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**THE EXTRACTION AND RECOVERY OF RARE EARTH
ELEMENTS FROM PHOSPHATE USING
PX-107 AND CHELOK® POLYMERS**

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THE EXTRACTION AND RECOVERY OF RARE EARTH ELEMENTS FROM
PHOSPHATE USING PX-107 AND CHELOK® POLYMERS

FINAL REPORT

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PERSPECTIVE

Patrick Zhang, Research Director - Beneficiation & Mining

Rare earth elements (REE) include 15 of the lanthanum series, as well as the non-lanthanides, yttrium and scandium. These elements are critical to the national security, the development of green energy from hybrid car to wind turbine, and advance in various high-tech fields from computer to network. They are also vital to many traditional industries such as petroleum refining, phosphor manufacturing and glass polishing. The demand for these elements cannot be presently met directly from rare earths mines, and alternative sources must be found with potential to fill this need. Florida phosphate could be one of the alternative sources. The FIPR Institute recently conducted a characterization study of REE in Florida phosphate, and found appreciable amounts of REE in currently mined ore, with one flotation concentrate analyzing above 900 ppm of total REE.

In January 2014, the Critical Materials Institute (CMI) and FIPR jointly organized the Workshop on Rare Earths and Uranium from Phosphate Ore to discuss strategies for recovering REE from various phosphate mining and processing streams. At that workshop, Periodic Products presented their preliminary research results on REE recovery from phosphogypsum by leaching using their patented leaching solution (PX-107) followed by REE extraction with a polymer (Chelok®). Promising preliminary results prompted FIPR to fund the current project to test both the leaching solution and polymer in details on phosphogypsum (PG), amine flotation tails and waste clay. Extraction of REE from phosphoric acid was also tested using the polymer.

The major challenge to recovering REE from any of the phosphate processing streams is high operating costs due to low REE content. One way to achieve a commercially viable separation scheme is to employ a material that will economically and selectively bind to various REEs in the presence of potential interfering ions, such as calcium and iron. Ideally, this process should be efficient, scalable, and have minimal environmental impact. The polymer tested under this project offers all those features, because it is inexpensive, non-toxic, water-insoluble, selective, and reusable.

Results show that Chelok® recovered nearly 100% of the rare earth metals leached out using PX-107 from PG, amine flotation tails and waste clay. Overall non-optimized extraction and recovery yields were generally around 60% with some elements having extraction and recovery yields approaching 80%. However, Chelok® was found to be ineffective for REE extraction from phosphoric acid.

Although PX-107 proved to be somewhat efficient for REE leaching, Chelok® demonstrated more potential for industrial application. One limitation with Chelok®, however, is its requirement for pH at or above 1.5, which needs either dilution or neutralization of most leaching solutions. Considering that Chelok® is a few orders of magnitude cheaper than regular REE extracting solvents, this project is very successful.

ABSTRACT

The extraction and recovery of rare earth elements from phosphate rock, phosphoric acid, and three phosphate fertilizer waste by-products, phosphogypsum, amine tailings, and waste clay, using a novel aqueous-based extraction solution and an adsorption polymer, poly 1-octadecene 2,5-furandione salt, are examined. Overall extraction and recovery yields were between 80% for gadolinium and 8% for praseodymium from amine tailings, between 70% for terbium and 7% for praseodymium from phosphogypsum, between 56% for scandium and 15% for praseodymium from phosphate rock, and between 77% for samarium and 31% for praseodymium from waste clay. Poly 1-octadecene 2,5-furandione salt effectively bound 100% of the rare earth elements extracted from the solids. Treatment of phosphoric acid with poly 1-octadecene 2,5-furandione salt did not effectively recover appreciable amounts of REEs. These results suggest that this process may be an efficient means of recovering rare earth elements from phosphate mining waste products, and that treatment of phosphogypsum stack water and leachate with poly 1-octadecene 2,5-furandione salt may effectively reduce metal contamination of both surface and groundwater.

ACKNOWLEDGEMENTS

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EXECUTIVE SUMMARY

The rare earth elements (REE) or rare earth metals consist of seventeen chemical elements, the fifteen lanthanides, scandium, and yttrium. Despite their relative abundance, most REEs are not found concentrated enough to make them economically exploitable. The United States, once able to domestically produce sufficient REEs, has, over the past 15 years, become totally reliant on imports, primarily from China, because of the low cost of operations. World demand for REEs exceeds 200,000 tons per year. To meet this demand, improved separation techniques, more efficient metal recovery processes, and improved recycling technologies will need to be developed and implemented.

Additionally, alternative sources for REEs are currently being explored. Because two phosphate minerals, xenotime and monazite, are also principal rare earth element mineral ores, phosphate rock has the potential become an important supplemental source of rare earth elements. It is estimated that in Florida alone, approximately 30,000 tons of rare earth elements are discarded with various phosphate mining waste by-products annually.

While numerous procedures to extract and recover rare earth elements from phosphate rock during the production of phosphate fertilizer have been reported, none have not seen widespread commercial acceptance due to various limitations, such as high cost, low efficiency, impact on phosphoric acid purity and yield, and the inability to economically extend the technology to large-scale operations. Clearly, there is a need to improve the extraction and recovery technology of REEs.

