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Idaho National Laboratory
Idaho Falls, Idaho 83415

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Recovery of Rare Earth Elements from Bio-leachates by Precipitation

Abigail Hasler

Oregon State University, Corvallis, OR

Idaho National Laboratory, Idaho Falls, ID

Prepared under the direction of David Reed, Ph.D., and Yoshiko Fujita, Ph.D. in the Biological and Chemical Science & Engineering Department at Idaho National Laboratory.

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I. ABSTRACT

Rare earth elements (REE) are essential components in electronic devices and clean energy technologies, but primary REE production in the US is limited. Consequently, interest in REE recycling from end-of-life materials is increasing. Common practices for REE recycling use concentrated acids or extreme heat, which can be detrimental to the environment. Alternatively, bioleaching uses microorganisms that produce organic acids as an environmentally friendly and economically viable process to recover REE. The bacterium *Gluconobacter oxydans* was used to produce a bio-lixiviant to dissolve REE. However, once REE are leached with bio-lixiviant, the dissolved REE need additional processing for concentration and refinement. One way to recover and separate the REE from other metals in the solution is to precipitate them prior to down-stream processing. In this study, bio-lixiviant produced by *G. oxydans* was used to leach REE from mobile device speaker magnets. Sodium sulfate and oxalic acid were then tested at varying stoichiometric excess concentrations with the bio-leachate to precipitate REE. The sodium sulfate reactions resulted in less total precipitate than the oxalic acid precipitations, and the oxalic acid at 8X and 12X excess concentrations precipitated all detectable REE.

II. INTRODUCTION

Rare earth elements (REE) are used in a variety of electronics; they are contained in magnets, hard drives, hybrid vehicle engines, lasers, and metal alloys found in smart devices.[1] Because the vast majority of REE are not mined in the US, it is imperative to find ways to create a sustainable source of these elements to meet the demand. Currently hydrometallurgical technologies are being used to recover these elements from end-of-life materials such as e-waste; however they often use chemicals such as sulfuric acid that are harsh for the environment.[2] Pyrometallurgy can also be used to harvest REE from spent devices, but it uses extremely high heat to do so, and releases large amounts of greenhouse gases.[3,4]

Bioleaching, a form of hydrometallurgy, has arisen as a viable way to recycle REE that is potentially as profitable as traditional hydrometallurgy, with similar efficiencies but at a much lower environmental impact. Biohydrometallurgy uses microorganisms to extract and recover metals from wastes or primary feedstocks like ores. In heterotrophic bioleaching organic acids are synthesized by microorganisms and are used to leach metals.[5,6]

The purpose of this study was to determine whether REE could be recovered from a bio-leachate using methods previously applied for recovering REE from conventional hydrometallurgical leachates. Mobile device magnets containing REE were leached using a biotically produced organic acid lixiviant and methods for downstream precipitation of REE were tested. The gram negative bacterium *Gluconobacter oxydans* was used to produce the low pH bio-lixiviant; it oxidizes glucose to primarily produce gluconic acid.[7] Oxalic acid and sodium sulfate were tested for recovering REE from the bio-leachate. Hydrometallurgical practitioners commonly use these reagents to precipitate REE from leachate solutions.[8,9,10]

Oxalic acid reacts with REE to precipitate rare earth oxalates, which can be subsequently converted to oxides. However, in solutions containing iron, precipitation of ferrous compounds can occur, as reported by Lui et al. (2019). [8] With sodium sulfate as a precipitant, iron will not precipitate until a pH around 5. However, when using oxalic acid, the strong iron complex created with the oxalate increases the likelihood of iron precipitating out, contaminating the REE precipitate. Lui et al. (2019) also reported that when sodium sulfate was at a stoichiometric excess of 8X, >99% of REE were recovered from the inorganic acid leachate solution.[8] Excess solutions of oxalic acid or sodium sulfate in hydrochloric and sulfuric acid leachate from magnets yield $REE_2(C_2O_4)_3{\bullet}2H_2O$ or $2NaREE(SO_4)_2{\bullet}2H_2O$ respectively, as shown in the equations below.[8]

Sodium Sulfate and Oxalic Acid Precipitations with Inorganic Leachates

$$\mathrm{REE_2(SO_4)_3 + Na_2SO_4 + 2}n\mathrm{H_2O \rightarrow 2NaREE(SO_4)_2 \cdot }n\mathrm{H_2O}\downarrow$$

$$\mathrm{2REECl_3 + 3H_2C_2O_4 + }n\mathrm{H_2O \rightarrow REE_2(C_2O_4)_3 \cdot }n\mathrm{H_2O}\downarrow \mathrm{+6HCl}$$

[8]

III. METHODS

Additional details of methods used are provided in the Appendices. Brief descriptions are provided below.

