



Article Characterization and Leaching Kinetics of Rare Earth Elements from Phosphogypsum in Hydrochloric Acid

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Abstract: The characterization and leaching mechanism of REEs from phosphogypsum (PG) in HCl was studied in-depth. REEs contained in the PG were 208 ppm, of which Y, La, Ce, and Nd were the four most abundant elements. The modes of occurrence of rare earth elements (REEs) in the PG were quantified using the sequential chemical extraction (SCE) method. Among the five REE occurrence species, the metal oxide form accounted for the largest proportion, followed by the residual, organic matter, and ion-exchangeable fractions, and REEs bound to carbonates were the least. From the comparison of the distributions of REEs and calcium in different occurrence states, it can be determined that REEs contained in the PG were mainly present in the residue state (existed in the gypsum lattice) and the metal oxide state (easily leached). The leaching results show that the suitable leaching conditions were acid concentration of 1.65 mol/L, S/L ratio of 1/10, and reaction temperature of 60 °C. At the condition, the maximum leaching efficiency for \sum REE was 65.6%, of which the yttrium leaching rate was the highest and reached 73.8%. Importantly, A new kinetic equation based on the cylindrical shrinking core model (SCM) was deduced and could well describe REE leaching process from PG. The apparent activation energy for \sum REE leaching was determined to be 20.65 kJ·mol⁻¹.

Keywords: phosphogypsum; rare earth elements; sequential chemical extraction; leaching kinetics; shrinking core model; HCl

1. Introduction

Phosphogypsum (PG) is a waste by-product generated from the processing of phosphate rock by the "wet acid method" of fertilizer production. During the process, phosphate ore is digested with sulfuric acid, as shown in the reaction (1) [1,2]. About 4~5 tons of PG are generated for every ton (P_2O_5) of product acid. World PG production is variously estimated to be around 100–280 Mt per year [3,4]. However, only 15% of world PG production is recycled as building materials, agricultural fertilizers, or soil stabilization amendments and as set retarders in the manufacture of Portland cement, while the remaining 85% is disposed of without any treatment [1]. In Florida, the gypsum has accumulated more than 1 billion tons, and in China, the PG stockpiles approximately 500 million tons produced from 2010 to 2018 [5]. Additionally, a huge amount of PG has also stacked up in Europe, Canada, Morocco, Togo, India, Korea, Russia, and other parts of the world [6,7]. The bulk



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). deposition of PG not only occupies the farmland but also leads to severe pollution in the surrounding environment.

$$Ca_{5}F(PO_{4})_{3} + 5H_{2}SO_{4} + 10H_{2}O \rightarrow 3H_{3}PO_{4} + 5CaSO_{4} \cdot 2H_{2}O + HF$$
(1)

PG is mainly calcium sulfate dihydrate (CaSO₄·2H₂O) but also contains lots of impurities, such as phosphorus, fluorine, organic matter, and some rare precious metal elements [8,9]. It is precisely because of the presence of these impurities that the PG utilization rate is very low. Although the PG pretreatment can eliminate the main impurities such as soluble phosphorus, fluorine, and organic matter, it has little effect on the metal elements. The existence of these metal elements not only affects the quality of PG products, but also is a waste of resources to the metal itself, especially rare earth elements (REEs), which are known as "industrial vitamins" and a "treasure" of novel materials [10–15]. With the increasing demand for REEs and the shrinking of easy-to-treat rare earth resources, it has become an urgent problem to find new REE resources. Although the REE content of PG (0.01–0.40 wt%) is low, the large volume of PG makes the total amount of REEs locked in them large, and thus PG is considered as an important secondary resource for REEs [16–19].

For the recovery of REEs from PG, researchers have carried out lots of studies, among which acid leaching is currently the most studied method to extract REEs from PG, and H₂SO₄, HCl, and HNO₃ are the most commonly used acids. Under normal lab conditions, low REE leaching efficiencies range from 12% to 40% with H_2SO_4 were obtained [3,17,20,21]. In order to enhance the leaching rates of REEs with H_2SO_4 , researchers introduced the mechanical activation, ultrasonic impact, resin-in-pulp process, and even their combination to reinforce the leaching process [17,22]. Compared with H_2SO_4 , HCl and HNO₃ have higher REE leaching recovery, which might be owing to the relatively higher solubility of $CaSO_4 \cdot 2H_2O$ in their solutions. The leaching efficiency of REEs from PG by 1.5 M HCl could reach more than 50% within 20 min [3]. In addition, high leaching recovery of REEs even up to 93.1% was achieved by 15% HNO₃ with L/S = 10.1 [23]. It is noted that the deposition form of REEs in PG has a decisive effect on the leaching efficiency of REEs from PG [13,16]. However, there are no uniform opinions about the deposition form of REEs in PG among researchers. Some of them reported that REEs mainly existed in the calcium sulfate structure by the form of isomorphous substitution [24,25]. The others agreed that REEs presented as an isolated amorphous form or nanophase with poor crystallinity, or precipitated on the crystal surface of gypsum [26–28].

