

Extraction of rare earth elements from upgraded phosphate flotation tailings

S. Al-Thyabat

Professor, Mining Engineering Department, Al-Hussein Bin Talal University, Ma'an, Jordan
Corresponding author email: althyabat@yahoo.co.uk

P. Zhang

Director of beneficiation, Florida Industrial and Phosphate Research Institute (FIPR), Bartow, FL, USA

Abstract

Phosphate rock contains traces of rare earth elements (REEs) and can be a secondary source of these critical materials as large tonnages of phosphate rock are mined annually. Attention has mostly focused on the extraction of REEs from phosphogypsum, which contains more than 70 percent of the REEs reporting to phosphate concentrate, with only limited work conducted on REE extraction from sand tailings and slime even though they account for 16 percent and 15 percent, respectively, of REEs mined with phosphate matrix.

In this work, phosphate flotation tailings were upgraded by gravity separation and froth flotation. Gravity separation was conducted using a laboratory shaking table, while flotation was conducted in a Denver D-12 flotation cell. The concentrated tailings were then leached by nitric acid followed by REE extraction with solvent and ion-exchange resin.

The sand tailings were assayed as having 2.6 percent phosphate (P_2O_5) and 198.1 $\mu\text{g/g}$ REEs. It was found that the shaking table could produce tailing concentrate assayed as having 8.6 percent P_2O_5 and 616 $\mu\text{g/g}$ REEs but with only 20 percent REE recovery, while the froth flotation produced froth concentrate assayed as having 8.1 percent P_2O_5 and 368.2 $\mu\text{g/g}$ REEs with 63.5 percent REE recovery. Leaching the flotation concentrate with 5.2 M (25 percent) nitric acid followed by extraction with solvent and ion-exchange resin yielded precipitates with REE contents of 0.926 and 0.314 percent, respectively, compared with 0.716 and 0.213 percent when table concentrate was used.

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Introduction

Rare earth elements (REEs) consist of a group of 17 elements: the 15 lanthanides along with yttrium (Y) and scandium (Sc). They are rare not because of their scarcity in the Earth's crust but because they are rarely found in economic and mineable deposits. REEs are called "seeds of technology" because of their importance to some critical technological industries such as renewable energy, hybrid cars, electronics and batteries. On average, an electric car or a hybrid car contains about 10 kg of REEs (Grasso, 2012; Radhika et al., 2011).

REEs are usually categorized into light (LREE) and heavy (HREE). LREEs consist of lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pr), samarium (Sm), europium (Eu), gadolinium (Gd) and scandium (Sc), while HREEs consist of terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), lutetium (Lu) and yttrium (Y). About 200 minerals contain traces of REEs, but only three are considered economically significant: bastnasite, with the formula $\text{La,Ce}(\text{CO}_3)\text{F}$; monazite, with the formula $(\text{Ce,La,Nd,Th})\text{PO}_4$; and xenotime, with the formula

YPO_4 (Jordens, Cheng and Waters, 2013).

Phosphate rock, assayed as having about 0.01-0.6 percent REEs, is regarded as a secondary REE source (Koopman and Witkamp, 2000; Preston, Cole, Craig and Feather, 1996). The REE distribution depends on the rock source. REEs usually substitute the calcium ions (Ca^{+2}) in apatite mineral, making their concentration proportional to phosphate (P_2O_5) concentration (Habashi, 1985; Lambert and Tognet, 1987; Jorjani et al., 2008).

Phosphate rock is usually mined by large draglines, which is followed by a series of beneficiation processes such as washing, screening, desliming and flotation to raise the phosphate grade to fertilizer production requirements. Phosphate beneficiation generates four main streams: flotation concentrate, pebble product, sand tailings and waste clay, or slime. The pebble product is usually ground and mixed with the concentrate, forming the fertilizer plant feed, and the concentrate is then reacted with a mixture of sulfuric acid and recycled phosphoric acid to produce crude phosphoric acid with 28-30 percent P_2O_5 along with phosphogypsum waste. In Fig. 1, which shows a flowsheet for the process of producing phosphoric acid, approximately 1 t of phosphate concentrate, with 30 percent P_2O_5 , is required to produce 1 t of crude phosphoric acid, with 30 percent P_2O_5 , and 5 t of phosphogypsum waste (Guan, 2009; Zhang, Yu and Bogan, 1997; Becker, 1987).

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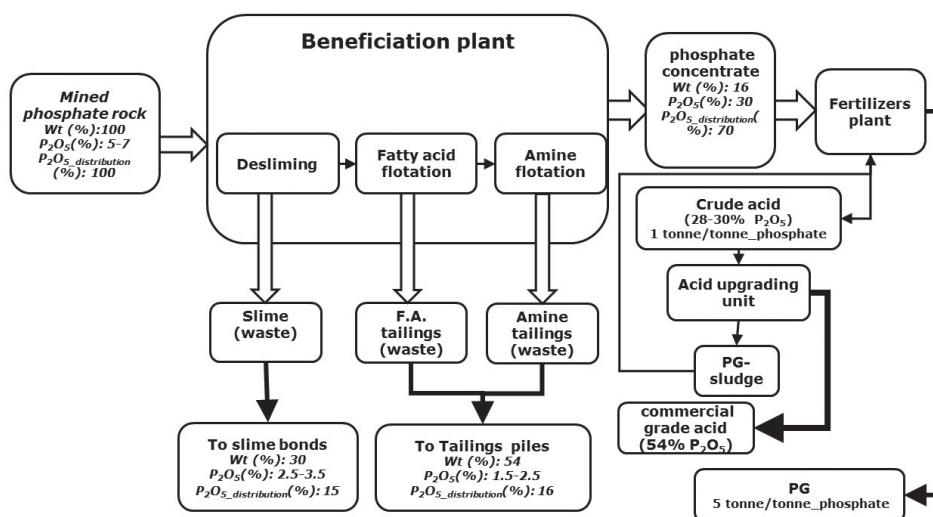


Figure 1 — Typical phosphate distribution in phosphoric acid production process.

