



Comprehensive recovery of rare earth elements and gypsum from phosphogypsum: A wastewater free process combining gravity separation and hydrometallurgy[☆]

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ABSTRACT

Comprehensive utilization of phosphogypsum (PG) has attracted much attention, especially for the recovery of rare earth elements (REEs) and gypsum due to the issues of stockpile, environmental pollution, and waste of associated resources. Traditional utilization methods suffered the issues of low REEs leaching efficiency, huge amount of CaSO_4 saturated wastewater and high recovery cost. To solve these issues, this study investigated the occurrence of REEs in PG and the leaching of REEs. The results show that REEs in PG are in the forms of (1) REEs mineral inclusions, (2) REEs isomorphous substitution of Ca^{2+} in gypsum lattice, (3) dispersed soluble REEs salts. Acid leaching results demonstrate that (1) the dissolution of gypsum matrix is the control factor of REEs leaching; (2) H_2SO_4 is a promising leachant considering the recycle of leachate; (3) the gypsum matrix suffers a recrystallization during the acid leaching and releases the soluble REEs from PG to aqueous solution. For the recovery of the undissolved REEs mineral inclusions, wet sieving concentrated 37.1 wt% of the REEs in a 10.7 wt% mass, increasing REEs content from 309 to 1071 ppm. Finally, a green process combining gravity separation and hydrometallurgy is proposed. This process owns the merits of wastewater free, considerable REEs recovery (about 10% increase compared with traditional processes), excellent gypsum purification (>95 wt% $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, with <0.06 wt% of soluble P_2O_5 and <0.015 wt% of soluble F) and reagent saving (about 2/3 less reagent consumption than non-cyclical leaching).

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1. Introduction

Rare earth elements (REEs) including the lanthanides, scandium and yttrium, play a critical role in functional materials, such as the permanent magnet material (Nd-Fe-B) that is vital importance for the electric vehicle and wind turbine. Considering the unevenly

distribution and supply risks, REEs have been defined as the strategic elements in the United States, Japan and the European Union.^{1,2} Recently, due to the depletion of high-grade ores and the rapid demand increase from functional materials, the recovery of REEs from second resources has attracted increasing attention.^{3–5} Phosphogypsum (PG), generally containing small amount of REEs, has been considered as a potential sustainable REEs resource due to its huge reserves.

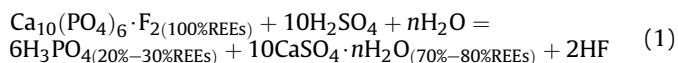
In phosphoric acid industry, it is estimated that about 1×10^5 t REEs (0.046 wt% REEs on average in about 2×10^8 t phosphate ores) loss annually, mostly ended up in PG (Eq. (1))⁶ which is close to the annual global REEs production.⁷ Generally, PG contains about 0.05 wt% to 1.5 wt% rare earth oxides (REO). On the other hand, PG is a bulk solid waste and its treatment is a worldwide problem in terms of the landfill issue and the environmental pollution brought

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by the trace radionuclides and heavy metals.⁸ 4–5 t of PG is generated for the production of each ton of phosphoric acid (counted by P₂O₅), when takes the 15 wt%–30 wt% of free water into consideration, the actual discharge of PG residue is about 5–6 t. That is, the annual global PG production is about 2×10^8 – 3×10^8 t, at present, most of them are stockpiled on land. It is estimated that, in the case of China, building of a dumping yard costs about 90 million RMB and the maintaining costs about 10 million RMB annually to treat a stockpile with 1.86×10^6 t PG. Even worse, storage of the untreated PG brings serious environmental problems, e.g., radioactive emission, permeation of radionuclides (²³⁸U, ²³⁴Th, ²³²Th, ²²⁶Ra, ²²²Rn, etc.), toxic elements (As) and heavy metals (Cr, Pb, Cd, Ni, etc.) into water bodies.⁹ And these hazardous matters may threaten humans' health via the radioactive irradiation, particle inhalation and food or drinking ingestion. Besides, the treatment of residual water in the abandoned stockpiles costs about \$25 to \$45 per 1000 gallons in Florida, USA. From both the perspective of environmental protection and resources recovery, the utilization of PG is of critical importance, especially the recovery of REEs and gypsum.¹⁰



To eliminate the environmental threatens and stockpile issue of PG, simultaneously achieve the comprehensive utilization of PG, many governments strictly reinforced the management regulations, e.g., Chinese departments require the phosphoric acid plants to utilize the new generated PG.¹¹ From the perspective of scientific research, pretreatments technologies of water washing, organic solvent aided acid leaching, neutralization, screening/hydrocyclone classification, flash burning, flotation, and ball milling have been developed for PG purification.¹² And the purified PG are used for soil amendments, cement retarder, building materials, etc.^{13,14} However, these studies majorly focused on the gypsum utilization but ignored the recovery of associated REEs, U, and some other valuable components. Even worse, these unrecovered components may cause second pollution in the long run, so far, it has not attracted enough attention. Therefore, a novel PG utilization way is to recover REE (and other valuable elements) during the purification treatment procedure and produce gypsum by-product at the same time.

To recover REEs from PG, firstly, the occurrence of REEs should be made clear. The general occurrence of REEs in PG has been found as the stable REEs independent minerals including monazite, xenotime^{15,16} and the unstable phases dominated by the isomorphs substitution.^{6,17} The REEs mineral inclusions are difficult to leach even with concentrated acids and the isomorphous substitution state REEs can only be released once the gypsum matrix is dissolved. Then, leaching of REEs from PG is mostly focused on the leaching of the unstable phases REEs.¹⁸ The operating conditions for leaching of REEs from PG are summarized in Table 1. Jarosiński et al. leached REEs from hemihydrate PG with 10 wt% H₂SO₄ followed by nonylphenylphosphoric acid (NPPA) extraction and fluoride precipitation and obtained 40 wt% REO product.¹⁹ Walawalkar et al.

