activity. The cost reached up to 100 million USD.
Brownfield Exploration	Brownfield exploration activity is different than greenfield activity. The geologists carry on existing mine or proximity operating mine. Brownfield exploration activity is much more interest because of low risk and low cost involve in this activity.

In greenfield exploration method, geologists are presently on the lookout for the evidence of metal enrichment involving measuring gravity, magnetism, or radioactivity. Greenfield exploration may include detecting radiations, measuring magnetisms, variations in magnetic field, satellite photography, and geologic mapping. The first method is detecting radioactive, things which are considered suitable to detect radioactive elements such as uranium and thorium emit radioactive source. The second method is measuring magnetism which has detected the magnetic mineral by means of using magnetometers. The third method is variations observed in magnetic field; this method helps detect mineral density within the crust of the earth by means of using gravimeters. The forth method is satellite photography in which geologist snap photos to identify certain deposit and satellite is then used to create the element in the maps. The fifth method is geologic mapping which is used by geologists to develop some research for mineral deposit in order to find locations and structures of the deposit element. Among the major equipment required for mining are mechanical supply (machine) and ventilation system, power and water supply, and other facilities. The construction usually begins after implementing environmental standards and safety standards.[32]

Mining

The second step is mining, which has a standard technique in developing several minerals and elements. Liu and Bongaerts had posited that most RE is mined by three conventional mining techniques, namely surface mining (i.e., open pit mining), underground mining and in-situ leaching.[26] Open pit technique is commonly employed in RE separation such as Bayan Obo mine (China), Mountain Pass mine (United States) and Mount Weld mine (Australia). This method involves removing the ores from the walls of the tunnels by blasting, excavating, which is followed by the ores being transported to the surface for the following process. Moving on, open pit is usually mined within 100 meters from the surface and large excavations open to the air are employed to extract the ore before processing. Notably, this method is less expensive but leaves large scars on the land surface and is harmful to the environment. Besides that, Lovozero complex (Russia) had mined hard rock RE ores by means of employing both techniques (i.e., open pit and underground) to extract REEs from Loparite. Underground mines are considered as more expensive and dangerous compared to open pit. Apart from that, ion adsorption deposits in Southern China are mined by using in-situ leaching.

Beneficiation Process

The third step is the beneficiation process of RE bearing minerals. Beneficiation process involves the physical separation the purpose of which is to remove undesired impurities, or to enhance the concentration of a desired product. The main unit operation in beneficiation process consists of sizing unit (i.e., crushing and grinding) and the separation of REO from other minerals either by means of froth floatation (i.e., mixer, froth flotation cell, concentrator), magnetic separation, and gravity separation, followed by dewatering the minerals (i.e., thickening and drying).[26] The RE ores are usually found to be combined with barite, fluorite, calcite, silicates and iron minerals which can be quite challenging to separate between RE minerals from other associations.[26,33,34]Each of the processes has increased the concentration of REEs. Firstly, the REO ores may go through the jaw crusher and ball mill to reduce the ores' sizes. The crusher is used to break the ores to a fine size (i.e., <1 cm diameter), followed by ball mill unit with steel ball which is used for grinding the ore to even a finer size (40-100 μm).[35] Most of the industries reportedly use crusher and grinder to obtain desired ores' particle size.[36] The slurry of ores is then pumped into the next beneficiation stage either by means of froth flotation, magnetic separation, electrostatic separation, gravity concentration, or a combination of all.[37] For instance, Bayan Obo may apply gravity separation and froth floatation to increase the efficiency of separation between monazite and basnaesite from the iron-bearing and silicate gangue materials.[28]All of these methods are used to separate RE minerals from impurity elements such as copper, zinc, lead, nickel, and other non-ferrous metals.

