

Rare-earth leaching from Florida phosphate rock in wet-process phosphoric acid production

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Abstract

Phosphorite, or phosphate rock, is the most significant secondary rare-earth resource. It contains high amounts of phosphate-bearing minerals along with low contents of rare earth elements (REEs). In Florida, about 19 Mt of phosphate rock are mined annually and most are used to manufacture fertilizers using a wet process, in which sulfuric acid reacts with phosphates to produce phosphoric acid and phosphogypsum. In the wet process, REEs are also leached out into solution and eventually get lost in the leaching residue and phosphate fertilizer. Recovering REEs from Florida phosphate rock in the wet process will be beneficial to broadening rare-earth availability, improving the quality of phosphoric acid product and protecting the environment.

This study focuses on the influences of wet-process operating conditions on REE leaching efficiency. The results indicate that REE leaching efficiency increases with phosphoric acid addition in the initial pulp. At a temperature of 75 °C, a stoichiometric ratio of sulfuric acid (H_2SO_4) to calcium oxide (CaO) of 1.05 and a weight ratio of liquid to solid of 3.5, REE leaching efficiency reached a relatively high value of 52.82 percent. The trends of REE leaching efficiency were similar to those for phosphoric acid (P_2O_5). Extensive tests on the leaching residue showed that during leaching, about 90 percent of the REEs were released from the phosphate rock but only 52.82 percent ended up in the leaching solution. This phenomenon can be attributed to two factors: (1) the effect of phosphate ions (PO_4^{3-}) in the solution, which caused REE ions to form REE phosphates and be precipitated into the leaching residue, and (2) the influence of large amounts of anions such as sulfate (SO_4^{2-}), dihydrogen phosphate ($H_2PO_4^-$) and hydrogen phosphate (HPO_4^{2-}) anions as well as the polar molecule H_3PO_4 , which surrounded the REE cations and formed an ion atmosphere that prevented the PO_4^{3-} from contacting and combining with REE cations. Interaction of these two opposite effects determined the REE distribution between leaching solution and residue.

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Key words: Phosphate rock, Wet-process phosphoric acid production, Rare earths, Leaching efficiency

Introduction

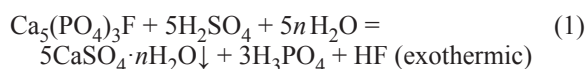
Phosphorite, or phosphate rock, is a sedimentary rock containing high amounts of phosphate-bearing minerals in which phosphate is mainly present as fluorapatite ($Ca_5(PO_4)_3F$), typically in cryptocrystalline masses, or as hydroxylapatite ($Ca_5(PO_4)_3OH$). Most of

the phosphorite mined is used in an industrial process, named wet process, to produce phosphoric acid, and the majority of the phosphoric acid is then converted into phosphate fertilizers (Becker, 1983).

In wet-process phosphoric acid production, sulfuric acid is used to digest the phosphate minerals. Taking fluorapatite as

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an example, the basic and simplified chemical reaction in the wet process can be expressed as (Zhang, 2014):

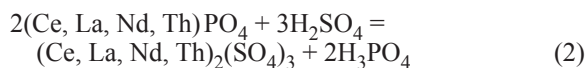


Depending on the value of n , the process is defined as: dihydrate ($n = 2$), hemihydrate ($n = \frac{1}{2}$) or anhydrate ($n = 0$).

The dihydrate process is the most widely used in phosphoric acid production plants because of its flexibility with regard to rock source and ease of operation (Becker, 1983). In this process, phosphate rock with 28 to 32 percent phosphoric acid (P_2O_5) content — P_2O_5 is generally used in the phosphate industry to represent phosphorus — is digested by sulfuric acid in a leaching tank (reactor). The pulp is then filtered, and a phosphoric acid product containing 27 to 30 percent P_2O_5 is obtained. The filter cake undergoes a three-stage, counter-current washing and is then disposed of to the stack, and the washing solution, containing approximately 16 to 19 percent P_2O_5 by weight, is recycled to the leaching tank. Generally, there are three important factors that need to be controlled in the leaching stage:

1. Sulfuric acid (H_2SO_4) addition: Determined by the amount of calcium oxide (CaO) in the solid feed. Usually, the stoichiometric ratio of H_2SO_4 to CaO is about 1.0.
2. Temperature: Controlled within a range of 70 to 80 °C by a cooling airflow or by a vacuum cooling system. Temperatures higher than 85 °C will lead to gypsum dehydration into hemihydrate calcium sulfate.
3. Ratio of liquid to solid: Usually about 3.5 by weight.

It is well known that there are some rare earth elements (REEs) in phosphorite, hosted in monazite ((Ce, La, Nd, Th) PO_4) or xenotime (YPO_4) or substituting for calcium in the phosphate crystals. Due to their low content levels, usually lower than 1 percent, and properties similar to other phosphates, these rare earth minerals cannot be economically beneficiated from the rock. In the wet process, these minerals also react with sulfuric acid according to the reactions:



Investigations by Abdel-Haleem et al. (2001) and Aydina et al. (2010) showed that most of the REEs in the phosphoric acid phase eventually end up in the phosphate fertilizer. Other researches indicated that rare-earth accumulation has a toxic effect on soil macrofauna community, and elements such as lanthanum (La), gadolinium (Gd) and ytterbium (Yb) in soil

at certain content levels can severely inhibit root elongation for some species of plants (Li et al., 2010; Ma et al., 2010), so application of REE-containing phosphate fertilizer may result in the long-term contamination of soil.

