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A Review of Rare-Earth Elements Extraction with Emphasis on Non-conventional Sources: Coal and Coal Byproducts, Iron Ore Tailings, Apatite, and Phosphate Byproducts

Meisam Peiravi¹ · Fahimeh Dehghani² · Louis Ackah³ · Azam Baharlouei^{1,4} · Justin Godbold⁵ · Jia Liu¹ · Manoj Mohanty⁶ · Tathagata Ghosh²

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Abstract

Primary economical deposits of rare-earth elements (REEs) are exhausting all over the world, and it has become necessary to find new sources and methods for their extraction. In addition, increasing the application of REEs in modern technological society has increased its demand globally. One of the important movements to compensate for the future shortages of critical metals is the recovery of REEs from recyclable materials. This paper presents a review of the classification and extraction methods, as well as general applications of REEs with emphasis on secondary sources such as coal and coal byproducts, iron ore tailings, apatite, and phosphate byproducts. An overview of the current state of knowledge on the various methods of REE beneficiation and extraction is covered. These methods include physical separation, as well as hydrometallurgical and bio-hydrometallurgical techniques. The application of these REE extraction techniques for enhanced recovery has been driven primarily by the unique industrial application of these important elements. This paper further explores the existing and potential environmental challenges associated with REE extraction. The authors have presented a wide array of literature, in-depth discussion of the subject, and a succinct summary of processes and relevant case studies.

Keywords Hydrometallurgy · Rare-earth elements · Strategic metals · Bioleaching · Biosorption

1 Introduction

The rare-earth elements (REEs) are a specific set of 17 chemical elements that appear on the periodic table. They consist of

scandium, yttrium, and the 15 elements of the lanthanide series including lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium, gadolinium, terbium (Tb), dysprosium, holmium (Ho), erbium (Er), thulium, ytterbium (Yb), and lutetium (Lu). The REEs may be classified based on differences in demand–consumption patterns, atomic number, weight, solubility, and different levels of abundance [1–3]. Applications and classification of REEs are given in Figs. 1 and 2.

A majority of the REEs around the globe were produced in China. It is estimated that China produced over 90% of the world's REE in the past decade [4]. The geopolitical environment of REE production has prompted research to find new reliable sources of REE and establish efficient techniques for their extraction. Although REEs are not particularly rare in abundance, they rarely occur in high concentrations, making traditional mining techniques inefficient. This unusual tendency of REEs combined with their increasing usage and the global economic environment has created a need for improved techniques to effectively recover REE from both conventional and non-conventional sources. Over the years, much attention

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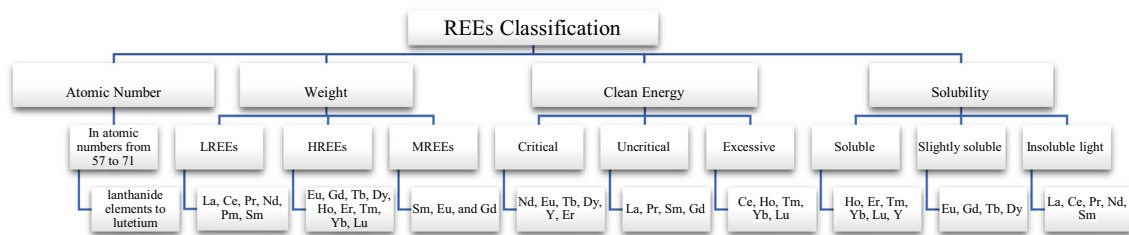


Fig. 1 Classification of REEs [5–10]

has been given to REE extraction and recovery from traditional sources. Nevertheless, the interest in the extraction and recovery of REE from alternative sources has been a major agenda pursued by the US Department of Energy. Current REE research projects tend to gear towards finding solutions to the technical constraints pertaining to achieving maximum efficiency and effectiveness of REE recovery using existing and newly introduced processing techniques. This review paper presents a discussion of the current body of knowledge regarding REE sources, the various physical beneficiation, and hydrometallurgical and bio-hydrometallurgical techniques that have been applied for commercial sources.

2 Beneficiation and Extraction of REEs from Primary Sources

2.1 Physical Separation

The economic feasibility of commercial REE production from primary and secondary sources is achieved through the application of a series of techniques [13–17]. Extraction methods such as hydrometallurgy, electrometallurgy, and pyrometallurgy are applied to further separate individual rare element oxides (REOs) from the mineral concentrate. Physical separation methods used for the REE recovery include gravity separation, magnetic separation, and electrostatic separations. These methods are usually used in combination. They are designed to beneficiate ore minerals from gangue by exploiting their respective physical and chemical properties [18, 19].

Magnetic Separation The difference in magnetic susceptibility of the REEs and the gangue minerals is used to remove the ferromagnetic or non-magnetic tailings from paramagnetic REE minerals [13, 20, 21]. This technique is used to eliminate highly magnetic gangue or to concentrate the desired paramagnetic REE minerals [16]. Magnetic separators have been applied in combination with gravity separators to recover more than 55% bastnasite without flotation [20]. In one study, a representative Saghand monazite ore deposit sample was upgraded by using a Humphrey spiral separator up to 58% REO recovery [22]. Fairly low separation efficiency associated with the use of gravity separation on very fine particles has been reported, which can

account for material and subsequent economic losses of valuable REE ores [23]. Gravity separations have also been successfully achieved with fine-grained mineralization [13, 24]. Magnetic separators are utilized in the beneficiation of Chinese bastnasite REE ores to eliminate Fe-bearing leaching rate gangue minerals prior to REE-specific separation steps, and as a cleaning step for flotation feeds and concentrates [25, 26]. Experiments were conducted on an Australian rare-earth ore to examine the use of magnetic separators to beneficiate REE minerals after being subjected to a roasting operation [27]. To improve magnetic separation efficiency, the main effective factors should be identified and controlled. These factors include the magnetic field strength and gradient, the magnetic susceptibility of the mineral particles, and accompanying fluid medium. Some of these factors are controllable. By controlling them, the REE recovery can improve [28].

Electrostatic Separation Xenotime is normally concentrated with ilmenite as they have similar gravity and magnetic properties; however, ilmenite has electrical conductivity and xenotime is a nonconductor of electricity. Thus, electrostatic separation is the only method that can upgrade xenotime [16, 20]. In addition, this method is used to separate monazite and xenotime from gangue minerals with similar specific gravity and magnetic properties but different electrical conductivity [21, 26]. The downside of the application of electrostatic separators, however, is that the feed materials are required to be completely dry [29], in most cases, prior to processes including gravity and magnetic separation, which are performed under wet environments. Therefore, the energy costs associated with drying fine size ore prior to an electrostatic separation step are anticipated to be cost-prohibitive for such a process to be applied on an industrial scale [20, 30].

Gravity Separation Gravity separation techniques are usually the most cost-effective beneficiation technology. Its efficiency of separation is partly dependent on particle size, where sufficiently coarse particles are preferred to move in accordance with Newton's law in a viscous medium such as heavy media, water, or, less commonly, air [31]. Due to relatively high specific gravities of REE minerals (between 4 and 7), gravity separation can be used to concentrate them by eliminating low specific gravity gangue minerals [26]. This method is widely used to concentrate REE mineral in beach sand deposits. The

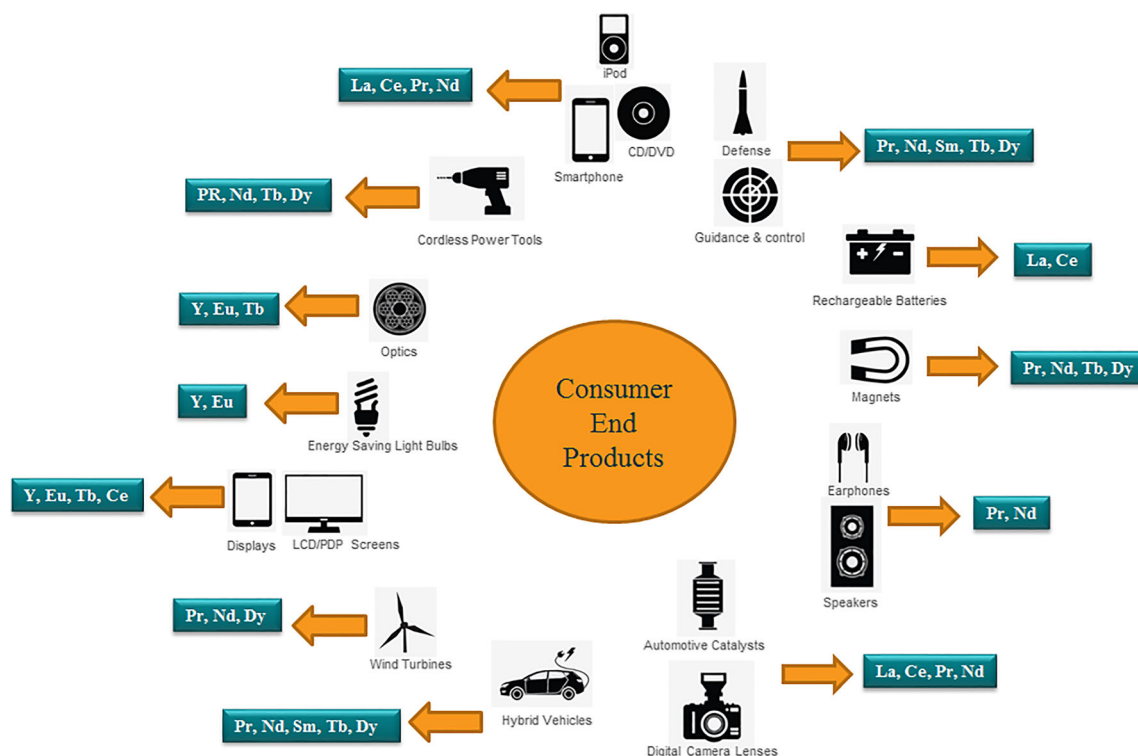


Fig. 2 Applications of REEs [11, 12]

most commonly employed gravity separators used for fine particle sizes are a centrifugal gravity [32], a concentrator spiral [16], a concentrator shaking table [33], spiral concentrators, and conical separators [25]. The Wilfley shaking table was used by Moustafa and Abdelfattah to reject low specific gravity gangue minerals via wet gravity concentration, followed by low-intensity magnetic separation to discard ferromagnetic minerals while concentrating paramagnetic monazite [33]. Ozbayoglu and Atalay used a Mozley multi-gravity concentrator to improve the REO grade from 28 to 35.5% with 48% recovery [13].

2.2 Froth Flotation

Flotation is a complex physicochemical separation process that has been successfully applied in commercial REE beneficiation. Several studies have been completed in the flotation of REE minerals of bastnasite in the Mountain Pass operation in the USA and Bayan Obo mines in China. Hydroxamates, fatty acids, sodium silicate, and sodium hexafluorosilicate are some collectors that are used in the flotation of bastnaesite [20, 26, 34, 35]. Various physical separation and flotation techniques are being used at different mineral processing plants to separate REOs from gangue minerals. Some of them are listed in Table 1. A review of REE extraction using flotation from bastnasite, monazite, and xenotime is given in Table 2.