As described above, there have been lots of studies on the acid leaching of REEs from PG. However, to the best of our knowledge, the modes of occurrence of REEs in PG, which crucially influences the REE leaching, are still controversial. Furthermore, investigations concerning the process kinetics have been rarely reported. To address the knowledge gap, this communication describes an experimental study where hydrochloric acid leaching tests were performed on the PG from Yunnan Phosphate Chemical Group to evaluate the viability of REE extraction. Leaching kinetic analysis and sequential chemical extraction (SCE) were conducted to explain the acid leaching mechanism. Based on this, we achieved a systematic understanding of REE extraction from PG.

2. Experimental

2.1. Materials

The PG was obtained from Yunnan Phosphate Chemical Group, Yunnan Province, China. Analytical reagent-grade hydrochloric acid (36~38 wt%), nitric acid (65~68 wt%), hydrofluoric acid (\geq 40 wt%), and perchloric acid (70~72 wt%) were purchased from Xilong Chemical Co., Ltd. (Shantou, China), and used for the SCE, the solid sample digestion, and acid leaching tests. Other analytical reagent-grade chemicals used for the SCE included magnesium chloride hexahydrate (MgCl₂·6H₂O, >99 wt%), sodium acetate trihydrate (CH₃COONa·3H₂O, >99 wt%), hydroxylammonium chloride (NH₂OH·HCl, >99 wt%), acetic acid (CH₃COOH), hydrogen peroxide (H₂O₂, 30 wt%), and ammonium acetate (CH₃COONH₄, >97 wt%), and they are also obtained from Xilong Chemical Co., Ltd. (China).

2.2. Sequential Chemical Extraction Tests

The sequential chemical extraction (SCE) method has been widely used to quantify the modes of occurrence of trace elements in solid samples [29]. In the extraction process, the solid specimen is sequentially reacted with a series of lixiviants under certain conditions, and trace elements of different modes are extracted in different steps. By measuring trace element concentration in the liquid obtained after each extraction, the distribution of trace elements in different solid phases can be quantified. Pérez-López, et al. [30] and Zhang, et al. [31] applied the BCR-sequential extraction procedure using CH₃COOH, HONH₂·HCl, H₂O₂, and NH₄OAc treatments to quantify the fractions of water/acid soluble/exchangeable, reducible, oxidizable, and residual species of trace elements in industrial by-product gypsum. Fu, et al. [32] classified trace elements in flue gas desulfurization gypsum into five forms according to the Tessier SCE procedure, i.e., ion exchangeable, carbonate, metal oxide, organic matter, and residual. Santos, et al. [33] further quantified six forms of trace elements in PG on the basis of the Tessier SCE procedure by determining the water-soluble species of trace elements by reacting with deionized water.

The SCE protocol used in this study as shown in Figure 1 was formulated based on the Tessier SCE procedure [34]. In the beginning, 1 g of solid was sequentially reacted with 1 M MgCl₂ and 1 M sodium acetate to extract the ion-exchangeable and carbonate species, respectively. The solid residue obtained from the carbonate extraction step was reacted with 25% (v/v) acetic acid to extract the metal oxide species. In this step, 0.04 M hydroxylammonium chloride was added to dissolve reducible phases such as iron, manganese, and cerium (IV) oxides. The fourth step shown in Figure 1 was used to extract the organic-associated species. After the organic matter extraction step, the solid residue was completely digested following the procedures listed in Section 2.4. The selective extractions were conducted in polypropylene centrifuge tubes (100 mL). After each extraction step, the sample was separated by centrifuging at 5000 rpm for 0.5 h. Then, the supernatant was removed with a pipet and analyzed for REEs and calcium, whereas the residue was rinsed with 8 mL of deionized water through centrifuging for 0.5 h, and the second supernatant was discarded. Three duplicates were performed and the accuracy of the extraction procedure was evaluated by comparing the bulk chemical analysis with the sum of the five individual associations. The recovery of REEs and calcium for the SCE process varied from 82.9% to 106.9% (as shown in Supplementary Materials), which was in the acceptable range of 70-130% [35,36].