On the other hand, as valuable metal elements, REEs are widely used in many industries and are seeing increasing demand. In the past few years, global rare-earth supply and prices underwent sharp fluctuations as a result of China's rare-earth export restrictions. Many developed countries have begun to support and encourage greater exploration for rare earths to ensure supply for their domestic needs (Massari and Ruberti, 2013; Humphries, 2013).

Some 50 Mt of rare earths are estimated to exist in phosphate resources around the world, nearly 100 kt of which are mined in the annual production of phosphate rock (Kanazawa and Kamitani, 2006; Zhang, 2014). Evaluation by Emsbo et al. (2015) indicated that the concentrations and quantities of heavy REEs in U.S. phosphorites exceed those of all known resources, and the easy-to-extract REEs hosted in phosphorites are a potential source to meet global demand. In recent years, more and more attention has been paid to recovering rare earths from phosphate rock, both to increase rare-earth availability and to improve the quality of phosphoric products (Altschuler, Berman and Cuttitta, 1967; Wamser and Bruen, 1976; Habashi, 1985; Weterings and Janssen, 1985; Bunus and Dumitrescu, 1992; Bunus, Miu and Dumitrescu, 1994; Bunus, 2000; Preston et al., 1996; Monir and Nabawia, 1999; Koopman and Witkamp, 2000; Krea and Khalaf, 2000; Jorjani et al., 2008; Wang et al., 2010; Chtara, 2012; Zhang, 2012).

Florida has a large quantity of marine sedimentary phosphate deposits in its central regions. Nowadays, there are about 19 Mt of phosphate rock annually mined in these areas to produce fertilizer (Jasinski, 2011). Several researchers demonstrated the existence of many kinds of REEs in the phosphate rocks. Although their contents are low in phosphate matrix, the total REE amount in the reserves is considerable (Waring and Mela, Jr., 1953; Giesekke, 1985; Zhang, 2012, 2014).

In order to recover REEs from Florida phosphate processing, 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 five phosphate mining and processing streams: (1) waste clay, (2) amine flotation tails, (3) phosphoric acid, (4) phosphogypsum and (5) sludge from phosphoric acid concentration and clarification. This paper is focused on the leaching of REEs from phosphate rock during the wet-process phosphoric acid operation.

Experimental

Phosphate rock sample and chemical reagents. About 100 kg of representative ground phosphate rock were pro-

Table 1 — Main chemical components and rare earth elements in the phosphate rock.

Component	P ₂ O ₅		CaO	Fe ₂ O ₃	MgO	Al ₂ O ₃	F		
Content (%)	27.38		40.10	1.24	0.62	1.08	3.24		
Element	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd
Content (ppm)	5.82	110.33	64.00	105.14	6.49	74.12	0.00	8.05	14.36
Element	Tb	Dy	Ho	Er	Tm	Yb	Lu	Total REEs	
Content (ppm)	1.73	12.16	0.00	8.50	3.03	7.42	1.19	422.34	

Table 2 — Particle-size distribution of the phosphate rock sample.

Screen mesh	Size (um)	Yield (%)	Content of chemical component (%)					
			P ₂ O ₅	CaO	MgO	Fe ₂ O ₃	Al ₂ O ₃	Total REE (ppm)
+14	+1,400	0.10	10.16	15.22	0.72	1.19	1.04	108.24
-14+30	-1,400+600	2.86	27.20	40.41	0.68	1.18	0.97	244.18
-30+50	-600+300	19.77	28.80	42.49	0.60	1.31	1.01	315.25
-50+70	-300+212	18.35	27.05	39.60	0.52	1.19	0.92	474.92
-70+100	-212+150	18.76	26.59	38.54	0.53	1.14	0.96	525.15
-100+140	-150+104	12.62	27.56	39.94	0.57	1.24	1.08	519.18
-140+170	-104+90	8.80	26.68	39.07	0.61	1.26	1.20	384.82
-170+200	-90+75	2.66	27.00	39.68	0.66	1.31	1.25	369.50
-200+270	-75+53	2.79	27.31	39.60	0.64	1.32	1.21	374.78
-270+325	-53+45	9.68	27.28	40.38	0.77	1.32	1.35	369.77
-325	-45	3.70	28.09	40.43	0.91	1.35	1.47	371.18
Total/Weighted average		100.00	27.40	40.07	0.60	1.24	1.07	423.89

vided by Mosaic Co. (Plymouth, MN), the largest phosphate fertilizer manufacturer in Florida. After thorough mixing in our laboratory, the phosphate rock sample was divided into aliquot portions of 400 g each, one for each experiment. The relative deviations of P₂O₅ and total REE contents and each size fraction yield tested among aliquots were no more than 1.0, 2.5 and 3.5 percent, respectively.

The phosphate rock sample was the beneficiation concentrate of the sedimentary phosphorite deposited in Polk County, FL. Mineralogical examination indicated that francolite was the main phosphorus-bearing mineral and contained about 95 percent of the phosphorus in the sample. The francolite was found to be white to tan and dark gray in all particle-size fractions. The principal gangue mineral was quartz, followed by calcite, dolomite, albite and potassium feldspar. In the slime portion, some clay minerals were found, including smectite, palygorskite and kaolinite. Monazite and xenotime were the main REE-containing minerals, and both of them were in minute amounts. Table 1 shows the content levels of the main chemical components and REEs in the sample, while Table 2 shows the particle-size distribution.

