


Review

Rare Earths' Recovery from Phosphogypsum: An Overview on Direct and Indirect Leaching Techniques

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Abstract: The need for rare earths elements (REEs) in high tech electrical and electronic based materials are vital. In the global economy, deposits of natural REEs are limited except for countries such as China, which has prompted current attempts to seek alternative resources of REEs. This increased the dependence on major secondary rare earth-bearing sources such as scrap alloy, battery waste, spent catalysts, fly ash, spent magnets, waste light-emitting diodes (LEDs), and phosphogypsum (PG) for a substantial recovery of REEs for use. Recycling of REEs from these alternative waste sources through hydrometallurgical processes is becoming a sustainable and viable approach due to the low energy consumption, low waste generation, few emissions, environmentally friendliness, and economically feasibility. Industrial wastes such as the PG generated from the production of phosphoric acid is a potential secondary resource of REEs that contains a total REE concentration of over 2000 mg/kg depending upon the phosphate ore from which it is generated. Due to trace concentration of REEs in the PG (normally < 0.1% wt.) and their tiny and complex occurrence as mineral phases the recovery process of REE from PG would be highly challenging in both technology and economy. Various physicochemical pre-treatments approaches have been used up to date to up-concentrate REEs from PG prior to their extraction. Methods such as carbonation, roasting, microwave heating, grinding or recrystallization have been widely used for this purpose. This present paper reviews recent literature on various techniques that are currently employed to up-concentrate REs from PG to provide preliminary insight into further critical raw materials recovery. In addition, the advantages and disadvantages of the different strategies are discussed as avenues for realization of REE recovery from PG at a larger scale. In all the different approaches, recrystallization of PG appears to show promising advantages due to both high REE recovery as well as the pure PG phase that can be obtained.



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Keywords: rare earths; phosphogypsum; acid leaching; bioleaching; recrystallization; carbonation

1. Introduction

Rare earths elements (REEs) are metals of the lanthanoids series on the periodic table commonly referred to as lanthanides, with atomic numbers ranging from 57 to 71. The REEs are usually classified in sub-groups as light (lanthanum to europium) or heavy (gadolinium to lutetium) based on their relative atomic weights [1]. Although, REEs have similar chemical properties, each individual REE displays unique characteristics and generally can not be substituted for specific applications [2]. The field of REE applications is extensive and their demand is high and mainly dominated by the magnetic, catalytic, metallurgical and polishing industries as shown in Figure 1 [3]. From their initial time of discovery, the utilization of REEs has developed from mischmetal to high purity separated REE metal used in current advanced technologies. This advancement has consequently led to a strong growth in the use of rare earth oxides (REOs) in the past few decades, from 75,500 tons reported in 2000 to 123,100 tons in 2016 and 167,500 tons in 2017 [4,5]. The mining and production of REOs have been dominated by China since 1990 and most of the

countries where these metals are part of the important innovation technologies depend on importations from China [6,7]. However, the past two decades have seen a rapid growth in the manufacturing industries in China ranking it among the major consumers of REEs, which has resulted in reduced yearly export quotas from China to other parts of the world [8]. REE supply and availability is therefore described to be at risk due to the current state of affairs, where China controls over 90% of REE production worldwide [9]. The Chinese control over the annual amounts of REO had led to significant price fluctuations, in particular for elements such as neodymium, dysprosium, europium, yttrium and terbium that are mostly used in sustainable applications. This control has prompted an urgent search for new deposits of REEs as well as the reopening of formerly exploited deposits such as the Mountain Pass mine in Nevada, United States of America, which was reopened in 2012 [7]. However, the search for new REE deposits or reopening of formerly existing REE mines is economically costly and alternative sources of these metals are needed to compensate for both the current scarcity and cost associated with conventional mining as the use of REEs is expected to increase and supply will affect several innovative areas in future [10,11]. Several studies have recently been carried out to investigate the feasibility of extracting REEs through recycling of low value waste streams such as bauxite residue, mine tailings, PG, slag and waste waters [12–14]. Amongst the aforementioned waste streams, PG has been identified as a promising source of REEs (Table 1) [15–17]. Despite the low concentration of REEs in PG when compared to primary REE bearing minerals such as monazite [18], the large volumes of PG, currently estimated to be 200–300 million tons per annum, makes it a potential source of REEs [19]. Furthermore, the extraction and recovery of REEs from PG has several advantages over conventional mining such as avoiding the costs of mining and its related infrastructure that are almost absent [18]. The low concentration of REEs in the PG and their occurrence as complex mineral phases could cause the extraction of REEs from PG to be highly challenging in both technology and economy. This paper therefore intends to review the progress achieved in the past 20 years regarding REE up-concentration from PG prior to their respective extraction and recovery by examining various approaches.

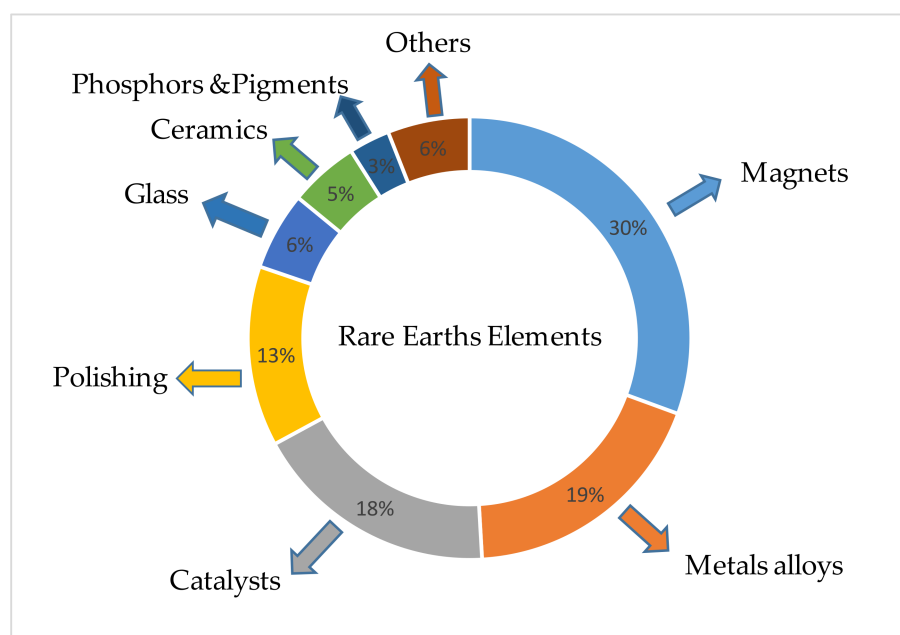


Figure 1. Estimation of global REE demand by applications in 2017 (adapted and modified from [3]).