Bio-lixiviant

The SixFors fermentation reactor system was used to produce the bio-lixiviant by growing *G. oxydans* in modified Pikoyskaya phosphate medium with 40 g/L glucose, as detailed by Reed et al. (2016).[11] Six batch reactors were monitored by the SixFors system and temperature, air flow, and stirring speed were controlled (Figure 1). The separate bioreactors were autoclaved prior to the run. The pH probes were calibrated, and the dissolved oxygen probes were polarized overnight and calibrated in the morning by using nitrogen gas and oxygen gas to secure high and low references. The pH and dissolved oxygen were monitored, and the optical density was measured at five time points during bio-lixiviant production. For a period of 40 hours, the temperature was held at 30°C, stirring speed at 600 rpm, and the air flow at approximately 1.06 liters per minute. After 40 hours in the bioreactors, the bio-lixiviant was centrifuged at 6000 g for half an hour and filtered (0.2µm PES). The bio-lixiviant was then stored at 4°C until use (Figure 2).

Bioleaching

Using sterile techniques to maintain sterility in the lixiviant bottle, 100 ml of bio-lixiviant was added to three one-liter Erlenmeyer flasks. The gluconic acid concentration of the bio-lixiviant was 253 mM and it had a pH of 2.17. Mobile device speaker sets, comprised of eight parts - an outer casing, inner frame, back plate, four side spacers (two long, two short), and the magnet - were separated from a collection of demagnetized speaker pieces. The speaker pieces were demagnetized by heating in a muffle furnace at 400°C and organized into 3 sets (Figure 3,4). The total weight of the magnet speaker set was measured with all eight pieces. The bio-lixiviant was also weighed to determine the exact lixiviant: solid mass ratio, or pulp density. In this experiment, the speaker set totaled 1.5 g, so the pulp density was approximately 1.5% (Table 1). The leaching was conducted for 72 hours at 20°C with shaking at 150 rpm. The bio-leachates were filtered (0.2µm PES). The filter cake and undissolved magnet pieces were weighed (Table 1) and discarded, and samples were taken for pH measurement and elemental analysis by inductively coupled plasma with mass spectrometric detection (ICP-MS).

Precipitation

Sodium sulfate and oxalic acid were used to precipitate REE from the bio-leachate solution. Concentrations that were 12, 8, and 4 times (e.g., 12X, 8X, 4X) the excess stoichiometric amounts were added to the bio-leachate according to the reaction expressions shown in the Introduction; the expected REE concentrations were based on previous experience leaching REE from the magnets.

Stocks of 2.4 M and 1.8 M were made of the sodium sulfate and oxalic acid respectively. The precipitation solutions were made using nanopure water and heated to 50°C to effectively dissolve the solid chemicals. When making the stock solutions for sodium sulfate and oxalic acid, larger quantities of each would have been easier to handle, but only 10 ml was made of each to prevent wasting materials. It was difficult to get the oxalic acid dihydrate and sodium sulfate to dissolve at these concentrations, however, after the solutions were heated to 50°C, and stirred on a hot plate they were able to go into solution.

Immediately after the solutions had been made, they were added to the bio-leachate. For each trial, 2 ml stock solutions, or their dilutions were added to 20 ml of bio-leachate so that each had the appropriate stoichiometric excess. The stock concentrations when added to 20 ml of bio-leachate were at 12X stoichiometric excess to REE concentrations. For the 8X and 4X stoichiometric tests, dilutions of the stocks were made and added to the bio-leachates. The reaction vessels were placed in the shaking incubator at 70°C for 1 hour and 200 rpm as outlined in Lui et al. 2019. [8]

The precipitate was filtered from solution using 0.7µm Whatman glass microfiber filters (can withstand heat in drying oven). Samples of the filtrate were collected for pH and ICP-MS. The filters were dried overnight for 14 hours at 100°C and weighed to determine the mass of solids recovered (Table 2). The ICP-MS measurements of the REE concentrations in the solutions from before and after the precipitations were used to calculate a mass balance and determine how much of the REE was recovered by precipitation.

