Rare Earths Recovery and Gypsum Upgrade from Florida Phosphogypsum

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Abstract

Phosphogypsum is a byproduct created during the production of industrial wet-process phosphoric acid. This study focused on recovering rare earth elements (REEs) from a Florida phosphogypsum sample and investigated the effects of removing detrimental impurities such as phosphorus pentoxide (P_2O_5), uranium (U) and fluorine (F) during the leaching process. Experimental results indicated that REE leaching efficiency increased rapidly, reached a maximum and then began to decrease with sulfuric acid concentrations ranging from 0 to 10 percent and temperatures ranging from 20 to 70°C. At a sulfuric acid concentration of 5 percent and leaching temperature of 50°C, REE leaching efficiency obtained a maximum value of approximately 43 percent. Increasing the leaching time or liquid/solid ratio increased the leaching efficiency. The leaching efficiencies of P_2O_5, U and F consistently increased with sulfuric acid concentration, temperature, leaching time and liquid/solid ratio within the testing ranges. A fine-grain gypsum concentrate, sized smaller than 40 μm, was separated from leached phosphogypsum through elutriation, in which the P_2O_5, U and F content levels were reduced by 99, 70, and 83 percent, respectively, from their content levels in fresh phosphogypsum.

Key words: Rare earth elements; phosphogypsum; leaching efficiency

1 Introduction

Phosphogypsum is a byproduct generated during the industrial wet process of phosphoric acid production, in which sulfuric acid is used to digest phosphate rock. Gypsum ($CaSO_4 \cdot 2H_2O$), the main component of phosphogypsum, usually accounts for 65 to 95 percent of phosphogypsum by weight. There are small quantities of impurities in phosphogypsum, such as phosphates (H_3PO_4, $Ca(H_2PO_4)_2 \cdot H_2O$, $CaHPO_4 \cdot 2H_2O$ and $Ca_3(PO_4)_2$), fluorides (NaF, Na_2SiF_6, Na_3AlF_6, Na_3FeF_6 and CaF), sulfates, trace metals and radioactive elements (Rutherford, Dudas and Arocena, 1996). Global phosphogypsum generation is estimated at 200 Mt/a (Parreira, Kobayashi and Silvestre, 2003; Yang et al., 2009), but only about 15 percent is recycled as building materials, agricultural fertilizers or soil stabilization amendments (Tayibi, Choura and Lopez, 2009).

The spreading of noxious components like arsenic, silver, barium, cadmium, chromium, lead, mercury, selenium, and residual phosphoric, sulfuric and hydrofluoric acids contained within the porous phosphogypsum may result in potential environmental contamination. Research on the leachability of these noxious elements from phosphogypsum indicated that radium (Ra), uranium (U), cadmium (Cd), copper (Cu) and zinc (Zn) can be leached using seawater, distilled water or dilute sulfuric acid solution (Al-Masri et al., 2004; Lysandrou and Pashalidis, 2008). Investigations on the migration of the radionuclides around phosphogypsum stacks verified the spread of these elements into the environment (Pérez-López et al., 2007).

On the other hand, phosphogypsum is regarded as an important secondary resource. Usually, there are about 0.04 to 1 percent of rare earth elements (REEs) in the waste. These elements are critical materials for green energy development due to their essential roles in items such as permanent magnets, lamp phosphors, catalysts and rechargeable batteries (Zhang, 2012; Sinha et al., 2016). Considering the billions of tonnes of phosphogypsum waste accumulated in the world, there is a large supply of REEs potentially available. Although research has been conducted, no technology has been developed that economically recovers these elements from the phosphogypsum waste (Lokshin et al., 2016; Kulczycka et al., 2016). Gypsum, widely used in the construction industry, is another potentially valuable component in the phosphogypsum stacks. However, the presence of impurities has given rise to many restrictions on the potential applications of phosphogypsum in this field. Research has shown that the residual phosphates and fluorides in phosphogypsum delay the setting time and reduce the early strength development of cement while the impurity atoms negatively affect gypsum crystal formation (Shen et al., 2012). Furthermore, the existence of radioactivity overwhelmingly restricts phosphogypsum utilization. In the United States, the use of phosphogypsum was banned in 1990 (Sumner, 1995) and in the European Union it was discontinued in 1992 due to its potential radiological impact.

