

Article

Rare Earth Element Recovery from Acidic Extracts of Florida Phosphate Mining Materials Using Chelating Polymer 1-Octadecene, Polymer with 2,5-Furandione, Sodium Salt

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Abstract: To meet the growing global demand for rare earth elements (REEs), nontraditional mining sources of these metals are being investigated. Phosphate ore and phosphate mining wastes have been identified as possible alternative sources to REEs. In this study, REEs were extracted from Florida phosphate mining materials using mineral and organic acids. The REEs were then recovered at high efficiencies using a chelating polymer, 1-octadecene, polymer with 2,5-furandione, sodium salt. At pH 1.5, the chelation polymer effectively bound nearly 100% of the rare earth elements extracted from the solids. 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. These results suggest that this chelating polymer efficiently recovers rare earth elements from acidic extracts of phosphate mining waste products.

Keywords: phosphate; phosphogypsum; acid extraction; REE recovery

1. Introduction

Phosphate mining and fertilizer production is a vital global industry and is essential to global agriculture and food markets. One of the most common phosphate sources is fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$), with monazite ($(\text{Ce},\text{La},\text{Nd},\text{Th})\text{PO}_4$, SiO_4) and xenotime (YPO_4) being phosphate-containing minerals commonly found with fluorapatite at around 1% by mass [1]. While monazite and xenotime are sources of phosphate, they are also an important source of elements known as rare earth elements (REEs). REEs are commonly substituted in place of calcium in the mineral structure. REEs are a group of 17 elements comprising the 15 lanthanide elements along with yttrium and scandium. Although not part of the lanthanide series of elements, yttrium and scandium are included because they have similar geochemical properties. The REEs are important elements because they are used in many technology- and energy-related applications: high-strength permanent magnets, lightweight alloys, electric motors, petrochemical refining, and fluorescent/optical displays [2].

During phosphate mining in Florida, the phosphate ore is purified and concentrated to attain phosphate rock, while the less concentrated portions, in the form of phosphatic clay and sand, are discarded. The phosphate is then extracted from the phosphate rock as liquid phosphoric acid, with the residual solid being CaSO_4 or phosphogypsum. Due to the presence of monazite and xenotime, Florida phosphate rock, phosphate clay, and phosphogypsum have been shown to contain significant levels of REEs [3–9]. It is estimated that 100,000 tons of REEs are co-mined with phosphate rock annually; these REEs become discarded as waste or remain in the phosphate-containing fertilizer or end product, making them a potential source for REEs [1].

While using phosphate rock and phosphate mining materials as a new source of REE metals is promising, there are technological hurdles that need to be addressed to make the process economically viable. Currently, the extraction and separation of REEs involves complex chemistries as well as advanced engineering and environmental considerations. One approach for extracting the REEs from phosphate mining materials is by leaching with different extraction liquids. Previous studies have used concentrated strong acids to extract REEs from phosphate mining materials; however, the use of concentrated strong mineral acids comes with economic and environmental drawbacks, including long reaction times often at elevated temperatures [10–13]. To circumvent the disadvantages of strong mineral acids, weak organic acids can be used to produce REE complexes that improve dissolution [14]. In addition, organic acids can act as reducing agents and can control the oxidation state of the REEs, preventing the formation of insoluble REE oxides and leading to enhanced extraction concentrations [15].

REEs leached from phosphate mining materials need to be recovered from the extraction medium. Previous studies have used phosphoric acid-based solvent recovery chemicals or ion exchange resins to recover REEs from acid leach solutions [16,17]. Other investigations have attempted to improve this recovery process by removing non-REE impurities by magnetic separation or selective precipitation [18,19]. However, these methods have not yet seen widespread commercial acceptance because of various limitations, such as high cost, low efficiency, and the inability to economically extend the technology to large-scale operations.