Solid samples (1 g)	
↓ 1 h with 8 mL of 1 M MgCl ₂ (pH 7.0) at 25 °C with continuous agitation	→Ion-exchangeable
↓	
0.5 h with 8 mL of 1 M CH ₃ COONa adjusted pH 5.0 with HOAc at 25 °C with continuous agitation	→ Carbonate
ŧ	
3h with 20 mL of 0.04 M $NH_2OH \cdot HCl$ in 25% (v/v) HOAc at 96 ± 3 °C with occasional agitation	→Metal Oxide
↓	
(1) 3 mL of 0.02 M HNO ₃ and 5 mL of 30% H ₂ O ₂ adjusted to pH 2 with HNO ₃ at 85 \pm 2 °C for 2h with occasional agitation; (2) A second 3 mL of 30% H ₂ O ₂ (pH 2 with HNO ₃) was then added and heated again to 85 \pm 2 °C for 3h with intermittent agitation; (3) After cooling to 25 °C, 5 mL of 3.2 M NH ₄ OAc in 20% (v/v) HNO ₃ was added and diluted to 20 mL with deionized water, and agitated continuously for 0.5h.	→ Organic Matter
+	
Acid digestion	→ Insoluble

Figure 1. Sequential chemical extraction procedure used for this study.

2.3. Leaching Experiments

The leaching tests were performed in a three-necked round bottom flask equipped with a reflux condenser, as shown in Figure 2. For each test, 300 mL of lixiviants with a certain concentration was first added into the flask and preheated to a predetermined temperature (30, 60, and 80 °C) on an oil bath and stirred with a magnetic stirrer at a constant rate of 100 rpm. Then, a certain quality of PG (based on the desired solid/liquid (S/L, g/mL) = 1/5, 1/10, or 1/20) was added to the acid solution and the timing was started. A schematic diagram of the apparatus is shown in Figure 2. Representative samples were taken by a pipette from the flask at regular time intervals (5 min, 15 min, 30 min, 45 min, 60 min, 90 min, 120 min) from the start of the leaching process up to a total reaction time of 2 h, and filtered using 0.8 μ m nylon syringe filters. Afterward, the samples were diluted three times with 1.0 M nitric acid and analyzed with ICP-OES to determine the concentration of REEs. Three duplicates were performed and the relative standard deviations (RSD) in the experimentally measured data were less than 5%.



Figure 2. A schematic diagram of the apparatus used for the acid leaching tests.

The leaching rate (α , %) was calculated using the following equations:

$$\alpha = 100\% \times C_{\rm f} \times 3 \times V/(C_{\rm s} \times 0.03) \tag{2}$$

$$\alpha_{\sum \text{REE}} = 100\% \times C_{f, \sum \text{REE}} \times 3 \times \text{V} / (C_{s, \sum \text{REE}} \times 0.03)$$
(3)

where C_f (ppm) represents elemental concentrations of the leaching sample diluted by 1.0 M nitric acid, V volume of the feed solution (0.3 L), and C_s (ppm) the elemental contents of the PG. Σ REE represents the total rare earth elements (only considering REEs with the highest concentration in the PG: Y, La, Ce, and Nd), and $\alpha_{\Sigma REE}$ the leaching rate for Σ REE.

2.4. Characterization

The structures of the samples were determined by X-ray diffraction (XRD, D8 Advanced, Bruker, Germany) using Cu K α radiation (λ = 1.54178 Å), with a scanning rate of 5°/min and a scanning 2 θ range 5° to 70°.

To gain information about the morphology of the solid phase and the distribution of REEs in the sample, the PG sample was characterized using a field-emission scanning electron microscope (SEM, Phenom ProX, Phenom World, Eindhoven, The Netherlands) in conjunction with an energy dispersive X-ray spectroscopy (EDS, Thermo Fisher Scientific, Waltham, MA, USA). To determine the REE concentration in the solid sample, the sample was digested by a combination of aqua regia, hydrofluoric acid, and perchloric acid according to HJ781-2016 (China National Environmental Protection Standard for solid waste), and analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, AvioTM 500, PerkinElmer, Waltham, MA, USA).

3. Results and Discussion

3.1. Phosphogypsum Characterization

As shown in Figure 3, the PG mainly presented as long rhombic flakes with occasional fragments. The XRD results (Figure 4) show that the main component of the PG was gypsum (CaSO₄·2H₂O), as well as a small amount of brushite (CaHPO₄·2H₂O) and quartz (SiO₂).



Figure 3. SEM image of the PG.



Figure 4. XRD pattern of the PG.