2.3 Hydrometallurgy Methods

2.3.1 Leaching

Understanding the leaching and extraction techniques for REE from primary resources is fundamental to their application in secondary sources. Leaching techniques have been widely used in the extraction of REEs, both from low-grade and high-grade ores. Leaching and roasting with or without additives have been studied for the enrichment of REE from primary REE resources including monazite, bastnasite, and xenotime.. The most common acids used in REE leaching from primary sources are sulfuric acid (H₂SO₄), hydrochloric acid (HCl), nitric acid (HNO₃), or their combinations.

Molarity of the acid and operating temperature have significant effects on the rate of leaching. The leaching rate increases with increasing temperature. Various applied technologies are discussed below.

Sulfuric Acid Baking Sulfuric acid baking is a common method for REE mineral leaching in both high and low temperatures. This process is carried out at 200–500 °C in an acid-resistant brick-lined furnace. The equation is as follows:

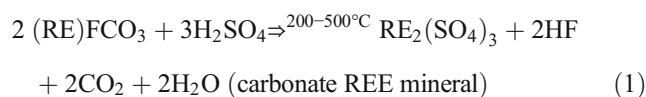
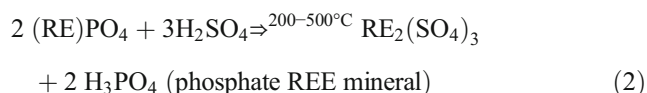
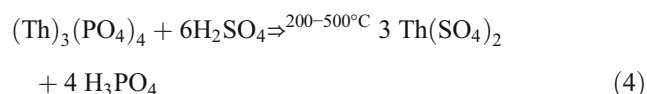
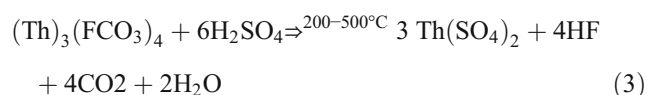


Table 1 Physical and flotation methods used by mines to recover REO [36]

Mine	Location	Technique	REO feed grade (wt.%)	REO concentrate grade (wt.%)
Lynas	Western Australia	Flotation	15	40
Molycorp	CA, USA	Flotation	3–6	60
Bayan Obo	Mongolia, China	Magnetic–flotation	6	65
Sichuan Mianning	Sichuan, China	Gravity–magnetic–flotation	3–6	60
Shandong Weishan	Weishan, China	Magnetic–flotation	3	60



Thorium in concentrate feed also will undergo the same reaction



In high temperature that is more than 300 °C, phosphate acid (H_2PO_4) decomposes in a reaction called dehydration and produces pyrophosphoric acid ($\text{H}_4\text{P}_2\text{O}_7$) [37].



Then thorium sulfate and pyrophosphoric acid will react and produce thorium pyrophosphate.



In a similar reaction, thorium metaphosphate is produced.

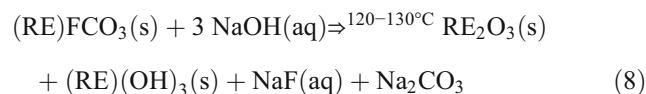


From an economic point of view, using sulfuric acid is cheaper than other leaching reagents, making the use of sulfuric acid very popular in China. However, a complex gas treatment is needed to treat gasses like sulfur oxide. Furthermore, it produces a large amount of solid wastes like gypsum after precipitation with carbonate or solvent extraction [37]. Both $\text{Th}(\text{PO}_3)_4$ and ThP_2O_7 are very stable and insoluble in water or strong acid. These two substances report to slag and increase the radioactivity of the slag. Thus, low temperature in this process is preferred when the thorium concentration is high [38].

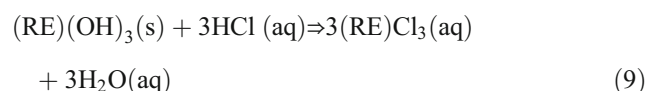
Roast Hydrochloric Acid Leaching This process was started and used by Molycorp, Inc. until 1995 to recover REEs from the mountain pass mine in CA. The process included one stage of calcination at 600–700 °C and leaching with hydrochloric

acid. The calcination process was to remove the gaseous hydrofluoric acid (HF) and oxidize the feed [37]. This process has a main problem: the impure cerium still contains some radioactive thorium. Moreover, it is not able to extract the REE fluorides. This problem led Molycorp, Inc. to design a new process based on caustic soda (NaOH).

Caustic Soda Leaching It was developed by Kruesi and Duker for bastnasite, a carbonate mineral. It is carried out in the temperature range of 120–130 °C and has three steps: (1) a mild HCl is used to treat the REE carbonate, (2) reaction with NaOH, and (3) leaching with HCl. There is an alternative process that ignores the first step; the reaction is as follows [39].



After cooling, hydrochloric acid is used to dissolve the REE hydroxide:

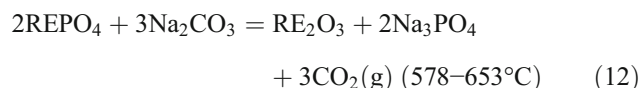
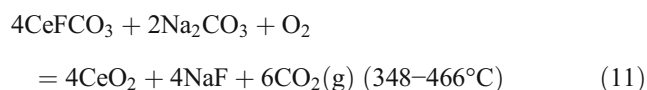
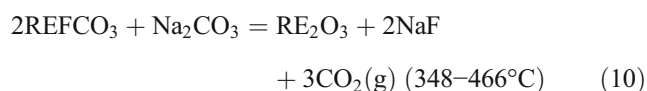


Thorium will undergo the same reaction but is removed from the solution as thorium hydroxide $\text{Th}(\text{OH})_4$. Barium chloride and sodium sulfate are also added to co-precipitate radium as radium/barium sulfate, and followed the solvent extraction stage. Advantages of this process are that thorium and radium are effectively removed, solid waste production is minimized, gaseous hydrofluoric acid is not produced, and there is no need for a complex process to capture HF, since fluorine is removed as NaF in aqueous phase. In general, in the caustic soda leaching process, sodium phosphate is a saleable byproduct and thorium is easily managed. In addition, there is no liquid waste produced in the reaction that is hard to manage [37, 40].

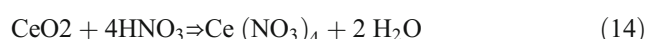
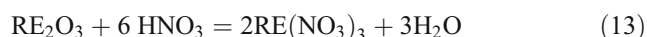
Sodium Carbonate Roasting Sodium carbonate roasting is considered a low-cost method. There is no strict requirement on particle size and high decomposing efficiency for silicates. The chemical reactions are as follows:

Table 2 Flotation studies on bastnasite, monazite, and xenotime samples from different deposits [35]

Mineral	Source	Test type	Iso-electric point (IEP)	pH of max recovery %	Collector	Depressant	Frother	Max recovery %
Bastnasite	Madagascar Mountain Pass, CA	Microflotation Zeta potential	6.3 8.1	9	Benzohydroxamic acid Phosphoric acid ester Sodium oleate	Sodium silicate	MIBC F150	95
Bastnasite	Mountain Pass, CA	Bench-scale flotation	9.5	9.5	K-octyl hydroxamate Fatty acid (sodium oleate)	Lignin sulfonate	NA	≈ 95
Calcite	Kansas	Microflotation	Positive throughout range tested					
Barite	South Carolina	Zeta potential Adsorption	Positive throughout range tested					
Bastnasite	China	Bench-scale flotation	7.8 (plain bastnasite)	5	Benzoic acid	Potassium alum	NA	≈ 95
Bastnasite	Brazil	Zeta potential Microflotation	8.1 (bastnasite w/ K alum) 4.9	9	K-octyl hydroxamate Fatty acid (sodium oleate)	NA	NA NA	≈ 95
Bastnasite	China	Bench-scale flotation Microflotation	8.0 (plain) 5.9b (w/ collector)	8.5–9.5	Modified hydroxamic acid	Sodium sulfide	NA	≈ 95
Monazite	China	Zeta potential Adsorption						
Monazite	China	Bench-scale flotation	4.7 (plain monazite)	5	Benzoic acid	Potassium alum	NA	≈ 95
Xenotime	Brazil	Zeta potential	6.9 (monazite w/ K alum)					
Zircon	Brazil	Microflotation Zeta potential	4 (zircon)	10	Hydroxamate (Flotisor V3759)	Sodium silicate Lignin sulfonate Starch	NA	≈ 98
Monazite	Brazil		5.2	9	K-octyl hydroxamate	Quebracho Amylopectin NA	NA	≈ 95
Monazite	Brazil	Microflotation	NA	10	Fatty acid (sodium oleate)	Sodium silicate	NA	≈ 95
Rutile	Brazil	Bench-scale flotation			Hydroxamate (Flotisor V3759)			
Zircon	Brazil				Sodium oleate			
Monazite	Australia,	Microflotation	5.5	≈ 90	Sodium dodecylsulfate	NA	NA	≈ 90
Xenotime	Malaysia, Thailand, USA	Zeta potential	7		Dodecylammonium chloride			
Monazite	Malaysia							
Rutile	Brazil	Microflotation	NA	10	Commercial hydroxamate (Flotisor V3759), Pure hydroxamate, sodium oleate	Sodium silicate Sodium sulfide	NA	≈ 95
Zircon	Brazil							
Monazite	Australia	Microflotation	5.3 (plain monazite)	8.5 (monazite)	Sodium oleate	NA	NA	≈ 98
Xenotime	Australia	Zeta potential Bubble detachment	3 (plain xenotime)	7.5 (xenotime)				
Monazite	Australia	Adsorption						
Xenotime	Australia	Bench-scale flotation	NA		Fatty acid (Actinol FA2)	Sodium silicate	NA	≈ 98
Xenotime	Australia	Bench-scale flotation	NA		Phosphoric acid esters	Sodium silicofluoride		
Xenotime	Australia	Bench-scale flotation	NA	10	F74286	Sodium silicate	MIBC	≈ 85



The nitric acid leaching reactions are as follows:



For the tailings (REO ~8%) from Baotou steel concentrator, applying sodium carbonate roasting at 700 °C and 2 M HNO₃ leaching, the leach rate of REE was as high as 93.2% [41].

Roasting, followed by leaching, has been used for mineral extraction in different scales. Some studies were done with the aim of optimizing the current technologies or developing a new technique to recover REEs from primary resources [42–46]. These techniques include (1) high-temperature carbon–chloride roasting, (2) ammonium chloride roasting, (3) calcium chloride (CaCl₂) and calcium carbonate (CaCO₃), and (4) CaO–NaCl–CaCl₂. Also, there are other leaching methods that have been obsolete due to associated environmental problems or their low yield [40, 47].