Recently, the use of sorbents during the extraction process has been investigated. Rychkov and co-workers [4,20] reported the use of Purolite C160 as a cation exchange resin for the separation of REEs from phosphogypsum acidic suspensions. Purolite C160 is a polystyrenic, macroporous, strong acid cation resin that contains sulfonic acid functional groups. This resin has been shown to exhibit Freundlich isotherm behavior and a regeneration efficiency of more than 95% [21]. When used for the recovery of REEs from acid mine drainage, this resin had affinities for calcium and magnesium, and showed adsorption yields for the REEs of 85% to 89% [22].

In this study, we investigate the use of a chelating polymer, 1-octadecene, polymer with 2,5-furandione, sodium salt, to recover REEs from acid leach solutions. This chelation polymer is water-insoluble, and has been shown to possess novel metal adsorption characteristics [23]. It demonstrates metal adsorption capacities substantially higher than those of other heterogeneous adsorbents and almost equivalent to those obtained with homogeneous adsorbents. Additionally, the polymer exhibits pseudo-second-order kinetics, and has an adsorptive behavior accurately characterized by the Dubinin–Radushkevich isotherm model. The working pH range of the polymer is 1.5 to 14.

1-Octadecene, polymer with 2,5-furandione, sodium salt, contains dicarboxylic head groups that have high affinity for several polyvalent metal ions, including the transition metals and lanthanides, while showing low affinity for calcium and magnesium. In addition, the chelating polymer does not contain nitrogen, sulfur, or phosphorus; it can be efficiently filtered from aqueous solutions; and it can be regenerated for multiple recovery processes, making it environmentally friendly and economically attractive [3,23].

In the present study, we investigate the recovery of REEs from acidic extracts of four materials produced during phosphate mining: phosphate rock, phosphatic waste clay, phosphogypsum, and amine flotation tailings. The chelating polymer (1-octadecene, polymer with 2,5-furandione, sodium salt) is used to recover the REEs from acid extraction solutions.

2. Materials and Methods

Nitric acid (trace metal grade), citric acid anhydrous (lab grade), and ascorbic acid were purchased from Fisher Scientific (Waltham, MA, USA) and used as received without further purification. Phosphate rock, phosphogypsum, waste clay, and amine tailings were obtained from the Florida Institute of Phosphate Research (FIPR) Institute (Bartow, FL, USA). Poly(maleic anhydride-alt-1-octadecene) was

purchased from Chevron Phillips Chemical Company (The Woodlands, TX, USA) and was converted to 1-octadecene, polymer with 2,5-furandione, sodium salt (also referred to as poly(2-octadecyl butanedioic acid)) [23]. The REE, uranium, and thorium content of the phosphate materials were determined by ACZ Laboratories, Inc. (Steamboat Springs, CO, USA) using EPA Methods M3050B and M6020. The REE, uranium, and thorium content of the extracts and polymer-treated filtrates were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) using a Horiba Activa M ICP (Edison, NJ, USA). ICP standard solutions were purchased from Exatol Chemical Corporation (Clearwater, FL, USA). Moisture content was determined using a Mettler Toledo HB43-S Moisture Balance. Particle size was determined by a Microtrac S3500 laser diffraction particle analyzer (Microtrac, Inc., Montgomeryville, PA, USA).

2.1. Acid Extraction Methods

The extraction of REEs from the phosphate rock, phosphogypsum, waste clay, and amine tailings was performed in triplicate and carried out as follows: Each phosphate material was dried overnight in an oven at 100 °C. After drying, 40 g of a given material was mixed with 300 mL of the desired acid extraction solution (Table 1) under magnetic stirring for 15 min at room temperature (25 °C). After 15 min, the extraction solution was collected using vacuum filtration. The solid filter cake was then washed with 50 mL of the same acid extraction solution and washed again with 50 mL of deionized water. The filtrate was then collected and analyzed for REE, uranium, and thorium content using ICP-OES.