Table 1 — Chemical analysis of flotation tailings.

Oxide	Major oxides Concentration (weight %)	Impurity distribution (%)
P ₂ O ₅	2.6	—
CaO	4.2	4.5
MgO	0.02	0.02
Al ₂ O ₃	0.25	0.27
Fe ₂ O ₃	0.37	0.39
Acid insoluble (A.I.)	88.9	94.9
Total impurities	93.7	100
Rare earth elements (REEs)		
REE	Concentration (µg/g)	Distribution (%)
Ce	53.0	26.7
La	27.0	13.6
Pr	7.7	3.9
Nd	1.7	0.8
Sm	4.0	2.0
Eu	6.0	3.0
Y	40.2	20.3
Gd	1.8	0.9
Tb	11.2	5.7
Dy	0.55	0.3
Er	0.28	0.1
Ho	2.5	1.3
Yb	30.9	15.6
Lu	7.8	3.9
Tm	1.6	0.8
Sc	2.1	1.1
Total REEs	198.2	100

Assuming that REE distribution follows that of phosphate and that about 70-80 percent of REEs in the phosphate concentrate report to phosphogypsum stacks, it follows that about 16 and 15 percent of the REEs in the mined phosphate rock are lost in tailings piles and slime ponds, respectively. Nevertheless, there has been little research on REE extraction from tailings piles and slime ponds, with most of the research conducted so far centered on REE extraction from phosphogypsum and phosphoric acid, which account for 70 percent of REEs in the mined phosphate rock. Furthermore, 54 and 30 percent by weight of mined phosphate rock end up in tailing piles and slime ponds, respectively, causing serious environmental problems for beneficiation plants, so any attempt to extract REEs or phosphate from these wastes may be justified from an environmental viewpoint at least (Koopman and Witkamp, 2002; Preston, Cole, Preez et al., 1996; Wang et al., 2010).

Various researchers have investigated REE extraction from conventional and secondary sources. Recent developments in REE mineral characterization and flotation reagents can be found in the works of Pradip and Fuerstenau (2013) and Lin, Hsieh and Miller (2013). Regarding secondary sources, extraction from phosphogypsum is explored in Al-Thyabat and Zhang (2015), extraction from phosphorus slag in Karshigina et al. (2015) and extraction from red mud, or bauxite residue, in Borra et al. (2015).

The present work is aimed at characterizing the distribution of REEs in upgraded sand tailings before their extraction with solvent and ion-exchange resin. Sand tailings were subjected to gravity separation and froth flotation in order to concentrate the REEs before leaching with dilute nitric acid and extraction with solvent and ion-exchange resin.

Materials and procedure

Sample preparation. Four drums, approximately 200 L each, of wet flotation tailings were received from a phosphate flotation plant in central Florida. Approximately 5 kg were collected from each drum and dried in an oven at 105°C for 24 hr. The samples were then mixed and separated by quartering and coning into 5-kg portions and stored in sealed bags. Representative samples were then riffled and used for chemical and size-distribution analyses.

Chemical analysis. Chemical analysis was conducted using a PerkinElmer Optima 8300 inductively coupled plasma atomic emission spectroscopy (ICP-AES) spectrometer. Each sample was prepared by adding 20 mL of 7.2 M (36 percent) nitric acid to 1 g of dry sample in a 100-mL flask and leaving to digest on a hotplate at 300°C for 10 minutes. The flask was then filled to the mark and filtered into plastic bottles for REE analysis. Samples of the digested solution were diluted 10 or 20 times for analysis of the major oxides: phosphorus pentoxide (P_2O_5), calcium oxide (CaO) and magnesium oxide (MgO). ICP standards for the REEs and major oxides were prepared from single-element standards purchased from Fisher Scientific and validated by a phosphate rock check 22 standard.

Chemicals used in the experiments were nitric acid, 70 percent, trace metal grade; sulfuric acid, 96 percent; hydrochloric acid, 38 percent; phosphoric acid, 85.6 percent; Dowex 50WX8 ion-exchange resin, 150 to 300 μ m; calcium carbonate, 100 percent; purified kerosene; tributyl phosphate (TBP), 99 percent; oxalic acid dihydrate; and ammonium hydroxide, 30 percent. All chemicals were purchased from Fisher Scientific.

Ultrapure nano water was used in the chemical analysis, while Bartow tap water was used in the flotation tests. Size analysis was conducted by standard wet sieve analysis. Each test was duplicated, and the average reported.

Gravity separation. An Outotec Model 13A-Lab laboratory-scale shaking table was used in the gravity separation experiments. In the preliminary experiments, the tilt angle, stroke frequency, stroke length, and wash-water flow rate were held constant, while water flow rate into the feed box was varied. Variation of the water flow rate into the feed box was inevitable with manual feeding due to changes in pulp density and therefore pulp volumetric flow rate.