Froth floatation is interactively applied in industries compared to other beneficiation techniques. This method uses chemical reagents (i.e., depressants and collectors) to separate the selection group of minerals to adhere to air bubbles.[36] The ore-water slurry from the mixer may go through froth floatation cell to separate the valuable metals and impurities.[35] The collector may have to be added to make RE minerals attached to the rising bubbles and float as it is shown in Figure 2. The air bubbles may in turn rise together with ore particle-water slurry.[38]In this regard, the RE particles may require at least an estimated 40-100 μm size diameter for optimum froth flotation feed.[39,]It is worth highlighting that the particles that are not attached with the bubbles may end up sinking. Most of the researchers have focused on basnaesite and monazite due to flotation response of their surface properties.[12]

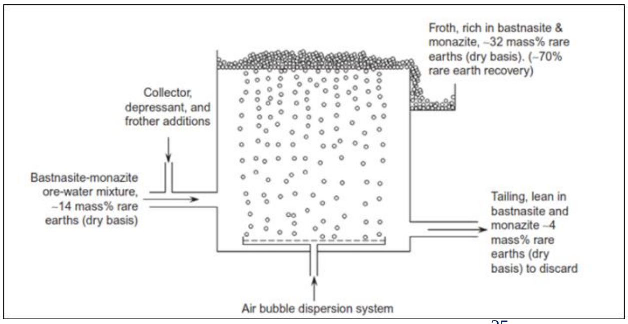

Figure 2: Schematic of froth flotation cell. [35]

In froth floatation, there are 2 types of chemicals which are widely used to separate REEs and others impurity elements which are called as depressants and collectors. Depressant is a chemical which is used to prevent the unwanted mineral floating whereas the collector is used to attach the minerals with air bubbles and to help raise them to the surface. The ores particles usually begin with depressant additions, followed by the collectors. The conventional chemical collectors for bastnasite minerals are mostly used for hydroxamats, fatty acids, dicarboxylic acids, and organic phosphoric acids in comparison with the mostly used depressants include sodium silicate, sodium hexafluorosilicate, lignin sulfonate, or sodium carbonate.[22] The effectiveness collector depends on the size of the particle to enhance the selectivity of a flotation process i.e., the feasible minerals which were initially floated together. Most of minerals float at a pH value of between 7.5 -11.5.[35]

Also, magnetic separation method is commonly employed in industry, in which, they are used to remove highly magnetic gangue from non-ferrous such as monazite or xenotime [17]. According to Spedding's theory, REEs have a series of electrons involving a shielded 4f sub-shell and these electrons have magnetic charge, which do not cancel out, and may in turn, resulted in a material with some degree of magnetism.[40] In Sichuan Maoniuping, China, the combination between magnetic separation and gravity separation without the use of froth floatation is employed. This combination enables a high concentration of REE from bastnasite deposit to be attained.[41]Paramagnetic mineral of xenotime is reported to be more susceptible to magnetic separation than monazite.[22] In fact, RE metals like neodymium and samarium are widely employed in constructing powerful magnets and minerals containing RE elements are only moderately paramagnetic. Jordens had summarized that most of REs are paramagnetic element, which refers to less magnetic minerals than ferromagnetic (i.e., strongly attracted to a magnet).[22] However, if the particle size of ore is less than 100 µm, floatation method is deemed favorable.[37,46]Several authors had pointed out that gravity separation is suitable to be applied when the minerals have huge specific gravities, which range from 4 to 7 and significantly less dense such as silica.[24,42] Monazite minerals such as Bayan Obo beneficiated monazite and bastnasite are commonly employed in gravity separation process, which were installed between the rougher and cleaner flotation circuits to separate both mineral from the iron-bearing and silicate gangue materials.[28,22] The disadvantage of gravity separation is its inefficacy to separate RE ores at very fine particles size, which resulted in considerable losses of REs.[43] However, if large differences in the specific gravity of the minerals such as gold from silicate gaugue exist, gravity separation maybe used even though the particles are very fine in size.[44-45]Based on literature, it is important to define a proper beneficiation method for physical separation according to ores properties. It is necessary to firstly analyses the physical and chemical properties of the ores mineral in order to determine the specific method for beneficiation process to considering low cost and time saving operation.

The final process in beneficiation process is Dewatering. The ore-water slurry is managed by passing the water into a huge concentrator or thickener. The particles are settling out of the slurry by means of gravity effect, followed by thermal drying such as rotary dryers, spray driers and rotary tray dryers.