Stock solutions of REEs for analysis were purchased from Fisher Scientific (Waltham, MA). Deionized water was used in solution preparation and washing residue. Unless indicated otherwise, all reagents were reagent grade.

Leaching studies. The dihydrate wet process of phosphoric acid production was simulated in a 2.5-L water-bath batch reactor to investigate the influences of main factors on REE leaching efficiency. In each leaching test, 400 g of phosphate rock were used, and the leaching solution was sampled every 15 minutes to monitor the leaching progress through chemical analysis. After leaching, the pulp was filtered, and the residue was washed three times. REEs, CaO, magnesium oxide (MgO), iron oxide (Fe₂O₃) and aluminum oxide (Al₂O₃) in both solution samples and residue were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) using an Optima 8300 spectrometer (PerkinElmer, Waltham, MA). P₂O₅ and fluorine (F) were determined using a spectrophotometer and a fluoride ion selective electrode, respectively. Based on our experience, the relative deviations of mass balances for P₂O₅ and total REEs in each leaching test were set as less than

2.0 and 3.0 percent, respectively. Any test beyond these two error limits had to be conducted again.

Results and discussion

Effect of leaching time. First of all, a series of conventional operation conditions in the wet-process practice were applied to the batch leaching of this study to determine the effect of leaching time. The results are shown in Fig. 1. After leaching for 165 min, the concentrations of the main REEs Y (yttrium), La (lanthanum), Ce (cerium) and Nd (neodymium) as well as total REEs and P₂O₅ in the pulp all nearly reached their maximums. After leaching for 180 min, all concentrations of these species leveled off, so the leaching time for subsequent tests was set at 180 min.

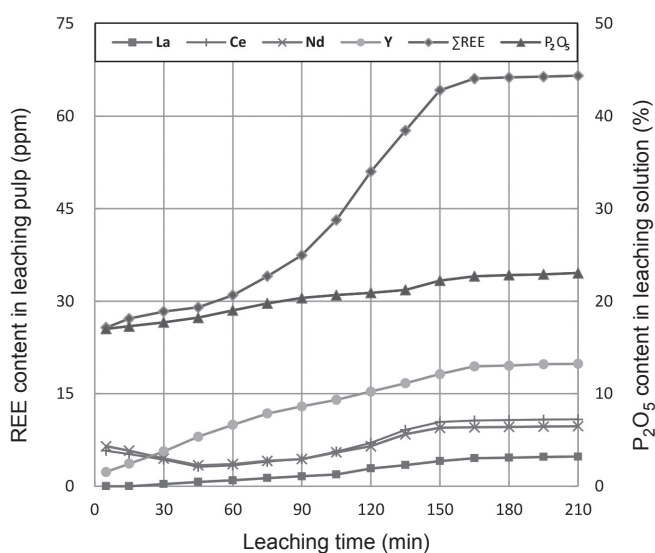


Figure 1 — Changes of four main REE and P₂O₅ contents in leaching pulp with time (leaching temperature = 75 °C; initial P₂O₅ content in pulp = 17 percent; stoichiometric ratio of H₂SO₄ to CaO = 1.05; ratio of liquid to solid = 3.5).

Effect of initial phosphoric acid concentration in pulp.

Studies by Wang et al. (2010) showed that adding phosphoric acid to the pulp before leaching is beneficial for both P_2O_5 and REE leaching. In this study, therefore, phosphoric acid was used as a lixiviant, and a series of experiments were performed with P_2O_5 concentrations ranging from 5 to 21 percent in the initial pulps. The results in Fig. 2 show that both P_2O_5 and REE leaching efficiencies increased with the initial addition of phosphoric acid, and they presented a similar trend.

Although the increase of phosphoric acid addition is beneficial to P_2O_5 leaching efficiency, it is not used in wet-process practice because high phosphoric acid concentration means high viscosity of the solution, which will cause more difficulties for subsequent solid/liquid separation. The only way that phosphoric acid is introduced into the leaching system in industrial operation is in the residue-washing liquid, which contains about 16 to 19 percent P_2O_5 and is recycled to the leading end of the leaching tank (Becker, 1983). In order to keep in line with wet-process practice, in this study the phosphoric acid addition was set at 17 percent P_2O_5 in the initial pulp in the following leaching experiments.

Effect of temperature. A series of experiments were performed to investigate the effect of temperature on REE leaching efficiency in the range of approximately 60 to 80 °C. The results shown in Fig. 3 reveal that the REE leaching efficiency first increased with temperature to about 52 percent — calculated value 52.82 percent — at 75 °C, and then dropped sharply.