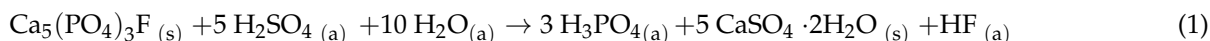
Table 1. REE content from various recycling waste streams (ppm).

Bearing Wastes	REEs																Ref
	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	Sc	
Acid mine drainage	0.9	0.09	0.03	0.1	0.06	0.02	0.1	0.02	0.07	0.01	0.03	0.002	0.01	0.002	NR	NR	[19]
Fly ash	91	196	24	89	18	3	16	3	13	3	7	1	7	1	62	NR	[20]
Mine tailings	903	2047	239	906	148	19	138	16	101	17	54	5	38	4	664	NR	[21]
NdFeB magnet	NR	NR	3	260	NR	NR	NR	NR	42	NR	NR	NR	NR	NR	NR	NR	[22]
NiMH batteries	237	67	NR	36	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	[23]
Phosphogypsum	1450	2310	235	899	163	35	99	7	46	7	16	1	6	0.6	180	1	[24]
Phosphor	4	5	NR	NR	NR	3	3	NR	NR	NR	NR	NR	NR	NR	112	NR	[25]

NR = not reported.

2. Phosphogypsum

Phosphogypsum (PG) is the chemical gypsum or by-product generated during the processing of phosphate ores (fluorapatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$) in acidic medium [11]. The names of the chemical gypsums are usually derived from its primary manufacturing products created during the chemical processing. For instance, phosphogypsum, phenologypsum and borogypsum are respectively by-products from phosphoric acid, phenol and boric acid processing [26]. For phosphogypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), the reaction involves a concentrate of $\text{Ca}_5(\text{PO}_4)_3\text{F}$ which is dissolved in a mixture of sulphuric acid (H_2SO_4) to produce phosphoric acid along with other products as described in Equation (1).



The phosphoric acid obtained in this process is mainly used in the production of phosphorus fertilizer while hydrofluoric acid is recycled in acidic process waters [27]. Hence, for each ton of phosphoric acid produced, about 1.7 tons of PG can be produced as a precipitate. Phosphate ore used in this process usually contains 20–40% of phosphate and the balance constitutes the impurities that mainly include aluminium dioxide, calcium oxide, carbon dioxide, fluorine, silicon dioxide, sodium dioxide, sulphur trioxide, iron oxide, magnesium oxide; heavy metals, U, Th and REEs. Of these impurities, REE content varies between 0.1–2 wt. % of which 70–95% gets concentrated into PG [24,28]. However, depending upon both the source of phosphate ores and the processing method, the concentration of REEs in PG can vary. For instance, the concentrations of REEs present in PG obtained through dehydrate (DH) and hemihydrate (HH) processes originating from America, Belgium, Brazil, Canada, Egypt, Poland, Russia, and Tunisia were found varying between 0.01 and 0.6 wt. % as shown in Table 2. However, it is important to highlight that, in a process where PG-HH is produced, almost 90–95% of the REEs can be transferred to PG waste, whereas only 70–80% is transferred in the PG-DH method [28,29]. Phosphoric acid processing associated with the production of PG-DH has globally been the most frequently used in recent years compared to a few processes where PG-HH is produced [28]. Therefore, the present paper will mainly focus on PG-DH generated from phosphoric acid processing.

Table 2. REE content from various types of phosphogypsum.

Country of Origin	Type of PG	REO Content (% wt)	Ref
America	DH	0.034	[30]
Belgium	DH + HH	0.55	[24]
Brazil	DH	0.52–0.54	[31]
Canada	DH	0.02	[32]
Egypt	DH	0.048	[33]
Poland	DH + HH	0.11–0.65	[16]
Russia	DH	0.47	[34]
Russia	HH	0.40–0.43	[34]
Russia	HH	0.59	[34]
Russia	HH	0.11	[35]
Russia	HH	0.46	[35]
Russia	DH + HH	0.3–0.9	[36]
Tunisia	DH	0.022	[37]

DH: PG-dehydrate, HH: PG-hemihydrate.

3. Phosphogypsum Disposal and Use Worldwide

The disposal of PG requires large land areas where it can be stacked. To date, more than a billion tons of PG has been produced and stockpiled on land worldwide leading to landfill issues [38]. Severe environmental problems have resulted due to the leaching of radioactive elements such as U, Ra, Th as well as heavy metals such as Cd, Ni [28]. These elements are known to percolate into groundwater and soils and cause contamination due to the long-term storage [39]. Furthermore, in some countries where phosphoric acid is produced such as Morocco, Mexico, Tunisia and South Africa, PG waste is directly poured into the ocean [40]. In an attempt to utilise such a huge amount of PG, several studies have focused on transferring PG into building materials, ammonia fertilizer and soil amendments [41]. However, over 85% of PG annually generated worldwide is disposed of on land or sea and only 15% is utilised in recycling processing such as building materials (plaster, wallboard etc.), soil stabilisation amendments or fertilizers or manufacturing of Portland cement (settling time controller) [42]. This is mainly due to some specific limitations of impurities such as radioactive and REEs being present in PG [43]. A few studies have investigated the phases in which REEs occurred in PG but their conclusions varied depending upon the source of the PG [44–46]. From these studies, it was found that REEs usually occur in four main phases namely as carbonates, phosphates, fluorides, and sulphates. The first two phases are usually referred to as associated phases and the last two as replacement phases for calcium in the crystal lattice structure. REEs found as associated mineral phases are readily soluble using mineral acids such as HCl, H₂SO₄ and HNO₃ while those in replacement phases require treatment processes to increase both chemical and physical reactivity of PG. However, apart from these phases, REEs can also be found as adsorbed ions in PG. REE occurrences in PG were recently investigated by Yang et al. [47] by combining mineral liberation analysis (MLA) and electron microprobe analysis (EMA) for mineral analysis and ICP-MS for elemental composition. Their results showed that gypsum (CaSO₄) was the dominating mineral phase in PG that contained over 72% of REEs present in the samples.