IV. RESULTS AND DISCUSSION

Magnet leach

After 72 hours of leaching the liquid in each of the flasks was murky because the magnet and four side spacers had partially dissolved. Flask 1 had a yellow-brown color, flask 2 was slightly darker than 1 and had a green tint, and flask 3 was the darkest and appeared green and red (Figure 5). All of the flasks had 3 speaker pieces still intact: the outer casing, inner frame, and back plate (Figure 6). The filtrates for 1 and 2 were similar colors, yellow and orange, but the filtrate for flask 3 was a much darker orange and red color (Figure 7). The filter cakes followed the same trend with one being lighter and three being the darkest color. The remaining speaker pieces weighed between 0.8-0.83 grams meaning that less than half of the speaker sets were dissolved during the leaching. The initial pH of the bio-lixiviant was 2.17. Post leaching pH readings for 1 and 2 were similar: 3.72, and 3.74 respectively, while 3 was significantly lower at 3.55. This difference might be attributable to a different composition of the pieces in speaker set 3 compared to the other speaker sets, as the undissolved pieces from speaker set 3 were different colors than those from speaker set 1 and 2.

Table 1: Initial and final pH values of magnet bio-leachates and masses of remaining speaker pieces

Speaker set	Initial bio-lixiviant (pH)	Final bio-leachate (pH)	Magnet speaker set weights (g)	Mass of remaining speaker parts (g)
1	2.2	3.7	1.55	0.81
2	2.2	3.7	1.56	0.82
3	2.2	3.6	1.54	0.80

<u>Precipitation</u>

Immediately upon the addition of all oxalic acid concentrations there was an obvious reaction between the bio-leachate and the oxalic acid; the solution turned yellow and foamed. A yellow precipitate fell out of solution immediately and settled to the bottom of the conical tube. There was no visible reaction with the sodium sulfate solutions. After precipitate was filtered out, the pH of the filtrates was measured. There was a large decrease from the initial pH of the combined bio-leachates at 3.5 for the oxalic acid reactions and a minimal change for the sodium sulfate precipitation reactions. The pH readings of the sodium sulfate concentrations were all around 3.5, not changing significantly from the initial pH of the bio-leachate. The oxalic acid reactions had very low pH values, ranging from 2.8 for the 4X sample to 1.2 for the 12X sample.

Table 2: Final pH values of precipitation reactions and mass of precipitates at different concentrations

Excess Concentrations	Initial pH (prior to stock addition)	Final pH	Precipitate mass (g)
Na_2SO_4 12X*	3.5	3.6	0.05
Na_2SO_4 8X	3.5	3.5	0.04
Na_2SO_4 4X	3.5	3.5	0.03
$C_2H_2O_4$ 12X	3.5	1.2	0.26
$C_2H_2O_4$ 8X	3.5	2.1	0.12
$C_2H_2O_4$ 4X	3.5	2.8	0.04

*See the equations: *Sodium Sulfate and Oxalic Acid Precipitations with Inorganic Leachates.*

The excesses were determined based off the 1:2 REE to sodium sulfate and 1:1.5 REE to oxalic acid ratios. For example, 12X would change sodium sulfate's ratio to 1:24.

The filter cake resulting from each sodium sulfate reaction was grey, all three of the reaction stoichiometries tested resulted in the same color after drying. The precipitate for the oxalic acid immediately after filtering was green for the 4X, muted yellow for 8X, and a bright yellow for the 12X. After drying the precipitate turned a darker yellow for all three concentrations. There was also an outer ring of dark grey that encircled the yellow filter cake. The yellow filter cake is likely iron (II) oxalate because in the precipitation reaction the iron would have created a complex with oxalate and fallen out of solution. At the higher pH values using a bio-leachate the iron would not have stayed dissolved. After drying, the yellow filter cake was not firmly attached to the filters and could easily be scraped off the filter and separated from the grey material.

The data collected from the ICP-MS indicated that the 12X and 8X oxalic acid precipitation reactions recovered the most REE compared to the 4X reaction and the sodium sulfate reactions. While the sodium sulfate was able to precipitate out praseodymium, neodymium, gadolinium, and dysprosium, the higher excesses of oxalic acid were able to precipitate out the majority of the detected REE (Table 3).

