UC Berkeley
UC Berkeley Previously Published Works

Title

Concomitant Leaching and Electrochemical Extraction of Rare Earth Elements from Monazite

Permalink

Journal

ISSN

Authors

Maes, Synthia
Zhuang, Wei-Qin
Rabaey, Korneel
et al.

Publication Date

DOI

Peer reviewed

Concomitant Leaching and Electrochemical Extraction of Rare Earth Elements from Monazite

Synthia Maes[†], **Wei-Qin Zhuang**[‡§], **Korneel Rabaey**[†], **Lisa Alvarez-Cohen**[§∥], and **Tom Hennebel**[‡†§]

[†] Center for Microbial Ecology and Technology (CMET), Ghent University, Coupure Links 653, B-9000 Gent, Belgium

[‡] Department of Civil and Environmental Engineering, The University of Auckland, Auckland 1142, New Zealand

[§] Department of Civil and Environmental Engineering, University of California, Berkeley, California 94720-1710, United States

[∥] Earth and Environmental Sciences Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, California 94720, United States

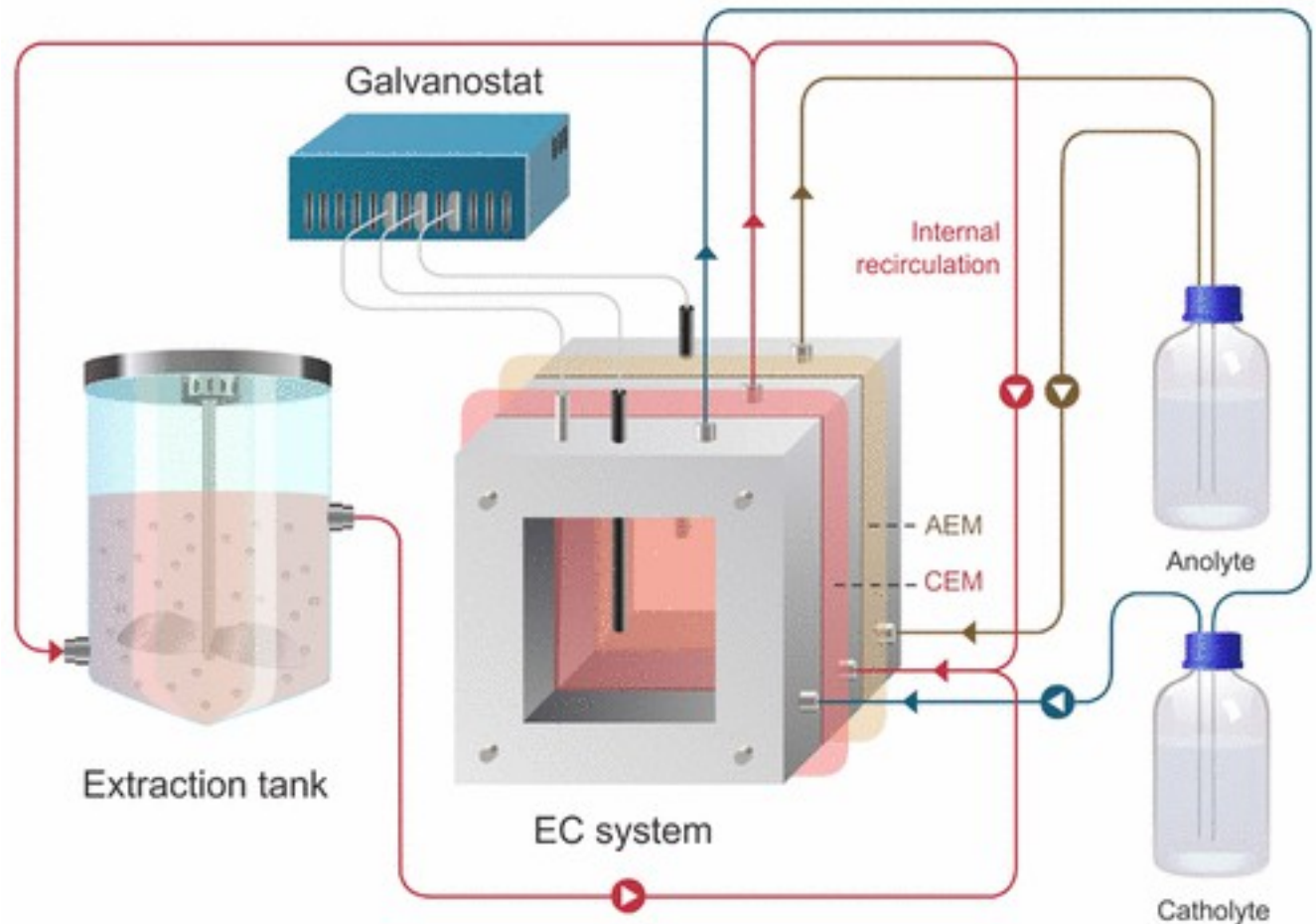*Center for Microbial Ecology and Technology (CMET), Ghent University, Coupure Links 653, B-9000 Gent, Belgium. E-mail: Tom.Hennebel@ugent.be. Telephone: +32(0)9 2645985. Fax: +32(0)9 2646248.

-

Abstract

Rare earth elements (REEs) have become increasingly important in modern day technologies. Unfortunately, their recycling is currently limited, and the conventional technologies for their extraction and purification are exceedingly energy and chemical intensive. New sustainable technologies for REE extraction from both primary and secondary resources would be extremely beneficial. This research investigated a two-stage recovery strategy focused on the recovery of neodymium (Nd) and lanthanum (La) from monazite ore that combines microbially based leaching (using citric acid and spent fungal supernatant) with electrochemical extraction. Pretreating the phosphate-based monazite rock (via roasting) dramatically increased the microbial REE leaching efficiency. Batch experiments demonstrated the effective and continued leaching of REEs by recycled citric acid, with up to 392 mg of Nd L^{-1} and 281 mg of La L^{-1} leached during seven consecutive 24 h cycles. Neodymium was further extracted in the catholyte of a three-compartment electrochemical system, with up to 880 mg of Nd L^{-1} achieved within 4 days (at 40 A m^{-2}). Meanwhile, the radioactive element thorium and counterions phosphate and citrate were separated effectively from the REEs in the anolyte, favoring REE extraction and allowing sustainable reuse of the leaching

agent. This study shows a promising technology that is suitable for primary ores and can further be optimized for secondary resources.