2.3.2 Extraction

Among extraction methods, solvent extraction is the most widely used. Because of the low yield and low productivity in the ion-exchange process and environmental difficulties, it has slowly been replaced by solvent extraction. Almost all REE plants are based on solvent extraction, as in China, USA, and Malaysia. Precipitation methods are used in some stages for impurities removal and in the REE compound production in solid form (oxides, phosphates, fluorides). In Table 3, different methods of extraction including crystallization, precipitation, solvent extraction, and ion exchange to recover REEs from phosphoric acid solutions are presented [16, 37, 48].

Industrially, REE separation processes are done in specific equipment called a battery of mixer settlers. Several factors are assessed for selecting the best solvents, such as selectivity, loading capacity, energy consumption, and chemical reagent consumption. The higher the selectivity of a solvent, the lower the number of stages it will require. The main extractants used in rare-earth separation processes are TBP, Aliquat 336, Versatic acid, HDEHP, and H(EH)EHP. The chemical reaction involved during the extraction will determine how to act on the extraction, and the energy consumption will depend on

the extraction mechanisms [16, 37]. Plenty of studies have been done for the extraction of various rare-earth metals by using solvent extraction processes using different organic extractants. Summary of them is given in Table 4.

3 Beneficiation and Extraction of REEs from Secondary Sources

3.1 Coal and Coal Byproducts

Recent studies have shown the existence of REEs in coal and coal byproducts. While the average concentration of REEs in coal fly ash is estimated at 445 ppm [62, 63], there are different regions such as Western Siberia, Inner Mongolia, and the Fire Clay coal bed in eastern Kentucky in the USA which show higher concentrations of REEs than this average. As REE concentrations as high as 2000 ppm were reported in coal seams and coal preparation rejects [64]. In one study, coal fly ash samples were analyzed from different power plants; REEs were found in the range of 187 to 600 ppm [65]. Coal ash samples from the UK and Poland had REO in the range of 297 to 579 ppm and 371 to 432 ppm, respectively [66]. REE minerals in coal were identified as aluminum phosphates, sulfates of the alunite super group, and carbonates [67].

3.1.1 Physical Separation and Flotation

To have identified economic concentrations of REEs in coal and coal products, several attempts have been made towards their recovery. Ronghong et al. examined the feasibility of selected physical separation techniques, including particle size, and magnetic and density separation methods, for the enrichment of REE from several sources including coal, coal ash, coal mining byproduct samples, clay, and shale [68]. REE concentration in the fly ash samples generally increased in finer particle size ranges, as corroborated by previous research. The observed trend is a result of a more efficient liberation of REE minerals in the fly ash samples than other samples. Furthermore, higher REE concentration in the coal ash samples could be the result of the low volatility of REEs during coal combustion and the subsequent even distribution in coal ashes [69–71].

Further magnetic separation experiments were performed by Lin et al. on the ash samples and found REE enrichment in the non-magnetic fraction [68]. Unlike Lin et al. results, Dai et al. found higher REE concentrations in association with the magnetic fractions of coal and coal mining byproducts. Dai et al. researched the different phases of fly ash by separating them into magnetic, mullite + corundum + quartz, and glass phases. It was found that REE concentrations in the glass phase were higher than in other non-magnetic and magnetic phases [72]. The difference in response of different coal and coal products to magnetic separation in concentrating REE is

Table 3 Various methods for extraction of REEs from phosphoric acid solutions [48]

Methods	Reagents or condition	Advantages	Disadvantages
Crystallization	Evaporation at 200 °C for 2 h	• REE recovery around 98%	• High energy consumption • Pressure-resistant apparatus
	CePO ₄ and CeF ₃	• Relatively high purity around 54 wt% REO • Using cycle leaching to concentrate REEs	• Passivation of seeds • Expensive seeds • Low REE recovery around 50%
Precipitation	Ammonia neutralization NaOH pH = 2.0–3.0 Fluorides: partial neutralization (20%) Using 15.4 g/L F ⁻ in WPA	• Simple process • Relatively high REE recovery almost 90% • Fe, Al removal simultaneously occur • High REE recovery almost 99.8% • Removal of U	• Required high dosage of chemicals • Low REE purity around 2.5 wt% REO • Impurity issue because of fluorine more than 15 g/L F ⁻ left in WPA
	Double sulfates: 10–15 wt% H ₂ SO ₄ , 23–35 g/L Na ₂ SO ₄ , or NaCl	• Relatively high REEs recovery around 91% • Low cost and availability of chemicals	• Impurity issue because of H ₂ SO ₄ in WPA more than 10 wt% • Low REE purity around 5 wt% REO
Solvent extraction	MEHPA D2EHPA D2EHAP + TBP/TOPO	• Mature technology for U • Recovery of U and HREEs simultaneously occur	• Insufficient for LREEs • Needed extra process to separate REEs from U (green cake)
	DOPPA DNPPA + TOPO DOPPA + TOPO	• Recovery of U, HREEs, and LREEs at the same time with high efficiency • Good extraction performance	• Needed extra process to separate REEs from U
Ion exchange	Tulsion CH-90, 93, 96, and T-PAR DOWEX-50WX4, 8	• Simple process	• Low recovery for REEs less than 60%

primarily a result of their different mineral structure and composition. In most commercial REE processing, like the Bayan Obo mine, the magnetic separation step aims to separate the magnetic iron materials, thereby leaving the REEs with non-magnetic and weakly ferromagnetic materials for subsequent processing [73, 74].

Inadequate separation of REEs from their host material is a major factor when determining the effectiveness of a physical separation process. With a few exceptions, almost all other discovered rare-earth deposits require some form of comminution for mineral liberation from gangue materials prior to efficient separation. Froth flotation works well with other physical separation processes in concentrating REE to higher grades and recovery. A summary of physical separation studies relating to REE extraction from coal or coal combustion byproducts is given in Table 5.

3.1.2 Hydrometallurgical Extraction

Direct acid leaching techniques in different temperatures are more common than the roasting followed by the leaching process [81]. Joshi et al. patented a process for the recovery of REEs from coal ash. Matyas et al. patented another process to recover REEs from coal ash. The concentration of REEs related to the ash was as follows: vanadium: 3322 ppm, Mo: 232 ppm, total rare-earth metal content: 2077 ppm, and actinides: 2500 ppm. Their proposed process claimed to have a leaching recovery rate of 80–90% using a sequential leaching process (water leaching → dilute alkaline digestion → dilute hydrochloric acid digestion) [82].

Many factors derive the REE recovery from coal ash using leaching procedures. These technical factors include mineralogy of the coal ash, characteristics of encapsulation, grain size, presence of complicating minerals, and their presence in the coal ash as refractory. Economic factors for leaching in larger scales are cost, leaching recovery rate, and environmental impact. All of these parameters are considered when selecting the final technique for leaching of REEs from coal ash. There is not any commercialized technique for leaching of REE from coal ash, and there have not been very many studies on the leaching process of REE. Therefore, further experimentation under a variety of conditions will be required to discover the most efficient and environmentally benign technique for the leaching of REE. Table 6 presents summary of studies on coal and coal byproducts using hydrometallurgical extraction.

3.2 Iron Ore and Apatite

The presence of REEs in tailings of iron ore and apatite has been studied. REEs were found in fluorapatite, monazite, allanite (ce-bearing), xenotime (Y), light rare-earth element (LREE)-bearing epidote, and REE fluorocarbonates [88, 89]. Yang et al. investigated apatite vein-type REE from Mushgia Khudag, South Gobi, Mongolia. Apatite was the main REE carrier in the samples, with an average REO content of 14.7%, and the highest values reached 20.8%. There was a minor amount of other REE minerals such as monazite, cheralite, parisite, and synchysite. The grain size of apatite varied from 0.1 to 4.0 mm. The whole-rock REE concentrations were from 2.2 to 8.3% [90].

Table 4 The results of rare-earth element extraction from different solutions using various extractants

Extractant	Solvent	Solution features	Reagents and test condition	Results	Ref
TEHDGA (N,N,N',N'-tetrakis-2-ethylhexyldiglycolamide)	Methanol	La, Nd, Y, and Er in nitric acid	These samples were dissolved in nitric acid by (1) acid-digestion method (2) fusion with NaOH + NaNO ₃ mixture	• There is selectivity in the extraction. The heavier the rare earth, the higher the K _d s at any given nitric acid concentration	[49]
	Kerosene	LREEs La, Ce, Pr, Nd, and HREEs like Tb, Dy, Y, Ho, Er, Yb, and Lu in phosphoric acid solutions	0.01 M nitric acid 3 M phosphoric acid 1 M TOPS 99	• The separation of REEs into three concentrates, two heavy rare-earth fractions including Yb + Lu and Tb, Dy, Ho, Y, Er, and one light rare-earth fraction	[50]
2,6-Bis(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine (n-Pr-BTP)	n-Dodecane/1-octanol	A mixture of Am ³⁺ and Eu ³⁺ in nitrate solution	Time of extraction was 6 h 0.03 M n-Pr-BTP in n-dodecane/1-octanol 1 M NaNO ₃ pH = 2	• Extraction of 85% Am ³⁺ and 6% Eu ³⁺	[51]
TOPS 99 PC88A Cyanex 272	Kerosene	Mixture of seven HREEs (Tb, Dy, Ho, Y, Er, Yb, Lu) and four LREEs (La, Ce, Pr, Nd) in phosphoric acid	3–5 M phosphoric acid TOPS 99, PC88 A and Cyanex 272, with varying concentration from 0.1 to 0.5 M	• Cyanex 272 has the lowest extraction efficiency of lanthanides from H ₃ PO ₄ • TOPS 99 has the highest extraction efficiency of lanthanides from H ₃ PO ₄ • The extraction of metal decreases as the acid concentration increases.	[52]
PC 88A	Paraffinic kerosene	Dy and Tb chloride solution	3.5 M HCl	• Most of the Dy and Tb are separated to yield a concentrate assaying > 50%D Dy ₂ O ₃ , 14% Tb ₄ O ₇ , 10% Gd ₂ O ₃ , 2.4% Ho ₂ O ₃ , and 21% Y ₂ O ₃ • Dy and Tb were recovered with a purity of 97% and 83% respectively	[53]
4-Sebacoylbis(1-phenyl-3-methyl-5-pyrazolone) (H2SP) and 4-dodecandioylbis(1-phenyl-3-methyl-5-pyrazolone) (H2DdP)	Chloroform	Actinides [Th(IV), U(VI)] and Ln(III) (Nd, Eu, Lu) in nitrate solutions	0.2 M nitric acid	• Metal ions were extracted as Th[30]2, Th(DdP)2, UO ₂ (HSP)2, UO ₂ (HDdP)2, Ln [30](HSP) and Ln(DdP)(HDdP) with H2SP or H2DdP	[54]
Cyanex 301 + Cyanex 923 (TRPO)	Xylene	Trivalent rare earths in nitrate solutions	0.1 M sodium nitrate pH 2.0–3.0	• Th(IV) selectively separated from U(VI) and Ln(III) • Trivalent REE ions extracted as MX ₃ -3HX with Cyanex 301. • La and Nd are extracted as MX ₂ -NO ₃ -TRPO in the presence of Cyanex 923 • Eu, Y, and other HREMs extracted as MX ₃ -HX-2TRPO	[55]
Cyanex 923 (TRPO)	Xylene	Trivalent lanthanides (La, Nd, Eu, Tb, Ho, Tm, Lu) and yttrium (Y) in thiocyanate and nitrate solutions	pH 2.5–3.0 on the extraction of the trivalent metal ions 1.0 M nitrate solutions 0.05 M Cyanex 923	• Trivalent metal ions have better selectivity and extraction efficiencies from thiocyanate solutions as compared with the nitrate system • Metal ions extracted from thiocyanate solution as M(SCN) ₃ -nTRPO in nitrate solutions; metal ions were extracted as M(NO ₃) ₃ -3TRPO.	[56]
	Xylene	La, Eu, Lu, and Am in chloroacetate	pH 2.7	• Metal ions were extracted as M(PMBP) ₃ -HPMBP using HPMBP.	[57]