reported that the nitric acid and hydrochloric acid were superior to sulfuric acid in REEs leaching from PG, and optimal conditions of 80 °C, 1.5 mol/L HCl, liquid to solid (L/S) ratio of 8 and 20 min were suggested.¹⁵ In addition, the consumed HCl solution was recycled with anhydrate seeding by mixing at 80 °C then cooling down to 25 °C and leaving for 12 h.²⁰ Rychkov et al. achieved a more than 70% of REEs leaching efficiency by using a combination of mechanical grinding treatment, ultrasonic impact and resin-in-pulp.²¹ Hammas-Nasri et al. enriched REEs in PG from 225 to 1672 ppm by a double stage H₂SO₄ leaching, and the H₂SO₄ solution was evaporated for cycle leaching after REEs recovery.²² However, from the perspective of industrial application, most of the previous processes suffered issues of (1) high residual acid in a large volume of leaching solution due to the high L/S ratio, (2) low REEs concentration in leaching solution in terms of the low REEs content in phosphate rock and high L/S ratio, (3) large volume of CaSO₄ saturated wastewater, (4) additional energy consumption for leaching heating and (5) loss of REEs contained in the undissolved REEs mineral inclusions. Therefore, characteristics of wastewater free, enrichment of REEs in leaching solution, mild reacting conditions, and higher leaching efficiency are vital to achieve the industrial production of REEs recovery from PG.

On the other hand, the value of REEs products could hardly cover the recovery cost due to the low concentration of REEs in PG and the cost increases significantly with decreasing concentration of REEs in PG. A novel solution which is used to purify PG for various applications, simultaneously recovers REEs and other valuable component to maximize the benefit of PG comprehensive utilization.

To solve the issues summarized above, this study first characterized the occurrence state of REEs in PG. Based on that, the acid leaching process of REEs from PG was systematically investigated to develop the leaching reinforcement strategies. Cycle leaching with mineral acids was also examined to reduce the generation of wastewater and enrich REEs in aqueous solution.

2. Experimental

2.1. Materials and reagents

The PG sample used in this study was a byproduct from phosphate rock processing provided by a Brazilian industrial company. The main chemical composition of materials (Initial free water content of 17.41 wt%, after drying at 70 °C for more than 24 h) is listed in Tables 2 and 3. It can be seen that the overall REEs content in dried PG was about 0.49 wt%, dominated by La, Ce, Pr, and Nd. And the critical elements (Dy, Eu, Nd, Tb, Y) possessed a considerable proportion of 26.2 wt%. All reagents (HCl, HNO₃, and H₂SO₄)

Table 2
Elemental compositions of the PG (XRF).

Elements	O	Ca	S	F	Si	Ba	Sr	Fe
w (wt%)	58.02	20.99	17.04	1.17	0.56	0.54	0.54	0.31

Table 1

Summary of operating conditions for leaching of REEs from PG.

Leaching reagents	Temperature (°C)	Time (h)	L/S	Efficiency (%)	Refs.
H ₂ SO ₄	<20	6	2	80	19
HCl	80	0.33	8	51	15
H ₂ SO ₄ +C-160 cation exchange resin	—	2	7.5	50	21
H ₂ SO ₄	10	2	1.3	50	22
HCl/HNO ₃	25	0.5	8	60–76	23
TBP	55	2	1	68.5	24

Table 3

Rare earth oxide concentrations in dried PG (ICP).

Oxides w (wt%)	La ₂ O ₃ 0.106	Ce ₂ O ₃ 0.179	Pr ₂ O ₃ 0.055	Nd ₂ O ₃ 0.114	Sm ₂ O ₃ 0.014	Eu ₂ O ₃ 0.003	Gd ₂ O ₃ 0.006	Tb ₂ O ₃ 0.001
Oxides w (wt%)	Dy ₂ O ₃ 0.002	Ho ₂ O ₃ <0.001	Er ₂ O ₃ 0.001	Tm ₂ O ₃ <0.001	Yb ₂ O ₃ <0.001	Lu ₂ O ₃ <0.001	Y ₂ O ₃ <0.001	TREO 0.492

used in this study were of analytical reagent grade and purchased from Sinopharm Chemical Reagents Co., Ltd.

2.2. Characterization

X-ray fluorescence spectroscopic analysis (XRF, ThermoFisher ARL Perform X 4200, USA) was adopted for the determination of the bulk elements content in PG. To measure the concentration of trace elements in PG, the particle sample was completely dissolved by aqua regia followed by deionized water dilution and tested by an inductively coupled plasma-optical emission spectrometer (ICP-OES, Agilent 5800, USA). An X-ray diffractometer (XRD, Rigaku Smartlab, Japan) was used to identify the crystal structure of PG and a laser particle analyzer (LPSA, Mastersizer 2000, UK) was used to measure the particle size distribution of the PG sample. To achieve an overall qualitative determination of REEs occurrence in PG, the sample was characterized using a field emission scanning electron microscope (SEM, MIRA4 LMH, Czech Republic). In addition, in order to obtain cross-section images of the particles, solid powders were embedded in a resin, and then finely ground with sandpaper on a metallographic polishing machine before polishing with a velvet cloth.

2.3. Experimental operations and analysis

The leaching experiments were conducted in glass beakers assisted with stirring paddle and electro-thermostatic water bath. After leaching, the slurry was filtrated and the concentration determination of metal ions was determined by ICP-OES. The error of experimental measurement data located within $\pm 5\%$ of certified values. In this study, the leaching efficiency (L) was calculated according to Eq. (2) because the trace amount of REEs in solid may cause big calculation error.

$$L = \frac{c_{aq} \cdot V_{aq}}{c_{ini} \cdot m_{ini}} \times 100\% \quad (2)$$

where c_{aq} : REEs concentration in leaching solution, V_{aq} : the volume of leaching solution, c_{ini} : REEs concentration in raw PG, m_{ini} : mass of raw PG.

