Scientific Research Publishing

Natural Resources, 2019, 10, 325-336
https://www.scirp.org/journal/nr
ISSN Online: 2158-7086
ISSN Print: 2158-706X

Phosphogypsum Processing for Rare Earths Recovery—A Review

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How to cite this paper: Yang, X.S., Salvador, D., Makkonen, H.T. and Pakkanen, L. (2019) Phosphogypsum Processing for Rare Earths Recovery—A Review. *Natural Resources*, **10**, 325-336.
https://doi.org/10.4236/nr.2019.109021

Received: May 20, 2019
Accepted: September 8, 2019
Published: September 11, 2019

Abstract

As a by-product from the phosphate fertilizer industry Phosphogypsum (PG) was considered a potentially valuable source of the rare earth elements (REEs). Because of trace concentration of REEs in the PG (normally <0.1% wt) and also their tiny and complex occurrence phases the recovery process would be highly challenging in both technology and economy. The studies on occurrences of REEs, REE recovery by physical methods and leaching using different lixiviants such as inorganic acids, H_2SO_4, HCl and HNO_3, and organic chemicals, the effects of mechanical treatment of PG by microwaving and grinding on leaching efficiency of REEs, and resin-in-leach process were reviewed in the paper.

Keywords

Phosphogypsum, Rare Earth Elements, Phases of Rare Earth Elements, Acid Leaching

1. Introduction

As a by-product from the phosphate fertilizer industry phosphogypsum (PG) mainly contains gypsum ($CaSO_4 \cdot 2H_2O$) and also notable levels of impurities originating from the source phosphate rock such as Sr, Ba, Si, P, Fe, Al, Ti, U, and Th etc., as well as rare earth elements (REEs). PG had been found to be potential in agricultural use (three of the essential elements for plants growth, calcium, sulfur and phosphorus), uses as construction materials (e.g. utilizing PG in cement) and as a chemical raw material such as for recovery of sulfur and subsequent sulfuric acid manufacturing, as well as for production of ammonium sulfate [1]. Meanwhile, these trace elements are considered one of the main environmental concerns associated with PG [2].

Rare earth elements (REEs) comprising 15 lanthanides plus Y and Sc were normally contained in the phosphate rocks in various contents of 0.03 to 1.0 wt% [3] [4]. PG was considered a potentially valuable source of REEs. For the phosphate rocks with different REE grades it was concluded that most (60% - 70%) of the initial REE contents were incorporated to the PG during the wet-process of phosphoric acid [5]-[11]. As much as 5 tonnes of PG were produced for each tonne of P_2O_5 affected by the composition of the phosphate rock [12]. It was estimated that 170 or even 280 million tonnes of PG were globally produced annually. If assume the average content of REEs in the PG being 500 mg/kg the potential source of REEs from the PG would be annually 85,000 - 140,000 tonnes. It was estimated that in Florida alone, approximately 30,000 tonnes of REEs were discarded with various phosphate mining wastes annually [1]. In South Africa up to 85% of REEs were precipitated with PG during the acidulation of Phalaborwa phosphorite with sulphuric acid [13]. Similarly, in Poland 70% of REEs were found in PG during dihydrate process for the Kola phosphorite [14]. In Finland, the Siilinjärvi mine annually produced 1.3 million tonnes of apatite concentrate and meanwhile, around 1.5 million tonnes of PG were produced from the processing of the apatite concentrate. It was estimated that the majority (60% - 80%) of REEs from the apatite concentrate, that is, over 2000 tonnes of REEs annually, were deposited into the waste in the mine.

However, processing PG for the extraction of REEs and other valuable elements had not been industrially realized. Trace concentration of REEs in the PG (normally <0.1 wt%) and also their tiny and complex occurrence phases could cause the extraction process of REEs from PG to be highly challenging in both technology and economy. In this paper, the studies and investigations on PG processing for REE extraction were reviewed and the potential feasibilities of approaches in economy are discussed.