*Table 3: Percentages of recovered REE** from precipitation reactions*

Excess Concentrations	Pr (%)	Nd (%)	Gd (%)	Dy (%)
Na_2SO_4 12X	8	11	30	24
Na_2SO_4 8X	12	12	20	19
Na_2SO_4 4X	5	8	28	14
$C_2H_2O_4$ 12X	100***	100	100	100
$C_2H_2O_4$ 8X	100	100	100	100
$C_2H_2O_4$ 4X	90	92	25	93

** At the time of this report preparation, final ICP-MS data for Tb and Fe were not available.

***100 indicates that less than 0.01 ppb was detected in the ICP-MS.

V. CONCLUSION

The mass of the filter cakes from the sodium sulfate precipitations were quantitatively much less than the mass of filter cakes resulting from oxalic acid reactions. Because they were generated from the same bio-leachate, the amount of dissolved iron should be the same in all reactions, suggesting that the iron in the sodium sulfate precipitations did not fall out of solution, or if it did, it did so to a minimal degree compared to the case with oxalic acid precipitation.

Based on the observations of the precipitation experiment, additional concentrations of oxalic acid should be tested. The mass of the filter cake was larger with increasing concentrations of oxalic acid. Lower concentrations of oxalic acid may produce a higher concentration REE precipitate because there would be less oxalate ions to complex with suspended iron and fall out of solution, but this could also lower REE recovery. According to the ICP data, the measurable amounts of REE recovered were the same between the 12X and 8X reactions, indicating that lower concentrations, perhaps between 8X and 4X could precipitate a comparable amount of REE, using less precipitant (Table 3).

Another modification would be to decrease the pH of the bio-leachate, because the lower the pH the less likely metals would be to precipitate out, therefore ensuring more iron would stay in solution, however this may interfere or limit REE precipitation. Future areas of research, in addition to altering pH and changing concentrations of precipitating reagents, include increasing REE yield by performing multiple precipitations on a single bio-leachate, perhaps using a combination of chemicals to do so, i.e. both sodium sulfate and oxalic acid.

VI. ACKNOWLEDGEMENTS

I'd like to acknowledge my mentors David W. Reed and Yoshiko Fujita from INL for their guidance and support throughout my internship. Thanks are also due to Caitlin A. McNamara for her continued training and direction, Mary E. Case for her instruction in the use of the TXRF, Kastli D. Schaller for analyzing my bio-lixiviant samples for organic acid content, and Luis A. Diaz Aldana for his advice regarding precipitation. I'd like to thank the Department of Energy and the SULI program and INL for allowing me to work here this summer. This work has also been supported by the Critical Materials Institute, an Energy Innovation Hub funded by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Advanced Manufacturing Office. Critical Materials Institute funding was provided at INL through DOE Idaho Operations Office Contract DE-AC07-05ID14517.

VII. APPENDICES

APPENDIX A: Bioleaching Procedure

1. Separate mobile device speaker parts from the demagnetized pile, find three sets of speaker parts and magnet.
2. Weigh the magnet separately and with the other speaker components. The weight should be around 1.5 g, so that the pulp density for leaching will be 1.5% if 100 ml of bio-lixiviant is used.
3. Using sterile techniques (Bunsen burner) add 100 ml of lixiviant each to magnet set, one-liter flasks with screw on lids. Weigh the lixiviant.
4. Speaker components do not need to be sterilized. Add speaker parts into the lixiviant in flasks.
5. Leach for three days at 20C, 150 RPM.

Harvest:

1. The leachate does not need to be centrifuged. Filter using vacuum and 250 ml filters (0.2μ PES), into separate bottles.

2. Collect 5 ml in a 15 ml conical for ICP, 1 ml in 1.5 ml microcentrifuge tube for TXRF, and 1 ml for pH in glass tube.
3. Measure pH and TXRF, send ICP out for testing.

APPENDIX B: Precipitation Procedure

1. Add two bio-leachates together to have enough for six trials. Record combined pH.
2. Add 20 mls of the combined bio leachate into 6 50 ml conicals, labeled with chemicals being used for precipitation.
3. Begin heating shaking incubator (70C).
4. Prep stock solutions.
    a. Using nanopure water create 2.4 M and 1.8 M stock solutions of sodium sulfate and oxalic acid, respectively.
    b. At 50 °C on a hot plate, mix the solutions for 5 minutes, or until completely dissolved.
    c. See Precipitation Concentration spreadsheet for calculations and stock solution measurements.
5. The determined stoichiometric excesses for these precipitations were 12, 8, and 4 for each sodium sulfate and oxalic acid. Depending on the amount of excess, add stock solution and autoclaved nanopure water (for a total of 2 ml added volume) to the conical tubes.
6. Shake in incubator at 70C for one hour.
7. Weigh filters. Label sample conical tubes for excess filtrate, pH, ICP, and TXRF analysis.
8. Filter using Whatman glass microfiber filters with 0.7µm pore size.
9. Section out filtrate for ICP (5 ml), TXRF (1 ml), pH (2 ml), and the remainder of the filtrate (12-15 ml) in another conical.
10. Place the filters in a metal tray for oven. Put the filters in a glass pan, and into the drying oven at 100C 12 hours/ overnight.
11. Measure pH of filtrate.