2.2. REE, Uranium, and Thorium Recovery Methods

The filtrates collected above were used to assess the REE metal recovery ability of 1-octadecene, polymer with 2,5-furandione, sodium salt. First, the pH of the filtrate was adjusted to pH 1.5 with sodium hydroxide. The pH values of the filtrates before adding NaOH were 1.44, 0.81, 0.89, and 0.79 for phosphate rock, phosphogypsum, waste clay, and amine tailings, respectively. Then, 5.0 mL of the pH-adjusted filtrate was diluted with 5.0 mL of deionized water, and 0.3 g (for phosphate rock, phosphogypsum, and waste clay) or 0.2 g (for amine tailings) of 1-octadecene, polymer with 2,5-furandione, sodium salt, was added to the diluted filtrate. The mixture was shaken for 1 h on a rotary shaker at 150 rpm and then syringe-filtered through 1.2 µm and 0.22 µm filters. The filtrates were analyzed for REE, uranium, and thorium content by ICP-OES.

2.3. Data Analysis

The REE, uranium, and thorium concentration in mg per g of material ($[REE,U,Th]_{mg/g}$) were calculated with the following equation:

$$[REE, U, Th]_{mg/g} = \frac{[REE, U, Th]_{ICP,ppm} \times Volume_L}{Mass\ of\ sample} \times Dilution\ factor, \quad (1)$$

where $[REE,U,Th]_{ICP,ppm}$ is the concentration from ICP-OES intensities in ppm and $Volume_L$ is the volume of acid used during the extraction in liters. A dilution factor was applied to the pH-adjusted extracts and the filtrates after polymer binding to account for the change in volume due to the addition of NaOH solution.

The standard deviation of the replicate extraction data was calculated using Equation (2):

$$S = \sqrt{(x_{i1} - x_{i2})^2 / 2}, \quad (2)$$

where x_{i1} and x_{i2} are the concentrations for REEs from separate individual extractions.

Table 1. List of Acid Extraction Solvents.

Acid Extraction Solution	Acid Composition
1	2.5% HNO ₃
2	2.5% H ₂ SO ₄
3	1.25% HNO ₃ + 1.25% H ₂ SO ₄ (2.5% total)
4	2.5% HNO ₃ + 5% Citric Acid
5	2.5% HNO ₃ + 5% Ascorbic Acid
6	2.5% H ₂ SO ₄ + 5% Citric Acid
7	2.5% H ₂ SO ₄ + 5% Citric Acid

3. Results and Discussion

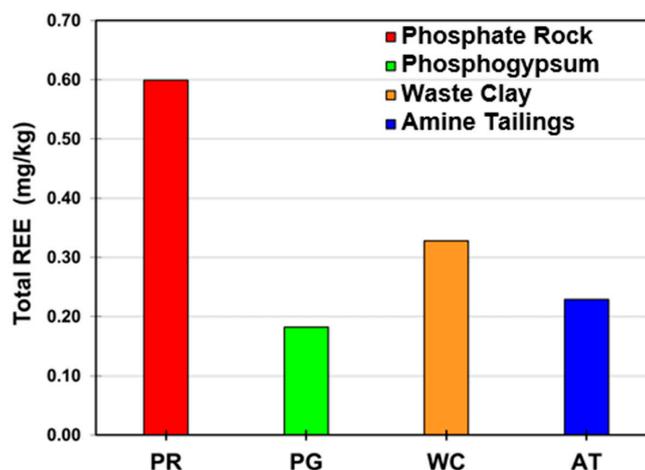
3.1. Acid Extraction

The physical characteristics for the phosphate materials tested can be found in Table 2. The particle size of the waste clay was difficult to determine because of its high moisture content; then, after drying, it formed large particles several millimeters in size. The moisture content of the phosphate rock showed no loss on drying, because it was supplied having been previously dried by FIPR. The mineralogy of the samples tested have been reported [6,8,9,24–26].