Chemical Treatment

The fourth step in RE processing requires chemical treatment, which is known as cracking process.[6] Acid treatment and alkaline treatment are the two routes in chemical treatment. Both routes are employed to increase the REOs concentration with an estimation of 90% purities and remove impurities. With regards to acid treatment, most industries employed inorganic acids such as sulfuric acid (H_2SO_4), hydrochloric acid (HCL) and nitric acid (HNO_3), while NaOH and Na_2CO_3 are commonly used in alkaline treatment. Some authors had pointed out that alkaline treatment is mostly applied in monazite and bastnasite due to the phosphate and carbonate–fluoride component contained in them.[37] In China, acid-roasting with high temperature andsulfuric acid (H_2SO_4) is used to remove fluoride (HF), sulfur dioxide (SO_2), sulfur trioxide (SO_3), and silicon tetrafluoride (SiF_4) were employed extensively.[37,47] Dangerous gasses including hydrofluoric acid (HF), acid sulfuric (H_2SO_4) and hexafluorosilicic acid (H_2SiF_6) will be adsorbed during the first and second scrubber before being released to the atmosphere.[47] The scrubber is diluted with Na_2CO_3 solution, which is used to treat the exhaust as it is being discharged.[6,37]The acid treatment is currently apply at the Bayan Obo mine in China, meanwhile the alkaline treatment was apply by Molycorp at the Mountain Pass mine before the company closed in 2002.[48]

To illustrate, monazite can be managed via alkaline treatment (i.e., dissolution by sodium hydroxide) or acid treatment (i.e., digestion by acid sulphuric). The leach solution, which is produced from sulphuric acid digestion, contains other elements namely uranium (U), thorium (Th) and ferum (Fe). In relation to acid treatment, there are 3 ways employed for monazite after removing thorium (Th) and uranium (U), which include sodium double sulphate precipitation, neutralization by ammonia hydroxide and neutralization by sodium oxalate.[25] For monazite after minerals sodium removing impurities and radioactive element, alkaline treatment is available in 4 ways including dissolution by HCL, H_2SO, and HNO_3.[25] In bastnasite processing, REO was leached by various routes including calcite REO between 800-900^oC, Flotation process and calcite by 10% of HCL or 30% of HCL at 620^oC or dissolution of H_2SO_4 at 480^oC.[25] In relation to xenotime processing, there are 3 ways to leach out REO, which include digestion by 93% of H_2SO_4 at 190-250^oC, roasting of Na_2CO_3 at 900^oC and fusion of NaOH at 400^oC. These methods are leached by using water or extracted by means of using NH_4CL

Separation Process

The fifth step involves the separation process in order to purify individual REOs. There are five common methods for separation process, namely supercritical, biosorption, electro-winning, solvent extraction and ion exchange. Among these methods, solvent extraction is the mostly employed method in chemical industries in separating RE in single element.[49] REE minerals exits in fluorocarbonates and phosphates form are required to be converted to carbonates or chlorides prior to the separation process by means of using exchange or solvent extraction.[50] With regards to this process, REO was estimated to attain 99% purity.[25]Nonetheless, the similar chemical and physical properties make it difficult for REE to separate, which in turn, may increase both time and cost operation.

Several methods to separate RE from the ores were identified, namely chemical precipitation,[51-53]reduction,[54]bio-sorption,[55-67] membrane extraction,[68-70]liquid membranes,[71-74]solvent extraction,[75-76,96]ion exchange[76]and electro-winning.[77-81]However, supercritical, bio-sorption, electro-winning, solvent extraction and ion exchange are the 5 most popular methods for extracting RE element. The increasing amount of various REE applications has led researchers to develop techniques for the extraction of REE. It should be noted that many researchers have been working on improving the hydrometallurgy method.[82]Hydrometallurgy method is a technique employed to extract metallurgy involving chemical in aqueous form to recovery precious metals from ores, concentration solvent and recycled residual materials. Hydrometallurgical method depends on the capability of chemicals to extract RE mixtures from the undesired component by changing the pH and acid/bases utilized.[83] It is challenging to separate individual RE from each other due to the fact that they tend to have identical physical and chemical properties.[25] Separation processes focusing on ion exchange and solvent techniques have been developed to produce high purity single RE solutions or compounds.