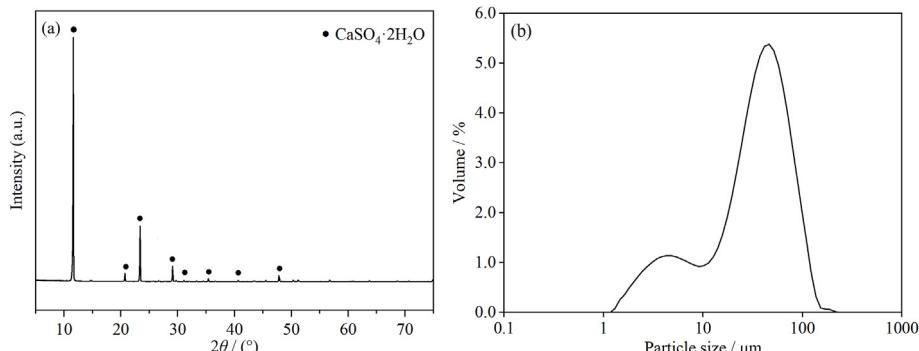


Fig. 1. The XRD pattern and particle size distribution of PG (initial PG sample without pretreatment).

3. Results and discussion

3.1. Characterization of PG samples

As shown in Fig. 1, only the pattern of matrix gypsum can be detected by XRD and the average particle size is about 49.1 μm . To determine the occurrence status of REEs in PG for the exploration of leaching mechanism and optimization of process, the microstructure of the sample was analyzed using SEM, including an overall microscopic photograph, partially zoomed photograph and elemental mapping images (Figs. 2 and 3, Fig. S1).

In these SEM photographs, it was found that most of the matrix gypsum particles displayed as gray plates and the impurities enriched particles are shown as white (or bright) aggregated particles. This greatly facilitated the recognition of the independent REEs mineral phases in PG, as the elemental maps and the spot characterization photographs (Figs. 2 and 3, Fig. S1) demonstrated that REEs independent minerals occurred majorly as REE phosphates and REE-Ba/Sr/Ti sulfates. However, REEs in the PG sample were dominated by the isomorphous substitution (Fig. 3(b), Ca^{2+} substituted by REE^{3+} and Na^+) dispersed in the huge amount of matrix gypsum particles even though the concentration of REEs was lower than that in the mineral inclusions.

3.2. Leaching of REEs from PG by mineral acids

Much previous research has proven that acid leaching is the most effective way to dissolve REEs from PG, and the leaching efficiency depends on the occurrence of REEs.²⁵ To examine the leaching performance of REEs from PG by mineral acids, the effect of types of acid, acid concentration, leaching temperature, and stirring time on the leaching efficiency of REEs were first systematically investigated. Then the relationship between the leaching efficiency and the occurrence state of REEs was clarified based on the microscopic characterization of the leaching residue, and a recovery strategy for different forms of REEs in PG was provided.

3.2.1. Effect of leaching conditions

Leaching contrast experiments were conducted by controlling proton concentration (H^+) at 4 mol/L with H_2SO_4 , HCl and HNO_3 , as shown in Fig. 4(a). HCl exhibited the best leaching efficiency of REEs from PG, then HNO_3 and H_2SO_4 . Known from section 3.1, REEs in this PG sample were dominated by the isomorphous substitution state, from which the leaching efficiency of REEs depends on the dissolution of gypsum matrix. Since REEs can only be released after the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ lattice was broken down, the reaction equation can be written as Eq. (3). Therefore, dilute solutions of HCl and HNO_3 have higher solubility of CaSO_4 than H_2SO_4 solution,

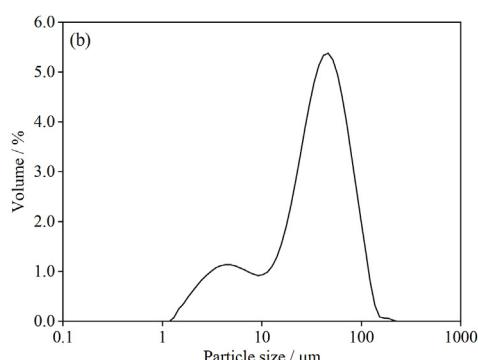


Fig. 2.

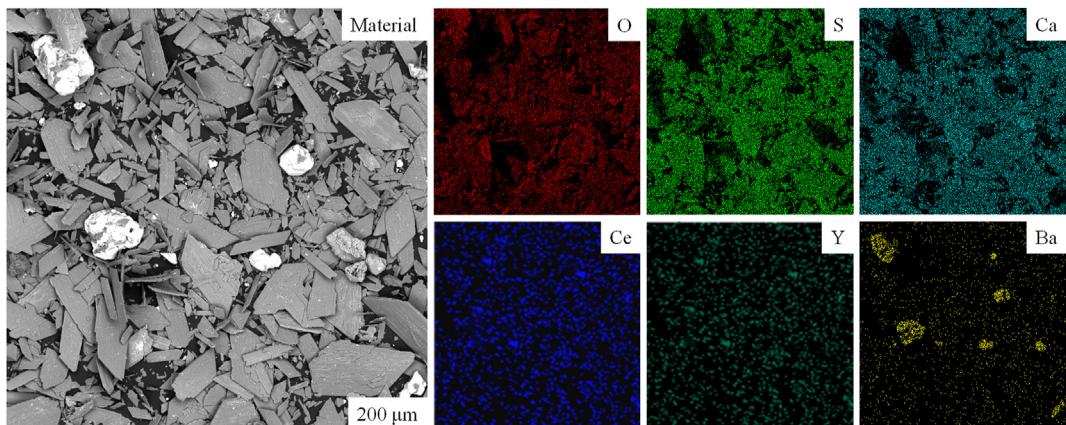


Fig. 2. Elemental mapping images of untreated PG material by SEM.