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

Sample Description	Sample Appearance	Average Moisture Content (before Drying)	Average Moisture Content (after Drying)	Average Particle Size (d50)
Phosphate Rock	Fine gray sand	1.14%	1.14%	257.3 µm
Phosphogypsum	Gray to beige powder	19.36%	0.89%	72.45 µm
Amine Tailings	Gray to brown wet powder	20.77%	0.23%	168.8 µm
Waste Clay	Gray	60.64%	1.70%	Not Determined

Figure 1 shows the amount of total REEs contained in each phosphate material. The levels of each individual REE can be found in Supporting Information. The highest levels of REEs were in phosphate rock, followed by waste clay, amine tailings, and phosphogypsum. The levels of REEs reported are commensurate with previous studies on Florida phosphate rock and phosphate wastes [1]. Phosphate rock contains the highest levels of REEs because it has the highest concentration of fluorapatite and the REE-bearing minerals monazite and xenotime.

**Figure 1.** Total rare earth elements (REEs) contained in phosphate rock and phosphate waste materials.

One goal of this study was to identify potential extraction conditions that lead to high REE extraction efficiencies while being compatible with the extraction polymer, 1-octadecene, polymer

with 2,5-furandione, sodium salt. High-temperature extractions are commonly advantageous for achieving higher extraction efficiencies; however, high temperatures can have adverse effects when dealing with phosphate rock and phosphate wastes. High-temperature acid extractions can lead to the increased dissolution of silicon and fluorine, which can lead to the formation of low-solubility REE fluorides [27]. Also at high temperatures, calcium sulfate will convert to the anhydrous state, which has a significantly lower solubility than the hydrated form [28]. Hence, room-temperature extractions were used throughout this study.

It should be noted that to assess the actual environmental and economic viability of these potential extraction methods, larger-scale studies would be required to address parameters such as waste moisture content (dewatering), particle size (milling), solid-to-liquid ratio, and mixing efficiency. This study was designed, in part, to determine the compatibility of the extraction polymer with previously reported acidic extract solutions of phosphate waste products rather than optimize the acid extraction process.

The results of the room-temperature extractions are shown in Figure 2. When using only mineral acids, the following trend was observed for the extraction efficiency of REEs: $\text{HNO}_3 > \text{HNO}_3/\text{H}_2\text{SO}_4 > \text{H}_2\text{SO}_4$. This trend was observed in all the phosphate materials tested. This can be attributed to the solubility of calcium sulfate, and is consistent with previous studies, including the recent work of Walawalker et al. [28]. Calcium nitrate has a higher solubility than calcium sulfate and is capable of dissolving more of the calcium minerals/salts; this leads to the better extraction of the REEs contained in the calcium minerals. While HNO_3 was more efficient at the extraction of the total REEs than H_2SO_4 , some individual REEs showed an increased percentage of extraction when compared to the total REEs when using H_2SO_4 , most notably, yttrium (Individual REE extraction data are contained in Supplementary Materials). When comparing the two REEs highest in concentration, cerium and yttrium, cerium showed an increased extraction in HNO_3 and an increased percentage when compared to the total REEs extracted (Figure 3a). Conversely, yttrium showed that a higher percentage was extracted in H_2SO_4 when compared to the other REEs (Figure 3b).

When adding organic acids, citric acid, when mixed with HNO_3 , increased the extraction of REEs in only phosphate rock and phosphogypsum (Figure 2). When citric acid was used with H_2SO_4 , it increased the REE extraction in phosphogypsum and amine tailings, but not phosphate rock or waste clay. Ascorbic acid showed an increased REE extraction in only waste clay, when using HNO_3 . When using H_2SO_4 , ascorbic acid had a slightly increased extraction in phosphate rock and phosphogypsum. Calcium ascorbate had a significantly higher solubility when compared to calcium citrate and calcium sulfate; hence, the increased solubility when adding ascorbic acid to H_2SO_4 can be attributed to the increased calcium dissolution from the phosphate materials, and is in agreement with the results of Mishelevich et al. [29]. However, as calcium has a high solubility in HNO_3 , the addition of ascorbic acid had minimal effects on the REE extraction when added to HNO_3 .