4. Beneficiation Methods

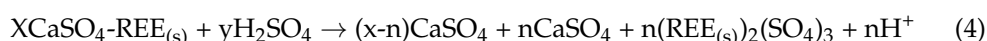
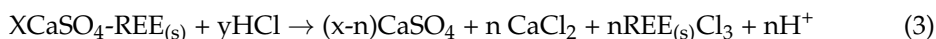
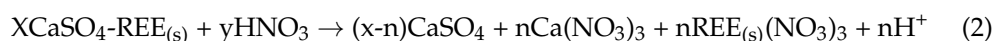
Physical and chemical pre-treatment methods have been used to upgrade the low concentrations of REEs present in PG prior to processing. Physical methods such as hydrodynamic, flotation, grinding and high gradient magnetic separation (HGMS) have been reported in the literature [46,47]. In a study by Yang et al. [48] four tests of physical enrichments were conducted on PG through treating it by HGMS alone, flotation combined with HGMS or mechanical grinding followed by flotation and HGMS, and hydrodynamic sedimentation followed by HGMS, respectively. Their results proved that PG was effectively enriched in REEs from an initial grade of 0.13 to 7.3 wt. %. In another trial, the authors used a centrifugal ball milling at 30, 60 and 90 min prior to the leaching process in a suspension of HCl or HNO₃. The results clearly showed that the milling had a significant effect on the extractability efficiencies of REEs as, in the samples milled, the extracted REEs increased for all the REEs as the milling time increased. According to these authors, this improvement of REE leaching efficiency using mechano-activation by grinding could be attributed to increased specific area and decreased virtual activation energy of ground material due to crystal interior defects. However, the recovery of individual elements differed because REEs in PG are carried by the gypsum mineral phase which was not completely enriched by the aforementioned physical methods. Therefore, the loss of REEs during the beneficiation process mainly resulted from that portion remaining in the gypsum. Microwave radiation has also been used by Reid et al. [49] and Lambert et al. [50] for enrichment of PG prior to REE leaching. It was found that microwaving PG resulted in dielectric heating of water molecules present in PG crystals causing the formation of pores in the PG matrix as the water vapour escaped. Chemical enrichment approaches have also been discussed by Hammas-Nasri et al. [51]. In their study the PG was treated consecutively with solutions of NaCl and Na₂CO₃ in an attempt to enrich the PG with REEs in the final

residue prior to the leaching process. Their methods consisted of washing 500 g of PG with 25 or 60 g/L saline Na_2CO_3 solutions (S:L = 1:200) resulting in approximately 81% and 84% increased rates of enrichment, respectively. Improvement of REE leaching from PG, through investigating the effects of mechanical treatments (grinding and ultrasonic impact) and chemical activation (sorption onto an ion exchange resin) were also reported by Rychkov et al. [17]. The study consisted of treating 40 g of PG with 300 mL of H_2SO_4 (S:L = 1:7.5) and it was found that upon exposure to highly concentrated H_2SO_4 , only 30% of REEs present in the PG was leached. The authors explained this low recovery was a result of strong chemical bonding between the REEs and the crystals of PG. Nevertheless, by applying grinding and ultrasonic impact treatment simultaneously in an attempt to reduce the particle size to between 6 and 8 μm while adding a strong acid cation exchange resin (Purolite C-160) directly to the H_2SO_4 leaching solution, the REE recovery was found to increase by a factor of 4. Moreover, by sorbing the REE ions directly from the leaching solution onto the strong acid cation exchange resin, the potential for precipitating the REEs as double sulphate and oxide complexes was minimized. The proposed process was able to increase REE recovery from 15–17% to over 70% by physical and chemical reactivity of the PG, which also led to a PG product containing less impurities. Although physical and chemical treatments of PG are promising approaches towards high leaching efficiencies of REEs, they involve additional costs particularly at large scale. To overcome this, PG could also be treated directly through hydrometallurgical processing such as direct and indirect leaching, without physical and chemical pre-treatments due to its smaller particle size [42].

The leaching is the first step in the hydrometallurgical process in which the operational parameters such as agitation speed, contact time (residence time), particle size, solid to liquid ratio (S:L), lixiviant type, and temperature are usually varied to obtain optimum conditions [52]. The leaching of PG is mainly possible as most REEs occur as adsorbed secondary phases onto the surface of PG. This surface adsorption suggests that REEs should be relatively susceptible to be extracted through aqueous chemical agents such as inorganic or organic liquids, compared to a case where REE are found incorporated within the crystal lattice of PG [53].

4.1. Direct Leaching

Strong inorganic acids such as H_2SO_4 , HCl and HNO_3 are the most commonly used lixivants in direct leaching of PG due to their strength and availability (Table 3). However, the leaching efficiency of REEs from PG is limited by the solubility of the gypsum (CaSO_4) in the system. Thus, as CaSO_4 reaches its solubility limit, no additional REEs can leach since the remaining REEs are trapped inside the undissolved PG particles. According to Kouraim et al. [54], the possible chemical reactions that can occur during the leaching of PG with HCl , HNO_3 or H_2SO_4 can be described as indicated in Equations (2)–(4).