XRF results (Table 1) illustrated that in addition to the main elements of S, O and Ca, the PG also contained impurities such as Si, P, Al, and F. If SO₃, CaO, and crystal water all

came from dihydrate gypsum (CaSO₄·2H₂O), the mass fractions of dihydrate gypsum in PG calculated from these three components were 90.95%, 92.38%, and 91.59%, respectively. XRD revealed that there was still a small amount of brushite (CaHPO₄·2H₂O) which also included CaO and crystal water in the PG. Therefore, the proportion of dihydrate gypsum calculated by SO₃ was relatively accurate, which implied that the PG contained more than 90% of dihydrate gypsum. In addition, neither XRD nor XRF detected the presence of REEs, which may be due to their low concentration.

Radicals	SO ₃	CaO	SiO ₂	P_2O_5	Al ₂ O ₃	F	K ₂ O
Mass fraction, %	42.30	30.08	6.68	0.68	0.38	0.31	0.19
Radicals	MgO	Fe ₂ O ₃	TiO ₂	BaO	PbO	Crysta	l water
Mass fraction, %	0.07	0.05	0.04	0.03	0.01	19	.17

Table 1. Chemical composition of the PG analyzed by XRF (%).

To further determine the REE content, the PG was digested according to the HJ781-2016 standard, and analyzed by ICP-OES. The elemental analyses (Table 2) show that the total content of REEs was 208 ppm, of which yttrium, lanthanum, cerium, and neodymium are the four highest content elements with the concentration of 74, 46, 32, and 30 ppm, respectively. Due to the very low concentration in other REEs, we only considered the four REEs (Y, La, Ce, and Nd) with the highest concentration in the PG.

Table 2. Contents of REEs in the PG.

Element	Content/ppm	Element	Content/ppm
Sc	<1	Gd	2
Y	74	Tb	<1
La	46	Dy	7
Ce	32	Ho	2
Pr	5	Er	2
Nd	30	Tm	<1
Sm	6	Yb	1
Eu	1	Lu	<1
∑REE	208	Ca	$2.09 imes10^5$

The sequential chemical extraction (SCE) was carried out to determine the occurrence modes of the 4 REEs and calcium. As stated in the experimental section, the elements in the PG were classified into five different modes of occurrence including ion-exchangeable, carbonate, metal oxide, organic matter, and insoluble (see Figure 1). Figure 5 shows the distributions of the four REEs and calcium in the different occurrence modes. In the PG, the distributions of La, Ce, Y, and Nd among the five occurrence modes were basically the same, of which REEs in the metal oxide form accounted for the largest proportion, followed by the residual, organic matter, and ion-exchangeable fractions, and REEs bound to carbonates were the least. This partially agreed with the findings of Santos, et al. [33], especially for lanthanum. The distribution of total REEs (Σ REE) among the five occurrence modes were 39% in the metal oxide fraction, 31% in the residual fraction, 18% in the organic matter fraction, 7% in the ion-exchangeable fraction, and 5% in the carbonate fraction, respectively. Among them, the ion-exchangeable, carbonate, and metal oxide forms are easy-to-leach REE minerals, which are more soluble in relatively weak acid conditions. The organic matter form requires strong acid solutions for dissolution, and the residual is difficult to dissolve.



Figure 5. The modes of occurrence of REEs and calcium obtained by the SCE method in the PG.

The distributions of calcium in the five occurrence modes were distinctly different from the REE distributions, of which the residual calcium (CaSO₄·2H₂O) accounted for the largest proportion of 56%, followed by the organic matter with 19%, and the least proportion was the metal oxide form with 5%. This was obviously controversial with the result that dihydrate gypsum accounted for more than 90% of the PG by XRF. The main reason for this result was the slight solubility of dihydrate gypsum, which resulted in the dissolution of part of the dihydrate gypsum in each of the first four steps of the SCE experiment, thereby reducing the calcium content in the residual forms. Additionally, this caused part of REEs contained in the gypsum crystals, which should be the residual REEs, to enter into the first four occurrence modes of the SCE experiment, and thus increased the REE content in the first four occurrence forms and decreased their content in the residual.

Although the distribution results obtained through the SCE experiment had a certain deviation, it was determined that REEs in the PG was mainly presented in the form of residuals (existed in the gypsum lattice) and metal oxides (easily leached) by the comparison of distributions between REEs and calcium among different occurrence modes.