2. Occurrences of REEs in PG

The occurrence phases of REEs in PG were concerned in many studies but conclusions were disputable [6] [9] [15]-[20]. Generally, according to these studies REEs occurred as sulphates, carbonates, fluorides and phosphates and also being adsorbed as $REEs^{3+}$ ions. Recently, REE occurrences in PG were studied [21] with a European sample. Chemical analysis by ICP-MS showed that all the REEs except Pm exist and La, Ce, Pr, Nd, Sm, Eu, Gd, Dy and Y were found with relatively high concentrations. The content of total REEs (TREE) was around 2200 mg/kg (0.2 wt%). Gypsum as the dominating mineral in the PG was detected by the mineral liberation analysis (MLA) and the electron microprobe analyses (EPMA) to be the major REE-bearing phase and carry most (over 72%) of REEs. Other REE-bearing phases are monazite and apatite etc.

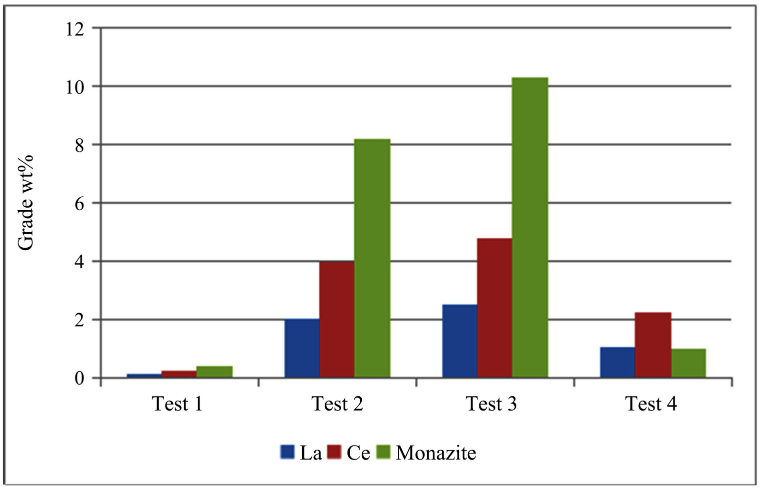
3. Recovery of REEs from PG by Physical Methods

Because of low grades of REEs an economical approach for recovery of REEs from PG should be firstly treated by physical methods to upgrade the REEs in the material prior to further processing such as leaching. The feasibility studies of enrichment of REE-bearing phases by physical methods such as hydrodynamic sedimentation, flotation and high gradient magnetic separation (HGMS) were conducted [22]. Ce and La, two REEs with high concentrations in the PG sample, had the grades of 0.1 wt% and 0.03 wt%, respectively. Monazite as the major REE-bering mineral in the material had the grade of 0.04 wt%. **Figure 1** shows the grades and recoveries of Ce and La, and monazite in the beneficiation concentrates for four tests. The testing conditions were: in Test 1 PG was treated by HGMS; in Test 2 PG was treated by flotation and HGMS; in Test 3 PG was ground first and then treated by flotation and HGMS; and in Test 4 PG was deslimed by hydrodynamic sedimentation and then treated by HGMS. It is seen that the REEs (Ce and La) and the mineral monazite in the PG could effectively enriched, that is, the grades of La and Ce can reach 2.5 wt% and 4.8 wt%, respectively, and the grade of monazite can reach 10.5 wt% (**Figure 1(a)**). However, elemental and mineral recoveries shown from **Figure 1(b)** were very different. The recoveries of the REEs were extremely low, only 4.9% - 8.5% for La and 3.3% - 5.8% for Ce, and the recovery of monazite was quite high reaching 22% - 55%.