In general, H_2SO_4 leaching is economically advantageous due to its much lower cost and therefore is mostly used. However, the key obstacle encountered with H_2SO_4 direct leaching of PG for REE extraction, is the inefficient diffusion of proton, sulphate ions and REE ions between the layers of calcium sulphate crystals to which calcium ions are tightly bonded. This effect was attributed to low solubility of PG in H_2SO_4 solution resulting from the common-ion effect [32]. For instance, under normal conditions of temperature and pressure, only low leaching efficiencies ranging from 12–40% have been attained [28]. Liang et al. [55] recently studied the extraction of REEs from PG (total REE concentration estimated at 218.42 ppm) generated at Mosaic Co. in Florida using 5% H_2SO_4 , at S:L ratio of 1:4 (300 g of PG per experiment) at a temperature of 50 °C for 120 min. Their results showed that a maximum leaching efficiency of 43% REE was obtained with increased

contact time and S:L ratios. However, the leaching of the impurities such as U, F and P also increased. In order to enhance the leaching efficiency, a few other approaches have been considered.

Ammas-Nasri et al. [37] conducted a study on REE recovery from PG using a double H_2SO_4 leaching step to enhance REE dissolution. In their study about 500 g of PG containing a total REE concentration of about 224.93 ppm was leached with H_2SO_4 solutions (S:L = 1:1.3). The results showed a high enrichment of REEs of about 86% (ΣREE concentration of 1671.89 ppm) in the crystallised solid obtained from the evaporation of the second leachate, which was a mixture of anhydrite-monetite ($\text{CaSO}_4\text{-CaHPO}_4$) phases. Notwithstanding the enrichment of REEs obtained in this approach, the evaporation process was energy consuming when considering scaling up the process. The evaporation of the leachate exerts a beneficial influence on the isolation of REEs from PG but the incurred costs related to the heating of the solution dominates among the production costs rendering the process unprofitable. Lokshin et al. [56] extended the leaching time to several weeks in an attempt to increase the REE extraction efficiency using a H_2SO_4 solution. In their investigation, 40 g of PG was leached with H_2SO_4 solutions (0.5–4 wt. %) for 3025 h (18 weeks) using a S:L ratio of 1:2. However, the leaching efficiency of REEs only increased by three times compared to the case where 1 h leaching was used under the same conditions. Other methods such as that developed at Prayon SA in Engis, Belgium, consisted of extracting the REEs from a diluted H_2SO_4 solution while stirring the suspension at a high speed of 6000 rpm and subsequent recovery of REEs using organic extractants in a solvent extraction process or precipitation with oxalic acid [24]. Valkov et al. [57] also reported an increased yield of REEs while leaching 50 g of PG using bubbling of air into the H_2SO_4 pulp at a temperature of 70–100 °C for 1–2 h and S:L of 1. Although the authors indicated that the residue of PG was environmentally friendly for applications such as road constructions, no percentage yield of REEs was given. Similar to H_2SO_4 , the leaching of REEs from PG was also found to be moderately low with HCl. The low leaching of HCl was mainly attributed to the relatively low solubility of calcium sulphate in the HCl solution because of the salt out effect that is associated with this process [32]. However, Ismail et al. [33] demonstrated that REE fluorides were obtained by HCl leaching of PG after the REEs were partially precipitated into the residue.

HNO_3 leaching of REEs from PG seems the most efficient compared to H_2SO_4 and HCl due to the relative higher solubility of calcium sulphate in HNO_3 solution. The leaching efficiency of REEs with HNO_3 can reach up to 50% when using a low S:L ratio. A study conducted on Egyptian PG by El-Reefy et al. [58] using a mixture of HNO_3 (2.0–3.0 M) and 0.8 M calcium nitrate for 8 h residence time and varying the S:L ratios showed that the leaching efficiency of REEs increased with increasing S:L ratio but decreased with low S:L ratios under the same conditions. Similar patterns were observed by Ismail et al. [33] where the temperature effect was investigated. Lokshin et al. [59], reported a high leaching efficiency of REEs up to 93% using 15 wt % HNO_3 concentration and S:L ratio 1:10. It was found that with a high S:L ratio, the leaching efficiency of REEs increased with increasing the concentration of HNO_3 below 15 % wt and decreased gradually with continuous increasing of the concentration from 15% wt and above. However, while leaching REEs and calcium ions from PG (S:L = 1:8) obtained at the Agrium fertilizer plant, only a slight improvement of 6% on the leaching efficiency of REEs and 29% for calcium were reached when increasing the HNO_3 concentration from 1.5 to 3.0 M [32]. Despite the fact that HNO_3 is reported to have moderately high leaching efficiencies compared to HCl, the latter is more economical and can be potentially considered as a better leaching agent of REEs from PG from an industrial point of view. Although a few moderate REE leaching efficiencies have been reported through direct leaching of PG, so far these methods have been deemed uneconomical especially for larger scales [60]. Furthermore, due to the limited solubility of PG, dissolving it completely in an attempt to recover only REEs is neither economical nor practically feasible as the concentration of REE to be extracted is low. Therefore, exploring technologies that involve indirect leaching of REEs such as

carbonation and recrystallization of PG for production of materials that have commercial and industrial utilization with subsequent extraction of REEs is advisable.

4.2. Indirect Leaching

In contrast to direct leaching, indirect leaching refers here to processes that consist of modifying the microstructure of PG into materials that could find commercial and industrial applications while releasing locked REEs. Processes such as carbonation and recrystallization of PG offer good potentiality to achieve such an approach. Applying such processes can render the extraction of REEs more economical and attractive due to high REE content in PG estimated at about 21 million tons as well as saleable products that can be obtained for industrial and commercial utilization [61]. Therefore, the following sections mainly discuss the development that has been performed so far in respect of the aforementioned approaches with a particular attention on the mild acid recrystallization of PG for the fabrication of calcium whiskers and subsequent recovery of REEs from PG.