-

Introduction

The transition to a low-carbon economy has resulted in a growing demand for rare earth elements (REEs, including neodymium and lanthanum) because these are vital to many green technology products such as wind turbines and (hybrid) electric vehicles.[1-3] REEs are mainly mined as byproducts, and together with China's dominance on the REE production market (currently producing 85% of the global supply[4]), this has led to a supply risk in the United States and European Union.[5-11] While the current low value of REEs (e.g., $37–42 kg^{-1} for Nd_2O_3)[4] makes end-of-life recycling financially challenging (recycling rate of <1% for Nd),[12] it is recognized that recycling could reduce the sensitive dependence on virgin materials, especially for resource-limited countries.[2, 3, 7] Furthermore, conventional techniques for extracting REEs from the main ores are typically energy (>140 °C) and chemical intensive (e.g., concentrated sulfuric acid or sodium hydroxide), producing toxic waste streams that possibly contain radionuclides such as thorium and uranium.[5, 13] Consequently, new green technologies are needed to extract and recover REEs from both primary ores and secondary resources, such as preconsumer and end-of-life residues.[1, 9, 14]

Biometallurgical technologies, i.e., metallurgy based on microbial–metal interactions, can potentially serve as more environmentally friendly alternatives for the extraction, processing, and recycling of metals.[1, 15] Microorganisms (fungi, yeasts, and bacteria) can allow heterotrophic bioleaching, i.e., the leaching of metals from solid waste streams by the production of organic leachates (e.g., citric, oxalic, or gluconic acid).[15-17] Citric acid is of special interest, as it forms stable complexes with trivalent REEs (e.g., stability constant log β = 7.7 for Nd citrate[18]). REE recovery was recently investigated via diverse pathways: chemical leaching from monazite by organic acids[18] and bioleaching from red mud using *Penicillium* sp.[19] or from monazite using phosphate-solubilizing bacteria or fungi.[13, 20, 21]

In subsequent steps, metal ions (e.g., Cu, Cd, Pb, and Zn[15, 22]) can be removed and recovered from liquid waste streams with minimal chemical usage by electrochemical (EC) and bioelectrochemical processes by means of electrodeposition, if readily reducible, or further concentration in smaller volumes.[23-25] However, although electrodeposition of REEs is not

feasible from aqueous solutions [e.g., $E°(Nd^{3+})$ = –2.3 V vs the standard hydrogen electrode (SHE)], [25] electrochemical processes can be used to extract and enrich elements to concentrations sufficiently high for conventional use or postprocessing; i.e., via application of a voltage across the cell, an EC process generates protons at the anode (oxidation of water: $2H_2O \rightarrow 4H^+ + O_2 + 4e^-$) and hydroxide ions at the cathode (reduction of water: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$), and electrons flow from the anode to the cathode. This electrical current induces electromigration of anions or cations to the corresponding electrode to balance the electron flux. The electrochemical processing of a few REEs was recently demonstrated using mobile electronics scrap.[25] Electrodialysis, based on electromigration across (pairs of) different membranes, has been used extensively for desalination and has been studied for the removal of heavy metal from wastewater.[26, 27]

This study was aimed at the development and investigation of a potentially environmentally friendly REE extraction and recovery approach based on bioleaching with microbially based organic acids such as citric acid and a spent fungal supernatant, followed by membrane electrolysis. The two-stage recovery strategy was tested with monazite (REE phosphate ore) and synthetic neodymium solid sources [$NdCl_3$, $NdPO_4$, and $Nd_2(CO_3)_3$] and focused on the recovery of neodymium as a proxy for the light REEs (lanthanum, cerium, praseodymium, and neodymium) into more concentrated liquid streams.

-

Materials and Methods

Batch Leaching Experiments

Leaching experiments were performed in 50 mL tubes (flat-bottom, polypropylene), containing 0.1 g of the monazite sample (untreated or roasted monazite; City Chemical LLC, West Haven, CT) and 20 mL of the leaching solution. Both citric acid (0.05–1 M, prepared with deionized water) and a spent fungal supernatant (harvested after growth for 6 days) were investigated as leaching solutions. Test tubes were incubated at room temperature (23 ± 2 °C) and their contents stirred at 250 rpm for 32 h (using a magnetic stirrer). Sequential batch treatments were performed, as well (24 h per cycle), in which either the supernatant or the monazite was recovered, while new monazite or lixiviant was replenished. Experimental details about the roasting of the monazite and the cultivation of the fungi can be found in the sections S1.1 and S1.2 of the Supporting Information.

Electrochemical Reactor Experiments

Experiments were performed in a three-compartment electrochemical cell [three chambers, each with internal dimensions of 8 cm × 8 cm × 2 cm and an effective volume of 128 mL (Figure S6)]. The

middle compartment of the electrochemical cell was separated from the anode and cathode with an anion exchange membrane (AEM) (AM-7001 Anion Exchange Membranes, Membranes International Inc.) and a cation exchange membrane (CEM) (CEM Type II, Fujifilm Membrane Technology), respectively. A stainless steel wire mesh was used as the cathode (Solana) and an IrOx-coated titanium electrode as the anode (Magneto Special Anodes BV). The anode and cathode had a projected electrode surface area of 64 cm^2 each. All electrochemical experiments were performed at a fixed current of 40 A m^{-2}, controlled by a VSP multipotentiostat (Bio-Logic). A Ag/AgCl-saturated KCl reference electrode was placed in the cathode compartment (distance to cathode, 0.5 cm). Reactor experiments were performed at room temperature (23 ± 2 °C). All three compartments were operated in batch mode with a recirculation rate of 24 mL min^{-1}.