In central Florida, there are large quantities of phosphate deposits in the Bone Valley region. Phosphate rock mining has produced 1 Gt of phosphogypsum in that area and approximately 30 Mt are additionally generated each year.

The Florida Industrial and Phosphate Research Institute, under the umbrella of the Critical Materials Institute, is carrying out a systematic study of REE recovery from phosphate mining and processing streams. While researching the recovery of REEs from phosphogypsum, phosphogypsum reutilization was also taken into account. The purpose of this research is not only to recover the valuable REEs but also to develop a method of reusing the phosphogypsum waste.

2 Materials and methods

Mineral acid, such as sulfuric acid or hydrochloric acid, leaches REEs from natural mineral and promotes the dissolution of impurity metals in phosphogypsum waste. Because rare-earth extraction follows the leaching process, sulfuric acid was employed as the leaching agent when investigating the REE leaching efficiency and the radionuclide removal rate. Elutriation was used to concentrate the gypsum from the leached phosphogypsum.

2.1 Phosphogypsum sample

About 100 kg of representative phosphogypsum were provided by Mosaic Co., the largest phosphate fertilizer manufacturer in Florida. The phosphogypsum sample appeared to be air-seasoned. Although agglomerated in different sizes, no agglomerate was larger than 40 mm in diameter. After drying at 105°C, the sample was mashed by hand and sifted through a 14 mesh, corresponding to 1.4 mm, screen to disperse the gypsum granules. It was then mixed thoroughly and divided into aliquot portions of 300 g per experiment. The chemical components in the phosphogypsum sample are presented in Table 1.

Table 1 Main chemical components and rare earth elements in the phosphogypsum sample

<table>
<tr><td>Component</td><td colspan="2">P_2O_5</td><td>CaO</td><td colspan="2">Fe_2O_3</td><td colspan="2">MgO</td><td>Al_2O_3</td><td colspan="2">F</td></tr>
<tr><td>Content (%)</td><td colspan="2">0.99</td><td>22.65</td><td colspan="2">0.13</td><td colspan="2">0.00</td><td>0.22</td><td colspan="2">1.06</td></tr>
<tr><td>Element</td><td>Sc</td><td>Y</td><td>La</td><td>Ce</td><td>Pr</td><td>Nd</td><td>Sm</td><td>Eu</td><td>Gd</td><td>Tb</td></tr>
<tr><td>Content (ppm)</td><td>0.34</td><td>43.36</td><td>36.38</td><td>63.84</td><td>5.01</td><td>45.13</td><td>0.00</td><td>1.40</td><td>6.87</td><td>0.14</td></tr>
<tr><td>Element</td><td>Dy</td><td>Ho</td><td>Er</td><td>Tm</td><td>Yb</td><td>Lu</td><td colspan="2">Total REE</td><td>U</td><td>Th</td></tr>
<tr><td>Content (ppm)</td><td>6.41</td><td>0.91</td><td>4.35</td><td>2.26</td><td>2.02</td><td>0.00</td><td colspan="2">218.42</td><td>31.59</td><td>0.09</td></tr>
</table>

The phosphogypsum sample was wet-sieved to investigate its particle size distribution and the main chemical contents in each size fraction. To avoid the influence of gypsum dissolution, gypsum-saturated water was used in the screening test. The test results are shown in Table 2.

Table 2 Particle sizes and main element distributions of the phosphogypsum sample

Screen mesh	size (um)	Yield (%)	Content of main chemical component			
			Total REE (ppm)	CaO (%)	U (ppm)	F (%)
+18	+1000	0.21	111.53	0.25	28.45	1.15
-18+100	-1000+150	38.01	92.94	4.76	33.32	1.05
-100+200	-150+75	12.38	199.07	16.44	31.39	1.02
-200+270	-75+53	5.93	353.20	32.03	29.61	0.99
-270+325	-53+45	2.43	330.76	31.83	31.27	1.06
-325+400	-45+38	3.56	356.33	34.53	31.45	0.99
-400+500	-38+25	7.63	327.55	39.12	31.55	1.00
-500	-25	29.85	308.99	40.94	29.37	1.08
Total/Weighted average		100.00	219.10	22.95	31.42	1.05