Increasing temperature can speed up the chemical reactions in the system, but it does not necessarily increase P_2O_5 and REE leaching efficiencies. High leaching efficiencies are dependent on good coordination and equilibrium between the fluorapatite digestion rate and the gypsum precipitation rate. In the leaching system, with the digestion going on, more and more calcium ions (Ca^{2+}) were released from minerals. When the ion product of Ca^{2+} and sulfate ions (SO_4^{2-}) exceeded the solubility product of gypsum, they began to build up gypsum crystals. Increasing Ca^{2+} concentration can promote the crys-

tallization speed, but there is a limit. In the case of high rate of crystallization, more hydrogen phosphate (HPO_4^{2-}) and REE ions as well as other impurities will be wrapped into the gypsum crystal lattice, resulting in low P_2O_5 and REE leaching efficiencies. If the mineral digestion rate is much higher than the crystallization rate, Ca^{2+} will accumulate in the solution to a high concentration, which will slow down the migration and diffusion of newly released Ca^{2+} from phosphate minerals and lead to a serious problem that Ca^{2+} and SO_4^{2-} position on phosphate mineral particle surfaces and form a gypsum crystal coating to protect the mineral from further attack by sulfuric acid. On the contrary, too low a temperature is not conducive to the attack to refractory phosphate mineral by sulfuric acid, also resulting in low leaching efficiencies.

It can be seen from the test results that, within the tested temperature range, REE leaching efficiency presents a similar trend to that of P_2O_5 , and all of them reached their highest values at 75 °C, so 75 °C was set in the following leaching tests.

Effect of stoichiometric ratio of H_2SO_4 to CaO . According to Eqs. (1) to (3), sulfuric acid addition to the system must meet the need for phosphate mineral digestion. Besides, sulfuric acid concentration in the solution exerts an important influence on REE and P_2O_5 leaching efficiencies, because it is closely related to mineral digestion speed. Increasing sulfuric acid concentration will speed up mineral digestion. But, as stated above about temperature effects, increased digestion speed will lead to more HPO_4^{2-} and REE ions lost in gypsum crystal lattice and result in the formation of a gypsum coating on phosphate mineral surfaces, so too much sulfuric acid addition is adverse to enhancing REE or P_2O_5 leaching efficiency. On the other hand, decreasing sulfuric acid concentration will weaken the acid attack on phosphate minerals and finally leave more refractory phosphate minerals undigested. In leaching tests, with the mineral digestion going on, sulfuric acid concentration decreased gradually. When it reduced to a very low level, the digestion reactions stopped.

From the results in Fig. 4 it can be seen that with increased

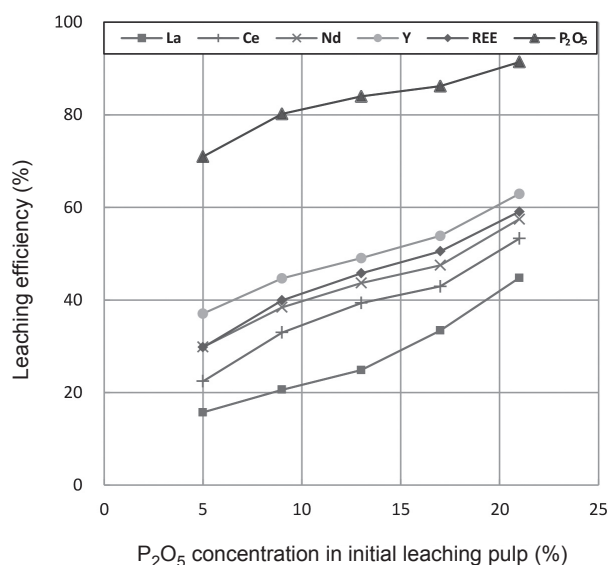


Figure 2 — Effect of phosphoric acid concentration in initial pulp on leaching efficiency (leaching temperature = 70 °C; stoichiometric ratio of H_2SO_4 to CaO = 1.05; ratio of liquid to solid = 3.5).

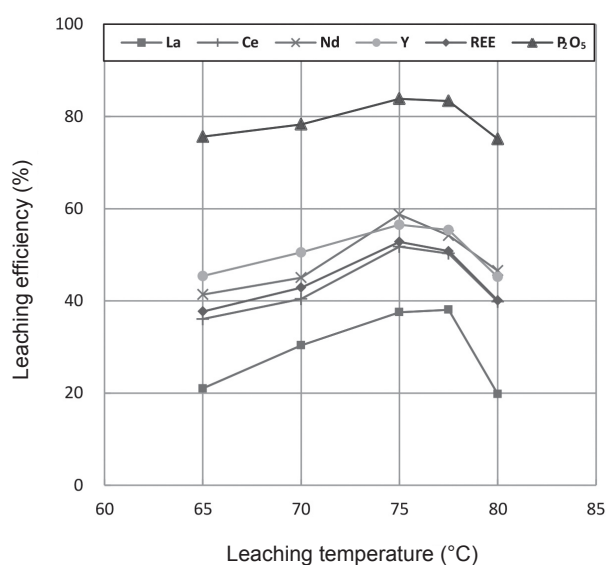


Figure 3 — Effect of temperature on rare-earth leaching efficiency (17 percent P_2O_5 in initial leaching pulp; stoichiometric ratio of H_2SO_4 to CaO = 1.05; ratio of liquid to solid = 3.5).