Flotation. Flotation tests were conducted in a Denver D-12 flotation cell. Flotation pulp was prepared with 57 percent solids. Both conditioning and flotation were conducted with a fatty acid collector for 5 min. Cleaning flotation and scavenging flotation were also conducted for 5 min, and the final concentrate was a combination of the cleaning and scavenging flotation concentrates.

REE extraction. Both table and flotation concentrates were subjected to nitric acid leaching in a 2-L Col-Int Tech double-walled glass reactor that was connected to a 5-L PolyScience water bath. In each test, 250 g of dry solids were leached with 500 mL of nitric acid at 72°C for 1 hr. The table concentrate

was leached with 1.5 M (8 percent), 3.9 M (20 percent) and 5.2 M (25 percent) nitric acid while the flotation concentrate was leached solely with 5.2 M nitric acid.

The leachates (5.2 M nitric acid) from both concentrates were subjected to extraction with solvent and ion-exchange resin. Solvent extraction was conducted by mixing 15 mL of 3M TBP diluted by kerosene with 10 mL aqueous solution of the leachate in a 50-mL beaker. The organic and aqueous phases, at an organic to aqueous ratio of 3:2, were mixed by a magnetic stirrer for 10 min and then poured into a 1-L separating funnel and left for 30 minutes for phase segregation. The loaded organic phase was stripped three times with 10 mL of 3 M (10 percent) hydrochloric acid, and 3 mL of both raffinate and stripped liquor were mixed with 20 mL of 7.2 M nitric acid in a 100-mL flask and left to digest for 10 min.

Ion-exchange-resin extraction was conducted by mixing 5 g of the resin with 20 mL of the leach liquor for 10 min in a 50-mL beaker. The loaded resin was then separated using a 150- μ m sieve and stripped three times with 20 mL of 3 M hydrochloric acid. Extraction efficiency was calculated by means of a mass balance of REE in the loaded liquor and raffinate.

REE precipitation. Ammonium hydroxide was used to neutralize the loaded liquors, and an excess amount of 1 M oxalic acid was then added to precipitate the REEs. After 24 hr, the precipitates were filtered, roasted at 900°C for 1 hr, and dried. The dried precipitates were then weighed and digested by nitric acid for ICP analysis.

Results and discussion

Chemical and size-distribution analyses of flotation tailings. Particle size analysis showed the D_{100} and D_{50} of the as-received flotation tailings to be 250 and 150 μ m, respectively. The tailings were assayed as having on average 2.6 percent P_2O_5 and 198.1 μ g/g REEs, with LREE content slightly higher at 52.1 percent compared with 47.9 percent for HREEs. Figure 2 shows a linear relationship between REE concentration and P_2O_5 concentration, indicating a strong relationship between the two. Table 1 shows the detailed chemical analysis of the as-received flotation tailings. Mineralogical study was not conducted in this work. However, the mineralogy of the original phosphate feed is well documented. The main phosphate mineral in Florida is francolite while the gangue consists of clay minerals, such as montmorillinite, palygorskite, and kaolinite, and quartz, or sand. The clay minerals are rejected during the desliming process while francolite is floated through the Crago

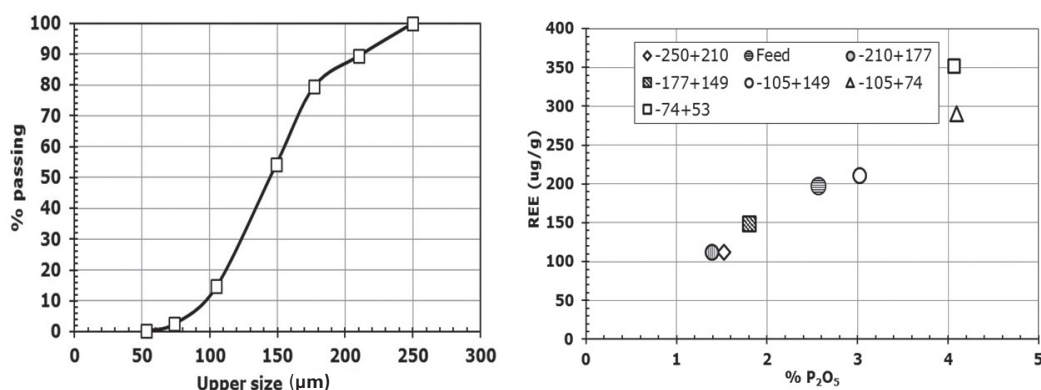


Figure 2 — Sieve size distribution of the as-received tailings (left), and the relationship between REE and P_2O_5 concentrations in each size fraction (right).

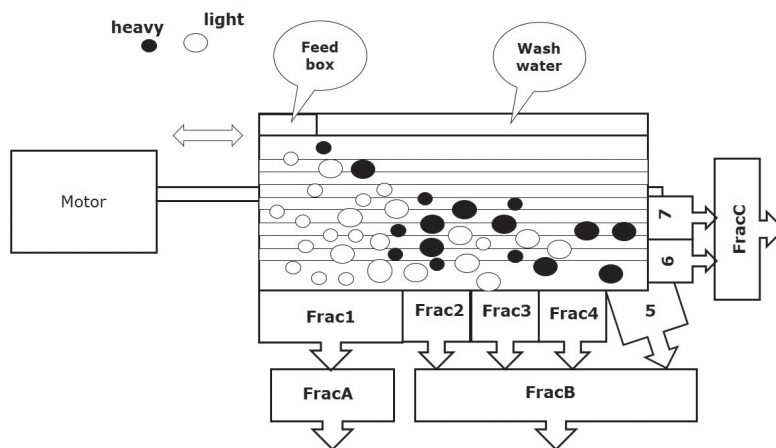


Figure 3 — Schematic diagram of densimetric table.