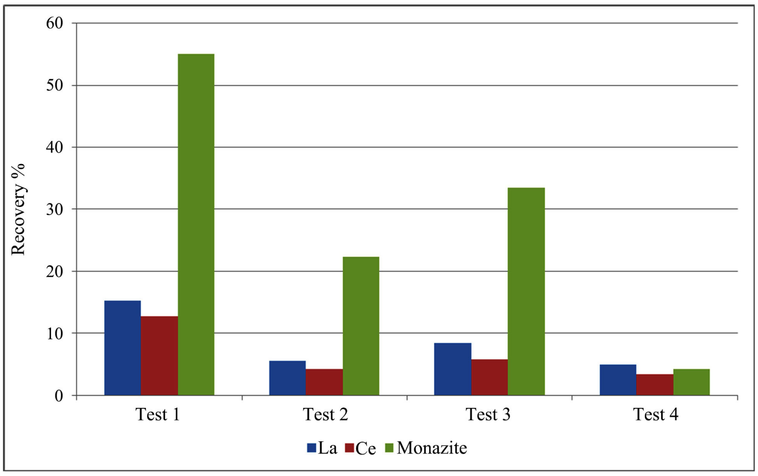
The results shown in **Figure 1** approved that the REE-bearing minerals in the PG such as monazite could be enriched by physical methods with a quite high recovery but the recovery REEs such as La and Ce in this study was very low. The main reason was that most (over 72%) of REEs in the PG are carried by gypsum which was not able to be efficiently enriched by physical methods. The lost REEs in the beneficiation process were mainly those carried by gypsum.

4. Acid Leaching of REEs from PG

Recovery of REEs from PG by acid leaching has been investigated extensively. Leaching with acids HCl, HNO_3 and H_2SO_4 was compared for the PG from Redwater Fertilizer plant in Alberta, Canada [19]. The XRD analysis revealed that the three main solid phases were gypsum ($CaSO_4 \cdot 2H_2O$) 84 wt%, anhydrite ($CaSO_4$) 8 wt%, and calcium phyllo-tetraphosphate ($Ca(P_4O_{11})$) 8 wt%. Y, La, Ce, Nd, Sm, and Pr were detected in both elemental as well as oxide form by TOF-SIMS (time-of-flight secondary ion mass spectrometry). The results showed that the leaching efficiency of REEs using H_2SO_4 was significantly lower than that of HCl and HNO_3 and the reason is that solubility of gypsum in H_2SO_4 is much lower than in HCl. It was observed that at 80˚C the solubility of gypsum in H_2SO_4 was about 4 times lower than that in HCl (0.075 mol/l vs. 0.3 mol/l, respectively) [23]. Similar results with HCl and HNO_3 were obtained that the average leaching efficiency (only considering REEs with high concentrations in the PG sample: Ce, La, Nd, Sm, and Y) after 20 min was 57% for the case of HNO_3 and 51% for the case of HCl, both at the conditions of 1.5 mol/l concentration, 80˚C, solid to liquid (S/L) ratio of 1/8, and 500 rpm agitation. The



(a)



(b)

Figure 1. REEs (Ce and La) and REE-bearing mineral (monazite) grades and recoveries of beneficiation concentrates by physical methods ((a) grade wt%; (b) recovery %) (Test 1: PG directly treated by HGMS; Test 2: PG treated by flotation and HGMS; Test 3: PG ground first and treated by flotation and HGMS; Test 4: PG deslimed by hydrodynamic sedimentation and treated by HGMS) [22].

leaching results showed that 80˚C, 1.5 mol/l concentration, S/L of 1/8 and 20 min were the most suitable operating conditions for the three acids.

Ismail *et al.* (2015) [24] also investigated the leaching of different lanthanides with HCl, H_2SO_4 and HNO_3 using the PG from Abu-Zaabal Company in Egypt. The total content of lanthanides in the PG was found to be about 480 mg/kg. Parameters of acid concentration, mixing time, and acid to PG (L/S) ratio as well as temperature were tested. The highest leaching efficiency was obtained at the conditions of 3.0 mol/l HNO_3, L/S 3.0, mixing time 3.0 h and room temperature (25˚C). After three cycles of leaching, the leached out lanthanides from the PG was more than 66%. It was found that the leaching efficiency was different for individual lanthanides and La had the highest leaching efficiency, that is, 73.4% La, 68.0% Ce, 62.3% Er, 55.1% Y and 39.5% Pr.