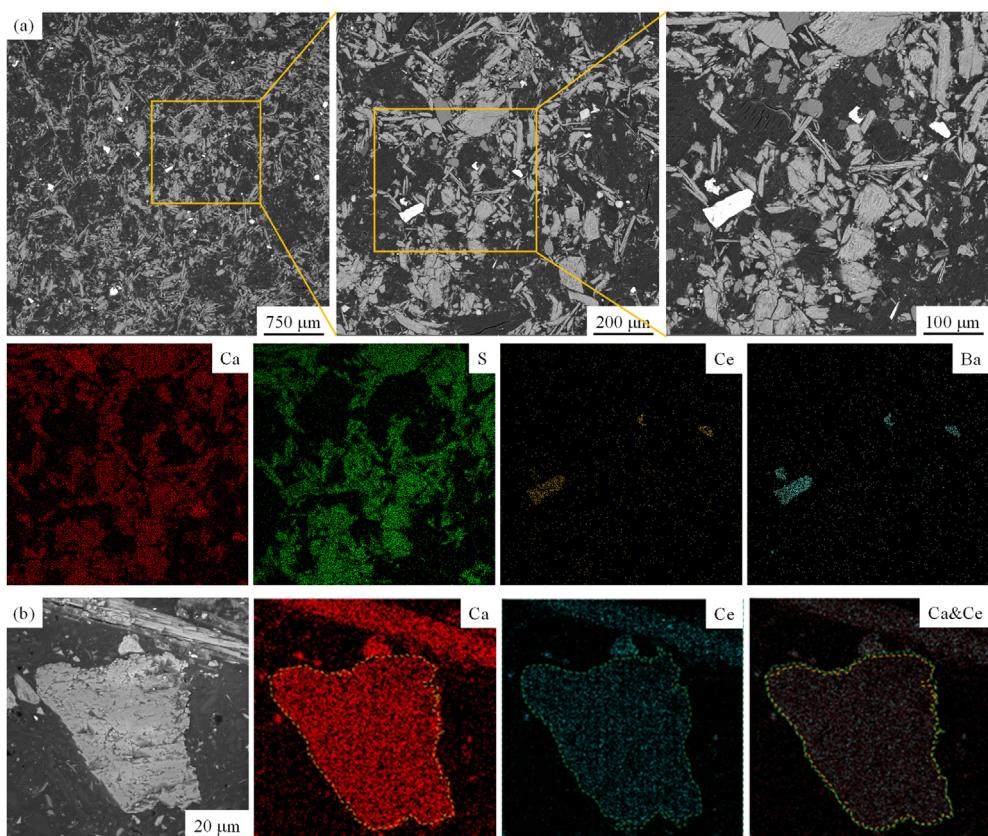
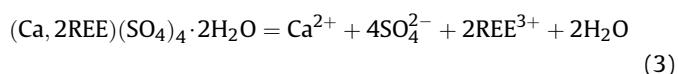


Fig. 3. Major (a) and local (b) elemental mapping images of polished PG sample by SEM.

providing a better chance for REEs dissolution.^{26,27} But in the view of some other proton diffusion affecting factors and the unevenly distribution of REEs, the leaching efficiency of REEs was not simply liner with the solubility of CaSO_4 . From the perspective of REEs recovery, HCl was considered as the optimum leachant, then the effect of various leaching conditions on REEs leaching was investigated using HCl.



As shown in Fig. 4(b), leaching efficiency of REEs obviously

increased with increasing concentration of HCl. However, further increase of HCl concentration did not provide much promotion of REEs leaching once over 4 mol/L. The increase of leaching temperature only brought slightly increase in leaching efficiency of REEs (Fig. 4(c)), but the heating of large volume slurry is an energy intense operation, violating the green principles. Even worse, elevated temperature led to a significant reinforcement of iron leaching. Therefore, ambient temperature is considered as the optimal leaching temperature. Leaching kinetics (Fig. 4(d)) demonstrated that 3 h was sufficient for REEs leaching from PG and a prolonged leaching time resulted in an increase of iron leaching efficiency. On the basis of conditional experimental results, the

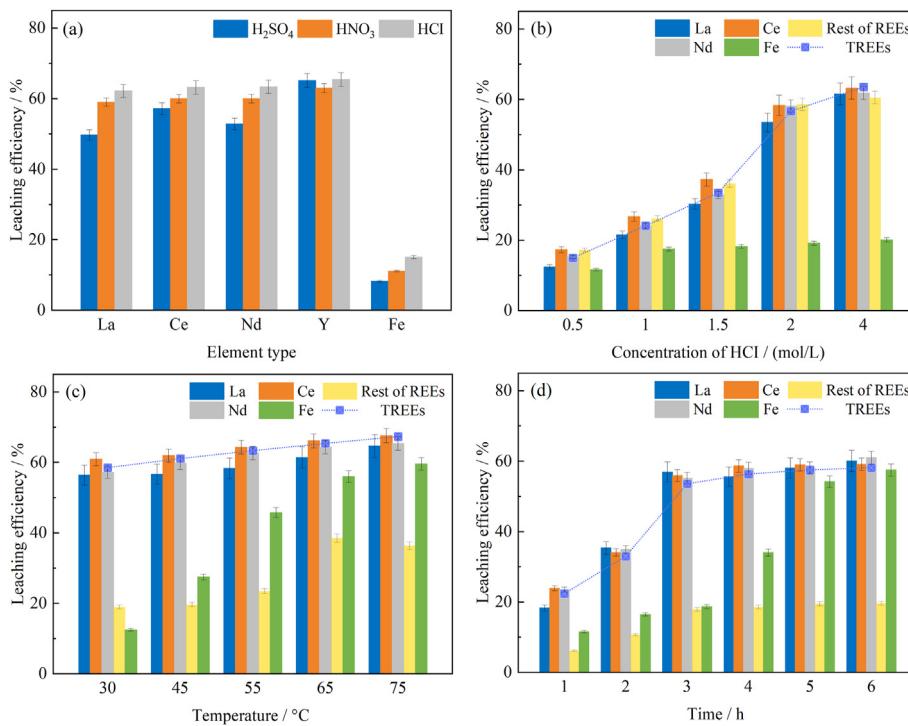


Fig. 4. (a) Leaching efficiency of REEs from PG by different acids (4 mol/L HCl and HNO_3 , 2 mol/L H_2SO_4 , 3 h, L/S = 4:1, 250 r/min); Effect of reaction conditions on the leaching efficiency of REE from PG by HCl: (b) 30 °C, 250 r/min, L/S = 4:1, 3 h; (c) 4 mol/L, 250 r/min, L/S = 4:1, 3 h; (d) 4 mol/L, 30 °C, 250 r/min, L/S = 4:1, where TREEs represents total rare earth elements.

optimal leaching conditions was considered as mixing PG with 4 mol/L HCl by a L/S ratio of 4:1 by stirring at 250 r/min and reacting for 3 h at ambient temperature.