Solvent extraction and ion exchange

Presently, solvent extraction is widely employed in many industries due to its capability to extract and purity RE products.[84-85] Several authors have reviewed the extraction of REE process, which employed chemicals and extractants [23,25]Solvent extraction is a process utilizing organic chemical (i.e., extractant) to transfer cations or anions from an aqueous phase into an immiscible organic phase.[86]REE is initiated by means of separating them in accordance with their group such as HREE and LREE using counter-current extraction.[87]The efficacy of solvent extraction is accomplished by the changes in different chemical nature between solvent and aqueous phases. Thus, the variables, which include the types of extractant, primary acidity, ores concentration and extractant concentration, may contribute to an effective RE separation.[23]

The desired individual element of RE, separation REEs with multiple unit mixer settlers is a common route.[25] The solvent extractant as organic phase and the RE leached as aqueous phases are mixed together in the mixer, in which, the particles are settler out and separated by gravity force. Notably, some cases in the industry have designed mixer with centrifugal force in order to mix both organic and organic phase. Various authors have delineated that the efficiency of the settler is limited by the settling time.[88 -95]Ion exchange technique was acknowledged as the most practical method used to separating the RE, just before the booming of RE industry by solvent extraction in the 1960s.[97]Although ion exchange is another way of separation RE, which has been employed in attaining 99.99% purities of REO, this technique is deemed not economical.[50]Most ion exchange techniques are employed to obtain high quality RE products either for electronic or analytical application.[98]Some authors posited that there are three major types of extractants, namely cation exchangers, anion exchangers and solvating extractants.[99-100] Among these extractant, solvating extractant is the commonly used in most of the industry. Some researchers stated that the conventional extractant, which is employed widely in the industry are di-2-ethylhexyl-phosphoric acid (D2EHPA or P204) and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (HEH/EHP or P507).[101-103]

Supercritical fluid

Supercritical fluid (SCF) method is a method employed to extract RE element by means of using carbon dioxide (CO_2). This method deals with carbon dioxide, which the temperature was elevated and compressed until above critical temperature and pressure are reached.[104]Most researchers are interested in REEs by SCF technique, in which, REEs extraction are expected to be improved by means of increasing the mass transfer between CO_2 and REEs.[104-111]The rapid and complete removal of the solute from the solvent is attained by means of gasification of carbon dioxide at atmospheric pressure, after the extraction. Shimizu and team had investigated RE extraction from secondary resources by employing supercritical fluid method.[111] Samsonova posited that SCF is suitable to be employed for recovery of actinides series in minimizing the radioactive aqueous and toxic organic wastes.[112] Mekki and group had studied the extraction of trivalent lanthanum and europium from an aqueous nitric acid solution to a supercritical CO_2 phase via an imidazolium-based ionic liquid phase.[113]Result showed 87% achieved in lanthanum and europium extraction.

Bio-sorption

Biosorption method is one of the emerging biological methods in sequestering metallic cations from diluted aqueous solutions and has received considerable attentions from researchers.[114-116]Most of the research focused on the heavy metal removal from industrial wastes.[117-121] A number of researchers have reported that the most empirical advantage of using biosorption is cost efficient due to the application of natural biomass to separate the RE element.[122-127] Table 3 summarizes the results of several research carried out, i.e., amongst the major studies published on REE biosorption. It should be noted that the sorption are contingent on the microorganism or bio-sorbent type, as well as on the experimental conditions. According to Das and team, there are various factors influencing the biosorption process and these parameters are with pH ranges from 4 to 7, bio-sorbent dosage of 15-200 mg/L, temperature of 25-60^{o}C, initial metal concentration of 15-300 mg/L and contact time of 300-480 min.[128]

Table 3: Summary of different types of adsorbents for bio-sorption process.