One way to achieve a commercially viable separation scheme is to employ a material that will economically and selectively bind to various REEs in the presence of potential interfering ions, such as calcium and iron. Ideally, this process should be efficient, scalable, and have minimal environmental impact. We have previously reported on a series of novel, non-toxic, water-insoluble polymer compounds that rapidly and efficiently remove several metal ions, including both light and heavy rare earth elements, from aqueous media. In this study, we employed one of these novel polymers, poly 1-octadecene 2,5-furandione salt, with an extraction solution, PX-107, to recover rare earth elements from phosphate rock, phosphoric acid, and three phosphate fertilizer waste by-products, phosphogypsum, amine tailings, and waste clay.

In this study, the polymer recovered 100% of the rare earth metals from the waste product extracts. Overall non-optimized extraction and recovery yields were generally around 60% with some elements having extraction and recovery yields approaching 80%. The results of this study suggest that PX-107 is a highly efficient and cost effective extraction solution for the removal of rare earth elements and other metals from phosphate mining waste products. The ability to reuse the adsorption polymer increases the economic viability of this process for REE extraction and recovery. The effect of particle size, drying temperature, and extraction solution temperature on REE extraction

rates should be investigated further. Further, treatment of phosphogypsum stack water and leachate with poly 1-octadecene 2,5-furandione salt may be an effective way to reduce the possibility of groundwater and surface water contamination by the heavy metals, thorium, and uranium associated with stack runoff.

INTRODUCTION

The rare earth elements (REE) or rare earth metals consist of seventeen chemical elements, the fifteen lanthanides, scandium, and yttrium (Connelly and Damhus 2005). Despite their relative abundance, most REEs are not found concentrated enough to make them economically exploitable (USGS 2007). The United States, once able to domestically produce sufficient REEs, has, over the past 15 years, become totally reliant on imports, primarily from China, because of the low cost of operations (Haxel and others 2002). Selected applications and end uses of the REEs are given in Table 1 (Jackson and Christiansen 1993, Humphries 2012).

Table 1. Selected REE Applications and End Uses.

Light Rare Earths	Application/End Use	Heavy Rare Earths	Application/End Use
Lanthanum	Hybrid engines, metal alloys	Terbium	Permanent magnets, phosphors
Cerium	Auto catalyst, metal alloys, petroleum refining	Dysprosium	Hybrid engines, permanent magnets
Praseodymium	Magnets	Erbium	Phosphors
Neodymium	Auto catalyst, laptop hard drives, headphones, hybrid engines, petroleum refining	Yttrium	Fluorescent lamps, ceramics, metal alloys
Samarium	Magnets	Holmium	Lasers
Europium	Red color for computer/TV screens	Thulium	Medical X-rays
Gadolinium	Magnets	Lutetium	Petroleum refining
		Ytterbium	Steel alloys, lasers

World demand for REEs exceeds 200,000 tons per year (Humphries 2012). To meet this demand, improved separation techniques, more efficient metal recovery processes, and improved recycling technologies will need to be developed and implemented. Additionally, alternative sources for REEs are currently being explored. Because two phosphate minerals, xenotime and monazite, are also principal rare earth element mineral ores, phosphate rock has the potential become an important supplemental source of rare earth elements. In a comprehensive investigation of rare earth elements in Florida phosphate obtained from monazite, recently completed by the Florida Industrial and Phosphate Research (FIPR) Institute, significant concentrations of rare earth elements were found in the waste clay, amine flotation tailings, and phosphogypsum. In this FIPR study, it was estimated that in Florida alone, approximately 30,000 tons of rare earth elements are discarded with various phosphate mining waste by-products annually (Zhang 2014).

While numerous procedures to extract and recover rare earth elements from phosphate rock during the production of phosphate fertilizer have been reported, none have not seen widespread commercial acceptance due to various limitations, such as high cost, low efficiency, impact on phosphoric acid purity and yield, and the inability to

economically extend the technology to large-scale operations. Clearly, there is a need to improve the extraction and recovery technology of REEs.

One way to achieve a commercially viable separation scheme is to employ a material that will economically and selectively bind to various REEs in the presence of potential interfering ions, such as calcium and iron. Ideally, this process should be efficient, scalable, and have minimal environmental impact. We have previously (Laurino 2008) reported on a series of novel, non-toxic, water-insoluble polymer compounds that rapidly and efficiently remove several metal ions, including both light and heavy rare earth elements, from aqueous media. In this study, we employed one of these novel polymers with an extraction solution, PX-107, to recover rare earth elements from phosphate rock, phosphoric acid, and three phosphate fertilizer waste by-products, phosphogypsum, amine tailings, and waste clay.

METHODOLOGY

CHEMICALS AND MATERIALS

Phosphate rock, phosphoric acid, phosphogypsum, amine tailings, and waste clay (both milled and unmilled) were obtained from the Florida Industrial and Phosphate Research (FIPR) Institute (Bartow, Florida). Poly 1-octadecene 2,5-furandione salt and PX-107 were obtained from Periodic Products, Inc. (Fort Lauderdale, FL, USA). Sodium hydroxide (ACS Grade), Whatman #1 filter paper, plastic syringes (10cc, Exelint International Co.), and syringe filters (0.22 μ [SLGP033RS] and 1.2 μ [03-376-223]) were purchased from Fisher Scientific (Waltham, MA, USA).