The anolyte and catholyte consisted of a 10 mM Na$_2$SO$_4$ solution (volume of 400 mL each). A 2 L Scott bottle was used as the extraction tank, containing the desired REE solid and a 0.5 M citric acid solution (4.7 g of monazite/L of leachate, volume of 750 mL), and they were stirred continuously at room temperature. The leachate from the extraction tank was continuously filtered prior to reactor circulation (seaweed membrane) to prevent the presence of microbial biomass and solid monazite particles in the EC system.

The settings and design of the electrochemical system were slightly modified for the last two experiments (results in [Figure 5](#)). A smaller cathode (8 cm × 8 cm × 0.6 cm) and a smaller catholyte volume (70 mL) were used to increase the "extraction tank to catholyte" ratio. The reference electrode was placed in the anode compartment instead of the cathode compartment. The extraction tank consisted of a different Nd solution, Nd$_2$(CO$_3$)$_3$ as the Nd source (159 mg of Nd L^{-1}), 73 mg of PO$_4^{3-}$ L^{-1} as Na$_2$HPO$_4$, and 0.5 M citric acid (total volume of 1 L, pH 2.5–2.9).

Analytical Methods

For analysis of REE, Th, and P, samples from batch and reactor experiments were collected, filtered through a 0.2 μm filter, and diluted 10–1000-fold in deionized water acidified with 1.5% nitric acid and 0.5% hydrochloric acid. Samples were analyzed on an Agilent Technologies 7700 series ICP-MS instrument. New calibration standards were prepared before each sample run. Citric acid was quantified using high-performance liquid chromatography (HPLC) with a Bio-Rad Aminex HPX-87H carbohydrate/organic acid analysis column with 5 mM H$_2$SO$_4$ as the mobile phase at a flow rate of 0.6 mL min^{-1} on a Waters 2695 HPLC system. Citric acid was detected using a Waters 2996 UV absorption detector to monitor absorption at 210 nm. A calibration curve was prepared using citric acid standard solutions for the concentration range of 0.5–20 mM.

Results and Discussion

Leaching of Rare Earth Elements from Monazite

Monazite was selected as a model source of REEs to investigate the leaching of light rare earth elements from solid streams. The mineral ore consists predominantly of REE phosphates, which have very low solubility ($\sim 10^{-13}$ M in water).[28] Two different monazite pretreatments were selected for this study to determine the most effective REE recovery strategy, untreated and roasted monazite [i.e., reacted at high temperatures with Na_2CO_3 and NaCl (see section S1.1 of the Supporting Information)]. The microbial leaching performance was studied using a combination of spent fungal supernatant (more details in section S1.2 of the Supporting Information) and citric acid and compared to that observed with citric acid alone as a benchmark of an organic lixiviant, typically produced by fungi.[17]

The first leaching experiments studied both the effect of the citric acid concentration and the roasting of the monazite (Figures S1 and S2). A 0.5 M citric acid solution was the most effective, within the tested range of 0.05–1 M, and was selected for subsequent leaching experiments (Figure S1). The 0.5 M citric acid concentration exhibited significantly improved leaching of neodymium and lanthanum from the roasted monazite (106 mg of Nd L^{-1} and 156 mg of La L^{-1} within 32 h) compared to that from untreated ore (2.5 mg of Nd L^{-1} and 1.4 mg of La L^{-1}) (Figure S2). In contrast, lower cerium levels (1.1 vs 3.0 mg L^{-1}) and similar amounts of thorium (0.8–0.9 mg L^{-1}) were leached from roasted monazite compared to those found with untreated monazite. These concentrations of REEs leached from untreated ore are similar to those published previously by Goyne et al.[18] but were obtained over a much shorter time frame (32 h vs 28 days) and using lower pulp densities (5 g of untreated monazite L^{-1} vs 10 g of untreated monazite L^{-1}). Moreover, it is clear that pretreatment of the monazite by roasting dramatically increases the efficiency of the leaching.

The rare earth elemental composition and proportional release during leaching were studied for both untreated and roasted monazite samples. On the basis of absolute concentrations, 40 and 50% of the total Nd and La, respectively, in the roasted monazite were extracted with 0.5 M citric acid, while <0.3% Nd and 0.2% La were leached from untreated monazite. When comparing the leaching results to the original ore compositions [mole fractions of REEs (Figure S3)], we see that Nd was preferably leached compared to its presence in both types of monazite, representing 32–33% in the leachate versus 21–23% in the ore. Roasting the monazite also induced a higher proportion of leaching of lanthanum (50%) compared to that of the untreated sample (18%) but resulted in a severely diminished level of cerium extraction (<1%) compared to that of untreated ore (40%).

Because Ce is relatively abundant and easy to obtain while Nd is in lower relative supply, the selective leaching of Nd and La (after roasting) can be considered advantageous.[9, 29] During roasting, REE phosphates are converted into REE oxides, facilitating the leaching of rare earth elements.[29] Cerium, however, is presumably rearranged from Ce(III) into Ce(IV), which is less prone to leaching, during roasting.[30, 31] The rate of release of Th into solution was low for roasted monazite with <0.0018 mol of Th/mol of REEs in leachate compared to 0.10 mol of Th/mol of REEs in the ore, confirming the preferential release of REEs over thorium in previous research.[13] Given the radioactive nature of Th, a process that results in the preferential release of REEs from ore while leaving most of the Th in ore residue is highly beneficial.