4.2.1. Carbonation

The carbonation process is one of the approaches that can be explored for the valorisation of PG by converting it to calcium carbonate (CaCO_3) or ammonia sulphate (AS) fertilizer and has been widely described in the literature [62,63]. Pure CaCO_3 can be used in a wide range of commercial and industrial applications such as for the manufacturing of concrete (Portland cement) and production of lime (soil stabilization and acid neutralization), water treatment and flue gas desulfurization [64]. CaCO_3 produced from PG processing has been found to be richly concentrated in REEs originally present in the PG waste [65]. This processing is therefore considered as an interesting method of up-concentrating REE prior to their recovery through dissolution of CaCO_3 using mineral acids followed by extraction [62]. However, as schematically presented in Figure 2, PG carbonation as such is generally used for the production of AS and both CaCO_3 and REEs are usually obtained as intermediate products from this process [66].

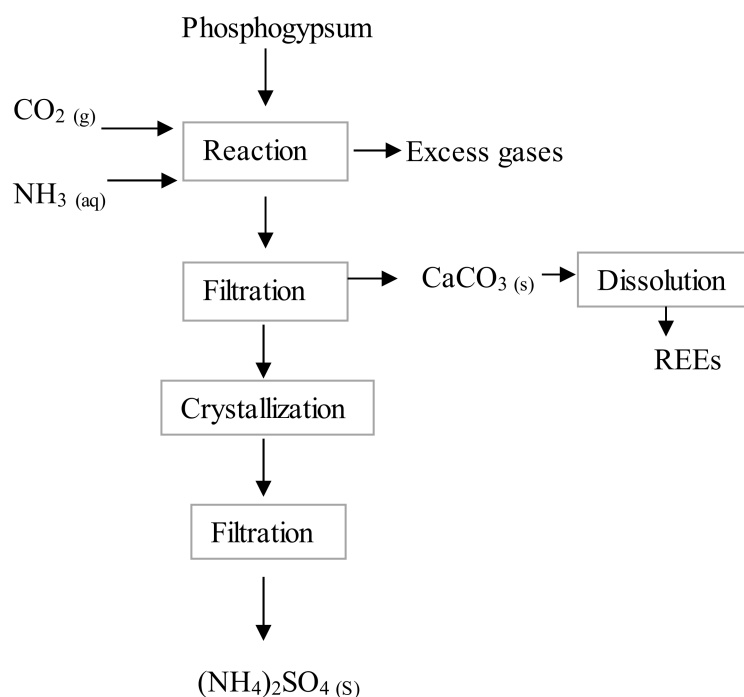


Figure 2. Mineral carbonation of phosphogypsum adapted and modified from [66].

Table 3. Leaching efficiencies of REEs from PG using various leaching agents.

Approach	REE Content (wt. %)	Lixiviant	S:L Ratio	Time (h)	Temperature (°C)	Efficiency (%)	Ref
Inorganic acid leaching	0.041	15% H ₂ SO ₄	1:3	2	100	60	[67]
	0.035	3 M HNO ₃	1:30	8	25	85	[11]
	0.17 *	2.5% HNO ₃	1:7.5	0.25	25	59	[68]
	0.032	1.5 M HCl	1:15	1	85	Nd: 80 Dy: 99 Y: 99	[50]
	2.6	H ₂ SO ₄	1:6	4.3	275	95	[18]
	0.19	0.01 M H ₂ SO ₄	1:20	20–22	24	15	[68]
	0.44	10% H ₂ SO ₄	1:3	20	2	52	[69]
	1.7	1 g/L H ₂ SO ₄	1:8	24	-	45–75	[70]
	0.44	10–30% H ₂ SO ₄	1:7.5	2	50	72	[17]
	0.022	10% H ₂ SO ₄	1:1.3	1–2	60	50	[37]
		1.5 M HCl				51	
	0.020	1.5 M H ₂ SO ₄	1:8	0.33	80	23	[32]
		1.5 M HNO ₃				57	
	0.042	36% HNO ₃	1:4	1	72	58	[30]
	0.034	90% H ₂ SO ₄ + 10% H ₃ PO ₄	1:6.7	1	72	49	
	3 M HNO ₃				43		
0.048	2 M HCl	1:2	3	25	12	[33]	
	4 M H ₂ SO ₄				13		
0.048	1 M C ₆ H ₈ O ₇	1:5	0.25	85	83.4	[71]	
Organic leaching	0.040	0.7 M TBP- 0.9M TOPO	1:1	2	55	70	[72]
		0.5 M Na ₂ CO ₃ + TPB-TOPO	1:1	2	55	80	
Bioleaching	1.3	Spent medium (<i>Gluconobacter oxydans</i> , 220 mM gluconic acid) Gluconobacter oxydants NRRL, B85	1:50	24	25	Y: 91.2 Ce:36.7 Nd: 42.8 Sm: 73.2 Eu: 50 Yb: 83.7	[53]

Note: * (mg/kg).

Masmoudi-Soussi et al. [43] recently developed a hydrothermal method that consisted of converting PG to CaCO₃ using a high-pressure and high-temperature Parr-reactor. Prior to the conversion, PG was washed with salt water (NaCl/25 g/L). The results were obtained at 80–100 °C for 2 h, and showed that the hydrothermal conversion was effective and led to a complete conversion of the sulphate matrix of PG to the corresponding carbonate, which was enriched in REEs at a rate of 66%. The authors indicated that the enrichment was related to the insertion of the REEs into the gypsum matrix by replacement of calcium ions in the PG as well as the known affinity of REEs towards carbonates in an alkaline pH. The leaching of the obtained carbonate using HCl solution (5–6%) at 80–90 °C for an hour in the presence of ascorbic acid as a reducing agent, allowed the migration of about 89% of REEs to the acid liquor. In a parallel approach, PG can also be directly decomposed by reaction with ammonium carbonate as shown in Equation (5). This decomposition is carried out in order to form AS fertiliser and CaCO₃ and as in the aforementioned approaches, REEs report significantly to CaCO₃ solid. Thus, the dissolution of CaCO₃ in HNO₃ or its calcination prior to a leaching with solutions such as ammonia chloride can result in a residue with high REEs content. Although, the carbonation of PG demonstrated interesting improvement in terms of REE extraction, the main disadvantages remain the high reagent cost and energy consumption as well as the limited market for CaCO₃ and AS, which is a common by-product in this process [61].