Table 4 (continued)

Extractant	Solvent	Solution features	Reagents and test condition	Results	Ref
Phenyl-3-methyl-4-benzoyl-pyrazalone-5 (HPMBP) + bis-(2-ethylhexyl)sulphoxide (B2EHSO)			0.01 M chloroacetate buffer solutions	• With B2EHSO, the synergistic adduct species were M(PMBP)3-B2EHSO and M(PMBP)3-2B2EHSO • With CMPO, the only complex extracted into the organic phase is M(PMBP)3-CMPO.	
Octyl(phenyl)-N,N-diisobutylcarbamoyl methylphosphine oxide (CMPO)	Chloroform	La(III), Ce(III), Eu(III), Th(IV), and U(VI) in HCl	The extraction of lanthanum, cerium(III) and europium(III) at pH 3.0–6.0, uranium(VI) at pH 2.5–3.2, thorium at pH 0.5–6	• The extraction of uranium decreases rapidly with increase pH above 3.2, whereas that of lanthanum, cerium, and europium does not	[58]
HPBI (3-phenyl-4-benzoyl-5-isoxazolone)			pH between 1 and 3 using mixtures of potassium chloride/hydrochloric and between 3 and 6 acid using sodium acetate-acetic acid	• The lower pKa value of HPBI is 1.14 • HPAl extracted REEs better than HPMBP and HTTA. • The perfect separation of thorium from lanthanum, cerium, and europium was around pH 1.	[59]
4-Methyl-2-pentanone (MIBK) containing 3-phenyl-4-acetyl-5-isoxazolone (HPAl)	Chloroform	La(III), Ce(III), Eu(III), Th(IV), and U(VI)			
1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP) and thenoyltrifluoroacetone (HTTA)					
1-Phenyl-3-methyl-4-trifluoroacetyl pyrazolone-5 (HPMTFP) + dicyclohexano-18-crown-6 (DCH18C6) + monobenzo-15-crown-5 (B15C5)	Chloroform	Trivalent metals (Am, Cm, Cf, and Eu) in NaClO4	0.1 M NaClO4 pH 2.70 0.01 M chloroacetate buffer	• With DCH18C6, the synergistic species extracted were (PMTFP)3-(HPMTFP) (DCH18C6), (PMTFP)3-(DCH18C6) with (B15C5) species are M(PMTFP)3-n(B15C5), n being 1 or 2 for all these metal ions. • In the present synergistic systems, the extraction order was found to be Am < Cm < Cf < Eu with both the crown ethers	[60]
1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP)	Chloroform	All RE ions (except Pm) and Y	0.1 M (Na, H) + ClO4 ⁻ 0.2 M sodium acetate-acetic acid buffer, pH 2–4	• The extraction order is different by using HPMTFP • Formation of Ln(PMBP)3, two-phase stability constants (logβ3-PLn(PMBP)3), pH for Using 5 × 10⁻² M HPMBP, 50% extraction of metal chelates (pH 50), and separation factors (S) between the adjacent elements have been evaluated.	[61]

Table 5 A summary of past physical separation studies relating to REE extraction from coal or coal combustion byproducts

Methods	Source materials	Results	Ref
Particle size	Coal fly ash	- The rare-earth elements and yttrium (REY) content increased from 608 to 896 $\mu\text{g g}^{-1}$ with decreasing particle size. - The highest REY content was measured at the minus 25-μm size fractions.	[75]
Magnetic separation		- The REY content increased with decreasing the magnetic susceptibility of the particles - The lowest and highest REY contents are 611 and 879 $\mu\text{g g}^{-1}$, respectively. - The non-magnetic fraction had the highest mass yield (– 57%), and 64% of REY occurred in this fraction.	
Density		- Through the destiny separation, REY were concentrated to a maximum value of 855 $\mu\text{m g}^{-1}$, in the separation gravity class of 2.4–2.6 g cm^{-3}. - Density separation has a low effect on the enrichment of REY.	
Particle size	Coal, coal fly ash, clay, and shale	- Higher REE concentration in the finer particle size of fly ash. - REEs enriched in the non-magnetic fraction of all ash samples. - In clay and shale, REE concentrations decreased with decreasing particle size.	[68]
Magnetic separation		All samples responded similarly to density separation.	
Density separation	Roof rock overburden	- Resulted in a separation yield of 37% magnetic material that showed a Total rare earth elements (TREE) of 330.8 mg/kg. - Yielded 44.3% of conducting material (TREE = 355.9 mg/kg) - Yielded 38.6% of insulating material (315.2 mg/kg)	[76]
Electromagnetic separation			
High-tension electrostatic separation		- Denser particle fractions accounted for the most REE content. - Respective REE concentrations included 263 ppm (1.9–2.4 g/cc), 235.3 ppm (2.4–2.9 g/cc), and 293.16 ppm (< 2.9 g/cc).	
Density separation			
Combined low-intensity and high-intensity magnetic separation	Coal fly ash	Concentrated REE from 266 to 1611.4 mg/kg with high recovery of about 80%.	[77]
Density separation	Coal and coal byproducts	Unsuccessful application of density-based separator due to the ultrafine grain size of RE minerals.	
Magnetic separation		Inefficient magnetic separation process due to low mass recovery of concentrated REEs in the magnetic fractions.	
Froth flotation		- Froth flotation was the only method that could be used for effective REE enrichment from the coal sources but not fly ash material. - REE concentration in coal processing was increased from 172 to 367 mg/kg.	
High-intensity magnetic separation (dry and wet conditions)	Coal	No significant separation under dry operation, whereas the wet high-intensity magnetic separation resulted in low yield of magnetic fractions of REE association.	[78]
Wet high-intensity magnetic separation	Coal	- This method was only effective for the removal of the pyritic content of coal. - It was inefficient for coal due to the low mass yields. - Flotation did not effectively concentrate REE from fine coal (< 149 μm) due to poor liberation.	[79]
Froth flotation			
Particle size	Coal and coal byproducts, clay and shale samples	- For all ash samples, the finer fraction had higher REE concentrations. - For the clay and shale samples, the REE concentrations decrease as the particle size reduces.	[68]
Magnetic separation		REEs are enriched in non-magnetic fractions for all ash samples.	
Density separation		- All samples responded similarly to density separation. - Among the three methods, density separation showed the highest enrichment of REE. - A combination of these methods is recommended.	
Shaker table	Coal and coal byproduct	The ultrafine grain size of REE minerals was identified as the major factor for the unsuccessful application of density-based separators.	[80]

Table 5 (continued)

Methods	Source materials	Results	Ref
Magnetic separation		The low mass recovery rendered the magnetic separation process inefficient, although it could concentrate REE in the magnetic fractions of the samples.	
Flotation tests		- Most effective methods except for fly ash - Grade of REE was increased from feed to flotation step from 172 to 367 ppm.	

Table 6 Summary of studies on hydrometallurgical extraction of REE from coal and coal byproducts

Summary of procedure	Source materials	Results	Ref
The optimum condition was found to be 400 rpm stirring rate, 3 M acid concentration (HCl) and 1:10 solid:liquid ratio at 60 °C leaching temperature, and 2-h leaching time period.	Coal fly ash	In this condition, leaching efficiency for preconcentrate product and raw coal fly ash (CFA) was 78% and 43%, respectively.	[75]
1 M HCl was used as leaching agent. Fly ash was leached using 1 M HCl for 4 h at 85 °C.	Fly ash from the Powder River Basin (PRB) and Appalachian Basin (APP)	- The recovery for total REEs for PRB ashes was 80–90%. - The recovery for APP ashes was 20–40% at pulp densities lower than 40 g/L. - The concentrations of soluble REEs generally increased with increasing pulp density.	[83]
Dilute sulfuric acid as a leaching reagent was investigated.	Industrial fly ash	- Leaching 70% of the REE with 0.4 M sulfuric acid. - Temperature had a very significant effect on the REE leaching recovery. - It was found to be quantitative but non-selective towards REE.	[81]
Recovery of REE from the sulfuric acid leachate was investigated using oxalate precipitation. Liquid–liquid extraction was tested with D ₂ EHPA.		It is most suitable to concentrate REE before precipitation as oxalates.	
Heated acid (nitric acid) in two stages was used to leach the minerals. The temperature of acid was raised to 90 °C to carry out the leaching experiment.	Coal ash	- REE can be leached from coal ash (recovery not specified). - Higher temperature leads to a more concentrated solution of REEs.	[82]
Solvent extraction (tributyl phosphate and kerosene) was used to extract the REE.		REE can be recovered from the aqueous solution using an organic solution.	
Sequential leaching process (water leaching, dilute alkaline digestion, dilute hydrochloric acid digestion).	Coal fly ash	Leaching of 80–90% of REEs.	[84]
The dissolution behavior of coal fly ash in a dilute H ₂ SO ₄ was investigated.	Coal fly ash	- It was concluded that REE in coal fly ash dissolve gradually in H₂SO₄ over time. - Dissolution rates of REE increased with the temperature of the H₂SO₄.	[65]
1 M ammonium sulfate was chosen as a lixiviant in the recovery of REE.	Coal products	57% recovery of REEs.	[76]
Leaching with nitric acid followed by solvent extraction was tested.	Coal ash	- The highest recovery rate of 90% for LREEs. - The highest recovery rate of 94% for HREEs. - Impurity recovery to the leachate maintained at less than 40%.	[85]
Cyanex 572 and D2EHPA and their combinations were tested.		- D2EHPA was found to be the best extractant in this solvent extraction test series. - REE recovery rate of nearly 99%.	
Leaching followed by solvent extraction was tested.	Coarse middlings	80% recovery of REEs.	[86]
Two-stage hydrometallurgical process (alkali fusion–acid leaching) to recover REEs.	Coal fly ash	- Optimum conditions for alkali fusion were 1:1 (mass ratio of CFA/Na₂CO₃), heating in 860 °C for 0.5 h. - Recovery of REE 72.78%.	[87]

3.2.1 Physical Separation and Flotation

In most cases, a combination of methods is used to economically beneficiate the REE-bearing minerals. Magnetic separators have been used with gravity separation, to beneficiate monazite from beach sands as a proposed step to eliminate strongly magnetic minerals, such as magnetite, before subsequent separation steps [20]. The operations have also been reportedly used to separate monazite from heavy mineral gangue materials which are paramagnetic and non-magnetic respectively [91]. A flowsheet was designed by Mustafa and Abdelfattah to concentrate monazite from Egyptian beach sands. Egyptian beach sands contain approximately 30 wt.% valuable heavy minerals, where low specific gravity gangue was discarded via wet gravity concentration, then low-intensity magnetic separation was used to discard any ferromagnetic minerals without removing paramagnetic monazite. A series of gravity, magnetic, and electrostatic separations were applied to exploit the different properties of the monazite and other minerals and produce the final concentrate streams [33]. Fangji et al. applied gravity and magnetic separations to produce a basanite flotation concentrate with a grade of 62% REO and a recovery of 80–85% [92]. Gravity separation has also been used in combination with flotation at many REE processing operations throughout China [25, 93]. The froth flotation process has been used on Pea Ridge iron ore's tailings to concentrate the REEs [94]. Yang et al. studied the beneficiation of vein-type apatite REE ore from Mongolia. Flotation tests were carried out with the apatite veins blended with syenite as the feed. The successful process resulted in over 90% Total rare earth elements (TREE) recovery [90]. A summary of the physical separation and flotation process is given in Table 7 for iron ore and apatite.