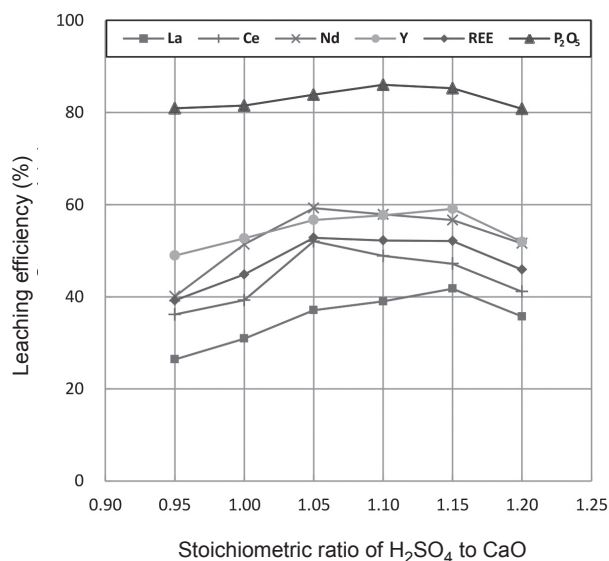


Figure 4 — Effect of stoichiometric ratio of H₂SO₄ to CaO on rare-earth leaching efficiency (17 percent P₂O₅ in initial leaching pulp; leaching temperature = 75 °C; ratio of liquid to solid = 3.5).

ratio of H₂SO₄ to CaO, both REE and P₂O₅ leaching efficiencies first trended upward and then descended. The maximum of total REE leaching efficiency, about 52 percent, occurred at the stoichiometric ratio of H₂SO₄ to CaO of 1.05, versus the ratio of 1.10 for maximum P₂O₅ leaching efficiency. This discrepancy may result from different reaction mechanisms between REE-bearing minerals and apatite, respectively, with sulfuric acid. In order to get higher REE leaching efficiency, the stoichiometric ratio of H₂SO₄ to CaO was set at 1.05 in the following experiments.

Effect of liquid to solid ratio. The effect of liquid to solid weight ratio on REE leaching efficiency was tested in the range of 2.50 to 4.50. The results in Fig. 5 show that the REE leaching efficiency significantly increased first as the ratio rose until it reached a maximum, about 52 percent, at the ratio of liquid to solid of 3.50 and then turned in the opposite direction.

Considered from the viewpoint of initial sulfuric acid concentration in solution, the trend of REE leaching efficiency in Fig. 5 is in accordance with that in Fig. 4. In Fig. 5, the initial sulfuric acid concentration reduced with the increase in liquid to solid ratio, whereas in Fig. 4 it increased with the rise of the stoichiometric ratio of H₂SO₄ to CaO. From the liquid to solid ratio of 3.50 to 2.50 in Fig. 5, both REE and P₂O₅ leaching efficiencies dropped with increased initial sulfuric acid concentration, similar to the trends in Fig. 4 from the H₂SO₄ to CaO ratio of 1.05 to 1.20. These trends can be attributed to the exorbitant initial sulfuric acid concentration in the solution. As stated earlier, too high a sulfuric acid concentration would lead to a very high mineral digestion speed and thus result in the problems of REE loss in gypsum crystal lattice and gypsum coating on phosphate mineral surfaces. On the other hand, comparing the changes from the liquid to solid ratio of 3.5 to 4.5 in Fig. 5 with the changes from the H₂SO₄ to CaO ratio of 1.05 to 0.95 in Fig. 4 showed that both REE and P₂O₅ leaching efficiencies decreased with the initial sulfuric acid concentration. This can be ascribed to the power of acid attacks on the phosphate minerals decreasing with sulfuric acid

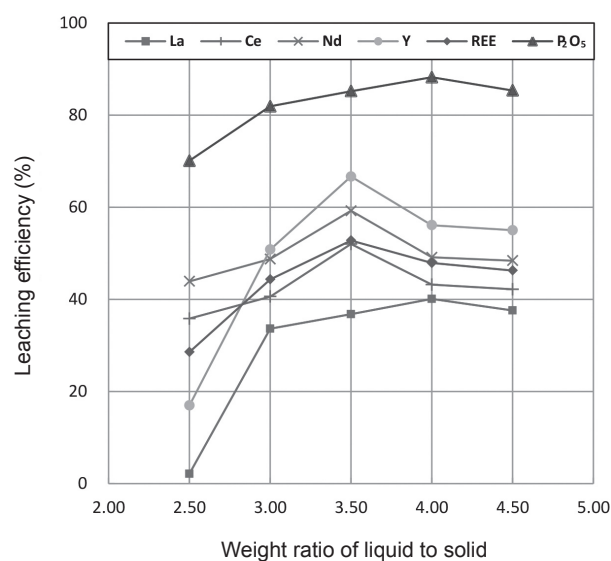


Figure 5 — Effect of ratio of liquid to solid on rare-earth leaching efficiency (17 percent P₂O₅ in initial leaching pulp; leaching temperature = 75 °C; stoichiometric ratio of H₂SO₄ to CaO = 1.05).

concentration. The initial sulfuric acid concentration therefore exerted a significant influence on REE and P₂O₅ leaching efficiencies. Besides, as the liquid to solid ratio decreased from 3.5 to 2.5, the leaching pulp became stickier, mainly due to the phosphoric acid dissolving in less water, which is another factor causing leaching efficiency to drop by depressing mass transfer velocity in the system.

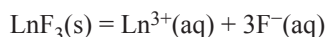
Analyses

Testing the REE distribution in the leaching residue revealed only about 10 percent REEs still existing in their primary mineral phases, which was also verified by phosphogypsum leaching tests, meaning about 90 percent of the REEs had been released from the phosphate rock in our leaching test. However, the experimental results above show only 52.82 percent of the REEs occurred in the leaching solution. It is essential to find out the reasons that caused this phenomenon.