Effects of Microbially Produced Organic Acids on REE Leaching

Previous research has shown that fungi can enhance REE leaching because of the production of additional organic substances beyond citric acid.[13, 19] This was further examined in this study using spent (substrate consumed) supernatant of fungal strain WE3-F (a *Paeciliomyces* spp. strain), combined with 0.5 M citric acid. The spent supernatant of this fungal strain contained at least acetic, gluconic, and succinic acids as major organic products.[13] However, the acidified supernatant exhibited only ~80% of the leaching efficiency of the citric acid control for Nd and La (Figure S2). Fungi are known to produce a diverse range of metabolites, with some, often unidentified, compounds that can enhance metal leaching.[13] Other metabolites such as oxalic acid[17] precipitate REEs and thus lower the recovery efficiency of an acidified supernatant. Furthermore, citric acid is a better chelating agent for REEs than acetic or succinic acid is, because of its three carboxylate groups.[32] Here we observed that for roasted monazite, cerium and thorium levels in the fungal leachate were similar to that of the citric acid only leachate. In previous studies with untreated monazite, Brisson et al.[13] observed that leachate containing fungal metabolites enhanced REE leaching compared to the leachate with single organic acids. They reported total REE concentrations of 30–45 mg L^{-1} by direct bioleaching (within 32 h) compared to 18 mg L^{-1} by abiotic leaching with citric acid (20 mM citric acid, acidified to pH 2.5 with HCl; 48 h). Abiotic leaching levels were similar to the values of this study, obtained at a 2-fold monazite concentration, i.e., 18 and 7.5 mg of total REEs L^{-1} for 10 and 5 g L^{-1} untreated monazite, respectively. Varying results in the literature indicate that the optimal leaching agent will depend on the REE source, the generated microbial products, and the experimental conditions.[13, 19, 20]

Assessment of Sequential Extraction Efficiency

Sequential batch tests with fresh lixiviant but the same monazite showed excellent initial leaching performances but lower leached REE concentrations over the course of five consecutive cycles

([Figure 1](#)). Approximately 80% of the Nd and La was recovered within the first 24 h cycle. As before, cerium and thorium did not leach very effectively as approximately 1 mg of Ce L^{-1} and 0.9 mg of Th L^{-1} were detected in the lixiviant (data not shown). Compared to the elemental composition of the roasted monazite, 43% Nd, 53% La, 0.3% Ce, and 0.6% Th were leached. Because the sequential leaching of monazite did not increase the level of extracted REEs substantially compared to the result of a single 32 h leaching cycle, we tested whether enhanced REE leaching could be promoted by recycling lixiviant with the addition of new monazite sand every cycle ([Figure 2](#) and [Figure S4](#)). Within seven consecutive cycles, a maximum of 392 mg of neodymium L^{-1} and 281 mg of lanthanum L^{-1} were leached with recycled citric acid. The recycled acidified spent supernatant extracted up to 279 mg of Nd L^{-1} and 287 mg of La L^{-1}. Cerium and thorium levels remained low throughout the consecutive cycles (maxima of 2.2 mg of Ce L^{-1} and 4.9 mg of Th L^{-1}). On the basis of the monazite feed, ~21% of the total Nd and ~13% of the total La were leached (by recycled citric acid). These lower leaching efficiencies were likely caused by the reprecipitation of REE phosphates. Hence, maximal concentrations of La and Ce were attained after three or four cycles, with no additional leaching in cycles 5–7. In contrast, an increased rate of extraction was observed again for Nd and Th in the seventh cycle. Phosphorus was leached concomitantly from the monazite, and its concentration increased to almost 2.8 g L^{-1}([Figure S5](#)).
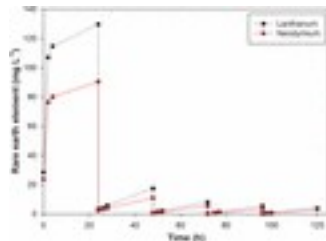

Figure 1. Leaching of neodymium and lanthanum by citric acid (0.5 M) from roasted monazite samples in a sequential batch experiment (same monazite dose and fresh lixiviant every cycle).
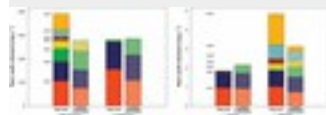

Figure 2. Solubilized neodymium, lanthanum, cerium, and thorium concentrations leached from roasted monazite over the course of seven consecutive cycles (n = 1). Citric acid (0.5 M; Citric Acid) and fungal supernatant acidified with citric acid (0.5 M; Acidified Supernatant) were used as leaching agents in the sequential batch experiment (recycled lixiviant with new monazite every cycle). Each cycle is indicated by a separate color. Note the different scales on the y-axes.

Brisson et al.[(13)] suggested several options for optimizing leaching of REE from (untreated) monazite, including the use of a different process design such as the repeated leaching of monazite by fresh lixiviant or by recycling the leachate. We demonstrate here that for roasted monazite, the former did not significantly enhance REE solubilization while the recycled lixiviants allowed the extraction of high REE levels, as long as generation of REE phosphates or other precipitates is prevented. Therefore, a reactor technology that selectively separates leached anions from cations could allow the recycling of lixiviants and favor the extraction of REEs.

Electrochemical Extraction of Neodymium

We applied membrane electrolysis to separate solubilized REEs from their phosphate counterions and to extract the REEs in more concentrated streams. The metal-containing leachate was introduced into the middle compartment of a three-compartment electrochemical cell (EC) ([Figure S6]). Briefly, the flow of electrical current allows migration of anions (e.g., citrate and phosphate) toward the anode via an anion exchange membrane (AEM) and cations (e.g., REEs) toward the cathode via a cation exchange membrane (CEM). The catholyte was characterized by a high pH (12.8–13.8), driven by the *in situ* production of OH^- due to the reduction of water and by the use of an anion-excluding membrane. Under these conditions, Nd precipitates as $Nd(OH)_3$ that can be harvested from the bottom of the cathode [as shown by thermodynamic calculations in OLI ([Figure S7])]. Nd precipitated mainly in the catholyte solution and presumably partly on the cation exchange membrane, as well. No visual precipitation was observed on the cathode. Following this precipitation, the net driving force of Nd^{3+} is maintained. Preliminary experiments using $NdCl_3$ investigated suitable ion exchange membranes and current densities (see [section S3 of the Supporting Information] and [Figures S8–S10]). Subsequently, the extraction of neodymium from a $NdPO_4$ solution was investigated (100 mg of Nd L^{-1}, 0.5 M citric acid; $\Delta t = 72$ h), at different current densities [0–40 A m^{-2} ([Figure 3])]. Overall, the mean Nd flux exhibited a linear increase as a function of current density (0.38 g of Nd m^{-2} day^{-1} at 20 A m^{-2} vs 0.74 g of Nd m^{-2} day^{-1} at 40 A m^{-2}). A current density of 40 A m^{-2} resulted in the highest neodymium recovery within the tested range; a maximal flux of 3.5 g of Nd m^{-2} day^{-1} was obtained during the first 4 h, compared to 0.6 g of Nd m^{-2} day^{-1} at 20 A m^{-2}. Simultaneously, ~27% of the citrate was extracted in the anolyte at 40 A m^{-2} within 72 h, resulting in a mean citrate flux of 1.2 kg of citrate m^{-2} day^{-1} (vs 0.16 kg of citrate m^{-2} day^{-1} at 20 A m^{-2}).
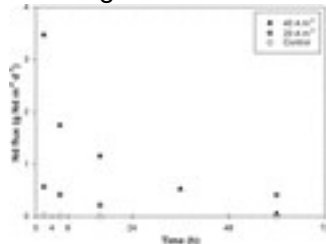
Figure 3. Influence of current density (0, 20, and 40 A m^{-2}) on the neodymium flux tested in a three-compartment system, using NdPO$_4$ (100 mg of Nd L^{-1}) as the neodymium source ($n = 1$). The neodymium fluxes were calculated on the basis of the increase in neodymium concentration in the catholyte between two sampling points and are indicated as intermediate points on the graph. The neodymium flux decreased over time.

