Leaching of Rare Earth Elements from Phosphogypsum Using Mineral Acids

Sicheng Li, Monu Malik, and Gisele Azimi

Abstract Rare earth elements (REEs) are critical metals for modern and emerging green technologies. Their increasing demand and limited supply have sparked the research on their recovery from secondary resources. The current study is focused on developing a hydrometallurgical process for the extraction of critical REEs from a waste byproduct, called phosphogypsum, and on elucidating the mechanism of the extraction process. Three types of mineral acids are used for the leaching, and a systematic study is utilized to assess the effect of operating parameters and to determine the optimum operating conditions. Thermodynamic modeling and solubility investigation shows the strong correlation between phosphogypsum solubility and leaching efficiency and the leaching process mechanism. Characterization results indicate that REEs can exist as isomorphous substitutions and/or separate phases inside phosphogypsum crystal. Based on these results, the destruction of phosphogypsum lattice is required to achieve improved extraction.

Keywords Circular economy · Hydrometallurgy · Leaching · Phosphogypsum · Process optimization · Rare earth elements

Introduction

Around the world, there is a growing push towards renewable energy generation and electrification of the transportation sector. With the increasing demand for wind turbines and electric vehicles, some rare earth elements (REEs) that are the building block of permanent magnets have been identified as critical elements [1]. The global market size of REEs was valued at $2.80 billion (USD) in 2018, and the demand

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A. Lazou et al. (eds.), *REWAS 2022: Developing Tomorrow's Technical Cycles (Volume I)*, The Minerals, Metals & Materials Series,
https://doi.org/10.1007/978-3-030-92563-5_28

for REEs was predicted to increase by 10.4% annually between 2019 and 2025 [2]. Considering the increasing demand, some REEs such as dysprosium (Dy) and neodymium (Nd) were predicted to face supply shortages in the foreseeable future [1]. Concerns regarding the availability of these REEs are due to their limited geological resources, adverse effects of primary-resource mining, and extraction complexities [3]. Therefore, many countries around the world have initiated activities to extract these elements from alternative sources. Industrial waste streams, such as phosphogypsum (PG), are considered as one of the potential supply sources.

The PG is the byproduct of phosphoric acid production in the fertilizer industry by digesting a concentrated slurry of pulverized phosphate ores using sulfuric acid (reaction (1)) [4]. The PG mainly consists of calcium sulfate dihydrate or gypsum ($CaSO_4 \cdot 2H_2O$), calcium sulfate hemihydrate ($CaSO_4 \cdot 0.5H_2O$), and anhydrite ($CaSO_4$).

$$\mathrm{Ca_{10}(PO_4)_6F_2} + 10\mathrm{H_2SO_4} + 20\mathrm{H_2}O \rightarrow 6\mathrm{H_3PO_4} + 10\mathrm{CaSO_4} \cdot 2\mathrm{H_2}O + 2\mathrm{HF} \quad (1)$$

The average concentration of REEs is around 0.01–0.4 wt% in PG [5]. Although the REE concentration per unit of PG is low, the total amount of REEs that can be extracted from this secondary resource is appreciable considering the vast supply of PG, with 100–280 million tonnes global annual generation [6]. Also, clean PG after trace metals removal (including REEs) could be used in the construction and fertilizer industries, thus offering added benefits. However, currently, only around 15% of PG is productively used in construction and agriculture industries, and the rest is landfilled or stored in stacks, losing the commercial benefits and causing potential environmental concerns [7].

The extraction process is one of the major steps in the REEs recovery, which conventionally relied on pyrometallurgy and/or hydrometallurgy, and the latter is preferred [8, 9]. Previous studies have the disadvantages of either low leaching efficiency, long leaching time, or high temperature [10, 11]. Besides low REE leaching efficiency, the occurrence of REEs in PG is another challenge. Although a few studies suggested some possibilities, the conclusions are still controversial [12]. Furthermore, because of the difficulty in determining the REEs occurrence, there is a lack of study on the mechanism behind the leaching process.

In the current study, a systematic investigation was performed to extract REEs (Y, Nd, Dy, and Ce) from a Canadian PG using three common mineral acids over a wide range of conditions. Solubility analysis, thermodynamic modeling, and kinetic analysis were used to explain the extraction trends and to identify the leaching process mechanism. The fundamental studies and novel findings from this study shed light on the physicochemical mechanisms behind REE leaching from PG, helping usher in an efficient extraction process that can be extended to any type of PG feeds with various REE concentrations.