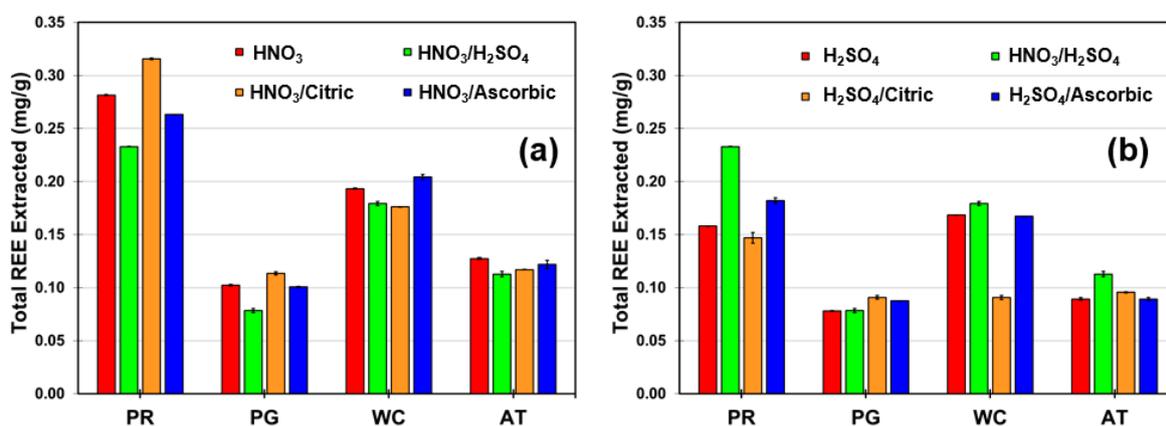


Figure 2. Extracted REEs using mixtures of (a) HNO_3 , (b) H_2SO_4 , citric acid, and ascorbic acid.

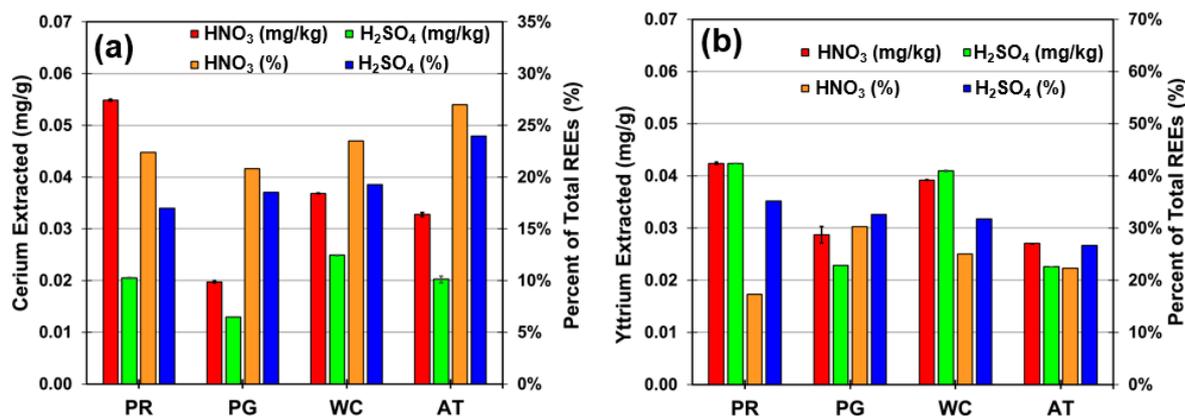


Figure 3. Extracted (a) cerium and (b) yttrium levels in HNO₃ and H₂SO₄.

Along with increasing the calcium/REE dissolution, ascorbic acid has the ability to act as a reducing agent; this ability could have an impact on cerium dissolution [15]. Cerium under mild aqueous conditions will occur in the Ce³⁺ state; however, at low pH and highly oxidative conditions, cerium can convert to the Ce⁴⁺ state, which forms insoluble Ce(IV) oxide [15]. In Figure 4, the addition of ascorbic acid to H₂SO₄ increased the cerium extraction in all phosphate materials; however, this could be a result of the increased calcium and total REE dissolution. When added to HNO₃, ascorbic acid only produced an increase in cerium extraction in waste clay (Figure 4). This could indicate more Ce(IV) being present in the waste clay when compared to the other phosphate materials.