No.	REM	Adsorbents	Adsorp-tion capacity (mg/g)	Refer-ences
1	La	*Sargassum* biomass	40.28	55
		Sargassum fluitans	101.401	56
		Pseudomonas sp.	120	57
		Agrobacterium sp. HNI	35.27	58
		Platamus orientalis leaf powder	28.65	59
		Activated carbon from rice husks	175.4	60
		Bamboo charcoal	120	61
2	Nd	*Monoraphidium* sp.	1511	62
		Penicillium sp., activated carbon	178	62
		Baker's yeast	313	62
		activated carbon	61	62
		Kluyveromyces marxiamus, Candida Colliculaosa, Debaromyces hansenii	12	63
		Colliculaosa, Debaromyces hansenii	10	63
		D113-III resin	232.56	64
3	Ce	*Platamus orientalis* leaf powder	32.05	59
		Agrobacterium sp. HNI	34.59	58
4	Er	D113-III resin	250	65
		Activated carbon from rice husks	250	60
5	Eu	*Sargassum* biomass	62.30	55
6	Sm	*Sargassum* biomass	105	66
7	Pr	*Sargassum* biomass	98	66
8	Yb	*Sargassum* biomass	48.45	55
		D113-III resin	265.8	67

Sustainability of sources and demand in future

Supply and demand

It is noteworthy that with huge demand in new technologies, especially in military, clean energy and consumer electronics sectors, REEs play a significant role for the whole world. Recently, there is an increase of attention in relation to these elements from the industry due to reliability to their supply.[131-132]To date, China began entering the RE market in early 1980s and represents the first world's REEs market in the early 1990s until today. China offered a lower price compared to Mountain Pass, which resulted in becoming a competitor to other producers. Also, China is the major consumer of electronics products for both domestic and export markets.Referring to Table 4, permanent magnets, metal alloys and catalysts are the primary area with the high RE demand compared other sectors.[150]The demand of the magnet sector may increase in the future.[133] On the other hand, permanent magnet is usually applied in clean technologies and high technology application such as motor, hard disk, loudspeaker, sensors, generators, wind power system, hybrid vehicle, refrigeration, and etc.[134]

In fact, Alonso and team had posited that since electric vehicles and wind turbines depend on the rare-earth magnets sector, the demand on dysprosium (Dy) may grow more than 700% and the demand on neodymium (Nd) elements may increase more than 2600% in the next 25 years.[133] The principal element for permanent magnet sector includes neodymium, praseodymium, samarium, dysprosium and terbium additives.[135] Dysprosium is an important element in the formation of permanent neodymium magnets due to its capability to maintain at high temperature and may beappliedin green technology such as wind turbines and electric vehicles.[136]Besides, neodymium element is also empowered with a special ability to stabilize their property even at high temperature. Spiegel online had reported that electromagnetic fields existed in Nd element are 25 times stronger than conventional ferrites. To illustrate, a Mercedes S 400 Hybrid car applies around 0.5 kg of Nd element.[137] However, to generate electricity, wind turbine requires only approximately 200kg of Nd.[137]Some authors had reported that 600 kg of REEs is needed to generate 3.5MW in wind turbine, which in average, was calculated around 171 kg of REEs per MW.[138]

Table 4: Global RE Demand In 2016 (in tonnes of TREO ± 20%).

End use	China	USA	Japan & SE Asia	Others	Total	Total %
PM	28K	2K	4.5K	1.5K	3.6K	22.5
MA	23K	2K	3K	2K	3K	19
Ct	15.5 K	5.5K	2.5K	1.5K	2.5K	16
PP	13K	2K	2K	1K	1.8K	11
P	8.5K	750	2K	750	1.2K	8
GA	7K	1K	1K	1K	1K	6
Cm	4K	2250	2.5K	1.25K	1K	6
Others	5K	8K	4K	2K	1.9K	12
Total	10.4 K	23.5 K	21.5 K	11K	160K	-
Mark-et share	65%	15%	13%	7%	100%	-

Note: Permenent magnet (PM); Metal alloy (MA); Cayalyst (Ct); Polishing Powders (PP); Glass addictive (GA); Ceramic (Cm)