Recovery of REEs Using Continuous Leaching and Electrochemical Extraction

A REE recovery flow sheet was proposed and further investigated, coupling the microbial leaching of monazite in a continuously stirred extraction tank with the electrochemical separation in a three-compartment EC reactor. This two-stage process was tested for the extraction of REE from roasted monazite (Figure 4) [4.7 g of monazite L^{-1} and 0.5 M citric acid (Figure S11)]. Within 6 days, up to 154 mg of Nd L^{-1} and 207 mg of La L^{-1} were extracted and concentrated in the catholyte, compared to only 7.3 mg of Ce L^{-1} and 0.08 mg of Th L^{-1}. Heating the extraction tank (at 70 °C) did not enhance the leaching process, except for cerium (maximum of 38 mg of Ce L^{-1}) (Figure S12). Maximal observed fluxes through the CEM were 2.6 g m^{-2} day^{-1} for neodymium and 3.7 g m^{-2} day^{-1} for lanthanum ($\Delta t = 24$–48 h). The concomitant leaching and electrochemical separation of REEs prevented accumulation and precipitation in the extraction tank (Figure 4 and Figure S12). Minor amounts of thorium were leached, as well; however, in contrast to the REEs, Th was transferred toward the anode, and thus part of a negatively charged anion complex (maximum of 2.9 mg of Th L^{-1}) was collected in the anolyte (Figure S12). This favors the selective separation of the radioactive thorium from the REEs, withdrawing the thorium in the extraction reactor when recycling the lixiviant. The other negatively charged ions were concentrated very efficiently in the anolyte; 87% of the citrate and nearly all leached phosphorus were recovered from the lixiviant (Figure 4). Concentrations of ≤1.6–1.8 times the initial citrate and phosphate concentration were obtained in the anolyte (Figure 4). Overall, a Coulombic efficiency of 24% could be obtained, meaning that 24% of the invested electrons were used for the transfer of Nd, La, Ce, citrate, or phosphate. This rather low Coulombic efficiency is due to electron fluxes for competitive ions,[33] such as Na$^+$ and Cl$^-$, coming from the highly saline lixiviant of the roasted monazite, as well as transport of protons and hydroxyl anions across the membrane recombining to water. Because no electrochemical separation was observed in the control run (no current applied), REE levels further increased in the lixiviant due to continuing leaching (Figure S12). The extraction from untreated monazite was ineffective as demonstrated before, with maxima of 0.7 mg of Nd L^{-1}, 1.0 mg of La L^{-1}, and 1.0 mg of Ce L^{-1} detected in the catholyte and 4.8 mg of Th L^{-1} in the anolyte (data not shown).
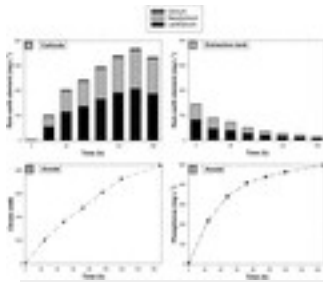
Figure 4. Extracted neodymium, lanthanum, cerium (milligrams per liter), citrate (millimolar), and phosphorus (milligrams per liter) concentrations in the three-compartment electrochemical system as a function of time (n = 1). Citric acid (0.5 M) was used as leaching agent for roasted monazite. Via application of a fixed current (40 A m^{-2}), the REEs were transferred toward the cathode while citrate and phosphorus were directed toward the anode.

To recover Nd more effectively at higher catholyte concentrations, additional electrochemical experiments were conducted on the basis of a smaller cathode, resulting in a higher "extraction tank to catholyte" ratio. This optimized reactor design was tested for the extraction of Nd from a synthetic $Nd_2(CO_3)_3$ solution (159 mg of Nd L^{-1}; 0.5 M citric acid). With this smaller cathode, neodymium concentrations of ≤880 mg L^{-1} were obtained in the catholyte after 4 days (Figure 5). Because Nd precipitated as $Nd(OH)_3$ in the cathode, Nd was recovered more effectively from the catholyte. Neodymium levels in the extraction tank dropped to 13 mg of Nd L^{-1}. Overall, the Nd mass balance could be closed for 76%. The gap in the balance was mainly due to sorption of Nd to the membrane as shown by Nd measurements after destruction of the membrane (39 mg of Nd was chemically extracted from both membranes after a series of tests). Overall, fluxes of 3.3–3.8 g of Nd m^{-2} day^{-1} were obtained, with maximal observed fluxes within the first 7 h (4.4–4.6 g of Nd m^{-2} day^{-1}). In the meantime, 606 mM citrate was extracted in the anolyte within 4 days (47–57% of initial loading), resulting in mean citrate fluxes of 1.9–2.2 kg m^{-2} day^{-1}. When the experiment was extended, up to 81% of the citrate was recovered in the anolyte (837 mM). Furthermore, 87–100% of the initial P loading was transferred into the anolyte (up to 50 mg of P L^{-1}). The combined electrochemical extraction of Nd, citrate, and phosphate was characterized by a Coulombic efficiency of 28–33%.
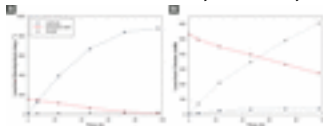

Figure 5. Extracted neodymium (milligrams per liter) and citrate (millimolar) concentrations in the three-compartment electrochemical system, with a smaller cathode, as a function of time (n = 2). Citric acid (0.5 M) was used to leach Nd from $Nd_2(CO_3)_3$ while a fixed current (40 A m^{-2}) was applied. Neodymium was transported toward the cathode, while citrate and phosphorus were attracted to the anode.