As shown in the chemical equations of Eqs. (1) to (3), with the mineral digestion going on in the leaching test, more and more Ca²⁺, phosphate (PO₄³⁻), fluoride (F⁻) and REE ions were released from the minerals. Most of the SO₄²⁻ and PO₄³⁻ transferred into the products gypsum (CaSO₄·2H₂O) and phosphoric acid, but there were still some SO₄²⁻, PO₄³⁻ and F⁻ in the solution. These anions all had the potential to combine with REE ions to form precipitates. The concentration of SO₄²⁻, PO₄³⁻ or F⁻ and the solubility of the corresponding REE salt Ln₂(SO₄)₃, LnPO₄ or LnF₃, with Ln representing any one of the REEs, were the main factors determining the generation and amount of each REE precipitate.

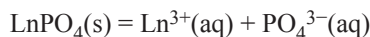
The solubilities of Ln₂(SO₄)₃, LnPO₄ and LnF₃ have been reported in the literature. Work by Spedding and Jaffe (1954) indicated that REE sulfates have moderate solubility in water. For the 10 REE sulfates tested, solubilities were all above 1 g in 100 g of water and the highest solubility, that of Yb₂(SO₄)₃, reached 36.01, whereas REE fluorides and phosphates showed very low solubilities at 25 °C in low-ionic-strength aqueous solution (Menon and James, 1989; Firsching and Brune, 1991;

Byrne and Kim, 1993; Liu and Bryne, 1997; and Cetiner, Wood and Gammons, 2005). In their saturated aqueous solutions, REE fluorides and phosphates are subject to the following dissolution-precipitation equilibria and ion concentration relationships:



$$K_{\text{sp}}^0(\text{LnF}_3) = \gamma_1 [\text{Ln}^{3+}(\text{aq})] \gamma_2 [\text{F}^{-}(\text{aq})]^3 \quad (4)$$

$$[\text{Ln}^{3+}(\text{aq})] = K_{\text{sp}}^0(\text{LnF}_3) / (\gamma_1 \gamma_2 [\text{F}^{-}(\text{aq})]^3)$$



$$K_{\text{sp}}^0(\text{LnPO}_4) = \gamma_3 [\text{Ln}^{3+}(\text{aq})] \gamma_4 [\text{PO}_4^{3-}(\text{aq})] \quad (5)$$

$$[\text{Ln}^{3+}(\text{aq})] = K_{\text{sp}}^0(\text{LnPO}_4) / (\gamma_3 \gamma_4 [\text{PO}_4^{3-}(\text{aq})])$$

where K_{sp}^0 is the activity product of REE fluoride or phosphate; γ_1 and γ_2 represent the activity coefficients of Ln^{3+} and F^{-} , respectively, in a saturated REE fluoride solution; and γ_3 and γ_4 denote the activity coefficients of Ln^{3+} and PO_4^{3-} , respectively, in a saturated REE phosphate solution. The solubilities of the REE sulfates, fluorides and phosphates reported are listed in Table 3.

Table 3 can be used to determine the kind of REE precipitates generated in the leaching system and explain the reason for the low REE leaching efficiency. In particular, taking the leaching test with the high REE leaching efficiency of 52.82 percent and conditions of 17 percent P_2O_5 in the initial leaching pulp, leaching temperature of 75 °C, stoichiometric ratio of H_2SO_4 to CaO of 1.05 and ratio of liquid to solid of 3.50 as an example to discuss this further.

Table 3 — Solubilities of REE sulfates, fluorides and phosphates in aqueous solution at 25 °C. (Data sources: $\text{Ln}_2(\text{SO}_4)_3$: Spedding, 1954; LnF_3 : Menon and James, 1989, corrected to $\log K_{\text{sp}}^0$; LnPO_4 : Liu and Bryne, 1997).

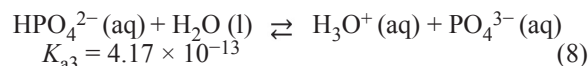
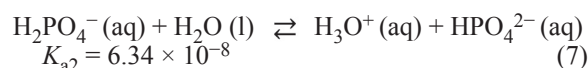
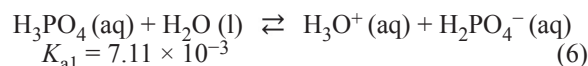
REE	$\text{Ln}_2(\text{SO}_4)_3$ (g per 100 g of water)	LnF_3 ($\log K_{\text{sp}}^0$)	LnPO_4 ($\log K_{\text{sp}}^0$)
Y	9.67	—	−25.02
La	2.14	−15.08	−25.75
Ce	5.06	−16.42	26.27
Pr	10.88	−16.93	−26.43
Nd	5.59	−17.79	−26.20
Pm	—	—	—
Sm	1.49	−15.90	−26.19
Eu	—	−15.35	−25.96
Gd	3.30	−17.13	−25.62
Tb	—	−16.00	−25.39
Dy	—	−15.15	−25.18
Ho	6.71	−14.04	−25.07
Er	15.19	−14.67	−25.13
Tm	—	−16.01	−25.03
Yb	36.01	−15.18	−24.89
Lu	—	−14.25	−24.75

The concentration of SO_4^{2-} in the leaching solution depended on the dissolution-precipitation equilibrium of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Gypsum solubility is 0.20 to 0.25 g per 100 g of water at 25 °C (Haynes, 2015), much lower than that of any of the REE sulfates shown in Table 3, so Ca^{2+} will take precedence over Ln^{3+} in combining with SO_4^{2-} in their mixed solution with same concentrations of Ca^{2+} and Ln^{3+} . Considering that the leaching solution was gypsum saturated, and that the REE concentration — 73.69 ppm total REE — was much lower than the Ca^{2+} concentration, it can be concluded that SO_4^{2-} did not lead to the REE precipitation in the leaching system.