2.2 Leaching tests and analysis

The leaching test was conducted in a 2.5-L water bath batch reactor to investigate the influences of four main factors – sulfuric acid concentration, temperature, leaching time and liquid/solid ratio – on the leaching efficiencies of REEs, P_2O_5, U and F. In each leaching test, 300 g of phosphogypsum was used. To monitor the leaching process, the solution was regularly sampled for chemical analysis. After leaching, the pulp was filtered, and the residue was rinsed three times. Concentrations of REEs, calcium oxide (CaO), magnesium oxide (MgO), iron oxide (Fe_2O_3), aluminum oxide (Al_2O_3) and U in both solution samples and residue were analyzed using an Optima 8300 inductively coupled plasma-optical emission spectrometer (ICP-OES) (PerkinElmer, Waltham, MA). P_2O_5 and F concentrations were determined using a spectrophotometer and fluoride ion-sensitive electrode, respectively.

2.3 Elutriation test

Elutriation was used to concentrate gypsum from leached phosphogypsum. In this test, 100 g of leached phosphogypsum was added to 10 L of gypsum-saturated water in a transparent plastic cylinder with diameter of 15 cm and height of 100 cm, and stirred to prepare a turbid liquid. After agitating and allowing a fixed time for sedimentation, the liquid above a certain height was siphoned out. The cylinder was refilled with gypsum-saturated water to 10 L, and the process was repeated until the siphoned liquid was no longer turbid. The cut size of the particle separated out each time was dependent on the sedimentation time and the height of siphoned liquid. Based on Stokes sedimentation law, their relationship can be written as:

$$d = \sqrt{\frac{18h\mu}{(\rho_s - \rho_l)gt}} \tag{1}$$

where d is the diameter in meters of the largest particles, or cut size, siphoned out after each repetition, h is the sedimentation distance in meters, μ is the dynamic viscosity of water, equal to 0.8949×10^{-3} kg/m·s at 25°C, ρ_s is the mass density of the solid particle in kg/m^3, ρ_l is the mass density of water, equal to 997.0 kg/m^3 at 25°C, g is the gravitational acceleration, equal to 9.8 m/s^2, and t is the sedimentation time in seconds.

3 Results and discussion

3.1 Effect of sulfuric acid concentration on leaching efficiency

The influence of sulfuric acid concentration on the leaching efficiencies of REEs, P_2O_5, U and F are presented in Fig. 1. The REE leaching efficiency initially increased with sulfuric acid concentration. At about 5 percent sulfuric acid concentration it reached a maximum of approximately 41 perent. At higher sulfuric acid concentrations, the efficiency decreased. For the other elements, the leaching efficiencies rose rapidly at low sulfuric acid concentrations, ranging from 0 to 3 percent, and then showed a slow growth trend.

These REE leaching efficiency trends are different from the test results of Kolokolnikov and Kovalev (2009), which showed a constant increase in REE leaching efficiency at sulfuric acid concentrations below 20 percent. This discrepancy can be attributed to the difference in REE content and the occurrence of REEs in the solid feed. For phosphogypsum, some researchers (Olmez and Yilmaz, 1988; Becker, 1983) argued that P_2O_5 and REEs exist in the gypsum crystal lattice by substituting the sulfate (SO_4^{2-}) and calcium (Ca^{2+}) ions, respectively. The gypsum dissolution allows for these REEs to transfer into the solution (Becker, 1983). In Kolokolnikov's test, the solid feed was the insoluble residue from phosphogypsum leaching by ammonium chloride (NH_4Cl), in which no calcium sulfate was left and the REEs had been concentrated up to 5.1 percent by weight of their rare earth oxides, Ln_2O_3, where Ln donates any REE. At increased sulfuric acid concentrations, additional REEs in the solid feed were dissolved into the solution. However, in the present study, the REE content in the phosphogypsum sample was only 218.42 ppm. At sulfuric acid concentrations below 5.0 percent, increasing the acid concentration helped the dissolution of the REEs in the leaching system. However as sulfuric acid concentration further increased, additional SO_4^{2-} in solution had an adverse influence on gypsum dissolution. This especially affected the fine gypsum particles with high REE contents (Table 2). In order to get a high REE leaching efficiency, the sulfuric acid concentration was set at 5.0 percent in subsequent experiments.