METHODS

General

Moisture content was determined using a Mettler-Toledo HB43-S moisture balance and represents the average of two analyses. Particle size was determined using a Microtrac S3500 laser diffraction particle size analyzer (Montgomeryville, PA, USA). Rare earth element and phosphorus content of the candidate materials were determined by ICP-OES by the Florida Industrial and Phosphate Research (FIPR) Institute (Bartow, FL, USA) with the following exceptions: holmium, terbium, and uranium concentrations in the waste clay, gadolinium, terbium, and thorium concentrations in phosphogypsum, and terbium in the amine tailings were determined by ACZ Laboratories, Inc. (Steamboat Springs, CO, USA) by ICP-MS. Rare earth element and phosphorus content of the leach solutions and polymer-treated solutions were determined using a Horiba Activa ICP-OES (Edison, NJ, USA) using standard solutions obtained from Exatol (Clearwater, FL, USA). The pH of the leach solutions was determined using a Thermo Scientific Orion Star AIII pH meter. Conductivities were determined with a LaMotte Tracer PocketTester (1749-KIT-01) (Chestertown, MD, USA).

Extraction and REE Recovery Methods

Phosphate Rock, Phosphogypsum, and Waste Clay

Forty grams of dried solid were stirred for 15 minutes in 300.0 ml of PX-107 extraction solution. The mixture was vacuum filtered using #1 Whatman filter paper, and the filter cake rinsed with 50.0 ml of PX-107 followed by 50.0 ml of deionized water. The filtrate was retained and the extraction procedure repeated on the filter cake. The filtrates were combined and adjusted to pH 1.5 with sodium hydroxide. Five ml of the pH adjusted filtrate were diluted with 5.0 ml of deionized water and 0.3 grams of poly

1-octadecene 2,5-furandione salt added to the diluted filtrate. The mixture was shaken for 1 hour on a rotary shaker and then syringe filtered through 1.2 μ and 0.22 μ filters. The filtrates were analyzed for REE content by ICP-OES.

Amine Tailings

Forty grams of dried solid were shaken on a rotary shaker for 15 minutes in 300.0 ml of PX-107 extraction solution. The mixture was vacuum filtered using #1 Whatman filter paper, and the filter cake rinsed with 50.0 ml of PX-107 followed by 50.0 ml of deionized water. The filtrate was retained and the extraction procedure repeated on the filter cake. The filtrates were combined and adjusted to pH 1.5 with sodium hydroxide. Five ml of the pH adjusted filtrate were diluted with 5.0 ml of deionized water and 0.2 grams of poly 1-octadecene 2,5-furandione salt added to the diluted filtrate. The mixture was shaken for 1 hour on a rotary shaker and then syringe filtered through 1.2 μ and 0.22 μ filters. The filtrates were analyzed for REE content by ICP-OES.

Analysis of Residual Leachates from Remediated Solids

Forty grams of each of the remediated solids obtained from the extraction and rare earth element recovery studies were washed with two 100 ml portions of deionized water and the filtrates analyzed for REE content by ICP-OES.

Determination of the Performance of the Recycled Polymer

Five ml of the pH adjusted filtrate were diluted with 5.0 ml of deionized water and 0.2 grams of poly 1-octadecene 2,5-furandione salt added to the diluted filtrate. The mixture was shaken for 1 hour on a rotary shaker and then syringe filtered through 1.2 μ and 0.22 μ filters. The filtrates were analyzed for REE content by ICP-OES. Between each of ten separate incubations, the polymer-metal complexes were treated with 2.5% nitric acid solution to remove the adsorbed metals and the polymer dried overnight prior to reuse.

RESULTS

PHYSICAL CHARACTERISTICS

Physical characteristics of the materials are summarized in Table 2. Phosphogypsum and amine tailings were dried overnight at 100°C, and waste clay dried overnight at 110°C prior to REE extraction with PX-107.

Table 2. Physical Characteristics of Phosphate Rock and Phosphoric Acid Waste By-Products.

Sample Description	Sample Identification #	Sample Appearance	Average Moisture Content (before drying)	Average Moisture Content (after drying)	Average Particle Size
Phosphate rock	PPJ107.29.14-PR	Fine gray sand	1.14%	1.14%	257.3 μ
Phosphogypsum	PPJ107.29.14-PG	Gray to beige powder	19.36%	0.89%	72.45 μ
Amine tailings	PPJ107.29.14-AT	Gray to brown wet powder	20.77%	0.23%	168.8 μ
Waste clay	PPJ107.31.14-WC01	Gray	60.64%	1.70%	> 2000 μ

RARE EARTH ELEMENT EXTRACTION WITH PX-107

The pH and individual REE concentrations of the combined filtrates from each of the treated solids were determined. The results are summarized in Table 3. For the amine tailings, REE extraction yields varied from 98% for gadolinium to 8% for praseodymium. Extraction yields for most of the rare earth elements in the amine tailings exceeded 60%. Small amounts of uranium, thorium, and phosphorus were also extracted from the amine tailings. Extraction yields for the REEs in the phosphogypsum varied from 71% for neodymium to 7% for praseodymium, and generally exceeded 60%. As was observed for the amine tailings, small amounts of uranium, thorium, and phosphorus were also extracted. For the waste clay, REE extraction yields varied from 82% for samarium to 31% for praseodymium, with most yields greater than 50%. Both uranium and thorium were also extracted, but phosphorus was not extracted from the waste clay by PX-107. REE extraction yields from the phosphate rock were generally lower, varying from 56% for scandium to 22% for lutetium and with most yields around 40%. The lower extraction yields for the REEs obtained from the phosphate rock were likely related to the higher pH of the filtrate. Small amounts of uranium and phosphorus were extracted from the phosphate rock, but thorium was not extracted with PX-107.

Table 3a. Extraction of Rare Earth Elements from Unmilled Solids with PX-107—Amine Tailings.