4.2.2. Recrystallization

REEs do not isomorphously cocrystallize with the lattice structure but rather exist in separate phases offering a good opportunity in terms of REE extraction and recrystallization of technically pure PG [73]. The dissolution and recrystallization of PG with attention to REE recovery is an emerging area of research and has been reported [29,73]. In view of this approach, a few trials have been performed both at laboratory scale and larger scale. For instance, Genkin et al. [73] described a process where PG-dehydrate was recrystallized in the presence of calcium nitrate (in terms of Ca²⁺) under acidic medium

(0.2–8 M, in terms of H^+). Subsequent to this method, over 98% of the REEs reported in the leaching solution. In this process, the solvent extraction method was suggested for subsequent recovery of REEs and further processing. Nevertheless, the proposed process was found to be unattractive from an economical and waste management point of view. Furthermore, although increased concentration of Ca^{2+} ions was favorable in terms of REE recovery, this increase made the formation of the targeted and purified PG less favourable. Another approach described by Koopman and Witkamp [29] consisted of introducing an ion-exchange resin for the extraction and recovery of REEs leached out during the recrystallization of PG-hemidihydrate to PG-dehydrate. Their results revealed a significant decrease of REEs in the final PG-dehydrate residue and the amount of REE released during the recrystallization process was found to be up to 53%. The authors indicated that REE extraction efficiency was mainly influenced by the recrystallization reaction but individual REEs that had a strong affinity to PG-dehydrate were least extracted. The main disadvantage of this process was that the sulfonic acid resin used also extracted calcium ions besides having a preference for trivalent REEs. A method developed at Mintek in Randburg, South Africa by Yahorava et al. [61] entailed hydrothermally treating PG containing slurry using an autoclave for the recrystallization and recovery of REEs. The process was tested on various PG samples and showed that REE recoveries were improved from 5% to 80% while recrystallizing the PG. Although the process carried a large potential for unlocking valuable REEs encapsulated in PG stock piles, there were still several parameters such as residence time in the autoclave, impact of seeding and solids content which required verification and optimization. Moreover, even though the process claimed to be “chemical free”, temperatures of up to 100 °C were required in the autoclave for high release of REEs during the recrystallization process. Similarly, the method developed at Integra.Ru Co Ltd. in Moscow, Russia by Kanzel et al. [74] consisted of decomposing PG while extracting released REEs using sulphuric acid in five consecutive stages. The resulting solid residue (cake) was technically a gypsum that could be used in the production of building materials (e.i. binders) and the liquid waste which was technically an industrial water contained high concentrations of REEs that were subsequently extracted using standard methods at a purity of 99%. However, the production of gypsum from PG in such a process is an energy intensive process since the PG binder is burned at higher temperatures than are traditionally used to obtain a binder from natural gypsum stone, hence making the proposed process economically unprofitable particularly when considering large scale processing [75,76].

The synthesis of calcium sulphate whiskers (CSWs) from PG due to high content of $CaSO_4$ is also an emerging area of research and has been recently discussed [77,78]. CSWs have been widely used for several applications such as reinforcing materials in plastics, paper mills, rubbers, grafting materials in bone and tissue regeneration, filters, paints and other products [79,80]. So far, efforts in this area have been made following three directions namely: the synthesis, modification of the crystal morphologies using additives, and the application of CSWs for constructional materials [81]. However, little effort has been made to develop a combined process in which both the synthesis of CSWs and REEs extraction could be sequentially achieved. CSWs are typically prepared through hydrothermal or atmospheric acidification synthesis or recrystallization. Compared to the hydrothermal synthesis, which is usually carried at high temperatures (>100 °C) and steam pressures [82], the atmospheric acidification of PG has advantages since it can be carried out at a mild reaction conditions (temperature < 90 °C and atmospheric pressure) [78]. Figure 3 shows a proposed flow diagram of this process with a subsequent extraction of REEs.

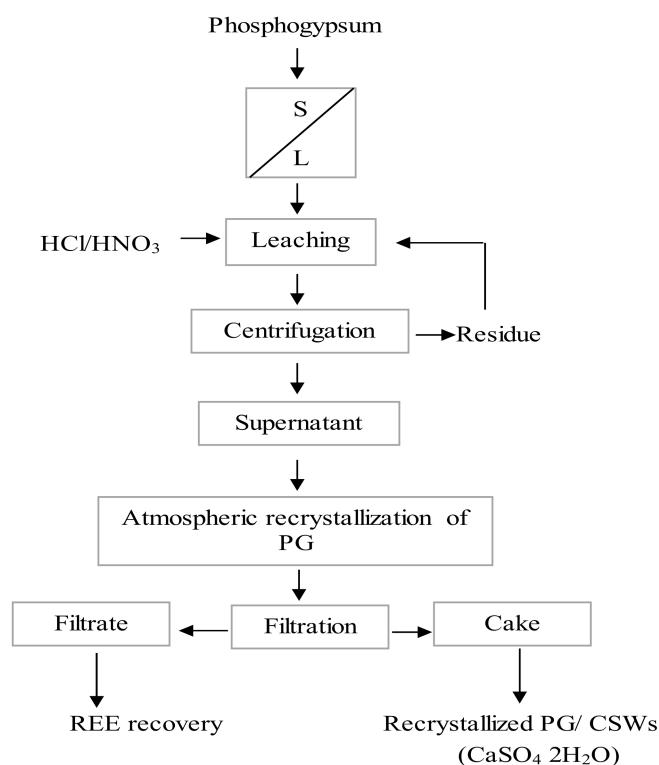


Figure 3. Proposed flowsheet of an atmospheric acid recrystallization of PG with subsequent extraction of REEs.