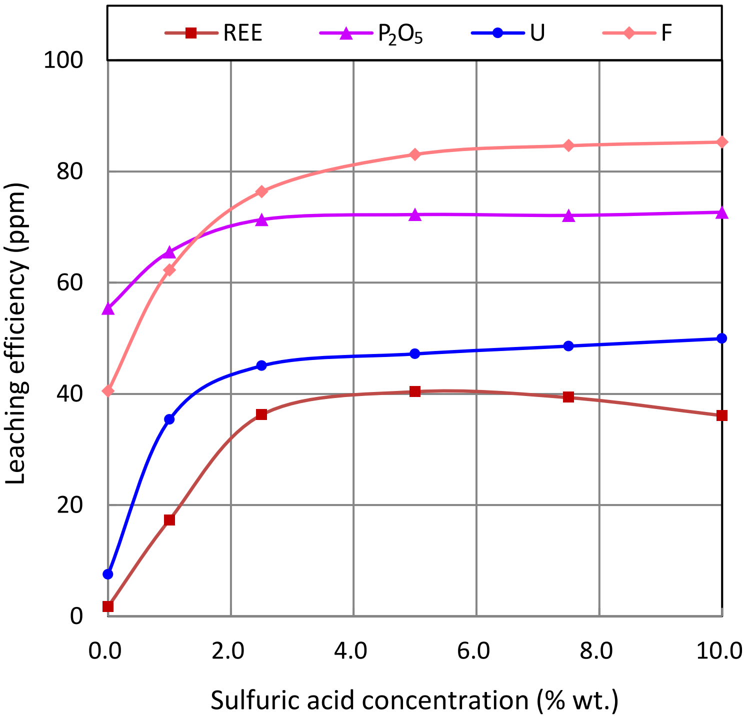

Figure 1 - Change of leaching efficiency with sulfuric acid concentration (leaching temperature = 50°C, leaching time = 120 min, liquid/solid = 4.0).

3.2 Effect of temperature on leaching efficiency

The effects of leaching temperature on the leaching efficiencies of REEs, P_2O_5, U and F are shown in Fig. 2. Comparing Figs. 1 and 2, leaching temperature had a similar effect as sulfuric acid concentration on REE leaching efficiency. The leaching efficiency of REEs trended upward initially, then dropped with temperature increase. At 50°C, it reached a maximum of approximately 43 percent. The leaching efficiencies for all other components displayed an increase with temperature.

The changes in REE leaching efficiency can be explained through the retrograde trend of gypsum solubility with temperature. Below 50°C, the dissociation of REE compounds increased with temperature and thus the REE leaching efficiency increased. Above 50°C, the decrease of gypsum solubility was the overwhelming factor, causing a decrease in REE leaching efficiency. In order to obtain a high REE leaching efficiency, the leaching temperature was set at 50°C in subsequent experiments.