Bastnasite minerals cover up to 90% of the world's REO, which is found in China and Mountain Pass in California (USA).On the other hand, monazite deposits was found to be the second largest REEs in the world, which has found in Australia, South Africa, China, Brazil, Malaysia, India and Russia. In the year of 2015, China continued dominating the global supply of REs. China's Rare Earth Industry Association highlighted that the REO consumption in China was predicted to increase from 98,000 tons in the year of 2015 to 149,000 tons in the year of 2020.[3] Most REEs were consumed by China by means of the application of magnet, abrasives, and catalyst, which estimated to be 35%, 18%, and 15%, respectively. Recent statistics showed that although China reserved 55,000,000 metric tons per year, they still control the world market, which produced 105,000 metric tons annually in the year of 2015.[3] Notably, there are 10 active China mines in RE production including Inner Mongolia, Shandong, Sichuan, Zhejiang, Jiangxi, Hunan, Fujian, Yunnan, Guangxi and Guandong.[139] Bayan Obo mine in China is the biggest RE resources in the world, which has the ability to reserve about 90% of REO. Chinese scientists in Bayan Obo (Inner Mongolia) initiated their research in the year of 1927 and run their production in the year of 1957. These deposits are rich in LREEs, especially in monazite and bastnasite minerals.[139] Apart from that, Sichuan and Shandong also produced light RE from bastnasite and several deposits were discovered in south China, which is estimated to be 80% of world's reserved HREEs in ion-adsorption minerals.[140] The second largest RE deposit is Mountain Pass deposit, which is located near the border in the southern parts of California, United States. This deposit started to be mined in the year of 1952 and closed in the year of 2002 due to the existence of several problems including environmental issues and competition from China.[141] However, Mountain Pass Mine operated back in the year of 2012 and the United States produced approximately 4,100 metric tons per year in the year of 2015.[3] Another mine production of REEs in Kola Peninsula's Lovozero, Russia mainly produced loparite minerals, which referred to oxides RE mineral, which was estimated for approximately 6500 metric tons of equivalent to REO.[142] Nevertheless, according to the USGS summary, Russia reduced their mine production to 2600 metric ton per year.[3] Although there are more than ten explored deposits, only three deposits were exploited, which include Kutessai in Kirghizia (yttrium group), Melovoye, Mangyshlak Peninsula in Kazakhstan (yttrium group), and Lovozerskoye, Kola (cerium group).[27]

Scenarios demand of future rare earth industry

In Alonso article had highlighted that only 10 elements out of 17 REEs are significant data on supply and demand, i.e., La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, and Y as presented in Figure 3.[133]From his review, five scenarios (i.e., rename as Scenario A,B,C,D,E) of future availability of REEs were identified based on previous analyses. This figure demonstrated that there are several sectors, which were predicted to be both cg increasing and decreasing. As mentioned before, permanent magnet sector and polishing compound were predicted to increase on the market demand. With this review, scenarios A and B employed historical data to estimate future trends in RE markets; Scenario C depended on the estimation by experts in the industry of RE demand; Scenarios D and E were limited for two mostly employed REE applications, including automotive and wind turbine generation.[133] Figure 3 (right) illustrated one of the examples from scenario B in various RE demand applications and individual REE demand between the year of 2010 and the year of 2035. The overall rate for scenario B is 5.3% between the years of 2010 and the year of 2035; while scenario A and C are predicted by experts in the industry to be approximately 3.6% and 8.6% annual growth demand, respectively.

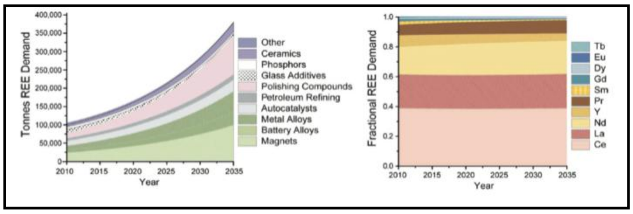

Figure 3: RE demand: Totals (left) and individual REE market share (right).