3.2.2. Linkage between the leaching efficiency and the occurrence of REEs

To achieve a targeted reinforcement of REEs leaching, a better understanding of the effect of the occurrence of REEs on its leaching is necessary. Then, statistics of REEs occurrence in leached PG was conducted, but not all the obtained photographs were posted in this study since most of them were similar.

As shown in Fig. 5, the area outline of REEs mineral inclusions left in the leaching residue could completely overlap with the map of Ce. Statistics of white particles (or bright) in Fig. 5 demonstrated that the proportion of REEs containing particles in total white particles has increased compared with initial PG. Most of REEs mineral inclusions are undissolved by dilute acids.

Characterizations of the gypsum plates showed that the area of REEs map was much smaller than that of Ca map, indicating that part of the embedded REEs in $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ lattice have been released, which was considered as impossible when the gypsum was not dissolved (Fig. 6). The most possible explanation is that the surface part of PG particles, containing REEs, must have been dissolved, and then recrystallized.^{19,28} To prove that mechanism, the dynamic concentrations of Ce and Ca were monitored during the leaching process. Two concentration peaks of Ca were found in several repeat leaching experiments, as shown in Fig. 7. The gypsum matrix must be dissolved and recrystallized during the leaching process.

For a better understanding of REEs occurrence in PG, 40 g PG sample was mixed with 2000 mL dilute HCl solution (2 mol/L) to dissolve the gypsum matrix, leaving 3.6 g residue. As shown in Fig. 8, the undissolved particles are dominated by impurity minerals such as Ba/Sr/Ti/REEs/Fe sulfates, silicates and phosphates. In

addition, it is known from Table S1 that REEs content in the leached PG is about 13 wt%.

Based on the characterization of PG before and after leaching, the occurrence states of REEs can be concluded as three kinds (Fig. 9): (1) undissolved independent REEs mineral inclusions including monazite, xenotime, REEs-Ba/Ca/Sr sulfates/silicates; (2) soluble REEs in the form of isomorphous substitution of Ca^{2+} in $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ lattice, but the REEs leaching limited by the liberation of matrix $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; (3) dispersed soluble REEs salts including sulfates, carbonates, hydrate phosphates and fluorides, but their dissolution may be hindered by $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ coating. The undissolved REEs minerals inclusions majorly occurred as dense ball-like particles with a relatively low surface area compared with the loose and plate-like gypsum particles, an inherent shortage for leaching kinetics. To recover this part of REEs, a gravity separation using wet sieving, chute or hydrocyclone was suggested. For the soluble REEs, assuming that they are uniformly embedded in the gypsum plates or co-crystallized in gypsum lattice, the key issue of recovery is to break down the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ lattice and release REEs without production of a large volume of CaSO_4 -saturated wastewater. Therefore, simple leaching reinforcement methods of recrystallization and cycle leaching were recommended and systematically investigated to enhance the release of soluble REEs engaged into matrix gypsum.

3.3. Cycle leaching of REEs from PG with HCl solution

As mentioned in section 3.2.1, HCl solution exhibited a superior leaching performance for REEs from PG. However, there are several issues faced all the traditional REEs leaching processes: (1) large volume of acidic CaSO_4 saturated wastewater; (2) extraction difficulty of low concentration REEs (less than 400 $\mu\text{g/mL}$ REEs in most cases) from leaching solution due to the much excessive acid; (3) separation difficulty of REEs from co-leached impurities, e.g., Fe^{3+}

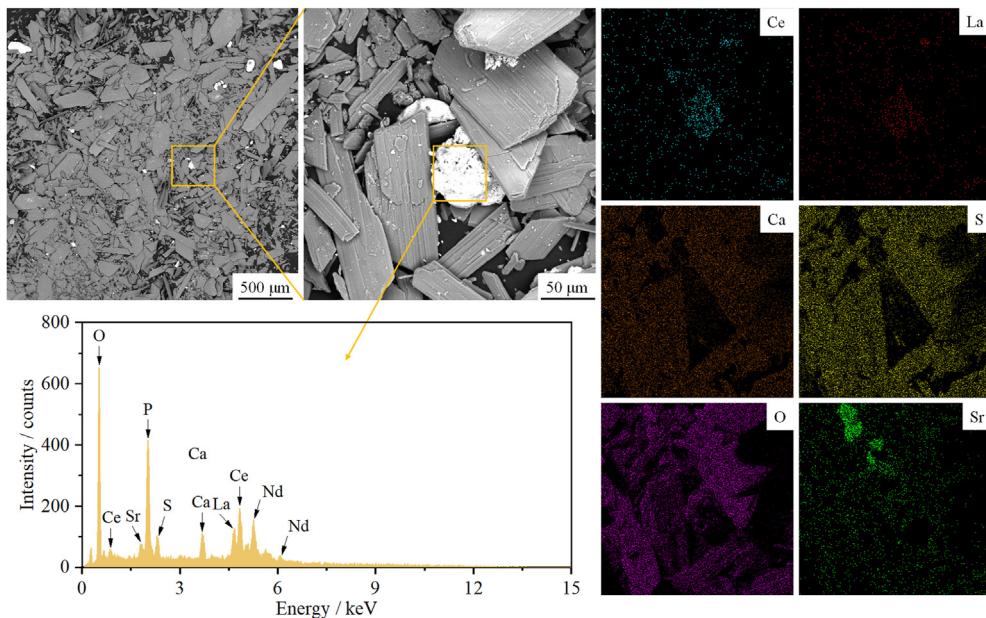


Fig. 5. Elemental mapping images and spot characterization for REEs occurrence in acid leached PG by HCl.