3.2.2 Hydrometallurgical Extraction

Roasting followed by leaching has been used for mineral extraction in different scales. Roasting can be used with some additives, such as CaCO_3 , CaO , and Na_2CO_3 , and NaCl . Na_2CO_3 roasting is considered a low-cost method, with no strict requirement on particle size and a high decomposing efficiency for silicates [41]. There are two main processes used for apatite leaching: sulfuric acid leaching and nitric acid leaching. During this reaction, 70–90% of the REEs end up in the product phosphogypsum with 10–30% going to the acid solution called green acid [37]. After using nitric acid leaching, mixed rare-earth nitrate solutions can be separated into individual rare-earth nitrate solutions directly by solvent extraction [98]. The solvent extraction of REEs and precipitation stripping were conducted using oxalic acid. Tributyl phosphate (TBP) was used to extract yttrium, lanthanum, cerium, and neodymium from an aqueous solution which was produced by nitric acid leaching of apatite concentrate. The

recoveries of 95%, 90%, 87%, and 80% were obtained for neodymium, cerium, lanthanum, and yttrium, respectively [99]. Table 8 summarizes the studies that have been done for the recovery of REE from iron ore and apatite tailings.

3.3 Phosphate Byproducts

The presence of REEs has been recognized in several phosphate secondary sources including phosphate tailings, phosphoric acid, and phosphate fertilizer byproducts. The extraction of REE from such sources has been explored and demonstrates the viability of reliable REE production from such sources. Research conducted by Ramos et al. has characterized the presence of both HREE and LREE in various South American phosphate-based manufactures, including those of fertilizers, di-calcium phosphates, and phosphogypsum. The results showed a high amount of variability in REE concentration from various phosphorite mines. Among the sites studied, the lowest REE concentration was found to be ~70 ppm [103]. The study, conducted by Khlifat et al. found that Jordanian phosphate contained up to 59.8 ppm of TREE, including Ce, La, Y, and Eu. As 83% of it is HREE, 17% is LREE [104].

Emsbo et al. found that there is a higher abundance of REEs in the US sediment deposits than current REE mining operations. The process used to leach and produce phosphates from this deposit is very similar to that required to extract the REEs. The similarities in the process and materials required to extract REEs and produce phosphates make the combined effort very cost-effective [105]. The Florida Industrial and Phosphate Research Institute utilized an absorbent polymer in combination with an extraction solution to separate the REE from phosphate waste products. In this study, the absorbent polymer, poly 1-octadecene 2,5-furandione salt, was used in combination with an extracting solution, PX-107, to recover 100% of the REEs present in the phosphate waste. These results demonstrate not only the efficiency of the absorbent polymer but also its cost-effectiveness, as the polymer can be reused for multiple batches [106]. Liang et al. studied the chemical extraction of REEs from phosphate waste sources. The study suggested that higher REE recovery is greatly influenced by the addition of phosphoric acid in the initial pulp. The results indicated that the optimum parameters released 90% of the REEs from the phosphate rock, with 52.82% making it into the leaching solution [107]. Different types of acids were used to extract REEs from phosphogypsum. More than 80% of REEs were recovered using 3 M HNO_3 that dissolved around 60% of gypsum and released the highest amount of impurities. Between 46 and 58% of REE was recovered using H_2SO_4 . Scandium was almost entirely recovered [108]. The physical separation of REEs from phosphate sources has also been tested. S. Al-Thyabat used both gravity separation and froth flotation to upgrade phosphate flotation tailings. The product was then leached with nitric acid. In the next step, solvent extraction and the ion-exchange process were used. Results

Table 7 A summary of studies on physical separations of REEs from iron ore and apatite

Methods	Condition	Source Materials	Results	Ref
Flotation tests	Flotation was done for magnetic preconcentrate (assaying a grade of 1.25% TREO, 39% Fe, and 9.47% Si) and non-magnetic tails (assaying a grade of 1.08% TREO, 11.90% Fe, and 27.70% Si). Collector: sodium oleate and hydroxamic acid. Depressant: sodium silicate and starch. The pulp pH was adjusted using hydrochloric acid and sodium hydroxide.	Iron oxide-silicate-rich tailing	i) Flotation of magnetic preconcentrate • Rougher-scavenger-cleaner (sodium oleate + hydroxamic acid) flotation obtained 70% TREO recovery at 1.17 enrichment ratio, with 25% Fe and 52% Si removed. • Rougher-cleaner hydroxamic acid flotation obtained 80% TREO recovery at 1.16 enrichment ratio, with 17% Fe and 62% Si removed. ii) Flotation of non-magnetic tails • Rougher-scavenger sodium oleate flotation obtained 49% TREO recovery at enrichment ratio 1.57, with 52% Fe and 80% Si removed. • Rougher-cleaner hydroxamic acid flotation obtained 78% TREO recovery at 1.80 enrichment ratio, with 22% Fe and 56% Si removed. • Recovered over 70% of the phosphates from the tailings.	[95]
Flotation tests	Particle size: $\sim 37 \mu\text{m}$ Solid%: 12 Collector: 0.27 lb/mt oleic acid Frother: 0.06 lb/mt pine oil Target minerals: phosphates 14.7% total REO in the carrier phase—apatite Collector: sodium oleate and the Aero 704-845 Depressant: Na_2SiO_3 Six flotation stages (one rougher, two scavenger, and three cleaner stages) Collector: tall oil collector Depressant: sodium silicate Feed has 1.53% REO	Iron ore tailing		[94]
Flotation tests		Apatite veins blended with syenite	• Resulted in over 90% TREE recovery.	[90]
Flotation tests		Apatite	• Concentrate grade was 94.8% apatite with a 94% phosphate recovery.	[34]
Gravity and magnetic separation		REE-bearing ore	• It was successfully rejected the diamagnetic, low specific gangue minerals in the RE ore.	[34]
A combination of cyclic magnetic separator, shaking table, and electrostatic	Monazite degree of freedom was between 75 and 105 μm	Iron ore Iron mine waste	• Total recovery and grade of the REE (Ce, La, Nd, Er, and Gd) concentrate obtained from the sample of 1499-ppm REEs were 67.1% and 1.2%, respectively.	[96]
Gravity separation (Knelson concentrator (KC) and Wilfley shaking table)	The KC was fed with a sample at a flow rate of 50 g/min. Solid pulp density was 25 wt%. The desk angle of Wilfley shaking table was $5-7^\circ$, water flow rate (2.5 L/min), and feed pulp density (25 wt%).	Iron oxide-silicate-rich tailing.	• Gravity separation using the KC on the unclassified and classified samples was not effective in selectively concentrating heavy mineral particles. • Tabling tests conducted on classified feed samples indicated no REE mineral upgrade when tests were conducted on particles $< 75 \mu\text{m}$ • Upgrade of Fe oxides was achieved in all the size fractions. • Separation efficiency decreased with decreasing particle size. • The results identified that the feed rate and feed size are the most significant operation parameters. • Under optimal conditions, the concentrate grade of rare-earth elements increased from 2860×10^{-6} to 6050×10^{-6} ppm • Recovery increased to 58%.	[97]
Humphrey spiral	Pulp was diluted and fed to a Humphrey spiral for upgrading.	REE-bearing ore		[22]

Table 8 Summary of studies on hydrometallurgical extraction of REE from iron ore and apatite

Summary of procedure	Source materials	Results	Ref
Solvent extraction and precipitation stripping were used to produce REE. TBP was used to extract REE from solution of nitric acid leaching of apatite concentrate. Hot, deionized water was used to scrub the impurities from the loaded organic phase. Precipitation stripping was studied.	Apatite–magnetite ores	95%, 90%, 87%, and 80% of neodymium, cerium, lanthanum, and yttrium, respectively, were extracted during optimum conditions. - The results showed that three stages of scrubbing with a phase ratio (V_a:V_o)_c of 5:1 removed approximately 80%, 30%, 27%, and 15% of Ca, Mg, Fe, and P, respectively. - Precipitation stripping was found to be a viable alternative to traditional acid stripping in the REE production process.	[99]
For the tailing (REO ~ 8%) from the Baotou Steel concentrator in China, applying Na ₂ CO ₃ roasting at 700 °C and 2 M HNO ₃ . Using nitric acid as leaching agent + (P350, B).	Iron ore tailing	Recovery is 93.2%.	[41]
The extraction of REE from apatite concentrate of the Chadormal plant, located in the Yazd Province of Iran.	Apatite concentrate	- Grade of mixed REO is more than 95% with yield over 98%. - Optimum conditions were found to be acidity: 60%, S/L ratio: 30%, leaching time: 30 min, agitation rate: 200 rpm, temperature: 60 °C, and particle size (d₈₀): 50 μm. - The recoveries of lanthanum, cerium, neodymium, and yttrium were achieved at 74%, 59%, 72%, and 73%, respectively.	[98] [100]
The assay and recovery of REE in the leaching process were determined.	Apatite concentrate	Optimum conditions: acidity 60 vol%, solid to liquid ratio 30 wt%, leaching time 30 min, agitation rate 200 r/min, and temperature 60 °C.	[101]
Neural network model was used to predict the effects of operational variables on recovery of REE.		The recoveries of La, Ce, Nd, and Y were achieved at 74%, 59%, 72%, and 73%, respectively.	
Apatite was dissolved in a 20% (v/v) nitric acid solution, at 60–70 °C during agitation.	Apatite	More than 98% of rare earths in apatite was recovered using a countercurrent extraction process with six stages, with phase ratio = 0.5.	[102]
The influence of the phase ratio, stage number, acidity, and salting-out agent on extractabilities of P350 was studied.		- The results show that rare earths can be separated from Ca, P, Fe, and other impurities with P350. - Mixed rare-earth oxides with a purity of up to 95% and a yield of up to 98% could be obtained.	

indicated that the shaking table procedure recovered 20%, while the froth flotation was able to recover 63.5% of REEs. For the flotation concentrate, the solvent and ion-exchange processes yielded REE contents of 0.93% and 0.31%, and for shaking table, 0.72% and 0.21%, respectively [109].