Small amounts of uranium and thorium were co-extracted with the REEs in HNO₃. Extraction yields for uranium were 29%, 38%, 47%, and 16% from phosphogypsum, phosphate rock, waste clay, and amine tailings, respectively. Extraction yields for thorium were 26%, 0%, 38%, and 20% from phosphogypsum, phosphate rock, waste clay, and amine tailings, respectively (see Supplementary Materials).

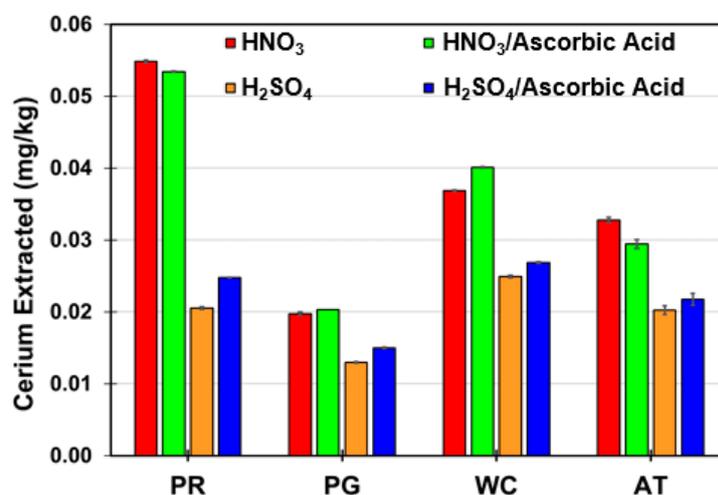
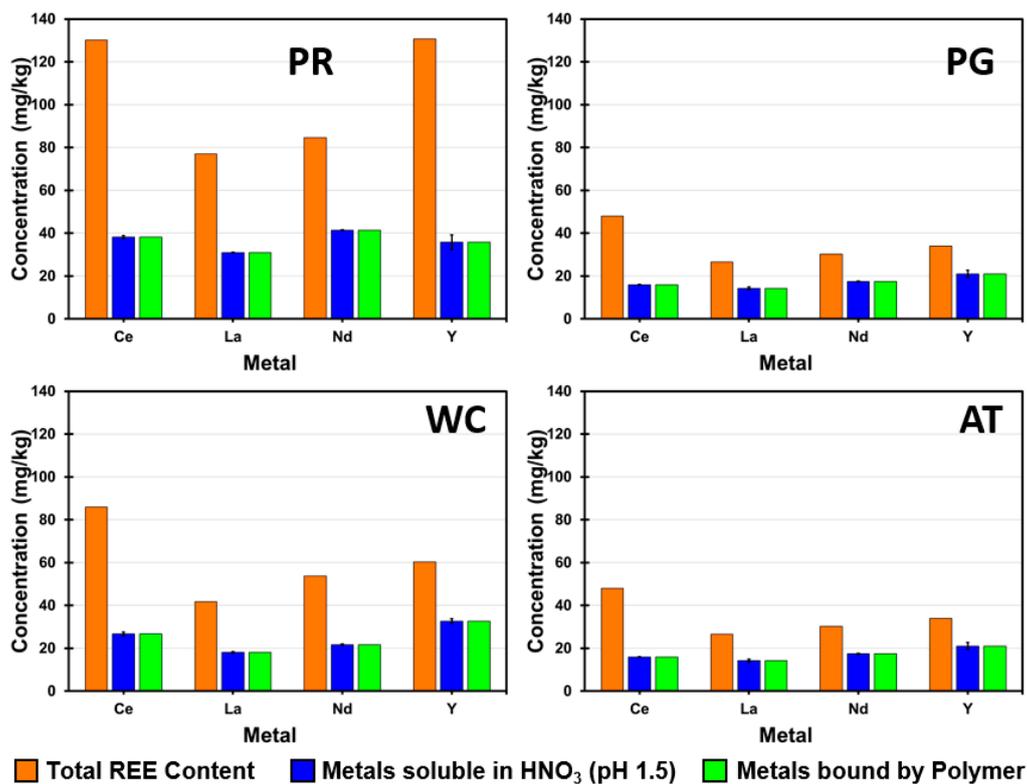