3.2. REE Leaching Tests

It can be seen from Figure 6 that at 30 °C, acid concentration of 1.65 mol/L, solidto-liquid (S/L) ratio of 1/10 and leaching for 2 h, the maximum \sum REE leaching rates of H₂SO₄, HCl and HNO₃ were 35.4%, 52.2% and 56.3%, respectively. Compared with other studies [3], the \sum REE leaching rate in H₂SO₄ was relatively high, which was mainly ascribed to the fact that a large part of REEs in the PG was presented in the form of metal oxides that were easily leached. However, in the presence of potassium ions (as shown in Table 1), it was easy to form insoluble rare earth sulfate double salts [37], especially in the cyclic leaching process, resulting in the loss of REEs in the H₂SO₄ leaching solution. Compared with H₂SO₄, HCl and HNO₃ were more effective leaching agents. In view of the small difference in leaching rate between HCl and HNO₃, and the price advantage of HCl, HCl was a more suitable leaching agent for leaching REEs from the PG [3].



Figure 6. The effect of the type of leaching agents on REE leaching rate at 30 °C, 1.65 mol/L and S/L ratio of 1/10 for leaching 2 h.

From Figure 7, increasing the acid concentration from 1.25 mol/L to 1.65 mol/L enhanced the leaching efficiency of \sum REE significantly, from 44.2% to 52.2%. In addition, a continued increase of acid concentration to 2.05 mol/L only increased the leaching rate slightly by 0.6%. As shown in Figure 8, the leaching efficiency increased with decreasing S/L ratio. When the S/L ratio decreased from 1/5 to 1/10, the \sum REE leaching rate increased remarkably from 37.5% to 52.2%, and the continued decrease in the S/L ratio to 1/20 only increased the REE leaching rate by 3%.



Figure 7. The effect of HCl concentration on REE leaching rate at 30 °C and S/L ratio of 1/10 for leaching 2 h.

From Figure 9, we can see that an increase in the reaction temperature could boost the leaching efficiency of \sum REE and calcium. When the leaching temperature was increased from 30 °C to 60 °C, the \sum REE leaching rate increased by 13.4%, while the calcium concentration only increased from 5.8 g/L to 6.6 g/L. With increased the leaching temperature to 80 °C, the \sum REE leaching rate increased by 9.6%, and the calcium concentration significantly increased to 14.1 g/L. The substantial increase of calcium in the leachate would greatly increase the burden of impurity removal in the subsequent process. Hence, the suitable leaching temperature for leaching REEs in the PG with HCl was 60 °C.



Figure 8. The effect of S/L ratio on REE leaching rate at 30 °C and 1.65 mol/L HCl for leaching 2 h.



Figure 9. The effect of leaching temperature on REE leaching rate and calcium concentration at 1.65 mol/L HCl and S/L ratio of 1/10 for leaching 2 h.

Therefore, comprehensive consideration of economy and leaching efficiency, the appropriate operating conditions of REE leaching from the PG using HCl as the leaching agent were acid concentration of 1.65 mol/L, S/L ratio of 1/10, and reaction temperature of 60 $^{\circ}$ C.

3.3. REE Leaching Kinetics

In order to study the leaching kinetics of REEs from PG in HCl solutions, the recovery data of La, Ce, Y, and Nd as a function of leaching time for different temperatures were illustrated in Figure 10. From Figure 10, the leaching process of the four REEs by HCl at different temperatures was roughly the same, which could be divided into three stages, i.e., quick leaching at the beginning, slow leaching at the middling, and basically reaching equilibrium after leaching 1 h. Among the four REEs, the yttrium leaching rate was the highest and reached 55.6%, 73.8%, and 88.4% at 30 °C, 60 °C, and 80 °C, respectively, which may be owing to its maximum content and the largest proportion of easily leached occurrence modes (as shown in Figure 5).



Figure 10. Leaching recoveries of REEs at different leaching temperatures ((**a**), 30 °C; (**b**), 60 °C; (**c**), 80 °C) as a function of leaching time under the conditions of 1.65 mol/L HCl and S/L ratio of 1/10.

To better understand the reaction rates and leaching mechanisms of REEs from PG, the data plotted in Figure 10a–c were analyzed by fitting the data to standard kinetic models. Since the leaching rates of REEs reached equilibrium or decreased after one hour, the kinetic analyses were only carried out within one hour of leaching time. Initially, the shrinking core model (SCM) for spherical particles (Figure 11), a common model used to describe multiphase solid–liquid reaction processes, was used to fit the data [38,39]. According to the model, if the reaction rate is controlled by the surface chemical reaction, the integral rate equation can be expressed as follows:

$$1 - (1 - \alpha)^{1/3} = k_c \cdot t \tag{4}$$

where k_c represents the surface chemical rate constant, α the leaching rate in decimal, and t the reaction time. Alternatively, if the reaction rate is controlled by diffusion through the product layer, the integral rate expression is as follow:

$$1 - 2/3\alpha - (1 - \alpha)^{2/3} = k_{sd} \cdot t$$
(5)

where k_{sd} represents the pore diffusion rate constant.