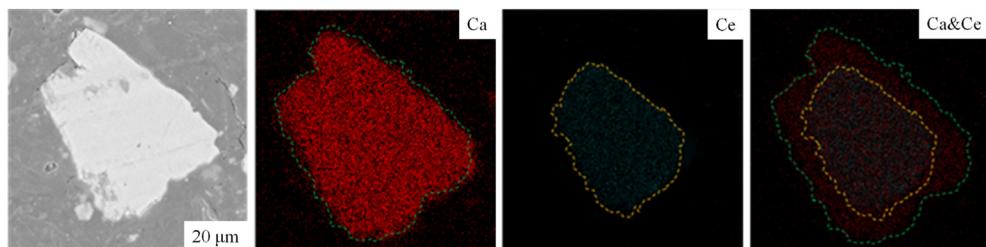


Fig. 6. Elemental mapping images of Ce and Ca in leached PG (by HCl).

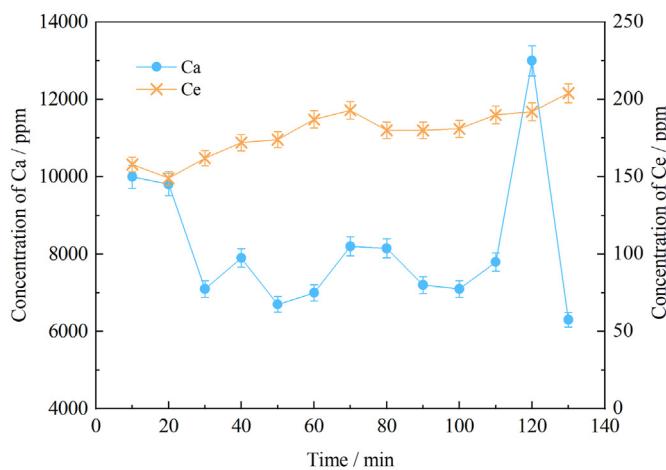


Fig. 7. Concentration variation of Ca and Ce during the leaching of PG with HCl (4 mol/L, 30 °C, 250 r/min, L/S = 4:1, 4 h).

(low leaching efficiency but substantial concentration compared with REE^{3+}). To solve these key-bottleneck issues, cycle leaching of REEs from PG with HCl solution was tested.

In cycle leaching, the recycled HCl solution was used to leach the fresh PG sample, as shown in Table S2 and Fig. 10, the leaching efficiency of REEs from PG decreased significantly with the increase

of leaching circulations. Even though the accumulated REEs in leaching solution were enriched to 1.12 g/L, the REEs leaching efficiency of the fourth leaching cycle dropped to less than 10%. This can be contributed to the saturation of CaSO_4 in leaching solution that hindered the further dissolution of matrix gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) from the fresh PG and the release of co-crystallized REEs. From another point, the leaching of REEs in the second, third and fourth leaching cycles can be attributed to the recrystallization of gypsum and the dissolution of a small amount of soluble REE salts. In addition, cycle leaching of HCl with adding extra $\text{H}_2\text{SO}_4/\text{Na}_2\text{SO}_4$ (less than 5 vol%) in cycled aqueous solution did not provide any improvement for the drop of the REEs cycled leaching efficiency. Consequently, cycle leaching of PG with HCl solution is not feasible for REEs leaching from PG.

3.4. Leaching reinforcement of REEs in the form of isomorphous substitution

Negative results of HCl cycle leaching and the find of recrystallization of gypsum indicated that H_2SO_4 cycle leaching might be a feasible alternative since part of the residual H_2SO_4 solution can be used as the slurring aqueous in phosphate rock processing. In this way, P_2O_5 entrained in PG can also be recovered and the REEs concentration can be enriched gradually.

As shown in Fig. 11, 2 mol/L was the optimal H_2SO_4 concentration for REEs leaching from PG taking the reagent saving into

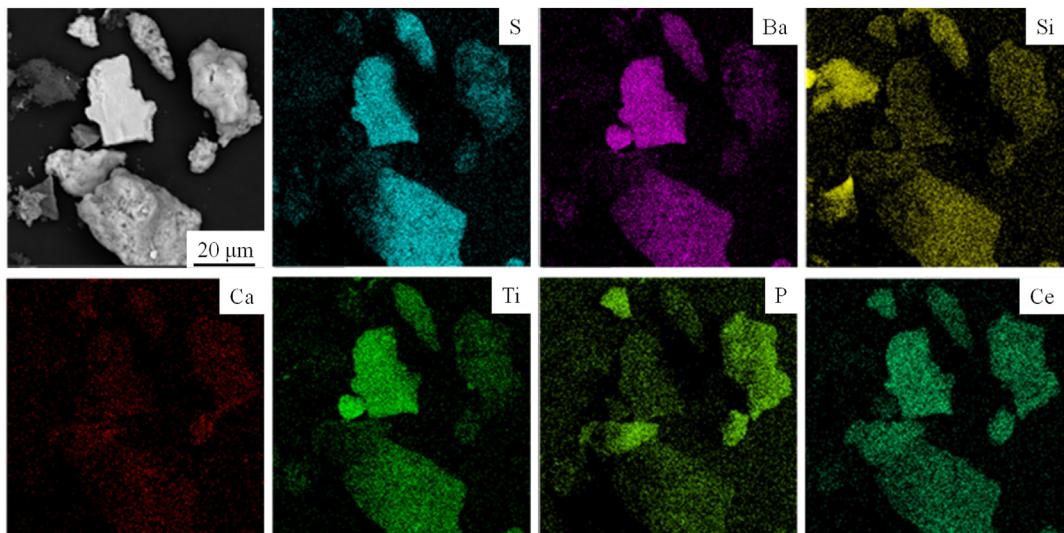


Fig. 8. Elemental mapping images of PG after complete dissolution of gypsum matrix by HCl.