During the experiments, the required cell potential evolved over time to a stable value (from 12.8 to 8.9 V; mean of 9.7 V) and was determined by a stable anode potential (+1.3 V vs SHE) and a varying cathode potential (−11.5 to −7.6 V vs SHE; mean of −8.4 V). The energy required to extract the REEs is determined by this cell voltage and the Coulombic efficiency. On the basis of an applied current of 256 mA, ∼0.06 kWh was consumed per day, resulting in an energy cost of €0.0238 for a 4 day experiment; this amounts to €0.279/g of Nd recovered in the catholyte or €0.0004/g of citrate recovered in the anolyte (€0.083/mol of citrate). The low efficiencies and high ohmic losses bring about rather high power requirements for this three-compartment cell. However, the cell potential and resulting power input can be decreased substantially by optimizing the reactor design, including the use of smaller compartments, better internal mixing, or the use of specialized membranes, which have lower resistance or are more selective.[34]

Implications

In general, microbial leaching of REEs from ores and solid residues such as monazite and red mud remains difficult and has not been adequately studied, as indicated by rather low leaching efficiencies.[13, 19] This indicates that some challenges need to be overcome before industrially relevant application of microbial REE leaching can be implemented. First, microbial REE leaching generates low-concentration metal solutions (100–200 mg L^{-1}),[13] mostly too diluted to allow effective chemical REE precipitation by NaOH. A hydrometallurgical flow sheet will have to make use of, for example, solvent extraction to produce higher metal concentrations (grams per liter), prior to chemical precipitation.[35] In this study, an electrochemical cell was used to up-concentrate REEs from diluted lixiviants by electrolysis of REE cations under the influence of an electric field via a CEM. These cations precipitate as REE hydroxides by *in situ* cathodically generated OH$^-$. The production of REE hydroxides allows a straightforward and effective separation of the REEs as solids. Second, the leached phosphates can reprecipitate solubilized REEs in the lixiviant, indicating the need for effective ion separation. Third, the limited leaching rates make the use of microbial organic lixiviants economically uninteresting. Therefore, the recovery of the organic acids is required. In this study, we showed that the leaching agent can effectively be recovered from the pulp by application in an electrochemical system. Next to the extraction of REE hydroxides in the cathode, the counterions phosphate and citrate will be separated in the anode, making it possible to recover citric acid as a microbial lixiviant and phosphate as an additional value-added product. To allow effective reuse of the anolyte as a lixiviant, phosphates should be removed to prevent up-concentration of phosphorus in the flow sheet. This phosphate purge can be achieved by precipitation, e.g., as iron phosphates. Alternatively, citric acid could be extracted from the anolyte by the use of solvents[36] or through the application of an ion exchange process or selective

membranes. An additional advantage of the system can be found in the separation of the radioactive element thorium from the targeted rare earth elements, preventing radioactive contamination of the obtained REE stream.

The leaching performance of REEs could be further improved through optimization of the overall flow sheet design and of its individual processes. The pretreatment of the monazite could be optimized as the maximal leaching efficiencies achieved suggest that the conversion of REE phosphates into REE oxides was incomplete, restricting the recovery of REEs. Better mixing during both leaching and electrochemical extraction is also crucial for enhancing REE recovery. Furthermore, optimized or alternative reactor designs could be developed to increase the overall recovery efficiency and improve the performance of the technology. For example, the separation of phosphate and citrate in an EC system could be targeted. More selective membrane and operating conditions could be selected to extract phosphate in the anolyte and leave citrate in the middle compartment, allowing the direct reuse of citrate as a leachate because phosphate and thorium are both removed through the anolyte.

Currently, the recovery of REEs from waste is very limited, because of the low market value of most REEs.(2, 4) Technologies for the recovery of REEs from waste streams will not easily become economically viable as long as REE prices remain low. For example, on the basis of the modified reactor design experiment and an energy cost of €0.1 ($0.11) per kilowatt hour, the power cost of extraction is calculated at €279 ($314) per kilogram of Nd transferred (2.79 kWh/g of Nd). The current market value of ~€55/kg of Nd is not sufficient to balance the power costs at the moment, (4) even excluding other operational costs and the capital investment in the system. If an improved reactor design that results in a lower cell potential can be designed, the power cost of extraction could be lowered, making this environmentally friendly technology more attractive. In addition, sudden changes in the demand for REE by rapid growth or changes in supply by export restrictions can be accompanied by highly volatile prices.(7)

This study was aimed at the development of an environmentally friendly technology suitable for the recovery of REEs from diverse solid sources. Compared to current chemical leaching processes that generate large amounts of hazardous and radioactive waste, microbial leaching occurs under much more mild conditions.(15) Whereas autotrophic microbial leaching requires S- or Fe-based resources, heterotrophic leaching can be applied to a larger variety of primary and secondary sources.(15) To implement the leaching process step, two main types of technologies exist: heap-based irrigation leaching and stirred tank leaching.(15) These leaching processes could be coupled to electrochemical cells, treating the leachates that can be sent back to the heaps or tanks after

metal recovery. Restrictions with regard to time, space, and capital investment will determine the choice of technology. Monazite was used in this study as a feed of REEs, but it can be envisioned that residues such as lamp phosphors, mine tailings, and metallurgical slags can be used as the feed source in a similar flow sheet.(14)

-

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b03675.