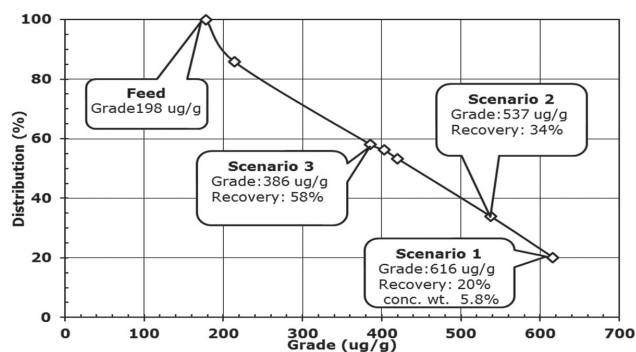


Figure 4 — Beneficiation scenarios of sand tailings by densimetric table.

process, leaving the quartz in the sand tailings (Guan, 2009; Zhang, Yu and Bogan, 1997). Specific mineralogical study on Florida sand tailings is limited but recently Zhang, Xiao and Zhang (2015) reported that REEs in Florida sand tailings mainly occur as monazite and xenotime.

Results of upgrading flotation tailings by gravity separation. The recovery versus grade relationship for all table fractions at different wash-water flow rates showed no clear trend, probably due to the small fractions of the table products. To overcome this problem, the table products were reclassified into three fractions (Fig. 3): light fraction (fraction A), middle fraction (fraction B) and heavy fraction (fraction C). The heavy and middle fractions were subjected to a re-cleaning stage before being combined to produce the final concentrate.

Even though reclassifying the table products reduced fluctuation in the results, slight variations in the manual feeding of solids caused significant variations in REE grade and recovery. Therefore, a peristaltic pump was used to pump the slurry into the feed box at a constant flowrate. A comparison between continuous and manual feeding showed that REE recovery to the middling (fraction B) was higher by about 12 percent for continuous feeding while REE grade was lower by 40 percent, indicating less REE loss to the tailings (fraction A). Continuous feeding also produced cleaner concentrate with almost the same recovery as manual feeding.

The REE distribution versus grade relationship, shown in Fig. 4, is used to identify the best scenario to upgrade flotation tailings. The first scenario is to pick the cleanest concentrate,

resulting from cleaning fraction C, which was assayed as having 616 $\mu\text{g/g}$ REEs but with low REE recovery of 20 percent. This scenario produced a concentrate with the highest enrichment ratio of 3.1, representing 5.8 percent of the original feed. The second scenario is to combine the concentrate and middling resulting from cleaning fraction C. This scenario improved REE recovery to 34 percent but slightly reduced the grade to 537 $\mu\text{g/g}$. The combined concentrate from this scenario was 11.3 percent of feed weight with enrichment ratio of 2.7. The last scenario is to combine the concentrate and middling resulting from cleaning fraction C with the concentrate and middling resulting from cleaning fraction B. This scenario produced a concentrate that was assayed as having 386 $\mu\text{g/g}$ REEs with 58 percent REE recovery. It was 26.8 percent of feed weight and its enrichment ratio was 2.0.

In order to provide enough material for REE extraction, the concentrates of several tail runs were combined and used in the leaching and REE-extraction experiments.

Results of upgrading tailings by froth flotation. The results of flotation tests showed that lower collector dosage produced cleaner concentrate, higher REE recovery and lower silica (acid insoluble) content. Increasing collector dosage improved REE recovery but reduced REE grade. For the purpose of comparison with table concentrates, flotation concentrates were combined from several flotation tests and used for leaching and REE extraction with solvent and ion-exchange resin. Table 2 shows the chemical analysis results of the table and froth flotation concentrates.

A comparison of the chemical analyses of the table and flotation concentrates (Table 2) with the as-received tailings (Table 1) shows that the flotation concentrate had higher REE and lower silica (acid insoluble) contents but also higher impurities content, consisting of the sum of the major oxides except P_2O_5 .

Results of REE extraction. Nitric acid leaching. Table 3 shows the results of the leaching tests. The REE concentration of the leached liquor and the efficiency of REE leaching from the table concentrate increased with increasing nitric acid concentration. Leaching with 5.2 M nitric acid had the highest efficiency for table concentrate, followed by feed and flotation concentrate. This may be due to the fine particle size of table concentrate compared with flotation concentrate.

Table 4 shows the REE distributions in the leach liquors. LREE contents are higher than HREE contents in both the table and flotation concentrates. LREEs make up 57 and 54

percent of the table and flotation concentrate leach liquors, respectively. The major REEs leached from table concentrate have the following order: Y > Ce > La > Nd. They make up 63 percent of the leached REEs. The major REEs leached from flotation concentrate have almost the same order: Y > Ce > Nd > La. They make up 70 percent of the leached REEs.

Solvent extraction. Tables 5 and 6 show the results of extracting REEs from the table and flotation concentrate leach liquors using 3 M TBP. REE extraction efficiency increased with increasing number of extraction stages for both table and flotation concentrates. After three extraction stages, extraction efficiency was about 75 percent for both table and flotation concentrates. However, after three extraction stages, the total extraction efficiency, or combined extraction and stripping efficiency, from flotation concentrate was significantly lower than from table concentrate at about 61 percent for table concentrate

Table 4 — REE distributions in leach liquors from table and flotation concentrates, using 5.2 M nitric acid.