In addition, the addition of $Ca(NO_3)_2$ to HNO_3 solution was found to increase the leaching efficiency of lanthanides, e.g. as $Ca(NO_3)_2$ concentration increased from 0.0 to 1.0 mol/l in 3.0 mol/l HNO_3 solution the leaching efficiency increased from 47.4% to 59.5% then it remained almost constant with further increasing $Ca(NO_3)_2$ concentration up to 2.0 mol/l. The addition of $NaNO_3$ or $Mg(NO_3)_2$ in the concentration range from 0.1 - 2.0 mol/l had no effect on leaching efficiency of lanthanides. The study by Preston *et al.* (1996) [13] also showed that the leaching of the rare earth values from the PG of a South Africa apatite ore by diluted HNO_3 was considerably enhanced by the addition of $Ca(NO_3)_2$ to the lixiviant, enabling recoveries of up to 85% achieved. The mechanisms could be that the addition of calcium ions lowered the concentration of free fluoride ion (it was observed that the concentration of REEs in the leach liquors might be dependent upon the various fluoride-related equilibria), or the high calcium concentration in solution naturally tended to displace the REEs from the solid phase, in which they were heterovalently substituted for calcium ions [13].

The studies above showed that HCl and HNO_3 were more efficient agencies than H_2SO_4 for leaching REEs from PG, but H_2SO_4 was still industrially preferred because of economical reasons. A two-step leaching method was introduced with H_2SO_4 as the lixiviant using a Tunisian PG [25]. The PG sample was firstly washed with distilled water and after solid–liquid separation underwent a double leaching with 10% H_2SO_4 solution at 60˚C, for 1 - 2 h of continuous stirring at L/S ratio of 1.3. After a first lixiviation with the acid solution, the first residue was obtained and was remixed with the same leach liquor for the second lixiviation. Then, after solid–liquid separation, the final filtrate was evaporated at 100˚C and a solid crystallization was resulted. After washing and filtration a REEs rich solid product was achieved. Analyses by XRD and ICP-MS showed that the impurities such as fluorides and phosphates were essentially dissolved in the first acid leaching, whereas the second leaching led to the dissolution of REEs in the H_2SO_4 liquor. The crystallized solid obtained after the evaporation stage corresponded to a mixture of anhydrite ($CaSO_4$) and monetite ($CaHPO_4$) phases with a total REEs enrichment of about 86%. This study showed that comparing to a single leaching the two-step leaching could improve the leaching efficiency of REEs which allowed a better solubilization of REEs. However, for some PG samples with low concentrations of the impurities such as fluorides and phosphates this process might not profit the leaching efficiency of REEs.

5. Leaching of REEs by Using Organic Chemicals as the Lixiviants

Treatment of PG using suitable organic extractants was investigated with a PG sample from Egypt [26]. Different types of organic extractants, such as tributylphosphine (TBP), trioctyl phosphine oxide (TOPO), triphenyl phosphine oxide (TPPO), and di-ethyl-hexyl phosphoric acid (DEHPA), dissolved in kerosene were experimented to investigate the effect of different solvents on the removal efficiency of radionuclides and REEs from the PG. Using 0.1 mol/l concentration for each solvent, the processes were carried out at room temperature (25˚C); contact time 1 h; and L/S ratio 1.0. The results showed that the highest efficiency (%) of REEs was obtained by using TBP. By the addition of TBP, 46% of REEs was removed. The optimized leaching conditions for treating the PG using TBP dissolved in kerosene determined by experiments were: contact time 2 h; concentration of TBP 0.5 mol/l (dissolved in kerosene); L/S ratio 1:1 (solution vol./PG wt.); temperature 55˚C (depending on the vapor pressure of the used solvent). At the conditions the obtained leaching efficiency of REEs reached 68.5%. The method was improved by using mixtures of TBP and TOPO in kerosene. In this case the REE recovery of 80% was achieved [27].