Element	mg REE per g Solid	mg REE in Solution per g solid at pH 0.69	% REE Extraction
Cerium	0.0657	0.0249	38
Dysprosium	0.0048	0.0038	79
Erbium	0.0028	0.0025	87
Gadolinium	0.0040	0.0039	98
Holmium	0.0011	0.0007	64
Lanthanum	0.0294	0.0195	66
Lutetium	0.00007	BLD	0
Neodymium	0.0397	0.0204	51
Scandium	0.0015	0.0010	64
Samarium	0.0049	0.0041	83
Terbium	0.0014	0.0007	50
Yttrium	0.0360	0.0262	73
Ytterbium	0.0023	0.0019	84
Praseodymium	0.0057	0.0005	8
Uranium	0.0248	0.0056	23
Thorium	0.0065	0.0018	28
Phosphorus	54.90	14.1498	26

Table 3b. Extraction of Rare Earth Elements from Unmilled Solids with PX-107—Phosphogypsum.

Element	mg REE per g Solid*	mg REE in Solution per g Solid at pH 0.73	% Extraction
Cerium	0.0480	0.0201	42
Dysprosium	0.0044	0.0028	63
Erbium	0.0025	0.0016	67
Gadolinium	0.0057	0.0033	58
Holmium	0.0011	0.0007	61
Lanthanum	0.0265	0.0173	65
Lutetium	0.0000	N/A	N/A
Neodymium	0.0303	0.0214	71
Scandium	0.00006	BLD	0
Samarium	0.0045	0.0025	55
Terbium	0.0008	0.0006	73
Yttrium	0.0340	0.0239	70
Ytterbium	0.0016	0.0010	66
Praseodymium	0.0058	0.0004	7
Uranium	0.0315	0.0101	32
Thorium	0.0012	0.0004	33
Phosphorus	26.20	7.8448	30

**Table 3c. Extraction of Rare Earth Elements from Unmilled Solids with PX-107—
Phosphate Rock.**

Element	mg REE per g Solid	mg REE in Solution per g Solid at pH 1.37	% Extraction
Cerium	0.1302	0.0378	29
Dysprosium	0.0136	0.0048	35
Erbium	0.0095	0.0035	37
Gadolinium	0.0164	0.0055	34
Holmium	0.0031	0.0008	25
Lanthanum	0.0770	0.0311	40
Lutetium	0.0014	0.0003	22
Neodymium	0.0846	0.0417	49
Scandium	0.0049	0.0027	56
Samarium	0.0118	0.0050	43
Terbium	0.0022	0.0009	41
Yttrium	0.1306	0.0367	28
Ytterbium	0.0086	0.0027	31
Praseodymium	0.0081	0.0012	15
Uranium	0.0885	0.0333	38
Thorium	0.0094	0.0000	0
Phosphorus	536.00	84.6272	16

**Table 3d. Extraction of Rare Earth Elements from Unmilled Solids with PX-107—
Waste Clay.**

Element	mg REE per g Solid	mg REE in Solution per g Solid at pH 0.84	% Extraction
Cerium	0.0860	0.0300	35
Dysprosium	0.0072	0.0050	69
Erbium	0.0046	0.0032	69
Gadolinium	0.0101	0.0050	49
Holmium	0.0018	0.0011	57
Lanthanum	0.0417	0.0192	46
Lutetium	0.0008	0.0004	45
Neodymium	0.0537	0.0234	44
Scandium	0.0061	0.0037	61
Samarium	0.0063	0.0051	82
Terbium	0.0016	0.0010	63
Yttrium	0.0602	0.0348	58
Ytterbium	0.0043	0.0027	63
Praseodymium	0.0026	0.0008	31
Uranium	0.0665	0.0322	48
Thorium	0.0059	0.0024	40
Phosphorus	115.90	0.0000	0

EFFECT OF PARTICLE SIZE ON RARE EARTH ELEMENT EXTRACTION

Solid samples were milled using a rod mill for ten (10) minutes and REE extractions performed as described in the Methods section above. The particle size results are summarized in Table 4. With the exception of phosphogypsum, which exhibited an average REE extraction increase of approximately 11%, the percent REE extraction did not improve, and often decreased, with decreasing particle size (see Table 5).

Table 4. Average Particle Size of Milled Solids.

Sample Description	Sample Identification #	Average Particle Size After Milling
Phosphate rock	PPJ107.29.14-PR	73.13 microns
Phosphogypsum	PPJ107.29.14-PG	72.45 microns
Amine tailings	PPJ107.29.14-AT	133.7 microns
Waste clay	PPJ107.31.14-WC01	178 microns

pH PROFILES OF SOLUBLE REE IN EXTRACTS

The pH was increased stepwise to pH 2 with sodium hydroxide and the REE content of the filtrates determined. The concentrations of the REE remaining in the filtrates at each pH are summarized in Tables 6 through 9 for the amine tailings, phosphogypsum, phosphate rock, and waste clay, respectively. As the polymer, poly 1-octadecene 2,5-furandione salt, has a working pH range from 1.5 to 14, the pH of the filtrates had to be adjusted accordingly. While the loss of REE in solution was substantial at a pH of 2, the loss of REE in solution at a pH of 1.5 was approximately 17%, 10%, 1%, and 6% from the amine tailings, phosphogypsum, phosphate rock, and waste clay extracts, respectively.