Methods and Materials

Feeds and Materials

Phosphogypsum was obtained from Nutrien Ltd.'s fertilizer operations located in Redwater, Alberta, Canada. Concentrated hydrochloric acid (ACS Reagent Grade, 36.5–38.0 wt% Assay), nitric acid (ACS Reagent Grade, 68.0–70.0 wt% Assay), and sulfuric acid (ACS Reagent Grade, 95.0–98.0 wt% Assay) were purchased from VWR.

Experimental Procedure

The as-received PG sample contains moisture; thus, it was dried at 40 °C for 24 h, followed by grinding by mortar and pestle to a fine powder. The leaching experiments were conducted inside 250 mL Erlenmeyer flasks placed inside a temperature-controlled water bath (Fisher Scientific ISOTEMP 4100 H21P) with continuous stirring at 500 rpm. The pre-determined amounts of solid PG and the acid solution were added, based on the desired solid to liquiud (L/S) ratio. The flask was covered with a rubber stopper to prevent the loss of water by evaporation. Samples were taken at the end of leaching time, the leaching solution was diluted with 5 wt% HNO_3 using a Hamilton Microlab 600 diluter/dispenser system (Hamilton Company, Reno, NV, USA), and the concentration was measured using ICP-OES.

Characterization

The concentration of REEs in raw PG was determined through aqua-regia digestion (MARS6 Xpress microwave digestion system) followed by inductively coupled plasma optical emission spectroscopy (ICP-OES) measurements. As PG is sourced from mineral ores, it contains some primary radionuclide. To quantify the concentration of the radioactive elements (thorium: ^{232}Th and uranium: ^{238}U) in PG, the concentration of digested PG was measured by inductively coupled plasma mass spectrometry (ICP-MS, Thermo Scientific iCAP Q).

Design of Experiments and Empirical Model Building

For all three mineral acids, factorial design of the experiment (DOE) and empirical modeling were utilized to assess the effect of the operating parameters on the REE leaching efficiency. The studied factors were selected as: leaching temperature

Table 1 List of experimental factor levels for the leaching response surface trials

Experimental factor	Units	− 1 level	0 Level	+1 Level
X_1: Leaching temperature	°C	45	65	85
X_2: Acid concentration	mol L^{-1}	0.5	1.5	2.5
X_3: Liquid to solids ratio	mL g^{-1}	10	20	30

(X_1), acid concentration (X_2), and liquid to solid (L/S) ratio (X_3). The coded levels corresponding to each parameter are listed in Table 1.

For all three acid systems, a full factorial design was designed, and the experimental data from each trial was fitted with an empirical model (Eq. 2) with variance assessment at $\alpha = 0.05$ significance level. The model parameters were fitted by multiple linear least squares regression (Eq. 3).

$$\hat{y}_i = \hat{\beta}_0 + \hat{\beta}_1 X_1 + \hat{\beta}_2 X_2 + \hat{\beta}_3 X_3 + \hat{\beta}_{12} X_1 X_2 + \hat{\beta}_{13} X_1 X_3 + \hat{\beta}_{23} X_2 X_3 + \hat{\beta}_{11} X_1^2 + \hat{\beta}_{22} X_2^2 + \hat{\beta}_{33} X_3^2 \quad (2)$$

$$\hat{\beta} = \left(X^T X\right)^{-1} \left(X^T Y_i\right) \quad (3)$$

where $\widehat{y}_i$ is the extraction efficiency, X_1 to X_3 is the experimental parameters, $\widehat{\beta}$ is model parameter vector including each of the model parameters ($\widehat{\beta}_0, \widehat{\beta}_1, \widehat{\beta}_2, \widehat{\beta}_3, \ldots$), X is the matrix, and Y_i is the response vector.

Results and Discussion

Characterization Results of Raw PG

As shown in Fig. 1a, the total content of REEs in raw PG is 295.21 mg/kg, and the concentrations of the radioactive elements (U and Th) are low, at 32.17 and 1.36 mg/kg, respectively. Considering the economic value of elements and the abundance in PG, Nd, Y, Dy, and Ce are mainly focused. Figure 1b indicates the concentrations of other elements in PG, and calcium (Ca) and sulfur (S) are the main components, accounting for 25.3 wt% and 19.9 wt%, respectively.