The rate constants and the corresponding adjusted coefficient of determination (R^2_{adj}) values for the SCM of chemical reaction control and diffusion control based on spherical particles are shown in Tables 3 and 4, respectively. As indicated by the R^2_{adj} values, the leaching of REEs from PG was more precisely fitted by the diffusion model relative to the chemical reaction model. Consequently, the data suggest that the leaching kinetics of REEs from PG were not controlled by the surface chemical reaction but rather by diffusion through the product layer.

Table 3. k_c and R^2_{adj} for the SCM of chemical reaction control based on spherical particles.

T/°C	30 °	C	60 °	°C	80 °	C
REE	k _c (×10 ⁻³)	R ² adj	<i>k</i> _c (×10 ^{−3})	R ² adj	<i>k</i> _c (×10 ^{−3})	R ² adj
La	4.77	0.8751	5.82	0.8995	7.46	0.8980
Ce	4.45	0.8590	5.32	0.9018	6.76	0.9040
Y	4.90	0.8756	6.84	0.8872	9.99	0.9235
Nd	3.56	0.8403	4.47	0.8995	5.26	0.8717
∑REE	4.55	0.8678	5.88	0.8932	7.77	0.9035



T/°C	30 °	С	60 °	C	80 °	C
REE	k_{sd} (×10 ⁻⁴)	R ² _{adj}	k_{sd} ($ imes 10^{-3}$)	R ² _{adj}	k_{sd} ($ imes$ 10 $^{-3}$)	R ² _{adj}
La	8.69	0.9574	1.26	0.9827	1.94	0.9798
Ce	7.63	0.9443	1.08	0.9831	1.64	0.9848
Y	9.14	0.9523	1.67	0.9738	3.13	0.9854
Nd	5.01	0.9281	0.78	0.9823	1.04	0.9638
\sum REE	7.97	0.9496	1.28	0.9791	2.07	0.9815

Table 4. k_{sd} and R^2_{adj} for the SCM of diffusion control based on spherical particles.

Figure 3 shows that the PG was mainly long rhombic flakes. Thus, we consider whether the cylindrical model can better illustrate the leaching kinetics of REEs from PG than the spherical model.

If the reaction rate is controlled by diffusion through the product layer of cylindrical particles, the integral rate expression is as follows [40]:

$$(1 - (1 - \alpha)^{1/2})^2 = k_{cd} \cdot t$$
(6)

where k_{cd} represents the pore diffusion rate constant for the SCM of cylindrical particles.

Table 5 shows the rate constants and the corresponding R^2_{adj} values for the shrinking core diffusion model based on cylindrical particles. By comparing Tables 4 and 5, we can see that the R^2_{adj} values based on cylindrical particles were all greater than those based on spherical particles for the linear fitting of REE leaching from PG. This indicates that the leaching of REEs from the PG can be more accurately fitted by the cylindrical shrinking core diffusion model than the spherical model.

Table 5. k_{cd} and R^2_{adj} for the SCM of diffusion control based on cylindrical particles.

T/°C	30 °	С	60 °	С	80 °	С
REE	k _{cd} (×10 ⁻³)	R ² _{adj}	k_{cd} ($ imes 10^{-3}$)	R ² adj	k_{cd} ($ imes 10^{-3}$)	R ² _{adj}
La	2.04	0.9595	2.99	0.9843	4.67	0.9831
Ce	1.78	0.9464	2.54	0.9841	3.92	0.9870
Y	2.14	0.9543	4.00	0.9767	7.77	0.9893
Nd	1.16	0.9298	1.83	0.9831	2.45	0.9665
∑REE	1.86	0.9517	3.04	0.9809	5.01	0.9849

To elaborate the kinetics of fluid-particle reaction more precisely, on the basis of diffusion control, we also considered the influence of interfacial transfer on the reaction rate [40,41], and deduced a new rate expression of SCM for the dissolution reaction of a cylindrical solid particle (Figure 12) under control of the interfacial transfer and diffusion across the product layer. The derivation process is as follows.



Figure 12. Schematic representation of the leaching of a cylindrical particle in bulk (r_0 , the original radius of the particle; r, the radius of the particle after reacting for time t; x, the distance that the solid-liquid interface moves inwards; l, the length of the particle).