4.3. Organic Liquid

REE leaching using organic solvents has also been discussed in the literature. This approach is referred to as solvometallurgy in comparison to hydrometallurgy where mineral acids are usually used. The solvometallurgical method allows a high selectivity of metals to be obtained and reduces both the consumption of acids and the volumes of leaching solutions [24,83]. A recent method proposed by El-Didamony et al. [72,84] aimed to remove the radioactive elements such as radium, uranium, thorium, cadmium, chromium etc. from PG while recovering REEs simultaneously using an organic solution of tri-*n*-butyl phosphate (TBP), tri-*n*-octylphosphine oxide (TOPO) and a mixture of TBP + TOPO in kerosene. The results revealed leaching efficiencies of between 66% and 73% for radioactive metals and 69% of total REEs when leaching PG with 0.5 M TBP using S:L ratio of 1 for 2 h at 55 °C. Two successive leaching steps were found to increase the removal efficiencies of both radioactive elements and REE metals while a third step did not bring any further enhancement. However, in the case of successive steps using a mixture of organic solutions namely TBP and TOPO with molar concentrations of 0.7 and 0.9, respectively, a considerable increase was obtained. Further investigation showed that pre-treating PG with hot sodium carbonate (0.5 M) prior to a leaching with a mixture of TBP and TOPO in kerosene had a significant effect on the extractability of these elements with an optimal removal efficiency of 94.6% and 80.1% that were achieved for radioactive elements and REE recovery, respectively. Although organic solvents have demonstrated relatively high recovery of REEs and other metals present in PG, the loss of organic reagents that were generally adsorbed and entered into the matrix of gypsum may lead to high costs due to the amount of organic solvents used as well as environmental concerns. Organic leaching processes are therefore promising but require more research and development before they can be implemented at a large scale.

4.4. Bioleaching

Bioleaching for metal extraction is an emerging technology, which is currently considered among other approaches to overcome some of the disadvantages encountered in direct leaching such as high operational cost, generation of both heavy metal pollution and sludge, and poor recovery [85–87]. Bioleaching processes can be performed by autotrophic or heterotrophic microorganisms and the selection of the latter depends on the type of the bearing mineral. Heterotrophic microorganisms have mostly been reported in the literature for REE extraction via bioleaching and includes the production of organic acids and metal-binding molecules [88]. The organic acids, namely oxalic, gluconic, acetic, citric, formic and malic acids decrease the pH allowing the leaching of REE while the metal-binding molecules act as chelating agent for separation of the targeted molecule out of the solution [61,87,89]. Bioleaching processes are relatively slow, most occur at lower pressures and temperatures and do not require the utilization of aggressive reagents [88]. Bioleaching has mostly been reported for REE extraction from other secondary REE sources such as bauxite but only a little information is available for PG. Bioleaching of PG for REE recovery is usually achieved using either anaerobic or aerobic microorganism species such as *Gluconobacter*, *Acidithiobacillus*, *Acetobacter* or *Desulfivibrio* and can be achieved through column or heap leaching processes [87,89]. Phosphate-solubilizing microorganisms (PSMs) have also been reported and used to solubilize the REEs from various bearing minerals [87]. Bacterial species such as *Pseudomonas*, *Bacillus*, *Rhizobium*, *Erwinia*, *Agrobacterium*, *Flavobacterium*, *Enterobacter*, *Micrococcus*, *Thiobacillus*, *Acetobacter*, *Clavibacter*, *Serratia*, and *Streptomyces* as well as some fungi such as *Penicillium*, *Aspergillus*, *Rhizopus*, and *Fusarium* have been found to be efficient in bioleaching processes using PSMs [89]. According to Glombitza and Reichel [90], mineral dissolution in bioleaching may proceed via one or several mechanisms which mainly include (a) complexation promoted dissolution (complexolysis), (b) proton promoted dissolution (acidolysis) and (c) redox reactions (redoxolysis). In these mechanisms, microorganisms produce metabolites by changing the pH of their surroundings and the formed metabolites form in turn complexes with the metals and therefore lead to their mobilization from solids (complexolysis). The dissolution of the solids (acidolysis) can similarly occur at reduced pH. The aforementioned mechanisms are systematically explained in Figure 4 where seven scenarios are expected to take place for bioleaching of REEs.

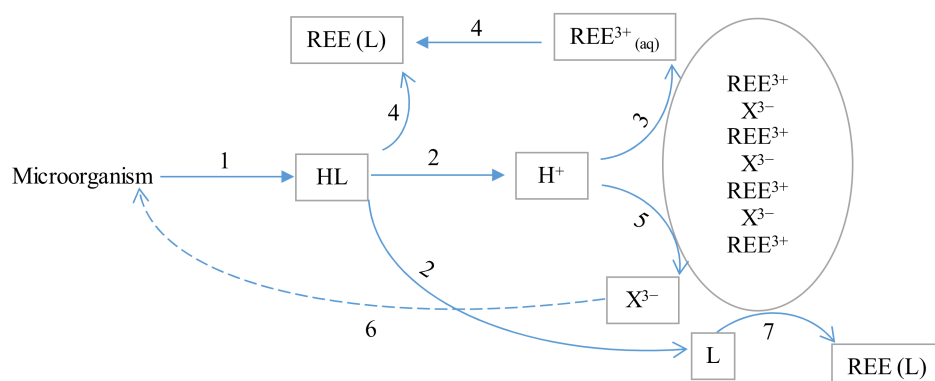


Figure 4. Possible mechanisms and reactions of REE bioleaching where (1) ligand (L) is secreted, (2) ligand dissociates, (3) proton promoted dissolution due to reaction with REE^{3+} , (4) reaction of $\text{REE}^{3+}_{(\text{aq})}$ with ligand protonated (HL), (5) dissolution of proton promoted due to reaction with arbitrary anion (X^{3-}), (6) X^{3-} up taking by microorganism, and (7) dissolution of ligand promoted. Adapted from [91].