REE	Table concentrate		Flotation concentrate	
	Concentration (mg/L)	Distribution (%)	Concentration (mg/L)	Distribution (%)
Ce	26.0	17.5	25.7	16.5
La	19.0	12.8	21.8	14.0
Pr	14.9	10.1	5.7	3.6
Nd	17.7	11.9	24.5	15.7
Sm	1.5	1.0	2.0	1.3
Eu	1.0	0.7	1.2	0.7
Y	30.4	20.5	37.6	24.1
Gd	4.3	2.9	5.4	3.5
Tb	2.4	1.6	3.3	2.1
Dy	4.6	3.1	5.5	3.5
Er	8.2	5.6	9.7	6.2
Ho	10.7	7.2	1.5	0.9
Yb	3.8	2.6	6.4	4.1
Lu	0.7	0.5	1.0	0.6
Tm	1.7	1.1	0.6	0.4
Sc	1.5	1.0	4.0	2.6
Total REEs	148.2	100	155.8	100

Table 2 — Chemical analysis of the concentrates from the shaking-table and froth-flotation experiments. (A.I. = Acid insoluble, N.D. = Not detected)

Oxide	Major oxides	
	Concentration (weight %)	
	Table concentrate	Flotation concentrate
P ₂ O ₅	4.8	8.4
CaO	7.0	8.5
MgO	0.05	0.07
Al ₂ O ₃	0.28	0.43
Fe ₂ O ₃	0.57	0.51
A.I.	81.7	76.4
Others	5.6	5.7
Total	100	100

REE	Rare earth elements (REEs)			
	Table concentrate		Flotation concentrate	
	ppm (µg/g)	Distribution (%)	ppm (µg/g)	Distribution (%)
Ce	71.0	23.9	82.3	20.4
La	49.8	16.8	64.4	15.9
Pr	5.0	1.7	12.7	3.1
Nd	45.7	15.4	61.2	15.1
Sm	4.3	1.5	3.9	1.0
Eu	2.3	0.8	1.7	0.4
Y	63.4	21.4	85.2	21.1
Gd	10.9	3.7	13.0	3.2
Tb	5.8	1.9	8.5	2.1
Dy	9.5	3.2	12.8	3.2
Er	19.8	6.7	27.6	6.8
Ho	2.1	0.7	5.8	1.4
Yb	3.4	1.1	15.3	3.8
Lu	N.D.	—	N.D.	—
Tm	N.D.	—	0.6	0.1
Sc	3.9	1.3	9.3	2.3
Total REEs	296.7	100	404.2	100

Table 3 — Results of nitric acid leaching.

Solids	Leach liquor			Residuals		
	Acid concentration (M)	REEs (g/L)	Impurities (g/L)	Leaching efficiency (%)	REEs (µg/g)	Acid insoluble (%)
Feed	5.2	82.9	26.4	82.9	31.7	97.5
	7.8	88.6	26.9	88.7	28.5	99.4
Table concentrate	1.5	145.4	38.3	98.0	100.3	96.4
	3.9	147.9	37.7	99.7	105.1	98.9
Flotation concentrate	5.2	148.2	36.7	99.9	103.9	98.7
	5.2	155.8	49.3	77.1	97.5	97.6

Table 5 — Results of REE extraction from table and flotation concentrates using solvent.

Extraction stage	Loaded liquor				Extraction efficiency (%)		Total efficiency (%)	
	REE concentration (mg/L)		Impurities concentration (g/L)		Table	Flotation	Table	Flotation
	Table	Flotation	Table	Flotation				
1-stage	29.3	20.5	3.9	2.3	42.3	27.4	37.7	8.9
2-stage	46.0	53.2	6.6	9.9	58.8	42.3	57.4	32.7
3-stage	35.2	32.2	8.0	6.1	75.3	74.5	61.2	40.3

Table 6 — REE distributions in loaded liquors from table and flotation concentrates, after three solvent-extraction and two stripping stages.

REE	Table concentrate		Flotation concentrate	
	(mg/L)	Distribution (%)	(mg/L)	Distribution (%)
Ce	7.8	22.2	5.9	18.4
La	7.0	19.8	8.5	26.5
Pr	2.3	6.6	0.6	1.8
Nd	4.5	12.7	3.8	11.8
Sm	0.2	0.5	0.2	0.5
Eu	0.3	0.9	0.4	1.2
Y	7.6	21.6	8.5	26.5
Gd	N.D.	—	N.D.	—
Tb	0.6	1.7	0.6	1.7
Dy	1.2	3.4	0.8	2.6
Er	1.0	2.8	0.6	1.7
Ho	1.6	4.4	1.1	3.3
Yb	0.8	2.3	0.9	2.8
Lu	N.D.	—	N.D.	—
Tm	0.2	0.6	0.1	0.4
Sc	0.1	0.4	0.2	0.8
Total REEs	35.3	100	32.2	100

and 40 percent for flotation concentrate. This is probably due to the higher content of impurities, especially iron (Fe^{+3}) and aluminum (Al^{+3}), in the flotation concentrate, which reduced stripping efficiency. The Fe^{+3} and Al^{+3} concentrations were 0.61 and 0.77 g/L in the table and flotation concentrate loaded liquors, respectively.