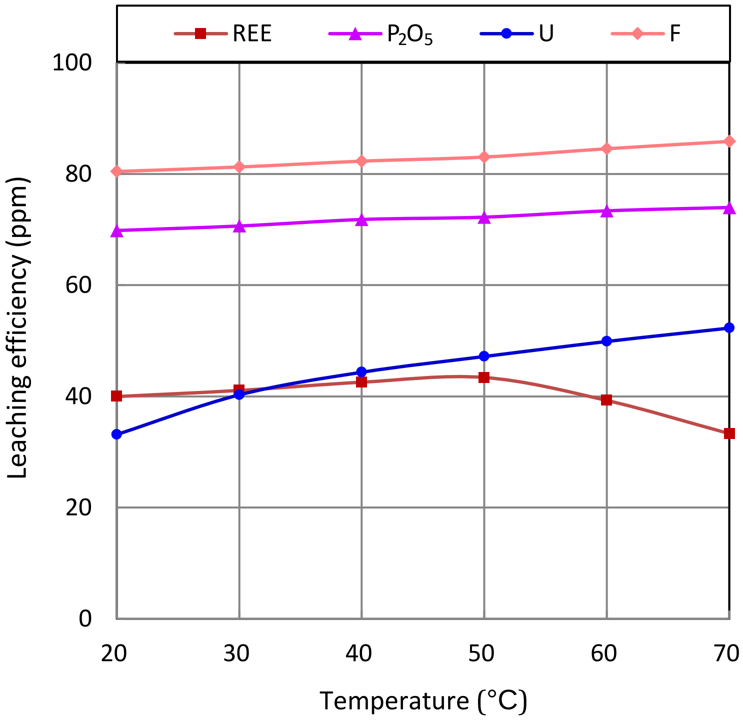

Figure 2 - Change of leaching efficiency with temperature (sulfuric acid concentration = 5.0%, leaching time = 120 min, liquid/solid ratio = 4.0).

3.3 Effect of leaching time on leaching efficiency

The effects of leaching time on the leaching efficiencies of REE, P_2O_5, U and F are presented in Fig. 3. All leaching efficiencies rose rapidly during the first 30 min and then slowed down. These changes can be ascribed to the occurrence states of these elements in the phosphogypsum feed. The REEs, P_2O_5, U and F existing in compounds of $LnPO_3$, $CaHPO_3$, Na_3SiF_6 or UO_2HPO_4 leach out immediately. However, there are still some uranium-containing compounds and fluorides coated by gypsum, and some REEs and P_2O_5 hosted in the gypsum crystal lattice (Fred and Wesley, 1980; Olmez and Yilmaz, 1988; Becker, 1983). These compounds require additional time to be leached out, and depend strongly on the gypsum dissolution and recrystallization in the system, leading to a slow growth of leaching efficiency with time.

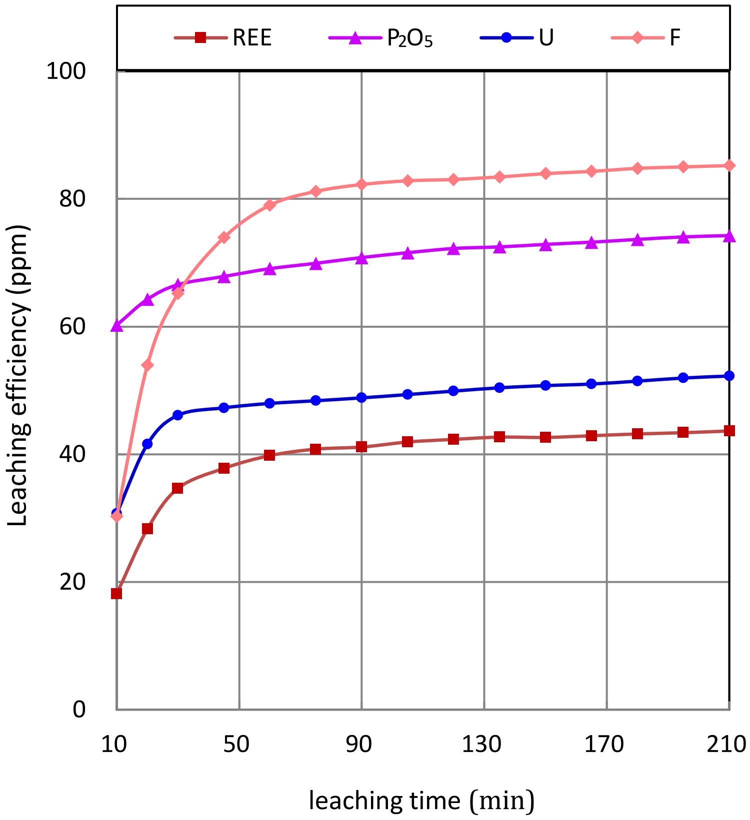

Figure 3 - Change of leaching efficiency with leaching time (sulfuric acid concentration = 5.0%, leaching temperature = 50°C, liquid/solid ratio = 4.0).