Leaching of lanthanides from PG using Nonyl Phenol Ethoxylate (NPE) associated with HNO_3 and HCl was conducted by Kouraim *et al.* (2014) [28] with the PG sample from the processing of Abu-Tartur phosphate ores in Egypt. The content of total lanthanides in the PG was 1387 mg/kg and highly concentrated in the fine size fraction (<20 μm). Leaching of lanthanides was carried out using either free acids HCl and HNO_3 or these acids associated with Nonyl Phenol Ethoxylate (NPE). Based on the experimental results relative to the corresponding free acids the leaching efficiency of lanthanides was increased by 30% using even small concentrations of NPE (>4 wt/v%) at temperature 25˚C. The factors affecting the leaching process were optimized. The kinetics of the leaching process was investigated as a function of temperature. It was found that the leaching process could be described by a shrinking-core model and in the leaching of lanthanides by the associated system the activation energy was decreased from 5.89 kJ/mol to 5.28 kJ/mol and 12.24 kJ/mol to 3.79 kJ/mol for HCl and HNO_3, respectively.

6. Influences of Mechanical Activations on Leaching of REEs

The effect of microwaving PG as the pre-treatment on acid leaching was investigated [29]. It was found that microwave radiation resulted in the dielectric heating of water molecules in the crystals and vaporization, causing the formation of breaks and pores in these particles as the vapour escaped.

An extraction method of REEs from a Russian PG was presented by processing the PG with sulfuric acid (0.3 - 0.6 mol/l) at high temperatures of 70˚C - 100˚C and S:L ratio of 1:1-3 for 1 - 2 h under stirring and bubbling of air into the pulp [30]. But the leaching efficiency was not revealed.

The influences of mechanoactivation by grinding on the overall solubility of $CaSO_4·2H_2O$ and of PG in water and in diluted acids (10% HCl, 7% H_2SO_4) as well as on the leaching efficiency of REEs from the PG were studied [31]. The PG sample was from Kola apatite processing. The content of REEs was 3700 mg/kg including La, Ce, Pr, and Nd. The grinding was performed in a centrifugal ball mill in air and in suspension with the acids. The results showed that the leaching of REEs from the PG was improved by the mechanoactivation in air, water and acids.

REEs recovery from a PG by leaching using a patented leaching solution (PX-107) followed by REEs extraction with a polymer (Chelok®) was reported [32]. The PG sample was milled using a rod mill for 10 minutes and the extraction rates of REEs were compared to those of the unmilled sample as shown in **Table 1**. It is clear that after the PG sample being milled the extracted REEs was increased for almost all the REEs.

The influence of mechanoactivation by grinding was investigated with a PG material from a mine in Europe [33]. The material was ground using a ball mill for 30, 60 and 90 min and acid leaching experiments were conducted with HCl and HNO_3. The leached rates of REEs including La, Ce and Y for unmilled and milled samples (at grinding time of 30, 60 and 90 min) were compared in **Table 2** and **Table 3**. It is seen the leaching efficiencies of REEs, La, Ce and Y, were improved by milling and also generally the leached rates increased as the milling time increasing.

Table 1. Comparison of extraction efficiencies of REEs for the unmilled and milled samples [32].

Extraction rate of REEs %	Ce	Dy	Er	Gd	Ho	La
Unmilled	47.72	74.46	79.92	59.54	39.20	72.65
Milled	49.54	85.25	89.89	68.12	58.87	87.37
Extraction rate of REEs %	Nd	Sm	Tb	Y	Yb	Pr
Unmiled	85.25	77.33	49.71	61.80	73.08	10.69
Milled	99.11	84.94	88.49	69.70	80.36	4.57

Table 2. Comparison of REE leached rates for unmilled and milled samples (HCl, 4.0 mol/l, 60˚C, 120 min) [33].

Extraction rate of REEs %		La	Ce	Y
Unmilled		51.80	54.76	46.11
Milled	30 min	64.47	60.48	70.79
	60 min	59.83	61.35	68.12
	90 min	72.21	62.86	84.56

Table 3. Comparison of REE leached rates for unmilled and milled samples (HNO_3, 4.0 mol/l, 60˚C, 120 min) [33].