A study by Barmettler et al. [92], has showed that a mixed culture of sulphur-oxidizing bacteria was able to extract 55–70% of REEs from PG after 30 days of incubation at pH 1.5–1.8. The authors attributed this leaching of REEs to the sulphuric acid generated by

sulphur-oxidizing bacteria. In another trial, where a sulfate-reducing bacteria *Disulfovibrio desulfuricans* was used, about 80% extraction was achieved for yttrium using a fixed-bed reactor. The ability of a gluconic acid dominated biolixiviant was also examined by Antonick et al. [53], conventional for the extraction of REEs from synthetic PG. The results indicated that although this biolixiviant was more effective for REE leaching compared to a commercial gluconic acid, its performance was very low in comparison with conventional H₂SO₄ acid leaching. The authors suggested more trials on real PG. However, more studies with regard to the costing and environmental impacts associated are still needed to decide whether or not bioleaching is a suitable option for REE recovery from industrial PG [92]. Compared to chemical leaching which uses strong acids (inorganic or organic) and complexants, bioleaching suffers from lower yield and rates [91]. The effectiveness of this process mainly depends on the ability of the microorganisms to oxidize and thus to leach the REEs and also on parameters such as particle size of the REE bearing mineral, the pH of the leaching media and the temperature [93].

Table 4 gives a comparative overview of various methods discussed in Section 4 of this review with particular attention to their advantages and disadvantages. Among other approaches, the atmospheric acid recrystallization of PG was found to be more promising as it can allow REE recovery and CSWs to be obtained separately and subsequently for both small and large scale.

Table 4. Overview of the advantages and disadvantages of the approaches discussed in this review.

Approach	Advantages	Disadvantages
Direct acid leaching	<ul style="list-style-type: none"> • High efficiencies • Applicable at small and large scale • No specific equipment required 	<ul style="list-style-type: none"> • High acid concentrations required • Generally uneconomical for large scale • Not environmentally benign
Organic liquid	<ul style="list-style-type: none"> • Selective • No specific equipment required • Mostly applicable at small scale 	<ul style="list-style-type: none"> • Loss of organic reagents generally adsorbed into the matrix of gypsum • High cost of organic solvents • Still required more research for large scale
Bioleaching	<ul style="list-style-type: none"> • No harsh conditions (temperatures) required • No specific equipment required • Mostly applicable at small scale • Environmentally safe 	<ul style="list-style-type: none"> • Low yields/rates • Required several hours/days • Effectiveness depends on the ability of the microorganisms to oxidize phosphogypsum particle
Carbonation	<ul style="list-style-type: none"> • Allows obtaining a carbonate reach in REEs • Specific equipment (reactor) required • Can be used at small/large scale 	<ul style="list-style-type: none"> • High reagent cost • High energy consumption • Dissolution of carbonates required for REE recovery • Generation of additional by-products such as ammonia sulphate
Atmospheric recrystallization	<ul style="list-style-type: none"> • Allows obtaining both REE and calcium sulphate whiskers (CSWs) separately • Mild reaction conditions (<90 °C) • Can be achieved in a loop system • No specific equipment required • Can be used at small/large scale 	<ul style="list-style-type: none"> • Use of acids required • REE recovery required solvent extraction or precipitation step

5. Methods of REE Recovery

The recovery of REE from PG leachates is usually carried out using common techniques as those developed for primary sourced REEs [28]. Methods such as precipitation, liquid–liquid extraction (solvent extraction), solid–liquid extraction (adsorption) and ion-exchange have widely been used for separation and purification since PG leachate is obtained as a mixture of REEs alongside with other metals. These methods are generally used in an attempt to produce REEs in a suitable form and purity. The ion-exchange consists of adsorbing REE ions from the leachates onto an exchanger that is specific and

selective for REEs. In a reverse process, REE ions are desorbed from the exchanger during an elution step [94]. The ion-exchange method has been used for decades and is highly selective. However, its cost limits its use except in certain processes where the production of extremely pure materials is required [3,95]. Similar to ion-exchange, solvent extraction, also known as liquid–liquid extraction, is highly selective and has the advantage over the ion-exchange method because it is fast, cost effective and can be used in a continuous process where large volumes of leachates are required. Solvent extraction is therefore the most commonly used commercial method for separation and purification of REEs from acid solutions [3]. Another emerging method for REE separation and purification is solid–liquid extraction. This method uses nanoporous materials such as polymeric fibres, or silica and carbon based sorbents to separate and purify the REEs [94,96]. In a recent study by Hu et al. [95], silica and carbon-based sorbents were reported for REE separation and purification. Their results highlighted four main aspects that were satisfactory namely a high enrichment factor, rapid adsorption kinetics, reduced solvent use and minimized waste generation obtained.

6. Conclusions

REEs are a critical and strategic resource of the modern world and to meet the growing industrial and technological needs, alternative secondary sources of REEs such as PG residues are continuously being explored worldwide. This review highlighted the research progress on various efficient leaching processes for the recovery of REEs from PG. This review provided information about the leaching of PG to provide an overview for the recovery of REEs contained in secondary wastes as critical raw materials. The first stage in REE recovery from waste materials is the leaching of elements from the solids. This knowledge is required in subsequent hydrometallurgical processing steps to recover REEs contained in these wastes. Direct leaching of PG for REE extraction using inorganic, organic and microorganisms is uneconomical and failed in most cases for large scale processing due to low concentration of REEs compared to other metal constituents in PG. Therefore, combining both REE extraction and subsequent recrystallization of PG for the synthesis of useful industrial materials such as calcium whiskers (CSWs) is a promising approach and could be feasible at small scale and large scale. Such a combination offers the possibility for exploitation of a secondary waste source of REEs, which may have a great impact on the economies of countries where primary sources of REEs are lacking. Furthermore, compared to the carbonation process which required dissolution of the carbonate reach in REEs, the recrystallization of PG offers the opportunity to extract the REEs directly from the filtrate.

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