Assuming that the ends of the cylinder are inactive [40] and the original radius of the particle equals r_0 , after reacting for time t, the radius is decreased to r and the solid-liquid interface moves inwards a distance x (namely $x = r_0 - r$). Based on the description, the fraction of unreacted solid on a volume basis is:

$$1 - \alpha = \frac{\pi (r_0 - x)^2 l}{\pi r_0^2 l} = \frac{(r_0 - x)^2}{r_0^2}$$
(7)

$$(1-\alpha)^{\frac{1}{2}} = \frac{r_0 - x}{r_0} = 1 - \frac{x}{r_0}$$
(8)

$$\frac{x}{r_0} = 1 - (1 - \alpha)^{\frac{1}{2}} \tag{9}$$

$$x = r_0 \left(1 - (1 - \alpha)^{\frac{1}{2}} \right)$$
(10)

$$\frac{dx}{d\alpha} = \frac{1}{2}r_0(1-\alpha)^{-\frac{1}{2}}$$
(11)

Integrating the Equation (11) gives,

$$\int_0^x dx = \int_0^\alpha \frac{1}{2} r_0 (1-\alpha)^{-\frac{1}{2}} d\alpha$$
 (12)

$$x = r_0 \left[1 - (1 - \alpha)^{\frac{1}{2}} \right]$$
(13)

$$r = r_0 - x = r_0 (1 - \alpha)^{\frac{1}{2}}$$
(14)

Moreover, it is assumed that the diffusion across the product layer follows the parabolic diffusion law, which defines that the rate of reaction is inversely proportional to the product layer thickness:

$$\frac{dx}{dt} = \frac{DV_m C_0}{x} \tag{15}$$

where *x* is the thickness of the product layer, *D* the diffusion coefficient (slowest transport), V_m the volume of the product layer formed from 1 mol of the slowest penetrating component, and C_0 the concentration of the penetrating species at the surface. When the diffusion across the product layer and the transfer across the contacting surface both control the rate,

$$\frac{dx}{dt} = \frac{DV_m C_0}{x} \cdot 2\pi r l = k_m \cdot \frac{r}{x}$$
(16)

where $k_m = 2\pi DV_m C_0 l$. Since both ends of the cylinder are inactive and thus do not diffuse, l is constant during the reaction process.

$$\frac{xdx}{r} = k_m dt \tag{17}$$

Substituting for *x*, *dx*, and *r* gives,

$$\left[(1-\alpha)^{-1} - (1-\alpha)^{-\frac{1}{2}} \right] d\alpha = \frac{2k_m}{r_0} \cdot dt$$
(18)

Integrating the above equation gives,

$$\int_{0}^{\alpha} \left[(1-\alpha)^{-1} - (1-\alpha)^{-\frac{1}{2}} \right] d\alpha = \int_{0}^{t} \frac{2k_{m}}{r_{0}} \cdot dt$$
(19)

$$-\frac{1}{2}\ln(1-\alpha) + (1-\alpha)^{\frac{1}{2}} - 1 = K_m t$$
⁽²⁰⁾

where $K_m = k_m / r_0$, and represents the apparent rate constant.

The K_m values of leaching process at different temperatures were calculated as shown in Table 6 from the slopes of the straight lines given in Figure 13a–c. As shown in Table 6, the new variant model fitted the leaching data better than the inner diffusion model, especially for the leaching at 60 °C and 80 °C with R^2_{adj} basically more than 0.98. Therefore, the leaching rates of REEs from the PG were controlled by the interfacial transfer and diffusion across the product layer.

Table 6. K_m and R^2_{adj} for the SCM of interfacial transfer and diffusion control based on cylindrical particles.

T/°C	30 °	С	60 °	С	80 °	С
REE	<i>K_m</i> (×10 ⁻³)	R ² _{adj}	K _m (×10 ⁻³)	R ² _{adj}	K _m (×10 ⁻³)	R ² adj
La	1.29	0.9705	2.03	0.9881	3.50	0.9943
Ce	1.11	0.9578	1.68	0.9856	2.82	0.9931
Y	1.37	0.9645	2.88	0.9858	6.96	0.9971
Nd	0.69	0.9395	1.15	0.9845	1.60	0.9793
∑REE	1.16	0.9623	2.07	0.9863	3.82	0.9968



Figure 13. Variance of $-1/2\ln(1 - \alpha) + (1 - \alpha)^{1/2} - 1$ between the experimental data and model predictions as a function of leaching time at different leaching temperatures ((**a**), 30 °C; (**b**), 60 °C; (**c**), 80 °C).