It should be noted that the global REE production was controlled by China, i.e., approximately 98% of current supply.[131,144] However, in the year of 2016, China was expected to decrease by 33% because the Chinese Ministry of Commerce (MOC) has control over the export quota of REs from China. Also, the government of China has started their initiatives to shut down polluted mines in order to give an allowance for the environmental remediation.[135] According to several authors this situation may reduce the RE export quota, which is one of the keys to increase RE prices.[145] Subsequently, the nations and industries may have significant solution to bring new outside China resources into the production such as reviving the Mountain Pass mine in the USA and the Mt. Weld in West Australia by Lynas Corporation.[146] The World Trade Organization (WTO) has rejected the proposal to limit the RE quota from China.[147]

Upon reviewing the literature, the researchers found that 34 countries have RE deposits in the world, in which, only six countries are actively producing REE in the world including China, Russia and Estonia, USA, India, Malaysia and Brazil.[148].Apart from that, 25 projects, which provide REE production of future supply were identified by most authors.[149-151] Notably, eight of them are current producers out of China, seven projects are under preparation producers and the remaining 9 projects are exploration-candidate suppliers. For instance, Lynas, Simelt of Estonia, MolyCorp, Great Western Group and three other joint ventures from Japan including Vietnam, India and Kazakhstan are producers of out from China.[148] Lynas Advanced Materials Plant (LAMP) has started their production at Gebeng, Pahang Malaysia since the year of 2012 by Lynas Corporation Ltd. The deposit was located at Mt. Weld, West Australia based on the richest known REEs deposit in the world. The biggest REEs producer in Europe is controlled by Silmet (Estonian Republic). It is worth highlighting that should all these projects from the outside China run; the suppliers may be more effective in the total production. China may decrease their supply to 64%, and in turn, another 36% will be left to other outside China producers. The total production of REE out of China after the year of 2015 was expected to be more than 170 thousand tons.[148]

According to Zhanheng article, RE deposits were found in 14 countries in Asia including Japanese companies (joint ventures with Vietnam, India, Mongolia, Kazakhstan and Kyrgyzstan) and Malaysia, which has RE factory processing in Mount Weld mine, Australia by Lynas Corporation.[148] Notably, Lynas has built their factory in Malaysia. Furthermore, other 6 countries from the Europe were discovered as RE deposit including Greenland, United Kingdom and Estonia from Russia. Although there are many RE reserves in Australia, they are still unable to develop due to environmental issues.[148] Other than that, MolyCorp had produced RE at Mountain Pass in North America. In Canada, several deposits were identified with HREEs, which has been developed into small scale because of the high price compared to LREEs. Great Western Group is a one of the companies, which developer RE processing in South Africa. In South America, Brazil has started their production in the year of 1884, which is known as the oldest country RE production. Moreover, 10 countries from South Africa have RE deposits and established Joint Venture with Canada-Great Western Group.

Conclusion

The present study is a review of extensive studies, which focus on the exploration of minerals to the purification process in relation to the market demand of REE and RE processing. The results of the studies are as the following:

•There are variety of separation process, which has been developed by many researchers and industry in accordance to the demand of REE, types of ores and engineering feasibility.

•The process involved in RE ores processing, from deposit exploration to the purification process are found to be important in RE production. The separation process of REEs involved both leaching and liquid-liquid extraction. The existing literature on the physical beneficiation of RE minerals mainly focused on three major REE (i.e., mineral, bastnasite, monazite, and xenotime) with combination technique by means of using froth floatation, magnetic separator or gravitational separation. Both acid and alkaline treatment leaching were extensively used in REs extraction from ores. However, most of the industries accepted the use of alkaline treatment compared to the acid route.

•Several methods of REs separation processes including supercritical method, electro winning, bio-sorption method, solvent extraction and ion exchange were employed. All of the methods used in the separation technique have their advantages and disadvantages, which were addressed to develop the RE separation processes in relation to cost, efficiency, and quality of REEs.

•The demand on REEs with variety of applications showed an increment recently due to the demand on permanent magnet application. There are several projects, which are still under development out of China due to the restrictions of Chinese export quotas. With regards to these projects, out of China may increase the production of REE, which in turn may contribute to good agreements in developing the world's technology.

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