3.4 Leaching of Cation Adsorption Clays

Clays and coal have a fairly low concentrations of REEs (0.05 to 0.5 wt.% REO). However, REE presence in clay is different from that in coal. REEs in clay are mainly present in an ion-exchangeable phase, which can be directly dissolved with suitable leaching reagents, such as NaCl and (NH₄)₂SO₄ [110]. The most common methods of leaching rare-earth cation adsorption clays are heap and in situ leaching. In China, both in situ and heap leaching are done at commercial scales. The conditions include pH between 3 and 4, ambient temperature, and pressure. Aqueous ammonium sulfate lixiviate is used as the leaching reagent. NH₄⁺-based salts, such as chloride, nitrate, and sulfate, are widely used in the extraction of REE from clays such as muscovite [111]. There are some studies focusing on the recovery of REE from the weathered crust elution-deposited rare-earth

ores (rare-earth mud) as well. The grade (REO) of rare-earth mud is 3–7%, and the particles are very fine at 1–10 μm. Zhu et al. conducted experiments to recover REE and manganese (Mn) from rare-earth mud, using 3.6 g/L Na₂SO₃ as a leaching agent. About 90% of Mn was dissolved, and the Mn–Fe amorphous structure was destroyed. The removed Mn mud was further roasted with ammonium chloride at 450 °C then directly dissolved by water. The recovery of REE was 73.4% [112]. Moldoveanu et al. investigated the leaching capability of (NH₄)₂SO₄ and NaCl for 5 different clays including MC₁ (light brown, very fine powder), MC₂ (pinkish orange, soft chunks, and some fine black sandy magnetic material), MC₃ (pinkish orange, very fine, occasional soft chunks), MC₄ (pinkish orange, higher content of coarse particles), and MC₅ (brownish orange, fine, occasional soft chunks). In the first part, 0.5 M (NH₄)₂SO₄ at room temperature was used. The initial REO of clays were MC₁ = 0.295%, MC₂ = 0.235%, MC₃ = 0.468%, MC₄ = 0.093%, and MC₅ = 0.125%. The total REE extraction for different clays was E (MC₁) = 62.4%, E (MC₂) = 63.0%, E (MC₃) = 76.1%, E (MC₄) = 23.4%, and E (MC₅) = 59.4%. They conducted another test with NaCl-based lixivants on the clays with the same experimental condition that resulted in a higher rate of

extraction (MC_1 , MC_2 , MC_3 , and MC_5). The results were $E(MC_1) = 46.0\%$, $E(MC_2) = 44.1\%$, $E(MC_3) = 44.0\%$, and $E(MC_5) = 40.2\%$. Two stages of leaching with $(NH_4)_2SO_4$ were studied for a possible increase in REE rate of extraction of MC_3 . It was observed that a two-stage leaching procedure has the ability to increase the overall REE extraction by an additional 10–20% depending on the individual REE. The highest rate of extraction for MC_3 was about 88.8% [110].

3.5 REE Recovery from Recycled Materials

Another approach to recovering REEs from secondary sources involves the extraction of REEs from recycled materials. Post-consumer electronics such as computers and cellphones have REEs in many of the components within the device. There are many obstacles standing in the way of developing an efficient REE recycling program. As less than 1% of REEs were recycled, the recycling rate of other metals such as lead, gold, and titanium were greater than 50%. Although many consumer electronics possess REEs, studies have found that REEs are among the least recycled metals, but this report indicated that recycling rates of REEs are expected to increase over the next couple decades, as new REE products such as wind turbines and electric vehicles enter the decline stage of the product life cycle [100, 113]. If the recycling rates of REEs can be improved, other obstacles must still be considered to efficiently recover the REEs from those recycled materials. One of them is the ability to effectively quantify the presence of REE in various post-consumer products. Research has been conducted to optimize REE detection methods in recycled materials. In a study, it was used polarized Zeeman atomic absorption spectrometry to measure the amount of Nd, Dy, Pr, Gd, and Sm in post-consumer magnets. The study found that it is an effective means to measure the presence of REEs in recycled rare-earth magnets [114].

Among the most abundant sources of REE containing post-consumer materials is hard disk drives recovered from various electronics such as laptops and cellphones. Hard disk drives contain relatively high amounts of neodymium, praseodymium, and dysprosium present in the magnets. It is estimated that the average hard disk drive contains 2.5 to 4.6 g of REEs [115]. One such study shreds hard drives through an industrial shredder and then uses demagnetization and grinding to produce a REE-enriched scrap. Two techniques were used to extract neodymium from the scrap. The first process utilized slag extraction before subjecting the slag to H_2SO_4 leaching. The second process skipped the slag stage and leached the enriched scrap directly. Both processes converted 98% of the REEs in the solution to a high-purity REE double salt which could be used for later REE component production. The study identified the scrap production phase as economically feasible. The results indicated that direct scrap leaching was favorable to slag treatment leaching [116]. Stuhlpfarrer et al. extracted REEs from hard disk drives using hydrochloric

acid in the leaching process instead of sulfuric acid. Using hydrochloric acid allowed high yields of RE oxalate recovery than sulfuric acid [117]. Zubiani et al. have conducted a study to analyze REE extraction from recycled materials using a solid sorbent, rather than solvent extraction. This study was directed at lanthanum extraction from a model solution. The model solution was used to represent a hard disk drive magnet leached in HNO_3 to produce a neodymium-rich solution. Lanthanum was targeted to represent the sorbent effectiveness at recovering other REEs, such as neodymium. The solution was tested with an activated carbon (AC) solid sorbent as well as a polymer-modified activated carbon solid sorbent. Both sorbents were effective in recovering (90%) lanthanum from the solution. These results showed the potential for neodymium recovery from hard disk drives [118].

Another source of REE containing post-consumer products comes from various lighting and optical equipment such as fluorescent lamps, lasers, and electronic video displays [119]. A study using fluorescent waste from a lamp processing facility showed the potential to extract REEs from the waste using solvent extraction. In the study, yttrium, cerium, europium, gadolinium, lanthanum, and terbium were all effectively leached from the fluorescent lamp waste. The study found that an increase in acid concentration during the leaching phase yielded higher efficiencies [120]. Yu et al. utilized this approach and used lighting waste produced by a fluorescent lamp production facility. Analysis indicated the presence of Y, Eu, Ce, and Tb in the waste samples. Ammonium chloride roasting followed by a subsequent water leaching process effectively recovered yttrium and europium from the waste phosphor. The procedure recovered 87% of yttrium and europium. The procedure boasts low operating costs, compared with traditional leaching methods [121]. Recycled batteries are also used as a potential source of REEs. The anode of a waste nickel–metal hydride batteries can contain up to 10% of REEs such as lanthanum, cerium, praseodymium, and neodymium. A study has investigated leaching and precipitation methods used on recycled batteries. In the study, Ni–MH waste batteries were collected and subjected to leaching, filtration, and precipitation. At the optimized conditions, 99% of rare-earth oxides were recovered from the waste nickel–metal hydride batteries [122]. Another novel approach to recycling REEs is to extract them from waste slag. Waste slag produced during metal smelting may contain REEs such as neodymium. Research has been conducted to use pyrometallurgy processes to extract the REE from the waste slag. Pyrometallurgy may have a lower cost than traditional hydrometallurgy methods. One such study identified two possible methods to extract the REEs from $CaO-SiO_2-Nd_2O_3$ slag. The two possible methods identified were precipitation of REE solid-phase material and concentrating of REE in a liquid + CS region [123].

Mining and purifying of REEs from primary sources are very difficult. In addition, they cause several environmental problems including water and air pollution, high energy

consumption, and radioactive byproducts. Hence, some measures should be taken to extract REEs from secondary sources. Unfortunately, current rates of recycling REEs are very low, even less than 1%. This is mainly because of technological difficulties and, until recently, low prices, and the lack of incentives. The technological issue (low amounts and different forms of REE in goods) causes it to be challengeable to establish a general approach to recycle REEs. Various studies have been conducted to develop an efficient recovery method of REEs from post-consumer products and secondary sources such as wastewater, electronics, and fluorescent lamps. The summary of these researches is given in Table 9.

3.6 REEs in Secondary Sources Versus REEs in Primary Sources

The primary sources to extract REEs include bastnasite, monazite, and xenotime. In 2019, total REE reserves were estimated 120 million t worldwide. They are distributed mainly in China (44 million t), Brazil (22 million t), Vietnam (22 million t), Russia (12 million t), India (6.9 million t), Australia (3.4 million t), Greenland (1.5 million t), the USA (1.4 million t), India, Canada, South Africa, and other countries.

On the other hand, in 2014, the total amounts of Y, Tb, and La used in the production of LEDs have been estimated to be 1200, 130, and 350 kg, respectively [137]. The fluorescent lamp waste is reported to contain > 20% REEs, mainly contributed by phosphors [138]. One of the most important constituents of electronic wastes is magnets. They contain almost 20–30% REEs [139]. In 2019, 53.6 million t and an average of 7.3 kg per capita of electronic waste were generated in the world. The highest quantity of electronic waste was generated by the Asia (24.9 million t), Americas (13.1 million t), Europe (12 million t), Africa (2.9 million t), and Oceania (0.7 million t), respectively. In 2030, the total global electronic waste generation is expected to increase up to 74.7 million t [140]. As can be seen in Table 10, in 2020, the ranges of recycling potential for REEs from magnets, lamp phosphors, and nickel–metal hydride batteries are about 5600 to about 10,700 t. The value of REE from recycled material is at least several hundred millions of dollars per year. Moreover, it is predicted that global in-use stock of REEs in 2020 is 375,000 t. The rapidly increasing usage of REEs in the manufacturing of new technologies should be a strong incentive for recycling of anthropogenic stocks, since these are the steady and increasing source for REEs is present in the anthropogenic stocks [138]. The global consumption of REE resource grows by more than 1% per year. However, REE recycling cannot replace extracted REE from primary mines, but it can mitigate it, especially for regions without primary REE production. Moreover, by finding innovative and cost-effective technologies, the environmental challenges can be reduced by REE recycling [141].

It was estimated based on the volume of acid mine drainage or AMD generated in Pennsylvania and West Virginia that there are

approximately 610 to 2700 t of REEs per year in the AMD sludge. This amount of REEs is roughly sufficient to supply the 800 t that the US defense industry needs each year. Besides, a survey of 154 AMD treatment facilities found 225 t of sludge (dry weight basis), with a REE value of \$122 million. From known coal reserves in Montana, Wyoming, Colorado, Utah, New Mexico, and Arizona, 6 million t of REEs could potentially be recovered. Around 5 million t was potentially available at the coal deposits of Pennsylvania, West Virginia, Kentucky, and Virginia. Also, several additional million t of REEs might be available in coal ash and coal mine refuse [142, 143]. Using the Hubbert linearization method, the total REE reserve in coal is estimated by Rutledge, Mohr and Evans, and World Energy Council. These quantities are 49.2, 50.7, 61.3 million t, respectively [141, 144, 145]. Phosphogypsum is reported to contain 0.01–0.4% REE with a production of 100–280 million t per year. Around 180 million t of red mud is generated each year that contains 500–1700-ppm REEs. Also, 600 million t of iron ore tailing is produced each year with REE concentration of 350 ppm [146–149].