Acid Leaching Results

Leaching of the REEs of interest was very fast for all three mineral acids, as the maximum leaching efficiency was reached within 20 min. Empirical models (Eqs. 2

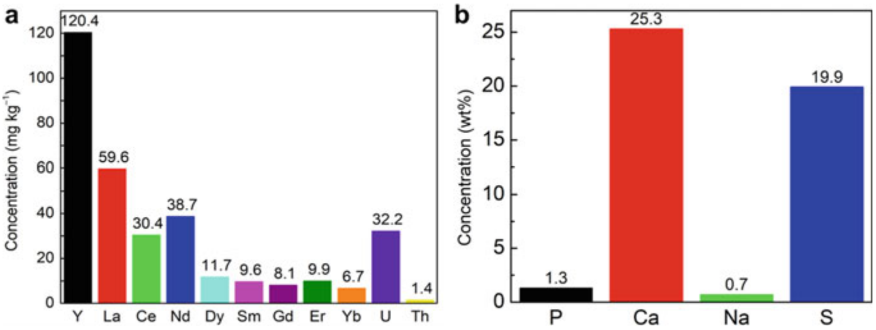


Fig. 1 Characterization of the raw PG sample: **a** content of REEs and radioactive elements (U, Th); **b** content of other elements in PG

and 3) were conducted to study the effects of operating parameters on the leaching process. It was found that acid concentration (X_2) and L/S ratio (X_3) have a positive effect on the extraction in the HCl system, whereas temperature (X_1) has a negligible effect. A similar trend was observed in the HNO_3 system, while temperature (X_1) has a positive effect in the H_2SO_4 system. Based on the overall leaching results, the optimized condition of the HCl system occurs at 45 °C, 2.5 M concentration, and 29.8 mL/g L/S ratio. For HNO_3 and H_2SO_4 system, the high leaching efficiency was achieved at much higher temperature (85 °C), and the optimal operating conditions of acid concentration and L/S ratio are 2.1 M, 1.3 M, and 27.7 mL/g, 30 mL/g, respectively. The best leaching efficiency of targeted REEs in each acid system (under optimized condition) is presented in Fig. 2, which indicates that HCl is the best leachant with the highest leaching efficiency (94.6%, 98.5%, 86.1%, 99.2% for Nd, Y, Dy, and Ce, respectively) under mild temperature condition (45 °C). Additionally, compared with HNO_3, HCl is less environmentally harmful and less expensive.

Fig. 2 Highest leaching efficiency was achieved for Nd, Y, Dy, and Ce in HCl, HNO_3, and H_2SO_4 system at 45 °C, 85 °C, and 85 °C, respectively

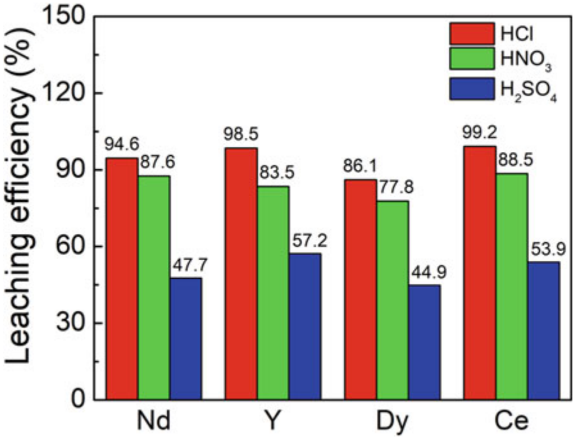
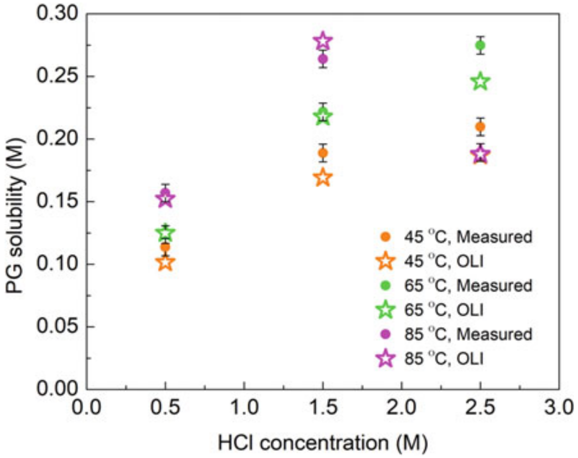


Fig. 3 Measured PG solubility and OLI simulation results in the HCl system as a function of temperature and acid concentration