RECOVERY OF THE RARE EARTH ELEMENTS FROM THE EXTRACTS AND PHOSPHORIC ACID USING POLY 1-OCTADECENE 2,5-FURANDIONE SALT

Extracts from each of the solids at pH 1.5 were treated with poly 1-octadecene 2,5-furandione salt, as described above, and the REE content of the polymer-treated filtrates determined by ICP-OES. As summarized in Tables 10a-10d, the polymer bound 100% of the rare earth metals in all of the extracts. The polymer also bound 100% of the uranium in the amine tailing and waste clay extracts, and 82% and 83% of the uranium in the phosphogypsum and phosphate rock extracts, respectively. Additionally, the polymer bound 100% of the thorium extracted from the amine tailings, phosphogypsum, and waste clay. As indicated above, thorium was not extracted from the phosphate rock.

Table 5. Extraction of Rare Earth Elements from Milled Solids with PX-107.

Element	% REE Extracted Phosphate Rock (Unmilled)	% REE Extracted Phosphate Rock (Milled)	% Change	% REE Extracted Amine Tailings (Unmilled)	% REE Extracted Amine Tailings (Milled)	% Change	% REE Extracted PG (Unmilled)	% REE Extracted PG (Milled)	% Change	% REE Extracted Waste Clay (Unmilled)	% REE Extracted Waste Clay (Milled)	% Change
Cerium	42.12	22.79	(19.34)	49.83	18.52	(31.31)	47.72	49.54	1.83	46.64	35.21	(11.43)
Dysprosium	56.82	41.14	(15.69)	76.86	74.04	(2.82)	74.46	85.25	10.79	83.26	72.41	(10.85)
Erbium	56.62	41.17	(15.45)	72.63	81.41	8.78	79.92	89.89	9.97	80.92	76.49	(4.43)
Gadolinium	48.17	34.54	(13.63)	99.36	90.48	(8.88)	59.54	68.12	8.58	62.97	49.74	(13.24)
Holmium	50.14	39.63	(10.50)	58.40	64.84	6.44	39.20	58.87	19.66	50.37	44.35	(6.02)
Lanthanum	56.28	48.27	(8.01)	72.84	49.68	(23.16)	72.65	87.37	14.72	57.40	45.96	(11.44)
Neodymium	76.38	50.86	(25.51)	54.68	33.20	(21.48)	85.25	99.11	13.86	50.14	42.50	(7.64)
Scandium	52.36	55.25	2.89	70.82	67.44	(3.38)	N/A	N/A	N/A	49.00	35.49	(13.51)
Samarium	69.81	46.45	(23.35)	89.41	79.56	(9.85)	77.33	84.94	7.61	98.70	78.33	(20.36)
Terbium	62.24	47.10	(15.14)	40.72	46.18	5.45	49.71	88.49	38.78	49.20	61.90	12.70
Yttrium	32.46	21.40	(11.06)	75.02	69.58	(5.44)	61.80	69.70	7.90	73.90	55.04	(18.86)
Ytterbium	42.81	30.93	(11.88)	71.67	79.09	7.42	73.08	80.36	7.28	77.35	66.65	(10.69)
Praseodymium	17.62	11.83	(5.78)	10.97	10.61	(0.36)	10.69	4.57	(6.12)	52.76	29.93	(22.83)

Table 6. pH Profiles of Soluble REEs in Amine Tail Extracts.

Element	mg REE per g Solid	mg REE in Solution per g Solid at pH 0.69	mg REE in Solution per g Solid at pH 1	% Loss mg REE at pH 1	mg REE in Solution per g Solid at pH 1.5	% Loss mg REE at pH 1.5	mg REE in Solution per g of Solid at pH 2	% Loss mg REE at pH 2
Cerium	0.0657	0.0249	0.0196	21	0.0168	32	0.0130	48
Dysprosium	0.0048	0.0038	0.0034	11	0.0032	14	0.0029	24
Erbium	0.0028	0.0025	0.0021	14	0.0020	19	0.0017	32
Gadolinium	0.0040	0.0039	0.0033	15	0.0032	18	0.0030	23
Holmium	0.0011	0.0007	0.0006	12	0.0006	16	0.0005	26
Lanthanum	0.0294	0.0195	0.0159	18	0.0140	28	0.0130	33
Lutetium	0.00007	BLD	BLD	BLD	BLD	BLD	BLD	BLD
Neodymium	0.0397	0.0204	0.0171	16	0.0159	22	0.0142	30
Scandium	0.0015	0.0010	0.0010	0	0.0011	-16	0.0003	64
Samarium	0.0049	0.0041	0.0034	17	0.0031	23	0.0030	26
Terbium	0.0014	0.0007	0.0006	13	0.0006	16	0.0005	29
Yttrium	0.0360	0.0262	0.0224	14	0.0212	19	0.0229	12
Ytterbium	0.0023	0.0019	0.0016	18	0.0015	24	0.0012	37
Praseodymium	0.0057	0.0005	0.0005	1	0.0005	1	0.0004	20
Uranium	0.0248	0.0056	0.0045	20	0.0039	30	0.0030	46
Thorium	0.0065	0.0018	0.0015	18	0.0013	27	0.0007	61
Phosphorus	54.90	14.1498	14.2696	-1	14.2646	-1	0.2570	98

Table 7. pH Profiles of Soluble REEs in Phosphogypsum Extracts.