The phosphate rock used in our test contained 3.24 percent fluorine (Table 1). Investigations by Becker (1983) discovered that fluorine undergoes a series of conversions during wet-process phosphoric acid production. Firstly, it is converted into hydrogen fluoride (HF) by sulfuric acid, as in Eq. (1), then most of the HF reacts with silica or aluminosilicate hosted in the phosphate feed to form hexafluorosilicic acid (H_2SiF_6) and aluminium hydrogen fluoride (H_3AlF_6). Some of these generated acids volatilize with water vapor during leaching, and most of the rest combine with Ca^{2+} , Mg^{2+} , Al^{3+} , sodium (Na^+), potassium (K^+) and other ions in the solution. Research by Frazier, Lehr and Dillard (1977) indicated that there are about 12 possible fluoride compounds eventually precipitating from the phosphoric acid product.

It is hard to accurately determine the amount of all the fluorine conversions in the system, because the emissions of volatile compounds such as HF and H_2SiF_6 and the precipitations of many fluoride compounds vary with operating conditions, and these changes last a long time. Even after leaching, these conversions still occur (Becker, 1983). In our test, the active F^{-} concentration in solution at the end of leaching was determined by a fluoride ion selective electrode as 1.29×10^{-4} mol/L (2.02 ppm, solution density 1.215 kg/cm³).

The concentrations of phosphate ions in the leaching solution cannot be analytically determined, but they can be calculated by using their dissociation equilibrium constants. In aqueous solution, phosphoric acid ionizes in three steps at 25 °C (Firsching and Brune, 1991):



In view of phosphoric acid dissociation constant $K_{\text{a1}} \gg K_{\text{a2}} \gg K_{\text{a3}}$, phosphorus in aqueous solution existed mostly in phosphoric acid (H_3PO_4) and dihydrogen phosphate (H_2PO_4^-). The relationships of H_3PO_4 , H_2PO_4^- , HPO_4^{2-} , PO_4^{3-} and hydronium (H_3O^+) in the leaching solution can therefore be expressed as:

$$[\text{H}_3\text{PO}_4] = C_{\text{T}} - [\text{H}_2\text{PO}_4^-] - [\text{HPO}_4^{2-}] - [\text{PO}_4^{3-}]$$

$$\approx C_{\text{T}} - [\text{H}_2\text{PO}_4^-] \quad (9)$$

$$[\text{H}_2\text{PO}_4^-] = K_{\text{a1}} \times [\text{H}_3\text{PO}_4] / [\text{H}_3\text{O}^+] \quad (10)$$

$$[\text{HPO}_4^{2-}] = K_{\text{a2}} \times [\text{H}_2\text{PO}_4^-] / [\text{H}_3\text{O}^+] \quad (11)$$

$$[\text{PO}_4^{3-}] = K_{\text{a3}} \times [\text{HPO}_4^{2-}] / [\text{H}_3\text{O}^+] \quad (12)$$

where C_{T} is the total phosphorus concentration, which was analyzed as 4.278 mol/L (25.0 weight percent P_2O_5 , solution density 1.215 kg/cm³).

Table 4 — REE concentrations in different dissociation-precipitation equilibrium solutions at 25 °C ($[F^-] = 1.85 \times 10^{-6}$ mol/L; $[PO_4^{3-}] = 1.00 \times 10^{-20}$ mol/L).

REE	Calculated REE concentrations in low-ionic-strength salt solution (M)		Analyzed REE concentrations in leaching solution (M)	
	LnF_3 ($\times 10^{-6}$)	$LnPO_4$ ($\times 10^{-6}$)	Leaching test solution ($\times 10^{-6}$)	Wet-process phosphoric acid product ($\times 10^{-6}$)
Y	—	9.53	342.17	661.71
La	292.28	1.77	75.94	173.79
Ce	14.65	0.54	114.91	259.86
Pr	4.63	0.37	4.29	5.18
Nd	0.58	0.63	95.08	198.49
Sm	46.32	0.64	0.00	0.00
Eu	146.49	1.09	23.14	32.46
Gd	2.92	2.39	20.54	25.31
Tb	36.80	4.07	3.60	3.46
Dy	232.16	6.59	14.10	14.52
Ho	2,922.75	8.49	0.00	0.00
Er	734.16	7.40	19.22	18.59
Tm	36.80	9.31	15.26	13.14
Yb	232.16	12.86	14.16	28.55
Lu	1,844.13	17.75	1.73	4.06