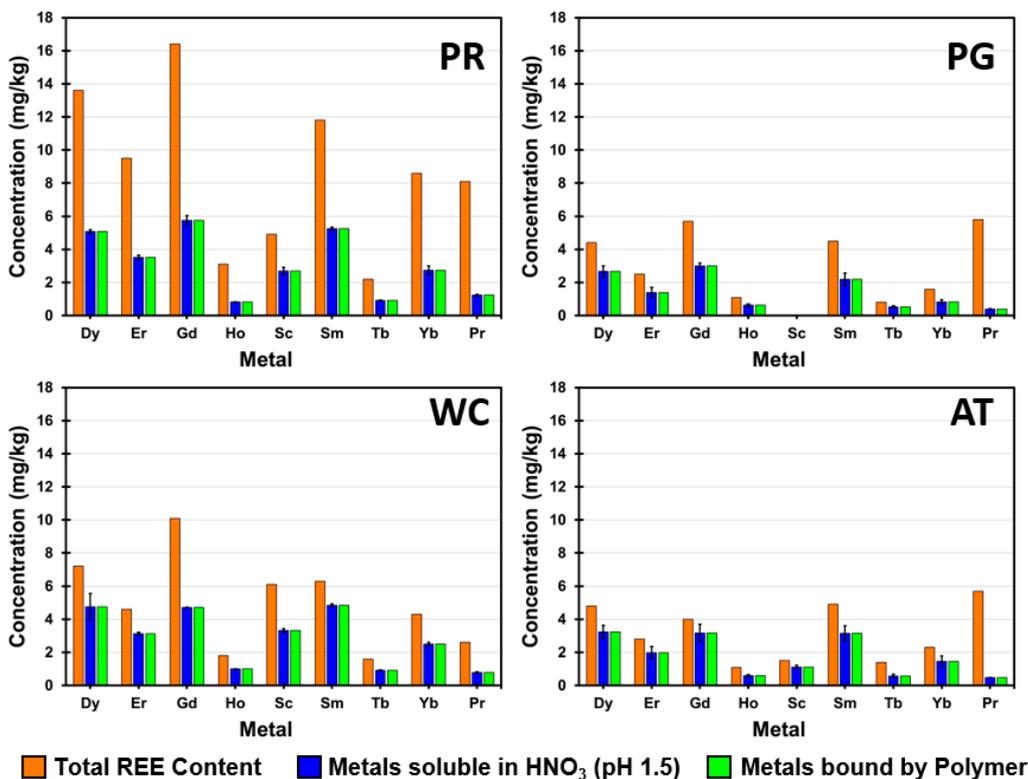
Figure 4. Extracted cerium levels with ascorbic acid.

3.2. REE, Uranium, and Thorium Recovery

REE recovery studies using 1-octadecene, polymer with 2,5 furandione, sodium salt, showed that the polymer bound REEs from all of the acid extract solutions. Due to the generally higher level of REEs extracted with the nitric acid solution, comprehensive REE recovery studies were performed using HNO₃ extraction solutions with the results being shown in Figure 5a (REEs present in high concentration) and Figure 5b (REEs present in low concentration).



(a)



(b)

Figure 5. (a) High-concentration REE recovery using 1-octadecene 2,5-furandione, sodium salt, in phosphate rock (PR), phosphogypsum (PG), waste clay (WC), and amine tailings (AT). (b) Low-concentration REE recovery using 1-octadecene 2,5-furandione, sodium salt, in phosphate rock (PR), phosphogypsum (PG), waste clay (WC), and amine tailings (AT).