Element	mg REE per g Solid	mg REE in Solution per g Solid at pH 0.73	mg REE in Solution per g Solid at pH 1	% Loss mg REE at pH 1	mg REE in Solution per g Solid at pH 1.5	% Loss mg REE at pH 1.5	mg REE in Solution per g Solid at pH 2	% Loss mg REE at pH 2
Cerium	0.0480	0.0201	0.0190	6	0.0159	21	0.0141	30
Dysprosium	0.0044	0.0028	0.0028	0	0.0027	4	0.0027	4
Erbium	0.0025	0.0016	0.0017	-2	0.0014	15	0.0016	2
Gadolinium	0.0057	0.0033	0.0031	6	0.0030	9	0.0027	18
Holmium	0.0011	0.0007	0.0007	0	0.0006	9	0.0005	28
Lanthanum	0.0265	0.0173	0.0157	9	0.0143	17	0.0136	21
Lutetium	0.0000	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Neodymium	0.0303	0.0214	0.0197	8	0.0174	19	0.0211	1
Scandium	0.00006	BLD	BLD	N/A	BLD	N/A	BLD	N/A
Samarium	0.0045	0.0025	0.0024	1	0.0022	10	0.0022	10
Terbium	0.0008	0.0006	0.0006	0	0.0005	4	0.0005	4
Yttrium	0.0340	0.0239	0.0231	3	0.0210	12	0.0206	14
Ytterbium	0.0016	0.0010	0.0010	0	0.0008	21	0.0008	21
Praseodymium	0.0058	0.0004	0.0004	0	0.0004	0	0.0000	100
Uranium	0.0315	0.0101	0.0094	7	0.0090	11	0.0090	11
Thorium	0.0012	0.0004	0.0004	0	0.0003	25	0.0000	100
Phosphorus	26.20	7.8448	7.6017	3	7.4372	5	7.4372	5

Table 8. pH Profiles of Soluble REEs in Phosphate Rock Extracts.

Element	mg REE per g Solid	mg REE in Solution per g Solid at pH 1.37	mg REE in Solution per g Solid at pH 1.5	% Loss mg REE at pH 1.5	mg REE in Solution per g Solid at pH 1.7	% Loss mg REE at pH 1.7	mg REE in Solution per g Solid at pH 2	% Loss mg REE at pH 2
Cerium	0.1302	0.0378	0.0381	-1	0.0203	46	0.0129	66
Dysprosium	0.0136	0.0048	0.0051	-6	0.0032	34	0.0022	55
Erbium	0.0095	0.0035	0.0035	-1	0.0022	36	0.0017	52
Gadolinium	0.0164	0.0055	0.0058	-4	0.0033	41	0.0021	63
Holmium	0.0031	0.0008	0.0008	-6	0.0007	14	0.0000	100
Lanthanum	0.0770	0.0311	0.0310	0	0.0281	9	0.0188	39
Lutetium	0.0014	0.0003	0.0003	0	0.0000	100	0.0000	100
Neodymium	0.0846	0.0417	0.0413	1	0.0261	37	0.0172	59
Scandium	0.0049	0.0027	0.0027	0	0.0024	13	0.0018	33
Samarium	0.0118	0.0050	0.0053	-4	0.0032	37	0.0023	55
Terbium	0.0022	0.0009	0.0009	-5	0.0006	26	0.0006	32
Yttrium	0.1306	0.0367	0.0358	3	0.0054	85	0.0028	92
Ytterbium	0.0086	0.0027	0.0027	-3	0.0012	54	0.0009	68
Praseodymium	0.0081	0.0012	0.0012	-1	0.0007	39	0.0000	100
Uranium	0.0885	0.0333	0.0329	1	0.0325	2	0.0235	29
Thorium	0.0094	0.0000	0.0000	0	0.0000	0	0.0000	0
Phosphorus	536.00	84.6272	85.2385	-1	87.4264	-3	73.9808	13

Table 9. pH Profiles of Soluble REEs in Waste Clay Extracts.

Element	mg REE per g Solid	mg REE in Solution per g Solid at pH 0.84	mg REE in Solution per g Solid at pH 1	% Loss mg REE at pH 1.0	mg REE in Solution per g Solid at pH 1.5	% Loss mg REE at pH 1.5	mg REE in Solution per g Solid at pH 2	% Loss mg REE at pH 2
Cerium	0.0860	0.0300	0.0276	8	0.0267	11	0.0133	56
Dysprosium	0.0072	0.0050	0.0048	4	0.0048	5	0.0048	4
Erbium	0.0046	0.0032	0.0031	4	0.0031	3	0.0029	8
Gadolinium	0.0101	0.0050	0.0047	6	0.0047	6	0.0046	8
Holmium	0.0018	0.0011	0.0010	6	0.0010	6	0.0009	13
Lanthanum	0.0417	0.0192	0.0181	6	0.0181	6	0.0129	33
Lutetium	0.0008	0.0004	0.0004	0	0.0003	6	BLD	100
Neodymium	0.0537	0.0234	0.0220	6	0.0217	7	0.0173	26
Scandium	0.0061	0.0037	0.0034	7	0.0033	10	0.0011	71
Samarium	0.0063	0.0051	0.0049	5	0.0048	5	0.0040	21
Terbium	0.0016	0.0010	0.0009	5	0.0009	7	0.0008	17
Yttrium	0.0602	0.0348	0.0333	4	0.0327	6	0.0291	17
Ytterbium	0.0043	0.0027	0.0025	7	0.0025	8	0.0025	8
Praseodymium	0.0026	0.0008	0.0008	0	0.0008	0	0.0009	-11
Uranium	0.0665	0.0322	0.0308	4	0.0311	3	0.0245	24
Thorium	0.0059	0.0024	0.0023	5	0.0022	25	BLD	100
Phosphorus	115.90	N/A	N/A	N/A	29.5518	N/A	20.0305	32

Table 10a. Polymer Binding and Percent Rare Earth Element Recovery—Amine Tailings.