Extraction rate of REEs %		La	Ce	Y
Unmilled		59.92	57.93	54.61
Milled	30 min	61.69	66.91	83.74
	60 min	75.43	70.32	88.30
	90 min	70.52	73.04	79.31

The improvement of mechanoactivation by grinding on leaching efficiency of REEs could be attributed to the increase of the specific area and the decrease of the visual activation energy of ground material because of crystal interior defects [34].

7. Resin-in-Leach

The study by Koopman and Witkamp (2000) [8] showed that during the wet-process of phosphoric acid production using sulfuric acid to the apatite concentrate the calcium sulfate hemihydrate (HH) was formed first, then recrystallized into calcium sulfate dihydrate (DH) or gypsum. REEs were incorporated to gypsum during the recrystallization. The extraction efficiency of lanthanides on the DOWEX C-500 resin (a strongly acidic cation exchange resin with 4.9 meg/g of sulfonic acid functional groups and a size of 465 - 635 μm) during the recrystallization of hemihydrate (HH) to gypsum was investigated. The experiments were carried out in the system of phosphoric acid, gypsum seeds, HH, and DOWEX C-500 resin at the temperature of 80˚C. The results showed that with 250 g resin/kg phosphoric acid, lanthanides can be removed during the recrystallization of HH to gypsum. Depending on the value of the distribution coefficient $K'_{A,DH}$ for each element, the removal percentages were 53% for Eu, 34% for La and 10% for Sm. Meanwhile, the results showed that the ion exchange resin also extracted bivalent calcium ions (Ca^{2+}) which could be selectively precipitated from concentrated hydrochloric or nitric acid solutions.

The resin-in-leach technology for extraction of REEs was studied by processing a PG material using sulphuric acid as the lixiviant in South Africa [35]. The process parameters including types of resin, unprocessed and processed PG by hydro-cycloning, with and without additives etc. were tested. The adsorbed REEs on the resins were eluted by using CaCl. The results indicated that resin-in-leach process was feasible for recovery of REEs from PG.

8. Conclusions

The occurrence phases of REEs in the PG were concerned in many studies but conclusions were disputable. According to these studies REEs occur as minerals and also being adsorbed as $REEs^{3+}$ ions. In a recently published study it was shown that gypsum as the dominating mineral in the PG was detected to be the major REE-bearing phase carrying over 72% of REEs in the material.

In a case study, physical beneficiation of PG by flotation and magnetic separation methods was investigated and the results showed that the REE-bearing minerals in the PG such as monazite could be enriched by physical methods but REEs such as La and Ce were not concentrated with high recoveries because gypsum, as a major REEs-bearing phase, carrying most of REEs in the PG, was not able to be efficiently enriched by physical methods.

Studies on acid leaching with H_2SO_4, HCl and HNO_3 were conducted. Acid concentration, temperature, solid to liquid ratio, operation time and the addition of $Ca(NO_3)_2$ to HNO_3 solution were found by experiments to be effective parameters for REEs leaching from PG. HCl and HNO_3 were found to be more efficient solvents than H_2SO_4 for leaching REEs from PG. H_2SO_4 might be still industrially preferred because of economical reasons. A study showed that two-step leaching using H_2SO_4 could improve the leaching efficiency of REEs for a PG material.

Some organic chemicals such as tributylphosphine (TBP) and trioctyl phosphine oxide (TOPO), or their mixture, dissolved in kerosene were proved by experiments to be effective lixiviants for leaching REEs from PG.

Influences of mechanical activations by grinding were found to be significant on leaching of REEs from PG. The activation mechanisms may need to be further studied for economical use of this process.

Resin-in-leach process using sulphuric acid as the lixiviant would be feasible for recovery of REEs from PG. The selectivity of the ion exchange resins to REEs ions and bivalent calcium ions could be the most important factor affecting practical use of the process.

Acknowledgements

The authors are grateful to the Academy of Finland (298094) for the financial support.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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