As shown in Table 6, LREE content was higher than HREE content in both table and flotation concentrate loaded liquors, at 62 and 60 percent for the table and flotation concentrates, respectively. In the table concentrate loaded liquor, the major REEs have the following order: $\text{Ce} > \text{Y} > \text{La} > \text{Nd}$. They make up 76 percent of the extracted REEs. In the flotation concentrate loaded liquor, the major REEs have the following order: $\text{Y} > \text{La} > \text{Ce} > \text{Nd}$. They make up 83 percent of the extracted REE.

Ion-exchange resin extraction. Tables 7 and 8 show the results of REE extraction from table and flotation concentrates using ion-exchange resin. REE extraction efficiency increased with number of extraction stages for both table and flotation concentrates, but the extraction efficiency for table concentrate

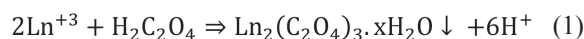
was higher than for flotation concentrate. After three extraction stages, extraction efficiency was about 75 and 45 percent for table and flotation concentrates, respectively. This may be due to high impurities content in the flotation concentrate loaded liquor. The total extraction efficiency of REEs from flotation concentrate liquor was higher than from table concentrate liquor, indicating insufficient REE stripping.

Table 8 shows the REE distributions in the loaded liquors from table and flotation concentrates. In both table and flotation concentrate loaded liquors, the major REEs have the following order: $\text{Y} > \text{La} > \text{Ce} > \text{Nd}$. They make up 66 and 79 percent of the REEs extracted from the table and flotation concentrate loaded liquors, respectively. LREE content was higher than HREE content for both table and flotation concentrates, at 75 and 84 percent, respectively.

A comparison of REE extraction from table concentrate loaded liquor with solvent and ion-exchange resin shows that the total extraction efficiency with TBP solvent was higher, at 61 percent, than with ion-exchange resin, at 31 percent, after three extraction stages. Solvent extraction efficiency increased with increasing number of extraction stages while ion-exchange-resin extraction efficiency peaked after two extraction stages.

The values for extraction efficiency and impurities in Tables 5 and 7 show that although both solvent and resin had equal extraction efficiency after three extraction stages, the ion-exchange resin extracted more impurities than the TBP solvent, indicating higher TBP solvent selectivity. In addition, leach liquor from leaching flotation concentrate responded differently to extraction by solvent and ion-exchange resin, with REEs extracted more efficiently by ion-exchange resin than TBP solvent. Nonetheless, after three extraction stages, both solvent and ion-exchange-resin extraction efficiencies were almost the same. This indicates that the nature of the liquor and its impurities content determine which extraction method can be used. In general, TBP solvent is more economical and easier for operations as no chemicals are used for stripping.

REE precipitation and separation. The loaded liquors from each test of both solvent and ion-exchange-resin extraction were combined and used for REE precipitation. The addition of ammonium hydroxide (NH_4OH) formed a cloudy, white solution that precipitated on the bottom of the beaker, probably due to the formation of metal precipitates, most likely calcium hydroxide ($\text{Ca}(\text{OH})_2$). REEs were precipitated from the loaded liquors by adding stoichiometric excess of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) according to (Chung et al., 1998):



Chung et al. (1998) reported that the solubility of REE oxalate depends on the oxalic and nitric acid concentrations: the solubility of the REE oxalate decreased as oxalic acid concentration increased, but it increased as the nitrate concentration increased. Other cations such as Ca^{+2} , Mg^{+2} , Fe^{+2} and Al^{+3} , if

present, will form oxalates of the ions that are co-precipitated with the REEs.

Analysis of the precipitates obtained from the TBP-solvent and ion-exchange-resin loaded liquors showed that REEs were precipitated from the TBP-solvent loaded liquor more efficiently than from the ion-exchange-resin loaded liquor. For table concentrate loaded liquor, the REE precipitation efficiency was 52.7 and 36.5 percent for TBP solvent and ion-exchange resin, respectively. The precipitation of impurities, consisting of the sum of major oxides except P_2O_5 , was about 11.2 and 8.2 percent for TBP solvent and ion-exchange resin, respectively. It is worth noting that the loaded liquor extracted by TBP solvent had lower impurities content, at 3.9 percent, than the ion-exchange-resin loaded liquor, at 2.7 percent.

The REE precipitation efficiency from flotation concentrate loaded liquor was 70 and 48.1 percent for TBP solvent and ion-exchange resin, respectively, while impurities precipitation was 9.8 and 9.3 percent for TBP solvent and ion-exchange resin, respectively. Loaded liquor extracted by ion-exchange resin had more impurities than that extracted by TBP solvent.

It was also found that CaO content was higher in the liquor extracted by ion-exchange resin from both table and flotation concentrates. This may be due to the affinity of ion-exchange resin to calcium ions, bearing in mind that Koopman and Witkamp (2000) reported that approximately 33 percent of ion-exchange resin capacity is occupied by Ca^{+2} ions. The CaO content in the REE precipitate from TBP-solvent loaded liquor was higher than in that from ion-exchange-resin loaded liquor. Similarly, the REE content in the TBP-solvent liquor precipitate was higher than in the ion-exchange-resin liquor precipitate. According to Chung et al. (1998), this may be due to the solubility of REE and Ca^{+2} ion oxalate in the loaded liquors. TBP solvent was stripped by water while ion-exchange resin was stripped by 3 M hydrochloric acid, therefore the acidity of the resin loaded liquor is expected to be higher than that of the TBP-solvent loaded liquor.