3.4. Leaching Apparent Activation Energy

The apparent activation energy is determined based on the Arrhenius equation, as follows Equations (21) and (22).

$$K_m = A e^{-E_a/RT} \tag{21}$$

$$lnK_m = -\frac{E_a}{R} \left(\frac{1}{T}\right) + lnA \tag{22}$$

where K_m is the apparent rate constant for the SCM of interfacial transfer and diffusion control based on cylindrical particles (min⁻¹), *A* the preexponential factor, *T* the reaction temperature (K), *R* the universal gas constant (8.314 J·mol⁻¹·K⁻¹), and E_a is the activation energy (kJ·mol⁻¹).

Figure 14 presents the linear Arrhenius plots of $\ln(K_m)$ vs. 1/T with the slopes (k_{slope}), and the related parameters of the linear Arrhenius plots are shown in Table 7. According to Equation (23), the apparent activation energy of La, Ce, Y, and Nd leaching from PG was calculated at 17.19, 16.04, 22.41, and 14.90 kJ·mol⁻¹, respectively, as shown in Table 7. In addition, the activation energy for the $\sum \text{REE}$ leaching was determined to be 20.65 kJ·mol⁻¹. In general, chemically-controlled reactions have an $E_a > 40$ kJ·mol⁻¹, while diffusion-controlled reactions have a lower E_a (<40 kJ·mol⁻¹) [42,43]. Furthermore, other scholars [44–46] have also obtained E_a values similar to this study during the leaching process under the control of interfacial transfer and diffusion across the product layer. Therefore, it is determined that the reaction rates of leaching REEs from the PG were controlled by the interfacial transfer and diffusion across the product layer.

$$E_a = -k_{slope} \cdot R \tag{23}$$



Figure 14. Arrhenius plots of leaching REEs from cylindrical PG under control of interfacial transfer and diffusion across the product layer.

Table 7. E_a and related parameters of the linear Arrhenius equation, $lnK_m = -k_{slope} \cdot (1/T) + lnA$.

	La	Ce	Y	Nd	∑REE
$k_{\text{Slope}} \ (\times 10^3) / \text{K}$	-2.068	-1.929	-2.695	-1.792	-2.484
lnA	0.127	-0.484	2.403	-1.374	1.393
R ² adj	0.9571	0.9525	0.9201	0.9990	0.9707
$E_a/kJ \cdot mol^{-1}$	17.19	16.04	22.41	14.90	20.65

4. Conclusions

The study investigated the characterization and leaching mechanism of REEs from PG in HCl. The characterization results show that the PG mainly presented as long rhombic flakes with the main component of dihydrate gypsum (CaSO₄·2H₂O). REEs contained in the PG were 208 ppm, of which Y, La, Ce, and Nd were the four most abundant elements. The SCE results indicate that among the distribution of REEs in the different occurrence modes, the metal oxide form accounted for the largest proportion, followed by the residual, organic matter, and ion-exchangeable fractions, and REEs bound to carbonates were the least. Additionally, the distribution of calcium among the five occurrence modes was extremely different from that of REEs, calcium was mainly present in the residual, and the metal oxide fraction made up a minimum proportion. Although the distribution results obtained through the SCE experiment had a certain deviation due to the slight solubility of dihydrate gypsum, it was determined that REEs in the PG was mainly presented in the form of residuals (existed in the gypsum lattice) and metal oxides (easily leached) by the comparison of distributions between REEs and calcium among different occurrence modes.

Acid leaching tests indicate that HCl was potentially a better leaching agent for REE leaching from the PG, and the suitable operating conditions were acid concentration of 1.65 mol/L, S/L ratio of 1/10, and reaction temperature of 60 °C. At the optimum conditions, the maximum leaching recovery for \sum REE was 65.6%, of which the yttrium leaching rate was the highest and reached 73.8%.

Kinetic analysis of the acid leaching results reflected that leaching kinetics of REEs from PG was not controlled by the surface chemical reaction but rather by diffusion through the product layer. Furthermore, the leaching data was better fitted by the cylindrical geometry than the sphere. To elaborate the leaching kinetics more precisely, a new shrinking core model (expressed as Equation (18)) for the dissolution reaction of a cylindrical solid particle under control of the interfacial transfer and diffusion across the product layer was deduced and could well describe the leaching process of REEs from the PG. The activation energy for the $\sum REE$ leaching was determined to be 20.65 kJ·mol⁻¹.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/min12060703/s1. Table S1: Distribution of REEs and calcium in different fractions of the PG sample according to the SCE procedure. Unit: ppm.

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