In this study, overall extraction and recovery yields for the rare earth elements 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. Polymer recoveries for uranium were 23%, 31%, 47%, and 16% from phosphogypsum, phosphate rock, waste clay, and amine tailings, respectively. Polymer recoveries for thorium were 26%, 38%, and 20% from phosphogypsum, waste clay, and amine tailings, respectively. As noted in Section 3.1, thorium was not extracted by HNO₃ from phosphate rock under the conditions used in this study (see Supplementary Materials).

1-Octadecene, polymer with 2,5 furandione, sodium salt, bound 100% of the extracted REE in the acidic solution, representing a significant improvement to the yields of 85% to 89% previously reported for Purolite 160 [22]. This is likely due to the Freundlich isotherm behavior exhibited by Purolite 160 and other cation exchange resins, indicating monolayer coverage of the adsorbent surface by the metal, equal adsorbent affinity for all the binding sites, and that the adsorption at one site does not affect the adsorption at an adjacent site [21]. By contrast, 1-octadecene, polymer with 2,5 furandione, sodium salt, exhibits behavior best characterized by the Dubinin–Radushkevich isotherm with a mean free energy of adsorption of 31.6 kJ·mol⁻¹, and a metal ion concentration-dependent Gibb's free energy of -6.50 to -11.61 kJ·mol⁻¹. This indicates that the polymer has a heterogeneous sorbent surface with spontaneous chemisorption (major) and physisorption (minor) properties [23].

The extraction polymer was able to retain its ability to bind REEs in the presence of high levels of calcium and total dissolved solids. This is an improvement to the selectivity reported by Felipe et al. for Purolite 160 [22]. Additionally, the polymer was stable to corrosive, low-pH environments, including nitric acid solutions. As the extraction polymer is water-insoluble, this recovery process avoids the reported limitations of organic solvent contamination and emulsion formation associated with solvent extraction techniques for REE recovery [27]. Additionally, the insolubility of the extraction polymer in water avoids the high cost and technical limitations associated with organic solvent-soluble metal binding ligands [30].

Previous studies have shown that the chelating polymer can be recycled and used for multiple recovery processes [3,23]. We have successfully eluted the REEs from the polymer with dilute mineral acid solutions, and reused the polymer for subsequent recovery studies for 20 cycles without loss of function.

4. Conclusions

The two main objectives of this study were to a) identify potentially efficient REE extraction conditions that show compatibility with the extraction polymer, 1-octadecene, polymer with 2,5-furandione, sodium salt, and b) determine the ability of the extraction polymer to bind rare earth metals in a corrosive, low-pH environment containing high levels of calcium and other dissolved metals.

The extraction of REEs from phosphate rock and phosphate materials was investigated in dilute mineral acids with the addition of organic acids. In general, phosphate rock contained the highest levels of REEs and, under the extraction conditions employed in this study, HNO₃ was the most efficient acid for extracting REEs. Additional large-scale extraction and processing studies will need to be conducted to determine the optimal extraction conditions and perform accurate mass balance calculations. Based on the results of this and prior studies, numerous parameters, such as the moisture content of the waste solid, particle size of the solids, solid-to-liquid ratio, mode(s) of agitation, and means of separating the extraction solution from the waste solids will need to be optimized, along with determining if the extraction solution can be reused. As these and other parameters are likely to significantly impact both the performance and economic viability of this extraction process, an economic analysis of this step of the process was not possible in this study.

The REEs were recovered from HNO₃ extraction solutions using 1-octadecene, polymer with 2,5-furandione, sodium salt. At pH 1.5, the chelating polymer bound 100% of the REEs from phosphate

rock, phosphogypsum, waste clay, and amine tailings, representing an improvement over strong acid cationic exchange resins such as Purolite 160.

The results of this study suggest that this polymer efficiently recovers rare earth elements from acidic extracts of phosphate mining waste products.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2075-163X/9/8/477/s1>, Table S1: Polymer Binding and Percent Rare Earth Element Recovery.

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Conflicts of Interest: The authors are current or former employees of Periodic Products, Inc. Intellectual property associated with 1-octadecene, polymer with 2,5-furandione, sodium salt is currently owned by Periodic Products, Inc.

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