- Experimental information about the roasting of monazite and fungal growth conditions (section S1) and additional results about the leaching of REEs from monazite (section S2), the selection of membranes and current density (section S3), and the electrochemical extraction of light REEs and Th from monazite (section S4) (PDF)

- **PDF**
  - o   es6b03675_si_001.pdf (1.89 MB)

Concomitant Leaching and Electrochemical Extraction of Rare Earth Elements from Monazite

fig**share**

Share**Download**

The authors declare no competing financial interest.

-

Acknowledgment

- [Reference QuickView](#)
-

References

This article references 36 other publications.

1. [1.](#)

   Zhuang, W.-Q.; Fitts, J. P.; Ajo-Franklin, C. M.; Maes, S.; Alvarez-Cohen, L.; Hennebel, T. Recovery of critical metals using biometallurgy *Curr. Opin. Biotechnol.* **2015**, 33, 327– 335 DOI: 10.1016/j.copbio.2015.03.019

   [Crossref], [PubMed], [CAS]

2. [2.](#)

   Rademaker, J. H.; Kleijn, R.; Yang, Y. Recycling as a Strategy against Rare Earth Element Criticality: A Systemic Evaluation of the Potential Yield of NdFeB Magnet Recycling *Environ. Sci. Technol.* **2013**, 47 (18)10129– 10136 DOI: 10.1021/es305007w

   [ACS Full Text], [CAS]

3. [3.](#)

   Nansai, K.; Nakajima, K.; Kagawa, S.; Kondo, Y.; Shigetomi, Y.; Suh, S. Global Mining Risk Footprint of Critical Metals Necessary for Low-Carbon Technologies: The Case of Neodymium, Cobalt, and Platinum in Japan *Environ. Sci. Technol.* **2015**, 49 (4) 2022– 2031 DOI: 10.1021/es504255r

   [ACS Full Text], [CAS]

4. [4.](#)

   Mineral commodity summaries 2016; U.S. Geological Survey: Reston, VA, **2016**.

5. [5.](#)

   Nassar, N. T.; Du, X.; Graedel, T. E. Criticality of the Rare Earth Elements *J. Ind. Ecol.* **2015**, 19 (6) 1044–1054 DOI: 10.1111/jiec.12237

   [Crossref]

6. [6.](#)

Graedel, T. E.; Harper, E. M.; Nassar, N. T.; Nuss, P.; Reck, B. K. Criticality of metals and metalloids *Proc. Natl. Acad. Sci. U. S. A.* **2015**, 112 (14) 4257– 4262 DOI: 10.1073/pnas.1500415112

[Crossref], [PubMed], [CAS]

7. 7.

Alonso, E.; Sherman, A. M.; Wallington, T. J.; Everson, M. P.; Field, F. R.; Roth, R.; Kirchain, R. E.Evaluating Rare Earth Element Availability: A Case with Revolutionary Demand from Clean Technologies*Environ. Sci. Technol.* **2012**, 46 (6) 3406– 3414 DOI: 10.1021/es203518d

[ACS Full Text], [CAS]

8. 8.

Nansai, K.; Nakajima, K.; Kagawa, S.; Kondo, Y.; Suh, S.; Shigetomi, Y.; Oshita, Y. Global Flows of Critical Metals Necessary for Low-Carbon Technologies: The Case of Neodymium, Cobalt, and Platinum *Environ. Sci. Technol.* **2014**, 48 (3) 1391– 1400 DOI: 10.1021/es4033452

[ACS Full Text], [CAS]

9. 9.

Binnemans, K.; Jones, P. T.; Blanpain, B.; Van Gerven, T.; Yang, Y.; Walton, A.; Buchert, M. Recycling of rare earths: a critical review *J. Cleaner Prod.* **2013**, 51, 1– 22 DOI: 10.1016/j.jclepro.2012.12.037

[Crossref], [CAS]

10. 10.

Report on critical raw materials for the EU. Report of the Ad hoc Working Group on defining critical raw materials; European Commission: Brussels, **2014**.

11. 11.

Critical Materials Strategy; U.S. Department of Energy: Washington, DC, **2011**.

12. 12.

Graedel, T. E.; Allwood, J.; Birat, J. P.; Buchert, M.; Hageluken, C.; Reck, B. K.; Sibley, S. F.;Sonnemann, G. What Do We Know About Metal Recycling Rates? *J. Ind. Ecol.* **2011**, 15 (3) 355– 366 DOI: 10.1111/j.1530-9290.2011.00342.x

[Crossref], [CAS]

13. 13.

Brisson, V. L.; Zhuang, W.-Q.; Alvarez-Cohen, L. Bioleaching of rare earth elements from monazite sand *Biotechnol. Bioeng.* **2016**, 113 (2) 339– 348 DOI: 10.1002/bit.25823

[Crossref], [PubMed], [CAS]

14.   14.

Binnemans, K.; Jones, P. T.; Blanpain, B.; Van Gerven, T.; Pontikes, Y. Towards zero-waste valorisation of rare-earth-containing industrial process residues: a critical review *J. Cleaner Prod.* **2015**, 99, 17– 38 DOI: 10.1016/j.jclepro.2015.02.089

[Crossref], [CAS]

15.   15.

Hennebel, T.; Boon, N.; Maes, S.; Lenz, M. Biotechnologies for critical raw material recovery from primary and secondary sources: R&D priorities and future perspectives *New Biotechnol.* **2015**, 32 (1) 121– 127 DOI: 10.1016/j.nbt.2013.08.004

[Crossref], [CAS]

16.   16.

Krebs, W.; Brombacher, C.; Bosshard, P. P.; Bachofen, R.; Brandl, H. Microbial recovery of metals from solids *FEMS Microbiol. Rev.* **1997**, 20 (3–4) 605– 617 DOI: 10.1111/j.1574-6976.1997.tb00341.x

[Crossref], [CAS]

17.   17.

Gadd, G. M. Fungal Production of Citric and Oxalic Acid: Importance in Metal Speciation, Physiology and Biogeochemical Processes. In *Advances in Microbially Physiology*; Poole, R. K., Ed.; Academic Press: New York, **1999**; Vol. 41, pp 47– 92.