Table 9 shows a comparison of the rare earth oxides in the table and flotation concentrates, and the calcined precipitates.

Conclusions

The following conclusions were drawn:

- Large tonnages of sand tailings resulting from Florida phosphate flotation may become a secondary source for REEs despite their low REE and phosphate contents. The sand tailings were assayed as having 2.6 percent P_2O_5 and 198.2 $\mu\text{g/g}$ REEs. Analysis of these REEs shows that LREE (Ce, La, Nd, Sm, Pr, Eu and Gd) content is slightly higher than HREE content at 52.1 and 47.9 percent, respectively.
- To concentrate these REEs and reduce the volume of leaching feed, the sand tailings can be upgraded using

a shaking table or froth flotation. This shaking table produced a concentrate assayed as having 8.6 percent P_2O_5 and 616 $\mu\text{g/g}$ REE but with only 20 percent REE recovery, while froth flotation produced a concentrate assayed as having 8.1 percent P_2O_5 and 368.2 $\mu\text{g/g}$ REE with 63.5 percent REE recovery.

- It was found that leaching the concentrated sand tailings with concentrated nitric acid followed by extraction with solvent or ion-exchange resin produced precipitates higher in REE content than the original feed. Leaching the flotation concentrate with 5.2 M (25 percent) nitric acid followed by solvent and ion-exchange-resin extraction yielded precipitates containing 0.926 and 0.314 percent REE, respectively, compared with 0.716 and 0.213 percent when table concentrate was used.
- However, the concentrations of the REEs in these precipitates are not high enough for them to stand alone as REE feed. Further upgrading is required. They may be combined with REEs obtained from other phosphate waste streams, such as phosphogypsum, waste clay or phosphoric acid sludge.

Table 8 — REE distributions in loaded liquors from table and flotation concentrates, after three resin-extraction and two stripping stages. (N.D. = Not detected)

REE	Table concentrate		Flotation concentrate	
	(mg/L)	Distribution (%)	(mg/L)	Distribution (%)
Ce	3.1	11.5	8.2	22.7
La	4.6	17.4	8.7	23.9
Pr	2.0	7.7	0.2	0.6
Nd	2.8	10.4	3.1	8.7
Sm	0.1	0.3	0.1	0.4
Eu	0.3	1.0	0.4	1.0
Y	7.2	27.1	8.6	23.8
Gd	N.D.	—	0.8	2.1
Tb	0.3	1.2	0.4	1.0
Dy	0.8	2.9	0.8	2.1
Er	1.3	4.8	1.2	3.4
Ho	1.4	5.3	0.9	2.4
Yb	0.8	3.0	1.1	3.1
Lu	1.5	5.5	N.D.	—
Tm	0.2	0.9	1.1	3.0
Sc	0.3	1.1	0.7	1.8
Total REEs	26.6	100.0	36.2	100.0

Table 7 — Results of REE extraction from table and flotation concentrates using ion-exchange resin.

Extraction stage	Loaded liquor				Extraction efficiency (%)		Total efficiency (%)	
	REE concentration (mg/L)		Impurities concentration (g/L)		Table	Flotation	Table	Flotation
	Table	Flotation	Table	Flotation				
1-stage	18.8	20.5	4.2	7.8	41.3	33.8	29.2	33.7
2-stage	35.3	53.6	8.4	10.6	59.5	46.6	45.4	46.4
3-stage	26.6	32.2	10.5	12.6	75.2	45.0	31.2	44.2

Table 9 — Comparison of rare earth oxides in the calcined precipitates and the corresponding feed for each extraction method. (N.D. = Not detected)

Rare earth oxide	Densimetric table concentrate			Flotation concentrate		
	Feed (µg/g)	TBP solvent (weight %)	Ion-exchange resin (weight %)	Feed (µg/g)	TBP solvent (weight %)	Ion-exchange resin (weight %)
Y ₂ O ₃	80.6	0.213	0.074	108.2	0.236	0.092
La ₂ O ₃	58.5	0.128	0.029	75.5	0.132	0.036
Ce ₂ O ₃	83.2	0.034	0.034	96.4	0.196	0.063
Pr ₂ O ₃	5.8	0.026	0.005	14.8	0.027	0.007
Nd ₂ O ₃	53.3	0.146	0.029	71.4	0.151	0.045
Sm ₂ O ₃	5.0	0.013	0.004	4.5	0.014	0.006
Eu ₂ O ₃	2.7	0.008	0.002	2.0	0.008	0.002
Gd ₂ O ₃	12.5	0.037	0.008	15.0	0.036	0.012
Tb ₂ O ₃	6.6	0.017	0.003	9.8	0.020	0.005
Dy ₂ O ₃	10.9	0.030	0.006	14.7	0.031	0.009
Ho ₂ O ₃	2.4	0.007	0.002	6.7	0.008	0.003
Er ₂ O ₃	22.6	0.006	0.001	31.6	0.008	0.002
Tm ₂ O ₃	N.D	0.002	0.002	0.659	0.002	0.005
Yb ₂ O ₃	3.9	0.029	0.010	14.0	0.037	0.015
Lu ₂ O ₃	N.D.	0.008	0.001	N.D	0.010	0.005
Sc ₂ O ₃	5.9	0.013	0.002	14.2	0.011	0.009
Total	353.7	0.716	0.213	479.4	0.926	0.314