According to Fig. 3, 210,000 t of REEs is produced in 2019 from primary sources. In the same year, more than 4.6 billion t of the mining tailing was generated that contain 1.96 million t of REEs. However, the quantity of REEs in the mine tailing is significant, but it is needed to consider how much of them are extractable from environmental and economic points of view. The extraction of REEs from mine tailings can reduce the environmental problems related to REE mining and processing. To get this goal, it is necessary to develop cost-effective methods and recycling flow sheet for the processing steps.

4 Bioleaching and Biosorption

To addresses the feasibility and efficiency of REE extraction using microorganisms, bioleaching of some REEs from Egyptian monazite with a purity of 97% was carried out via *Aspergillus ficuum* and *Pseudomonas aeruginosa*. The results showed that the bioleaching process is more effective than the chemical process using organic acids [150]. To increase the recovery of the REE from mineralized gibbsite ore material of Um Bogma formation, an autotrophic bacteria *Acidithiobacillus ferrooxidans* was used as a bioleaching agent. In this study, the metals from sulfate leach liquor were recovered in the form of marketable products [151]. *Aspergillus ficuum* and *Pseudomonas aeruginosa* have been used to extract thorium, uranium, and REEs from thorium–uranium concentrate. *P. aeruginosa* was able to produce siderophore to change the pH and increase chelation of Th^{4+} and UO^{2+} . The results indicated that the best pH for bioleaching was 5.3, which resulted in a 68% recovery of uranium and a 65% recovery of thorium [152].

To develop a biological leaching process of REE from monazite-bearing ore, the feasibility of 10 phosphate solubilizing

Table 9 A summary of studies conducted to extract REEs from recycled material

Raw material	REEs	Recovery process	Recovery performance	Ref
Cracking catalysts	La, Ce	Leaching, two-step solvent extraction	89% of cerium and 72% lanthanum	[124]
Cracking catalysts	La, Ce	Leaching, solvent extraction	90% lanthanum and 82% cerium	[125]
Cracking catalysts	La, Ce	Roasting, leaching solvent extraction	72.8% lanthanum and 86.4% cerium	[126]
Voice coil motor (VCM) from hard disk drive (HDD)	Pr, Nd, Dy	Dismantling, demagnetization, chemical etching, oxidizing, roasting, acid leaching, synthesis of metallic-bis amide, electrodeposition	- The Separation of Fe and REE can be done by using the wet separation process - Electrodeposition was used to recover Nd	[127]
Nd-Fe-B magnets	Nd, Pr, Gd, Dy, and H0	Pretreatment and pressure leaching, REEs oxalate precipitation	- Oxidative roasting and adding NaNO₃ both can promote the selective separation of REEs. > 99% of REEs and < 0.01% of Fe could be extracted by using the pressure leaching process.	[128]
Hard disk drives, magnets	Ne, La	Slag extraction, leaching, solvent extraction, solid sorbent	Up to 98% of REEs using leaching in H₂SO₄.	[114–118]
Computer monitor scrap	Y, Ce, Nd, Sm, Eu,	Leaching (hydrochloric acid + sulfuric acid)	Up to 90% of REE using solid sorbents	[129]
Phosphor powder from waste lamp	Y, Eu, La, Ce, Pr, Tb, Sr,	Leaching (using H ₂ SO ₄ and HNO ₃), solid–liquid separation, liquid–liquid extraction (N,N-diethylglycol amic acid)	Solution had 16.5 g/L Y, 0.55 g/L Eu, 59.0 g/L	[130]
Phosphor powder from waste lamp	Y, Eu, La, Ce, Pr, Tb, Sr	Two-stage flotation scheme	The separation of REEs and Fe, Al, and Zn occurred effectively.	[131, 132]
Deep sea nodule	Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er, Tm, Yb, Lu, Th,	Leaching using H ₂ SO ₄	- The recovery of phosphor is about 70–90% - Newton's efficiency is about 0.26–0.37	[133]
Industrial waste water	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Sc, Y, Lu	Leaching using nano-Mg(OH) ₂	REEs extraction about 58%	[134]
Nickel–metal hydride (Ni–MH) rechargeable	La, Ce, Pr, Sm,	Leaching using H ₂ SO ₄ , solvent extraction with 25% bis(2-ethylhexyl) phosphoric acid in kerosene, precipitation with oxalic acid, calcination	- A mixed REO of about 99.8% - T total yield of REEs about 93.6%	[135]
Fluorescent lamps, lasers, electronic display screens	Ce, Eu, Gd, La, Tb, Y	Leaching, solvent extraction, chlorination roasting, water leaching	Higher concentration of acid in the leaching phase resulted in higher REE recovery.	[119–121, 136]
Nickel–metal hydride batteries	La, Ce, Pr, Ne	Leaching, precipitation	87% of Y and Eu were recovered. 99% of REOs were recovered.	[122]
Metallurgical slag	Ne	Pyrometallurgy	- Two possible extraction methods were identified for further investigation: - precipitation of REE solid-phase material in liquid + Ca₂+xNd₈x(SiO₄)₆O_{20.5}x - Concentrating of REE in a liquid + CS region.	[123]

Table 10 Recycling potentials for REE from magnets, lamp phosphors, and nickel–metal hydride batteries in 2020 [138]

REE application	Estimated REE stocks (tons)	Estimated average lifetime (years)	Estimated REE old scrap (tons)	Pessimistic scenario: recycled REE (tons)	Optimistic scenario: recycled REE (tons)
Magnets	300,000	15	20,000	3300	6600
Lamp phosphors	25,000	6	4167	1333	2333
Nickel–metal hydride batteries	50,000	10	5000	1000	1750
Total	375,000		29,167	5633	10,683

bacteria (PSB) species was investigated by halo zone formation on Reyes minimal agar media supplemented. The results showed that *Pseudomonas fluorescens*, *Pseudomonas putida*, *Pseudomonas rhizosphaerae*, *Mesorhizobium ciceri*, *Bacillus megaterium*, and *Acetobacter aceti* formed halo zones. *A. aceti* had the widest zone among all the strains. It has been concluded that the determination of halo zone creation was a useful method when selecting a high-capacity bacterium in the REE leaching process [153]. *Thiobacillus thiooxidans* has been used to understand the mechanism of bioleaching of aluminum and iron from coal fly ash [154]. They have studied the interactions between bacteria, metabolic products, coal fly ash [154], and leaching products by suspending up to 10% (w/v) coal fly ash (CFA) in *T. thiooxidans* growth medium containing cell inoculum. It was indicated that over biological and chemical interactions, which include the several constituents, bacterial growth and the number of metals leached from the CFA were coupled. The results showed the same leaching levels using sulfuric acid and bioleaching of CFA, and the insignificant contribution of other metabolites [155].

Biomaterials such as bacteria, algae, fungi, resin, activated carbon, and carbon-based materials were used as potential adsorbents for the uptake of rare element metals [156]. Carbon nanotubes (CNTs) can be used in a variety of research area such as electronics, electrochemical sensors, and adsorbents due to their large surface area [157]. Ramasamy et al. investigated different modification schemes of CNT for selective sorption of REEs [158]. Palmieri et al. studied biosorption of lanthanum using *Sargassum fluitans* in a batch system as another option to

recover this silvery white metal. A complete recovery of lanthanum adsorption in this study shows the possible method in order to eliminate and recover this REE [159]. A study on biosorption of some bioleached REEs from Egyptian monazite using pretreated *Aspergillus Ficum* and *Pseudomonas aeruginosa* has been investigated. *P. aeruginosa* showed higher recovery compared with *A. Ficum* [160]. A research study has been carried out on the leaching of rare-earth elements and their adsorption by using blue-green algae (*Phormidium*). In this study, REEs were dissolved from a Vietnamese ore by using $(\text{NH}_4)_2\text{SO}_4$. The leaching ratio of Nd was 67.3% when the concentration of ammonium sulfide was 1%. The adsorption density of Nd was found to be 182 mg/kg at a *Phormidium* dosage of 0.2 kg/L. It has been concluded that these results were similar to the adsorption density of other absorbents, such as activated carbon, Fe-based absorbent, and calcinated dolomite [161].

Yoshio et al. have reported the recovery and separation of REE using columns loaded with DNA attached to cellulose (DNA filter hybrid). In the study, the possibility of using DNA for REE recovery and separation was investigated. DNA–cellulose filter paper hybrid along with N,N'-disuccinimidyl was used as a cross-linker substance to fix the DNA onto a fibrous cellulose filter. The results indicate DNA filter hybrid to have an appropriately high affinity to adsorb REE [167]. Table 11 summarizes the studies of bioleaching and biosorption of REEs from different sources. In addition, Table 12 presents the summary of different types of adsorbents that are used for the biosorption process.

Fig. 3 Cumulative REEs in mine tailings and recycled waste generated in 2019 were compared with the extracted REEs from primary sources in 2019. The graph also shows the individual secondary sources of REEs in mine tailings and recycled waste generated in 2019