In the leaching solution, the H^+ came from the sulfuric acid and was mainly consumed by the formation of HPO_4^{2-} , $H_2PO_4^-$ and H_3PO_4 . The total sulfuric acid added to the leaching system was 3.008 moles. Analyses and tests on the leaching residue indicated that there were 0.059 mole of MgO , 0.019 mole of Fe_2O_3 and 0.036 mole of Al_2O_3 — respectively representing actual Mg-bearing, Fe-bearing and Al-bearing minerals — leached out from the phosphate rock, and 0.210 mole of CaO — accounting for 7.33 percent of total CaO in the phosphate feed — still existed in its original minerals. On the basis of stoichiometry of sulfuric acid reacting with MgO , Fe_2O_3 , Al_2O_3 and CaO , it can be calculated that there still was 0.214 mole of spare sulfuric acid left in the final leaching solution. In addition, according to Eq. (1), the solution mass at the end of leaching changed to 1,211.0 g, disregarding the small changes from sulfuric acid reacting with other minerals, in which the calculated H_3O^+ concentration was 0.429 mol/L.

By combining Eqs. (9), (10), (11) and (12) and substituting the values for C_T , K_{a1} , K_{a2} , K_{a3} and $[H_3O^+]$, the values of $[H_3PO_4]$, $[H_2PO_4^-]$, $[HPO_4^{2-}]$ and $[PO_4^{3-}]$ can be derived as:

$$[H_3PO_4] = 4.21 \text{ mol/L}$$

$$[H_2PO_4^-] = 6.97 \times 10^{-2} \text{ mol/L}$$

$$[HPO_4^{2-}] = 1.03 \times 10^{-8} \text{ mol/L}$$

$$[PO_4^{3-}] = 1.00 \times 10^{-20} \text{ mol/L}$$

The REE equilibrium concentration can be calculated by applying the solubility products of LnF_3 and $LnPO_4$ (Table 3), and Eqs. (4) and (5), respectively, to a very dilute aqueous solution — for example, a solution with LnF_3 and NaF or $LnPO_4$ and Na_3PO_4 — in which LnF_3 or $LnPO_4$ reaches the dissolution-precipitation equilibrium and the concentration

of F^- or PO_4^{3-} is exactly the same value as in our leaching solution: that is, 1.85×10^{-6} or 1.00×10^{-20} mol/L. Since the ion concentration in these two solutions is very low, all the activity coefficients in Eqs. (4) and (5) can be recommended as 1.0. The calculated values and the analysis results of REE concentrations in our laboratory leaching solutions and in a Florida wet-process phosphoric acid product (28.67 percent P_2O_5 , solution density 1.254 kg/cm³) are shown in Table 4.

It can be seen from Table 4 that except for Nd and Gd, all of the other REE equilibrium concentrations in the LnF_3 saturated solution are much higher than those in the $LnPO_4$ saturated solution. As the Nd and Gd concentrations in the leaching solution were very low, it can be inferred that PO_4^{2-} was the determinant for REE concentrations in the solution.

On the other hand, it can be seen in Table 4 that each of the analyzed REE concentrations in either our laboratory leaching solution or wet-process phosphoric acid product is higher than the calculated value in the low-ionic-strength $LnPO_4$ solution, except for those low-concentration elements terbium (Tb), lutetium (Lu), samarium (Sm) and holmium (Ho). The largest difference appears for cerium (Ce), whose concentration in the leaching solution was up to 213 times higher than the calculated value in $LnPO_4$ solution. These discrepancies can be attributed to the ionic strength difference between these two solutions. Compared with the low-ionic-strength solution, the leaching solutions had many more anions such as SO_4^{2-} , $H_2PO_4^-$ and HPO_4^{2-} as well as polar molecule H_3PO_4 that could attract and surround the REE cations, forming a strong ion atmosphere to prevent PO_4^{3-} from contacting and combining with REE ions. As a result, many REE ions were kept in the leaching solution, so it can be concluded that ionic strength, especially anion concentrations in solution, is a decisive factor for determining REE concentration, and that adjusting ion atmosphere restriction to REE ions should be an important approach to control REE concentration in the leaching solution.

Conclusions

Laboratory experiments indicated that the REE leaching efficiency of Florida phosphate rock was affected significantly by four factors: (1) phosphoric acid content in the initial pulp, (2) leaching temperature, (3) sulfuric acid addition and (3) ratio of liquid to solid. As the phosphoric acid addition increased from 5 percent to 21 percent in the initial pulp, the REE leaching efficiency rose steadily. Within the ranges of leaching temperatures of 65 to 80 °C, stoichiometric ratio of H_2SO_4 to CaO of 0.95 to 1.20 and weight ratio of liquid to solid of 2.5 to 4.5, a high REE leaching efficiency of 52.82 percent was achieved at a temperature of 75 °C, H_2SO_4 to CaO ratio of 1.05 and liquid to solid ratio of 3.5. In all of the leaching tests, REE leaching efficiency showed similar trends to P_2O_5 leaching efficiency.

Analyses indicated that PO_4^{3-} in the leaching solution was the main species that combined with REE ions to form REE phosphates and precipitated into the leaching residue. However, there were large amounts of anions such as SO_4^{2-} , H_2PO_4^- and HPO_4^{2-} as well as the polar molecule H_3PO_4 , which surrounded the REE cations and formed an ion atmosphere to prevent PO_4^{3-} from contacting with them. Interaction of these two opposite effects determined the REE distribution between leaching solution and residue.

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