3.4 Effect of liquid/solid ratio on leaching efficiency

The effects of liquid/solid ratio on the leaching efficiencies of REEs, P_2O_5, U and F are shown in Fig. 4. Each shows a significant increase with liquid/solid ratio. Because the concentrations of these elements were very low in the phosphogypsum feed, solubility of the compounds was an important factor in the element leaching efficiency. As the liquid/solid ratio rose from 2 to 7, the REE concentration in the leaching solution rapidly decreased from about 34 ppm to 16 ppm. This is unfavorable for the subsequent REE extraction from the leaching solution. A liquid/solid ratio range of 3 to 4 was applied in this study.

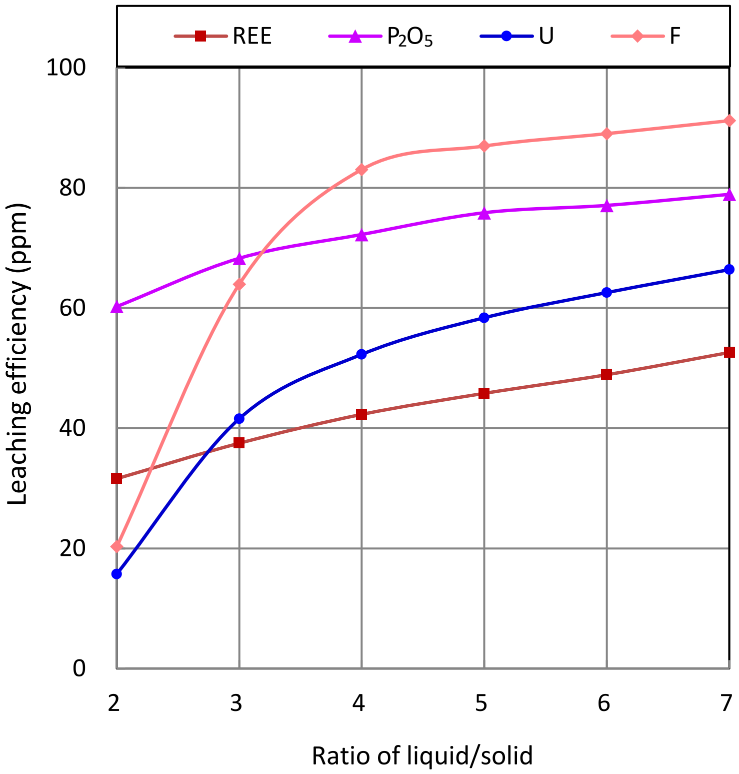

Figure 4 - Change of leaching efficiency with ratio of liquid/solid (sulfuric acid concentration = 5.0%, leaching temperature = 50°C, leaching time = 120 min).

3.5 Elutriation

The results in Table 1 indicate that the gypsum content in the phosphogypsum sample was not more than 70 percent, with CaO content at 22.65 percent. The acid-insoluble test also confirmed there was approximately 35 percent silica and other undigested minerals in the phosphogypsum. The screening results in Table 2 show that the gypsum content in the phosphogypsum increased as particle size decreased. In order to get purer gypsum, elutriation was used to concentrate gypsum from leached phosphogypsum. The cut size was set at 40 µm, and the sedimentation height was 50 cm. Using Eq. (1), the sedimentation time was calculated as 6.47 s. The test results are presented in Table 3.

The gypsum was concentrated in the fine fraction with a yield of 43.62 percent and CaO content up to 39.45 perent. Compared with fresh phosphogypsum, the contents of P_2O_5, U and F decreased by 99, 70 and 83 percent, respectively.