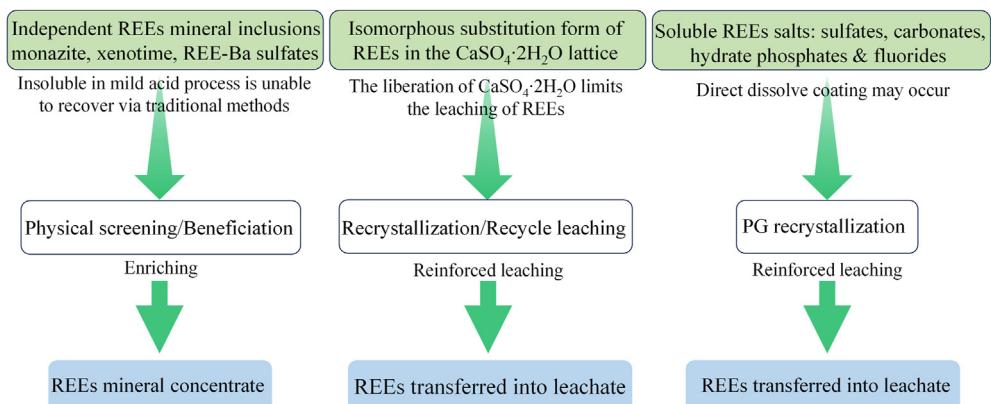


Fig. 9. Strategies for REEs recovery from PG based on their occurrence states.

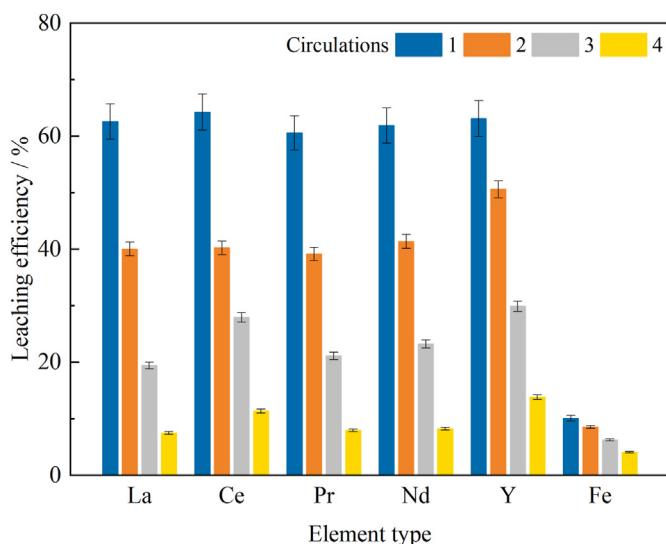


Fig. 10. Leaching efficiency of REEs from PG in 4 cycles with HCl solution (4 mol/L, 30 °C, 250 r/min, L/S = 4:1, 3 h).

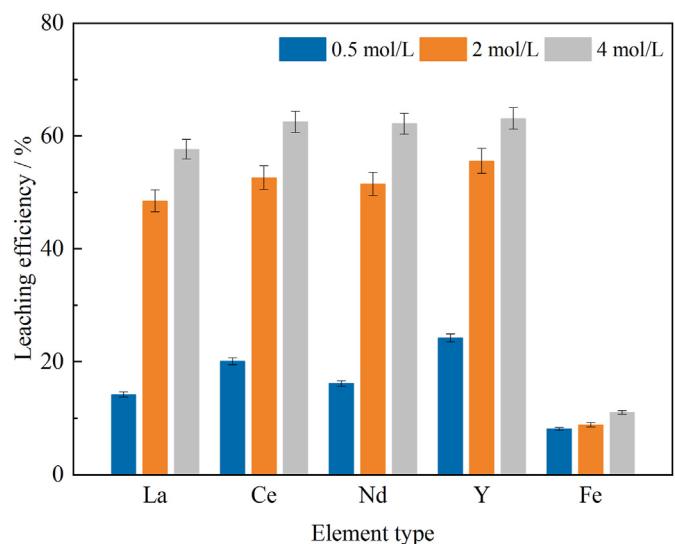


Fig. 11. Effect of H_2SO_4 concentration on the leaching efficiency of REEs from PG (3 h, 30 °C, L/S = 4:1, 250 r/min).

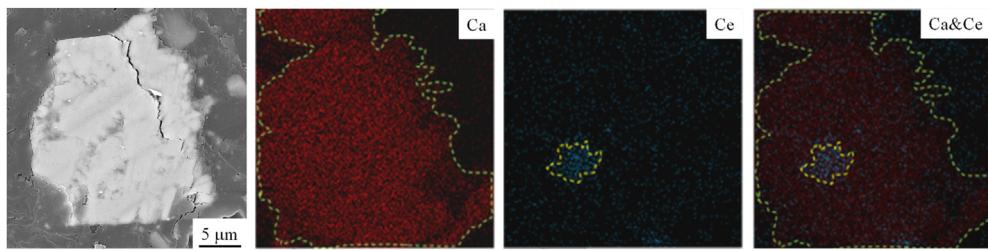


Fig. 12. Recrystallization phenomenon detected in the partial acid cycle leaching process ($2 \text{ mol/L H}_2\text{SO}_4$, $L/S = 4:1$, 30°C , 3 h).

account. Under a similar condition to HCl optimal leaching, three-stage leaching of fresh PG samples with mixed H_2SO_4 solutions consisting of 2/3 recycled and 1/3 fresh acid was conducted. Good leaching efficiency of REEs was obtained in each cycle (50.2%, 45.8%, and 43.4% for the first, second, and third cycles). The reinforcement of REEs leaching was majorly attributed to the recrystallization of gypsum plates that released the entrained REEs, as shown in Fig. 12.

3.5. Recovery of the undissolved REEs from the leached PG

According to the SEM photographs and elemental maps of raw PG and leached PG, three categories of REEs occurrence states in raw PG have been detected. Unfortunately, most of the REEs mineral inclusions cannot be leached even with high acidity solutions. However, it was found that most of REEs enriched phases are white dense sphere-like particles, but the gypsum matrix is dominated by the large gray loose plates. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) possesses a density of about 2.0 g/cm^3 and the density values of SrSO_4 , BaSO_4 , $\text{La}_2(\text{SO}_4)_3$, $\text{Ce}_2(\text{SO}_4)_3$ are 3.96 , 4.50 , 3.60 , 3.91 g/cm^3 , respectively. Based on these physical property differences, gravity separation methods such as screening, reselection, hydraulic cyclone are strongly recommended.