[Crossref]

18.   18.

Goyne, K. W.; Brantley, S. L.; Chorover, J. Rare earth element release from phosphate minerals in the presence of organic acids *Chem. Geol.* **2010**, 278 (1–2) 1– 14 DOI: 10.1016/j.chemgeo.2010.03.011

[Crossref], [CAS]

19.   19.

Qu, Y.; Lian, B. Bioleaching of rare earth and radioactive elements from red mud using Penicillium tricolor RM-10 *Bioresour. Technol.* **2013**, 136, 16– 23 DOI: 10.1016/j.biortech.2013.03.070

[Crossref], [PubMed], [CAS]

20. [20.](#)

Shin, D.; Kim, J.; Kim, B. S.; Jeong, J.; Lee, J. C. Use of Phosphate Solubilizing Bacteria to Leach Rare Earth Elements from Monazite-Bearing Ore *Minerals* **2015**, 5 (2) 189– 202 DOI: 10.3390/min5020189

[[Crossref](#)]

21. [21.](#)

Hassanien, W. A. G.; Desouky, O. A. N.; Hussien, S. S. E. Bioleaching of some Rare Earth Elements from Egyptian Monazite using Aspergillus ficuum and Pseudomonas aeruginosa *Walailak Journal of Science and Technology* **2014**, 11 (9) 809– 823

22. [22.](#)

Modin, O.; Wang, X.; Wu, X.; Rauch, S.; Fedje, K. K. Bioelectrochemical recovery of Cu, Pb, Cd, and Zn from dilute solutions *J. Hazard. Mater.* **2012**, 235–236, 291– 297 DOI: 10.1016/j.jhazmat.2012.07.058

[[Crossref](#)], [[PubMed](#)], [[CAS](#)]

23. [23.](#)

Nancharaiah, Y. V.; Venkata Mohan, S.; Lens, P. N. L. Metals removal and recovery in bioelectrochemical systems: A review *Bioresour. Technol.* **2015**, 195, 102– 114 DOI: 10.1016/j.biortech.2015.06.058

[[Crossref](#)], [[PubMed](#)], [[CAS](#)]

24. [24.](#)

Fu, F.; Wang, Q. Removal of heavy metal ions from wastewaters: A review *J. Environ. Manage.* **2011**, 92 (3)407– 418 DOI: 10.1016/j.jenvman.2010.11.011

[[Crossref](#)], [[PubMed](#)], [[CAS](#)]

25. [25.](#)

Lister, T. E.; Wang, P. M.; Anderko, A. Recovery of critical and value metals from mobile electronics enabled by electrochemical processing *Hydrometallurgy* **2014**, 149, 228– 237 DOI: 10.1016/j.hydromet.2014.08.011

[[Crossref](#)], [[CAS](#)]

26. [26.](#)

Ebbers, B.; Ottosen, L. M.; Jensen, P. E. Comparison of two different electrodialytic cells for separation of phosphorus and heavy metals from sewage sludge ash *Chemosphere* **2015**, 125, 122– 129 DOI: 10.1016/j.chemosphere.2014.12.013

[[Crossref](#)], [[PubMed](#)], [[CAS](#)]

27. 27.

Bagotsky, V. S. *Fundamentals of Electrochemistry*, 2nd ed.; John Wiley & Sons, Inc.: Hoboken, N, **2005**.

[Crossref]

28. 28.

Firsching, F. H.; Brune, S. N. Solubility products of the trivalent rare-earth phosphates *J. Chem. Eng. Data***1991**, 36 (1) 93– 95 DOI: 10.1021/je00001a028

[ACS Full Text], [CAS]

29. 29.

Franken, K. M. A Roast-Leach Process for Extraction of Rare Earths from Complex Monazite-Xenotime Concentrates *Sep. Sci. Technol.* **1995**, 30 (7–9) 1941– 1949 DOI: 10.1080/01496399508010386

[Crossref], [CAS]

30. 30.

Merritt, R. R. High temperature methods for processing monazite: II. Reaction with sodium carbonate *J. Less-Common Met.* **1990**, 166 (2) 211– 219 DOI: 10.1016/0022-5088(90)90002-2

[Crossref], [CAS]

31. 31.

Shuchen, S.; Zhiying, W.; Xue, B.; Bo, G.; Wenyuan, W.; Ganfeng, T. Influence of NaCl-CaCl2 on Decomposing REPO4 with CaO *J. Rare Earths* **2007**, 25 (6) 779– 782 DOI: 10.1016/S1002-0721(08)60024-1

[Crossref]

32. 32.

Wood, S. A. The aqueous geochemistry of the rare-earth elements: Critical stability constants for complexes with simple carboxylic acids at 25°C and 1 bar and their application to nuclear waste management *Eng. Geol.* **1993**, 34 (3) 229– 259 DOI: 10.1016/0013-7952(93)90092-Q

[Crossref]

33. 33.

Desloover, J.; Abate Woldeyohannis, A.; Verstraete, W.; Boon, N.; Rabaey, K. Electrochemical Resource Recovery from Digestate to Prevent Ammonia Toxicity during Anaerobic Digestion *Environ. Sci. Technol.***2012**, 46 (21) 12209– 12216 DOI: 10.1021/es3028154

[ACS Full Text], [CAS]

34. [34.](#)

Clauwaert, P.; Aelterman, P.; Pham, T. H.; De
Schamphelaire, L.; Carballa, M.; Rabaey, K.; Verstraete, W.Minimizing losses in bio-
electrochemical systems: the road to applications *Appl. Microbiol.
Biotechnol.* **2008**,79 (6) 901– 913 DOI: 10.1007/s00253-008-1522-2

[[Crossref](#)], [[PubMed](#)], [[CAS](#)]

35. [35.](#)

Ginley, D. S.; Cahen, D. *Fundamentals of Materials for Energy and Environmental
Sustainability*; Cambridge University Press: New York, **2012**.

36. [36.](#)

Kristiansen, B.; Linden, J.; Mattey, M. *Citric Acid Biotechnology*; Taylor & Francis: Abingdon-
on-Thames, U.K., **2002**.