Table 3 Results of elutriation test for leached phosphogypsum (gypsum particle density = 2320 kg/m^3)

Product	Yield (%)	Content of main chemical component				
		CaO (%)	Total REE (ppm)	P_2O_5	U (ppm)	F (%)
Fine (-40μm)	43.62	39.45	81.68	0.01	9.45	0.18
Coarse (+40μm)	56.38	9.17	157.32	0.48	20.82	0.13
Total/Weighted average	100.00	22.38	124.33	0.27	15.86	0.15

4 Analyses

The occurrence states of the REEs, P_2O_5, U and F in the phosphogypsum play an important role in their leaching performance. In Wing's study (2015), a portion of the REEs in phosphogypsum was incorporated with phosphate into calcium sulfate. The REEs and phosphate substituted for the Ca^{2+} and SO_4^{2-} ions, respectively. Investigation by Becker (1983) indicated that about 25 percent of the P_2O_5 in phosphogypsum is present as phosphoric acid, 12.5 percent exists in the undigested apatite, and the remaining 62.5 percent occurs in the gypsum crystal lattice as PO_4^{3-}, HPO_4^{2-} and $H_2PO_4^{-}$. Becker's study also confirmed that fluorine in phosphogypsum exists mainly in Na_2SiF_6 precipitate. Research by Hurst (1981) indicated that in phosphogypsum, uranium occurs mainly as U^{4+}, dispersing in the gypsum crystal lattice to replace Ca^{2+}, or as U^{6+}, being adsorbed as UO_2HPO_4 on the surface of gypsum. The results of the present study are inconsistent with their findings. The addition of sulfuric acid introduced hydrogen (H^+) ions and enhanced the hydrolytic actions for $LnPO_4$, $Ca_3(PO_4)_2$, $Ca(HPO_4)$, $Ca(H_2PO_4)_2$, Na_2SiF_6, UO_2HPO_4 and others. Therefore, more Ln^{3+}, HPO_4^{2-}, $H_2PO_4^{-}$, UO_2^{2-} and H_2SiF_6 entered the liquid phase. On the other hand, the gypsum dissolution and recrystallization in the leaching solution occurred constantly, whether or not a dynamic equilibrium was achieved. This caused Ca^{2+} and SO_4^{2-} to replace more impurities located in the gypsum crystal lattice. However, at high sulfuric acid concentration, excess SO_4^{2-} depressed the gypsum dissolution and crystallization process.

The major challenge to recovering REEs from phosphogypsum is high operating costs due to low REE content. The results of this study indicate that REE leaching may also clean the gypsum. Once the radioactivity of phosphogypsum is reduced to a level that meets the US Environmental Protection Agency (EPA) requirement, it can be used in the construction industry. Considering the huge economic and environmental benefits in this field, the process used in this study would be a promising approach for realizing phosphogypsum reutilization.

Conclusions

Laboratory experiments indicated that sulfuric acid solution could leach out REEs from phosphogypsum in addition to some detrimental impurities such as P_2O_5, U and F. When leaching for 120 min at a liquid/solid ratio of 4.0, REE leaching efficiency increased rapidly, obtained a maximum and then began to decrease. Tests were conducted at sulfuric acid concentrations ranging from 0 to 10.0 percent and temperatures ranging from 20 to 70°C. At a sulfuric acid concentration of 5.0 percent and a leaching temperature 50°C, REE leaching efficiency reached a high value of approximately 43 percent. Increasing the leaching time or liquid/solid ratio was beneficial to enhancing REE leaching efficiency. The leaching efficiencies of P_2O_5, U and F constantly increased with sulfuric acid concentration, temperature, leaching time and liquid/solid ratio within the testing ranges.

The location of the element within the phosphogypsum is a major factor affecting the leaching performance. Leaching efficiency is affected by gypsum dissolution and recrystallization if the REE, P_2O_5 and U are located within the gypsum crystal lattice. Addition of sulfuric acid could increase leaching efficiencies by enhancing dissolutions of $LnPO_4$, $Ca_3(PO_4)_2$, $Ca(HPO_4)$, $Ca(H_2PO_4)_2$, Na_2SiF_6, UO_2HPO_4 and so on. Additionally, longer leaching times resulted in greater REE, P_2O_5 and U leaching from the gypsum. Elutriation test results indicated that in the fine-grain gypsum concentrate, sized smaller than 40 μm, the contents of P_2O_5, U and F decreased by 99, 70 and 83 percent, respectively, compared with those in fresh phosphogypsum.

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