Herein wet sieving and shaking table were tested for the recovery of undissolved REEs from the leached PG. As shown in Table S3, wet sieving concentrated 37.1 wt% of the REE in a 10.7 wt% mass, increasing REE content from 309 to 1071 ppm. One stage shaking table enriched 8.5 wt% of the REEs in a 2.0 wt% mass (Table S4), increasing the REEs content from 260 to 1100 ppm in the leached PG, moreover, it enriched 14.6 wt% of the REEs in a 3.1 wt% mass and increased the REEs content from 490 to 2300 ppm using raw PG. Regarding the high recovery, wet sieving was adopted to recover the undissolved REEs in leached PG which provided extra about 20% of REEs from raw PG. Furthermore, the used water for slurring can be directly recycled for next wet sieving.

3.6. Promising process for REEs recovery from PG combining gravity separation and hydrometallurgy

On the basis of oriented reinforcement of REEs leaching according to the occurrence, a wastewater free recycle leaching process was proposed, as shown in Fig. 13. This process leaches most soluble REEs from PG with dilute H_2SO_4 solution ($0.5\text{--}2 \text{ mol/L}$, depends on the content of soluble REEs), enriches undissolved REEs by screening or gravity separation, and adopts cycle leaching with partial recycled leachate to enrich REEs concentration in leachate and reduce the leaching of gypsum matrix. REEs in leachate are recovered by carbonate/oxalate precipitation and the precipitation mother liquor can be used for phosphate ore processing after simple treatment with CaO neutralization. In this process, wastewater is eliminated, REEs leaching is significantly enhanced, and gypsum matrix is purified, which is considered as a green process.

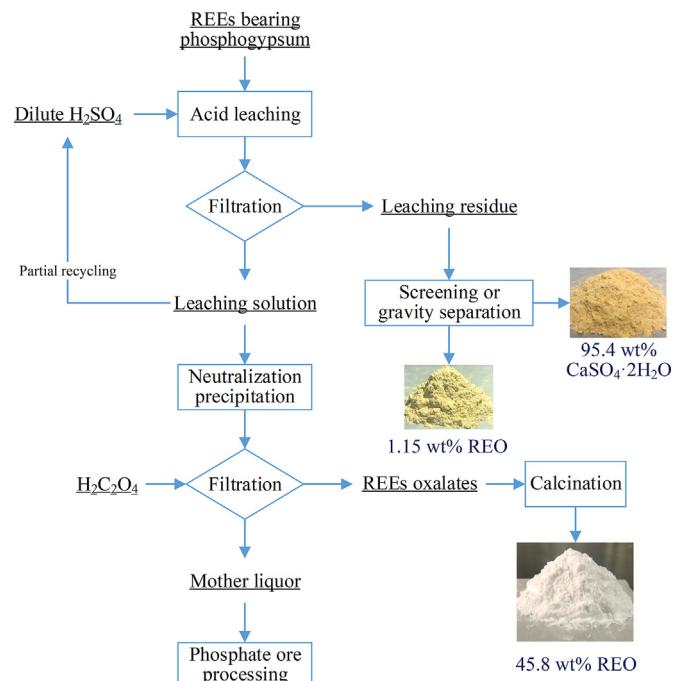


Fig. 13. Process for the comprehensive recovery of REEs and gypsum from PG.

To examine the REEs recovery of this process, a 5-stage cycle leaching was conducted by recycling 2/3 leaching solution with 1/3 fresh acid solution ($2 \text{ mol/L H}_2\text{SO}_4$), and two-stage countercurrent leaching was adopted to increase REEs leaching efficiency. As shown in Fig. S2, the falloff trend of REEs leaching efficiency in cycle leaching with partial leaching solution was much slower than that in direct cycle leaching. In addition, the REEs concentration in recycled leaching solution was accumulated into 726 mg/L with 5 leaching cycles. After then all of the accumulated leaching solutions were neutralized with CaO and 95.3 wt% of REEs in leaching solution was enriched in solid by oxalic acid precipitation (Table S5). Moreover, about 10.2% REEs from raw PG were enriched in fine particles (less than 500 mesh) with 1.15 wt% REO via wet sieving. And high-purity gypsum with >95 wt% of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, <0.06 wt% of the soluble P_2O_5 and <0.015 wt% of the soluble fluorine was also produced, the purified gypsum has a broad market as the cement retarder. Taking 1.0 kg PG as an example, a preliminary economic assessment was performed (Table S6). The cost of the product obtained by the proposed process was \$0.0444. The cost of reagent consumption was \$0.0372. Thus, without considering the energy consumption, cost of equipment and the costs of labor, the revenue of the whole process is about \$0.0072, which means that a profit of \$7.2 per ton of PG can be obtained.

4. Conclusions

REEs occurrence in PG was tested and three REEs occurrence states in PG are deduced: (1) isomorphous substitution, (2) independent REEs mineral inclusions and (3) soluble REEs salts. Based on that the targeted reinforcement methods for REEs leaching from PG were developed, including the cycle leaching of partial leachate based on the recrystallization of gypsum matrix and gravity separation based on the difference in morphology and specific gravity between REEs mineral inclusions and gypsum matrix. High total REEs recovery of 75% can be achieved. It can also be concluded that sacrificing partial REEs recovery for cost reduction might significantly improve the industrial feasibility of REEs recovery from PG. Then, a comprehensive recovery process that recovers both REEs and gypsum is proposed. Furthermore, this process owns the merits of wastewater free and reagents saving, according with the green development principles. A cycle leaching test achieved about 52.9 wt% overall REEs recovery (42.7 wt% in REO, 10.2 wt% in REEs enrichments), simultaneously, high-purity gypsum with >95 wt% of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, <0.06 wt% of the soluble P_2O_5 and <0.015 wt% of the soluble fluorine was obtained.

Declaration of interest statement

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

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jre.2024.01.013>.

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