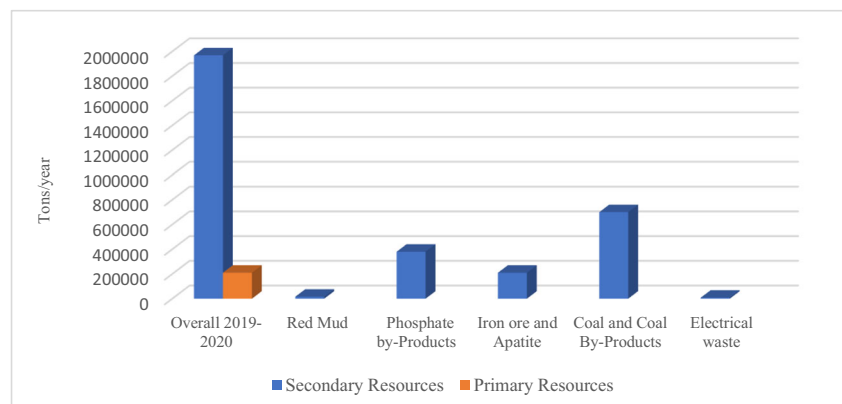


Table 11 Summary of case studies on REE bioleaching and biosorption

Summary of procedure	Source materials	Results	Ref
Bioleaching approach was used to dissolve the coal refuse material from various US-based mine sites.	Coal waste materials	- The ferric ions generated from bio-oxidation oxidize sulfide minerals such as pyrite, which generates acid. - Both acid and ferric ions are helpful for leaching REEs, as well as for removing residual sulfides. - The rate of ferrous ion bio-oxidation increased substantially by increasing the stirring rate - The bacteria are limited by oxygen availability at the lower speed.	[162]
An <i>Escherichia coli</i> strain harboring a lpp-ompA-dLBTx8 expression plasmid was grown in media supplemented with 50 µg/mL ampicillin. <i>nicotianae</i> ATCC 15236 was grown.	Coal byproducts	- Biosorption enables selective extraction of rare earths from coal leachates. - Recovery efficiency of light rare earths is most sensitive to leachate matrix effects. - An acid wash step between adsorption and desorption improves rare-earth purity. - Biosorption predicted to improve the efficacy of downstream REE precipitation steps. - The Mg/Ca impurities can be further reduced by incorporation of a low-pH wash step between the adsorption and desorption steps. - REE recovery is 80% and 50% for lignite and Powder River Basin coal fly ash, respectively. - With the exception of Sc, REEs remained largely soluble (93% and 88% remained in solution for lignite and PRB, respectively) in both feedstocks at pH 5.	[163]
Bioleaching of some REEs from Egyptian monazite with a purity of 97% was carried out by <i>Aspergillus ficuum</i> and <i>Pseudomonas aeruginosa</i>	Egyptian monazite	- The efficiency of bioleaching using <i>A. ficuum</i> was reported as 75.4% and 63.8% at a pulp density of 0.6, 1.2% (w/v) from monazite and (Th-U) concentrate, after 9 days of incubation. - The maximum percentages of bioleaching by <i>P. aeruginosa</i> was 63.5% and 52.6%. - The bioleaching process is more effective than the chemical one using organic acids.	[150]
Bioleaching recovery of the REE using autotrophic bacteria <i>Acidithiobacillus ferrooxidans</i>	Mineralized gibbsite ore material of Um Bogma	Leaching efficiencies of 67.58, 54.99, 49.91, and 22.36% for the REEs, uranium, zinc, and aluminum, respectively, were obtained.	[151]
<i>Aspergillus ficuum</i> and <i>Pseudomonas aeruginosa</i> were used to extract thorium, uranium, and REEs	Thorium–uranium concentrate	<i>P. aeruginosa</i> was able to produce siderophore to change the pH and increase chelation of Th⁴⁺ and UO²²⁺. - The best pH to bioleach was 5.3. - Resulted in 68% of uranium and 65% of thorium to be dissolved. <i>Aspergillus ficuum</i> leached 30% of uranium and 29.12% of thorium, 20% of lanthanum, 33% of cerium, and 2.51% at a pH of 3.0.	[152]
Bioleaching of REE using <i>T. thiooxidans</i>	Coal fly ash	- The same leaching levels using sulfuric acid and bioleaching of CFA, and the insignificant contribution of other metabolites. - CFA inhibits the growth rate due to the alkaline components released by the CFA that caused an increase in the pH, and the arbitrary attachment of the bacteria to both the sulfur particles and the barren CFA particles. - It is assumed that the mechanism of extracellular polymeric substance production is related to the existence of the particulate solid phase.	[155]

Table 11 (continued)

Summary of procedure	Source materials	Results	Ref
Leaching of rare-earth elements and their adsorption by using blue-green algae was studied	Vietnamese ore	During a leaching time of 3 h, and a solid/liquid ratio of 0.09, the leaching of neodymium was 67.3%, using 1% ammonium sulfide.	[161]
Blue-green algae (<i>Phormidium</i>) was used to adsorb the REEs		The adsorption density of Nd was found 182 mg/kg when dosage of <i>Phormidium</i> was 0.2 kg/L.	
The <i>Phormidium</i> biosorption for the adsorption of Nd was investigated		The contact time was 30 min, and the temperature was 298 K, while pH was kept at the initial value of 5.6.	
The equilibrium sorption isotherm of Nd onto <i>Phormidium</i> via the Langmuir isotherm equation was described		The pseudo-second-order kinetic model fitted the experimental data well.	
Phosphate solubilizing bacteria was used to leach REEs	Monazite	5.7 mg/L of cerium (0.13% of leaching efficiency) and 2.8 mg/L of lanthanum (0.11%) were leached by <i>Acetobacter aceti</i>, <i>Azospirillum brasilense</i>, <i>Azospirillum lipoferum</i>, <i>P. rhizosphaerae</i>. <i>M. ciceri</i> leached 0.5–1 mg/L of both cerium and lanthanum (0.005–0.01%).	[153]
Biosorption of lanthanum using <i>Sargassum fluitans</i> in batch system was investigated	Mixture of REE	- Maximum biosorption coefficient (q_{max}) up to 0.53 Mm at pH 5 from lanthanum sulfate was obtained. - Using lanthanum chloride a higher q_{max} (0.73 mM) was reported at the same pH. - Their proposed process claimed to have a complete recovery of lanthanum adsorption.	[159]
Parameters including the dynamics of biosorption, effect of pH, and desorption of lanthanum were studied.			
Biosorption of some bioleached REE using pretreated <i>Aspergillus Ficum</i> and <i>Pseudomonas aeruginosa</i>	Egyptian monazite	- The highest percentages of biosorped REE from monazite liquor were 85.00% by <i>P. aeruginosa</i> - The highest percentages of biosorped REE from monazite liquor were 80.00% by <i>A. Ficum</i> biomasses, respectively. - Mineral acids like H₂SO₄ could recover more than 95% of biosorped REE by <i>P. aeruginosa</i> - HCl recovered about 92% of the biosorped REE by <i>A. ficum</i>.	[160]
An overview of past achievements and current state of the biosorption studies	–	Several techniques have been developed for the recovery of REMs, but most of them are not economically attractive.	[156, 164–166]
Biosorption as a biotechnological technique exhibits a profitable exceptional tool for the recovery of rare-earth metals.			
The possibility of using DNA for REE recovery and separation was investigated	REE solution	- The results indicate DNA filter hybrid as an appropriately high affinity to adsorb REE. - The adsorption capacity was 0.182 mg/g for Nd. - REEs with higher atomic numbers have a higher affinity to DNA.	[167]
Identification of the binding site of REE in DNA was studied.		- Phosphate was in charge for REE adsorption onto the hybrid. - Whole separation of single REE from other REE may be difficult, but due to the different affinity among REE, group separation of REE is applicable. - Nd and Fe(III) were isolated from a synthetic solution of Nd magnet waste.	

Table 12 Different types of adsorbents used in the biosorption process to extract REEs [26]

La		Nd		Ce		Eu	
Adsorbents	Ref	Adsorbents	Ref	Adsorbents	Ref	Adsorbents	Ref
<i>Sargassum</i> biomass	[168]	<i>Monoraphidium</i> sp.	[169]	<i>Platamus orientalis</i> leaf powder	[170]	<i>Sargassum</i> biomass	[168]
<i>Sargassum fluitans</i>	[159]	<i>Penicillium</i> sp., activated carbon	[169]	<i>Agrobacterium</i> sp. HNI	[171]	Sm	
<i>Pseudomonas</i> sp.	[172]	Baker's yeast	[169]	Er		<i>Sargassum</i> biomass	[173]
<i>Agrobacterium</i> sp. HNI	[171]	Activated carbon	[169]	D113-III resin	[174]	Yb	
<i>Platamus orientalis</i> leaf powder	[170]	<i>Kluyveromyces marxianus</i> , <i>Candida</i>	[175]	Activated carbon from rice husks	[176]	<i>Sargassum</i> biomass	[168]
Activated carbon from rice husks	[176]	<i>Colliculaosa</i> , <i>Debaromyces hansenii</i>	[175]	Pr		D113-III resin	[177]
Bamboo charcoal	[178]	D113-III resin	[179]	<i>Sargassum</i> biomass	[173]		

To extract REEs when concentrations of the target metals are low, conventional physicochemical methods including dissolution, electrochemical technologies, fractional crystallization, ion exchange, and solvent extraction are often inefficient. Therefore, considering novel methods and approach like bioleaching and biosorption is valuable. Bioleaching relies on the ability of microorganisms to solubilize and release metal elements from a solid matrix, and it has gained attention in recent years because of its potential for lowering costs and energy requirements, and improving environmental sustainability. Besides, radioactive elements and other hazardous components can also be removed from the leaching materials during the bioleaching process, which leads to a harmless treatment of the waste materials.

5 Summary

Usually classified based on differences in demand–consumption patterns, atomic number and weight, solubility, and different levels of abundance, the global interest in REEs is primarily driven by their unique properties that are harnessed for various technological and industrial applications. Due to limited economic reserves of conventional sources and other major influencing factors including demand and supply characteristics influenced by the geopolitics of REE production, there has been renewed interest towards the search for new reliable alternative sources of REE. Many types of research have been conducted to recover REEs from identified and proven secondary sources such as coal and coal byproducts, iron ore tailings, and phosphates through the application of a series of techniques including physical separation, hydrometallurgical, and bio-hydrometallurgical techniques to concentrate rare-earth elements. This paper presented a critical review of the application of various REE extraction techniques and the environmental impacts associated with REE processing.

The various physical separation methods (i.e., gravity separation, flotation, magnetic separation, and electrostatic separations) were able to separate REE minerals from gangue primarily based on differences in distinct physical and chemical properties, but at lower yields except for flotation which consistently proved effective to separate REE minerals. In practice, however, a combination of physical separation processes is employed in a processing flowsheet to enhance recovery efficiency.

Hydrometallurgical extraction of REEs from sources including coal byproducts, iron ore tailings, apatite, and phosphate byproducts has been mostly successful. However, there is limited information about the large-scale application of this extraction technique of REEs from these sources. Subsequently, current research pursuit in this area is focused on scale-up and optimization of hydrometallurgical REE extraction processes.

To reduce the direct impact of acid leaching on the environment, biological processes, mostly bioleaching and biosorption, have also been employed at specific operating conditions with success. REE and associated element extraction has been achieved using microorganisms via bioleaching with strains such as *Aspergillus ficuum*, *Pseudomonas aeruginosa*, *Acidithiobacillus ferrooxidans*, *Aspergillus ficuum*, and *Pseudomonas aeruginosa*. Biomaterials such as bacteria, algae, fungi, resin, and activated carbon have also been studied as capable adsorbents for the uptake of REMs.

Although REEs help to reduce global reliance on non-renewable resources through their application in the development of clean energy technologies, like most mining activities, rare-earth mineral mining and subsequent downstream processing bring about a series of environmental concerns. Reviewed case studies of the environmental impact of REE mining and processing in many parts of the world raise concerns with regard to associated land degradation and loss of biodiversity, improper management and disposal of tailings which affect the surrounding ecosystem, and lastly the

emission of greenhouse gasses during processing. It was found that although measures have been adopted to contain these issues, design failures, negligence on the part of the mining companies, and weak environmental laws of REE-producing countries remain a challenge for the industry towards achieving sustainable mining in the future. In retrospect, the need remains for fundamental research to develop and optimize the various separation processes to enhance the economic and environmentally benign recovery of REEs from proven unconventional sources to meet future demands.

Compliance with Ethical Standards

Competing Interests The authors declare that they have no conflict of interest.

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