Element	mg REE per g Solid	mg REE in Solution per g Solid at pH 1.5	mg REE Bound by Polymer per g of Solid at pH 1.5	% Binding by Polymer at pH 1.5	% Total REE Recovery
Cerium	0.0657	0.0168	0.0168	100	26
Dysprosium	0.0048	0.0032	0.0032	100	68
Erbium	0.0028	0.0020	0.0020	100	71
Gadolinium	0.0040	0.0032	0.0032	100	80
Holmium	0.0011	0.0006	0.0006	100	54
Lanthanum	0.0294	0.0140	0.0140	100	48
Lutetium	0.00007	BLD	BLD	N/A	N/A
Neodymium	0.0397	0.0159	0.0159	100	40
Scandium	0.0015	0.0011	0.0011	100	75
Samarium	0.0049	0.0031	0.0031	100	64
Terbium	0.0014	0.0006	0.0006	100	42
Yttrium	0.0360	0.0212	0.0212	100	59
Ytterbium	0.0023	0.0015	0.0015	100	64
Praseodymium	0.0057	0.0005	0.0005	100	8
Uranium	0.0248	0.0039	0.0039	100	16
Thorium	0.0065	0.0013	0.0013	100	20

Table 10b. Polymer Binding and Percent Rare Earth Element Recovery—Phosphogypsum.

Element	mg REE per g Solid	mg REE in Solution per g Solid at pH 1.5	mg REE Bound by Polymer per g of Solid at pH 1.5	% Binding by Polymer at pH 1.5	% Total REE Recovery
Cerium	0.0480	0.0159	0.0159	100	33
Dysprosium	0.0044	0.0027	0.0027	100	60
Erbium	0.0025	0.0014	0.0014	100	57
Gadolinium	0.0057	0.0030	0.0030	100	53
Holmium	0.0011	0.0006	0.0006	100	55
Lanthanum	0.0265	0.0143	0.0143	100	54
Lutetium	0.0000	N/A	N/A	N/A	N/A
Neodymium	0.0303	0.0174	0.0174	100	57
Scandium	0.00006	BLD	BLD	N/A	N/A
Samarium	0.0045	0.0022	0.0022	100	49
Terbium	0.0008	0.0005	0.0005	100	70
Yttrium	0.0340	0.0210	0.0210	100	62
Ytterbium	0.0016	0.0008	0.0008	100	52
Praseodymium	0.0058	0.0004	0.0004	100	7
Uranium	0.0315	0.0090	0.0073	82	23
Thorium	0.0012	0.0003	0.0003	100	26

Table 10c. Polymer Binding and Percent Rare Earth Element Recovery—Phosphate Rock.

Element	mg REE per g Solid	mg REE in Solution per g Solid at pH 1.5	mg REE Bound by Polymer per g of Solid at pH 1.5	% Binding by Polymer at pH 1.5	% Total REE Recovery
Cerium	0.1302	0.0381	0.0381	100	29
Dysprosium	0.0136	0.0051	0.0051	100	37
Erbium	0.0095	0.0035	0.0035	100	37
Gadolinium	0.0164	0.0058	0.0058	100	35
Holmium	0.0031	0.0008	0.0008	100	27
Lanthanum	0.0770	0.0310	0.0310	100	40
Lutetium	0.0014	0.0003	0.0003	100	22
Neodymium	0.0846	0.0413	0.0413	100	49
Scandium	0.0049	0.0027	0.0027	100	56
Samarium	0.0118	0.0053	0.0053	100	45
Terbium	0.0022	0.0009	0.0009	100	43
Yttrium	0.1306	0.0358	0.0358	100	27
Ytterbium	0.0086	0.0027	0.0027	100	32
Praseodymium	0.0081	0.0012	0.0012	100	15
Uranium	0.0885	0.0329	0.0274	83	31
Thorium	0.0094	0.0000	0.0000	N/A	N/A

Table 10d. Polymer Binding and Percent Rare Earth Element Recovery—Waste Clay.

Element	mg REE per g Solid	mg REE in Solution per g Solid at pH 1.5	mg REE Bound by Polymer per g of Solid at pH 1.5	% Binding by Polymer at pH 1.5	% Total REE Recovery
Cerium	0.0860	0.0267	0.0267	100	31
Dysprosium	0.0072	0.0048	0.0048	100	66
Erbium	0.0046	0.0031	0.0031	100	67
Gadolinium	0.0101	0.0047	0.0047	100	47
Holmium	0.0018	0.0010	0.0010	100	54
Lanthanum	0.0417	0.0181	0.0181	100	43
Lutetium	0.0008	0.0003	0.0003	100	42
Neodymium	0.0537	0.0217	0.0217	100	40
Scandium	0.0061	0.0033	0.0033	100	55
Samarium	0.0063	0.0048	0.0048	100	77
Terbium	0.0016	0.0009	0.0009	100	59
Yttrium	0.0602	0.0327	0.0327	100	54
Ytterbium	0.0043	0.0025	0.0025	100	58
Praseodymium	0.0026	0.0008	0.0008	100	31
Uranium	0.0665	0.0311	0.0311	100	47
Thorium	0.0059	0.0022	0.0022	100	38

The complete removal of the rare earth elements and thorium, and the nearly complete removal of uranium (82%) from the phosphogypsum extract by poly 1-octadecene 2,5-furandione salt suggests that treatment of the phosphogypsum stack “pond” water or stack leachate (generally having a pH around 1.5) with the polymer may be an effective means to control potential ground and surface water contamination.