Thermodynamic Modelling and Solubility Investigation

To further study the chemistry and mechanism behind the leaching process (focused on the best leachant–HCl system), the solubility of rare earth elements in HCl system was calculated from thermodynamic models, employing OLI software (Version 9.6) with modification on database developed by Azimi et al. [13]. As shown in Fig. 3, from the prediction via OLI, the solubility of gypsum increases with increasing HCl concentration; however, a significant drop is observed at 85 °C by increasing the acid concentration from 1.5 to 2.5 M. This decrease could be attributed to two reasons: the transformation of gypsum to anhydrite at high temperature and high acid concentration, and the solvation of more ions in the solution which leads to fewer water molecules available to participate in dissolution [13, 14]. The gypsum solubility trends explain the effect of operating parameters on REE extraction, which indicates the direct link between gypsum dissolution and REE leaching (Eq. 4 in general).

$$\mathrm{REE} - \mathrm{CaSO_4} \cdot n\mathrm{H_2O_{(s)}} + \mathrm{HCl_{(aq)}} \rightarrow \mathrm{CaSO_{4(aq)}} + \mathrm{CaCl_{2(aq)}} + \mathrm{H_3O^+_{(aq)}} + \mathrm{(REE)Cl_{3(aq)}} \tag{4}$$

where n = 0, 0.5, and 2 correspond to anhydrite, hemihydrate, and gypsum, respectively. As a result, increasing the solubility of gypsum leads to matrix destruction, allowing more REEs to be extracted.

Mechanistic Investigation—Proposed Mechanism

On the basis of experimental leaching and thermodynamic modeling results, it is concluded that the destruction of PG lattice is required to achieve high leaching

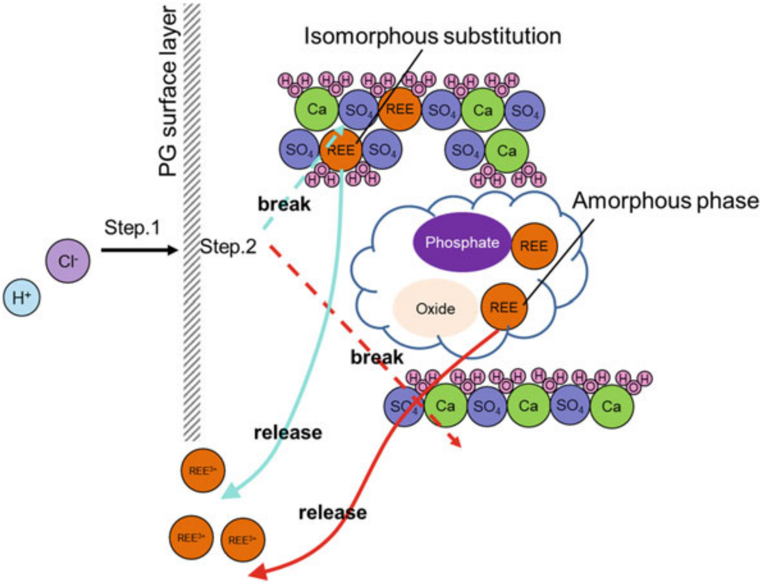


Fig. 4 Schematic diagram of the proposed leaching mechanism

efficiency. Although there are different possibilities of REEs occurrence, the leaching of REEs is highly correlated with the dissolution of gypsum regardless of whether they exist as their own phases or incorporate in PG lattice. The REEs that form separate phases are more easily leachable compared with the other case [12], which could cause the difference in the leaching efficiency of different REEs.

Overall, to improve the leaching process of REEs from PG, gypsum solubility is considered as an important factor, as its dissolution destructs the lattice, allowing the release of REEs substituting Ca^{2+} ions (isomorphous phase) and/or existing as separate phases (amorphous phase) within the PG lattice. The acid leaching mechanism is proposed as following steps (Fig. 4):

1. Acid diffuses and reaches the surface of PG particles.
2. Acid breaks the PG lattice (the bond between calcium and sulfate ion). Both REE phases inside PG and the isomorphous REEs substituting the Ca^{2+} ions are released into an aqueous solution due to the dissolution of the PG lattice.

Conclusions

In this study, the effect of various operating parameters on the leaching of REEs from PG was investigated for three mineral acid systems, and the optimum operating conditions were determined through systematic experimental and theoretical approaches based on the design of experiment. The HCl was identified as the best leachant, and the optimum operating conditions were determined to be 2.5 M HCl at 45 °C and 29.8 mL/g liquid to solid ratio which resulted in the highest extraction for all four targeted REEs. The developed HCl leaching process results in significantly higher leaching efficiency at a lower temperature compared with previous literature. Moreover, leaching results are explained via thermodynamic modeling and solubility investigation, which further elucidates the leaching mechanism.

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