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References

- Al-Thyabat, S., and Zhang, P., 2015, “REE extraction from phosphoric acid, phosphoric acid sludge, and phosphogypsum,” *Minerals Processing and Extractive Metallurgy*, Vol. 124, No. 3, pp. 143-150, doi: <http://dx.doi.org/10.1179/1743285515Y.0000000002>.
- Becker, P., 1987, *Phosphates and Phosphoric Acid: Raw Materials, Technology, and Economics of the Wet Process*, 2nd edition, Marcel Dekker Inc., New York, NY.
- Borra, Ch., Pontikes, Y., Binnemans, K., and Gerven, T., 2015, “Leaching of rare earths from bauxite residue (red mud),” *Minerals Engineering*, doi: <http://dx.doi.org/10.1016/j.mineng.2015.01.005>.
- Chung, D., Kim, E., Lee, E., and Yoo, L., 1998, “Solubility of rare earth oxalate in oxalic and nitric acid media,” *Journal of Industrial Engineering Chemistry*, Vol. 4, No. 4, pp. 277-284.
- Grasso, V., 2012, “Rare Earth Elements in National Defense: Background, Oversight Issues, and Options for Congress,” <http://www.Fas.org/sgp/crs/natsec/R41744.pdf>, accessed Dec. 18, 2013.
- Guan, C., 2009, “Theoretical background of the Crago phosphate flotation process,” *Minerals & Metallurgical Processing*, Vol. 26, No. 2, pp. 55-64.
- Habashi, F., 1985, “The recovery of the lanthanides from phosphate rock,” *Journal of Chemical Technology and Biotechnology*, Vol. 35(A), pp. 5-14.
- Jordens, A., Cheng, Y., and Waters, K., 2013, “A review of the beneficiation of rare earth element bearing minerals,” *Minerals Engineering*, Vol. 41, pp. 97-114.
- Jorjani, E., Bagherieh, A., Mesroghli, Sh., and Chehreh Chelgani, S., 2008, “Prediction of yttrium, lanthanum, cerium and neodymium leaching recovery from apatite concentrate using artificial neural networks,” *Journal of University of Science and Technology Beijing*, Vol. 15, No. 4, pp.367-374.
- Karshigina, Z., Abisheva, Z., Bochevskaya, Y., Akcil, A., and Sargelova, E., 2015, “Recovery of rare earth metals and precipitated silicon dioxide from phosphorus slag,” *Minerals Engineering*, Vol. 77, pp 159–166.
- Koopman, G., and Witkamp, J., 2000, “Extraction of lanthanides from phosphoric acid production process to gain purified gypsum and lanthanide valuable by-product,” *Hydrometallurgy*, Vol. 58, pp.51-60.
- Koopman, C., and Witkamp, G., 2002, “Ion-exchange extraction during continuous recrystallization of CaSO₄ in the phosphoric acid production process: lanthanide extraction efficiency and CaSO₄ particle shape,” *Hydrometallurgy*, Vol. 63, No. 2, pp.137-147.
- Lambert, J., and Tognet, J., 1987, “Essentially Complete Recovery of Uranium, Yttrium, and Thorium, and Rare Earth Values from Phosphate Rock during Wet Process Production of Phosphoric Acid,” U.S. Patent 4636369.
- Lin, C.L., Hsieh, Ching-Hao, and Miller, J.D., 2013, “Characterization of rare-earth resources at Mountain Pass, CA, using high-resolution X-ray microtomography (HRXMT),” *Minerals & Metallurgical Processing*, Vol. 30, No. 1, pp. 10-17.
- Pradip, and Fuerstenau, D.W., 2013, “Design and development of novel flotation reagents for the beneficiation of Mountain Pass rare-earth ore,” *Minerals & Metallurgical Processing*, Vol. 30, No. 1, pp. 1-9.
- Preston, J., Cole, P., Craig, W., and Feather, A., 1996, “The recovery of rare earth oxides from phosphoric acid by-product. Part 1: Leaching of rare earth values and recovery of a mixed rare earth oxides by solvent extraction,” *Hydrometallurgy*, Vol. 41, pp. 1-19.
- Preston, P., Cole, A., Preez, M., Fox, A., and Fleming, M., 1996, “The recovery of rare earth oxides from a phosphoric acid by-product. Part 2: The preparation of high-purity cerium dioxide and recovery of a heavy rare earth concentrate,” *Hydrometallurgy*, Vol. 41, pp. 21-44.
- Radhika, S., Nagaphani, K., Kantam, L., Ramachandra, B., 2011, “Solvent extraction and separation of rare earths from phosphoric acid with TOPS 99,” *Hydrometallurgy*, Vol. 110, pp. 50-55.
- Wang, L., Zhiqi, L., Huang, X., Yu, Y., Cui, D., and Zhang, G., 2010, “Recovery of rare earth from wet-process phosphoric acid,” *Hydrometallurgy*, Vol. 101, pp.41-47.
- Zhang, P., Yu, Y., and Bogan, M., 1997, “Challenging the “crago” double float process ii. amine-fatty acid flotation of siliceous phosphates,” *Minerals engineering*, Vol. 10, No. 9, pp. 983-994.
- Zhang, X., Xiao, W., and Zhang, P., 2015, “Enrichment of Rare Earth Elements from Phosphate Flotation Tailings,” *Beneficiation of Phosphate VII*, March 29-April 3, Melbourne, Australia.

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