Adjusting the pH of the phosphoric acid from 0.53 to 1.5 resulted in a loss of REE metals that varied between 19% and 70%. Poly 1-octadecene 2,5-furandione salt was also less effective in removing the REE metals from phosphoric acid at a pH of 1.5, binding only 6% to 60% of the metals. The polymer did not bind any of the phosphorus present in the acid.

DETERMINATION OF RARE EARTH ELEMENT CONCENTRATION IN RESIDUAL LEACHATES FROM REMEDIATED SOLIDS

Remediated solids were treated with deionized water and the leachates analyzed for REE content by ICP-OES, pH, phosphate, and conductivity. As shown in Table 11, leachates from the amine tailings, phosphate rock, and waste clay did not contain measurable amounts of rare earth elements. The leachate from the remediated phosphogypsum contained small amounts of cerium, lanthanum, neodymium, and yttrium. The pH of the leachates varied from 1.5 for waste clay to 4.2 for phosphate rock. Phosphate concentration varied from 0.6 ppm for the amine tailings to 21.30 ppm for the phosphogypsum, and conductivity varied from 104.5 μ S for the amine tailings to 10.45 mS for the waste clay.

RECYCLED POLYMER PERFORMANCE

As shown in Table 12, loss in polymer performance over ten treatment cycles with the various extracts was not observed. Due to the variable moisture content of the recycled polymer at the start of each run, and the normalization of the metal binding data in milligrams of metal per gram of polymer, the standard deviations of the means of the ten determinations were relatively high. A consistent pattern indicating loss of polymer performance was not observed.

Table 11. Determination of Rare Earth Element Content in Residual Leachates of Remediated Solids.

Element	Amine Tailings	Phosphogypsum	Phosphate Rock	Waste Clay
Cerium	BLD	86.61 ppb	BLD	BLD
Dysprosium	BLD	BLD	BLD	BLD
Erbium	BLD	BLD	BLD	BLD
Gadolinium	BLD	BLD	BLD	BLD
Holmium	BLD	BLD	BLD	BLD
Lanthanum	BLD	61.64 ppb	BLD	BLD
Lutetium	BLD	BLD	BLD	BLD
Neodymium	BLD	51.88 ppb	BLD	BLD
Scandium	BLD	BLD	BLD	BLD
Samarium	BLD	BLD	BLD	BLD
Terbium	BLD	BLD	BLD	BLD
Yttrium	BLD	22.68 ppb	BLD	BLD
Ytterbium	BLD	BLD	BLD	BLD
Praseodymium	BLD	BLD	BLD	BLD
Uranium	BLD	BLD	24.18 ppb	BLD
Thorium	BLD	BLD	BLD	BLD
Phosphorus	0.60 ppm	21.30 ppm	13.55 ppm	1.21 ppm
Conductivity	104.5 μ S	2.88 mS	215 μ S	10.45 mS
pH	4.10	2.65	4.23	1.58

Table 12. Recycled Polymer Performance.

Element	Average REE Bound (10 cycles) Amine Tailings (mean \pm SD)	Average REE Bound (10 cycles) Phosphogypsum (mean \pm SD)	Average REE Bound (10 cycles) Phosphate Rock (mean \pm SD)	Average REE Bound (10 cycles) Waste Clay (mean \pm SD)
Cerium	91% \pm 11%	84% \pm 17%	88% \pm 10%	83% \pm 12%
Dysprosium	91% \pm 11%	78% \pm 19%	82% \pm 15%	81% \pm 13%
Erbium	94% \pm 12%	79% \pm 21%	81% \pm 15%	80% \pm 13%
Gadolinium	91% \pm 11%	74% \pm 18%	82% \pm 16%	79% \pm 14%
Holmium	96% \pm 14%	90% \pm 22%	74% \pm 23%	77% \pm 17%
Lanthanum	92% \pm 10%	85% \pm 16%	81% \pm 15%	80% \pm 15%
Lutetium	N/A	N/A	100% \pm 0%	100% \pm 0%
Neodymium	94% \pm 7%	89% \pm 14%	87% \pm 10%	85% \pm 12%
Scandium	69% \pm 23%	N/A	69% \pm 17%	100% \pm 0%
Samarium	92% \pm 10%	80% \pm 18%	84% \pm 13%	84% \pm 12%
Terbium	96% \pm 14%	88% \pm 26%	77% \pm 20%	83% \pm 19%
Yttrium	85% \pm 16%	68% \pm 29%	84% \pm 14%	72% \pm 17%
Ytterbium	96% \pm 11%	89% \pm 25%	82% \pm 17%	80% \pm 14%
Praseodymium	95% \pm 17%	100% \pm 0%	86% \pm 16%	83% \pm 23%
Uranium	80% \pm 12%	82% \pm 15%	70% \pm 13%	85% \pm 15%
Thorium	98% \pm 7%	100% \pm 0%	N/A	100% \pm 0%

CONCLUSIONS AND RECOMMENDATIONS

The results of this study suggest that PX-107 is a highly efficient and cost effective extraction solution for the removal of rare earth elements and other metals from phosphate mining waste products. Additionally, recovery of the extracted metals from PX-107 using poly 1-octadecene 2,5-furandione salt was nearly quantitative at a pH of 1.5. The ability to reuse the adsorption polymer increases the economic viability of this process for REE extraction and recovery. The effect of particle size, drying temperature, and extraction solution temperature on REE extraction rates should be investigated further. Treatment of phosphogypsum stack water and leachate with poly 1-octadecene 2,5-furandione salt may be an effective way to reduce the possibility of groundwater and surface water contamination by the heavy metals, thorium, and uranium associated with stack runoff.

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