APPENDIX C: ICP Serial Dilutions

1. Add 50 µl of concentrated nitric acid to the 5 ml of sample used for ICP analysis.
2. Take 0.1 ml of the previous solution and add to 50 ml of 0.2 M nitric acid, vortex this solution.
3. Add 0.1 ml of the previous solution to 50 ml of 0.2 M nitric acid and vortex.
4. Add 0.5 ml of the previous solution to 15 ml of 0.2 M nitric acid and vortex. This results in a final dilution of 1:7,500,000 which is used for ICP analysis.

APPENDIX D: Picture Documentation

Figure 1: Hasler, A., 2020. SixFors Reactor

Figure 2: Hasler, A., 2020. Bio-lixiviants

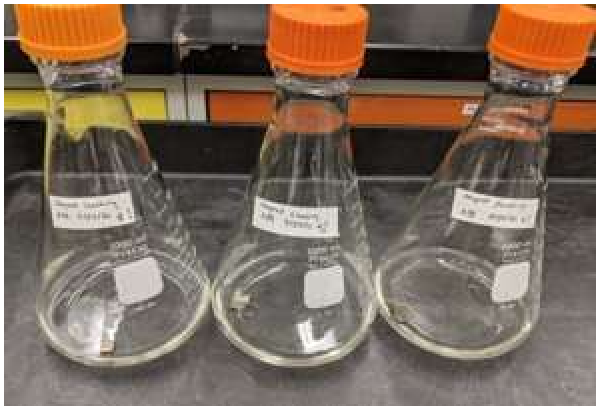

Figure 3: Hasler, A., 2020. Bio-lixiviant and Magnets Prior to Leaching

Figure 4: Hasler, A., 2020. Speaker Magnet Sets

Figure 5: Hasler, A., 2020 Magnet Bio-leachate

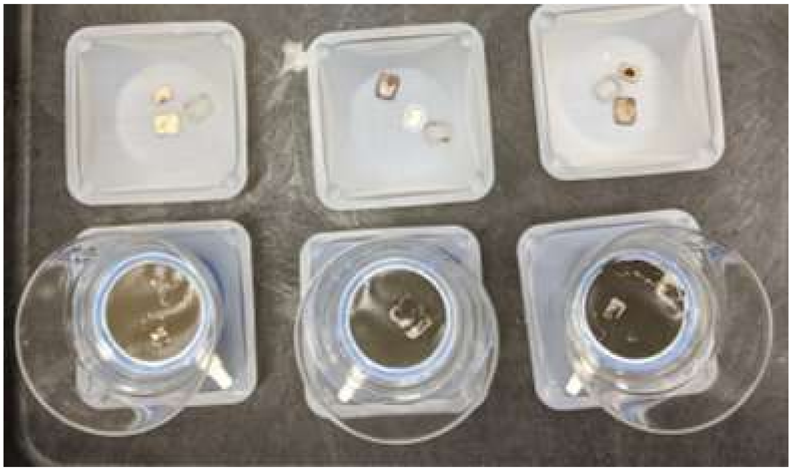

Figure 6: Hasler, A., 2020. Magnet Filter Cake and Remaining Speaker Pieces

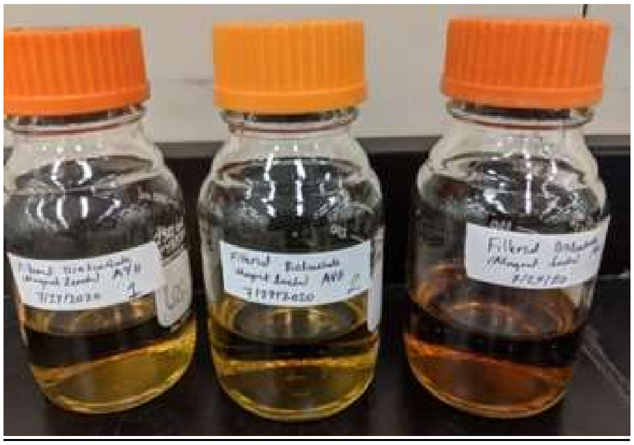

Figure 7: Hasler, A., 2020. Filtered Bio-leachate

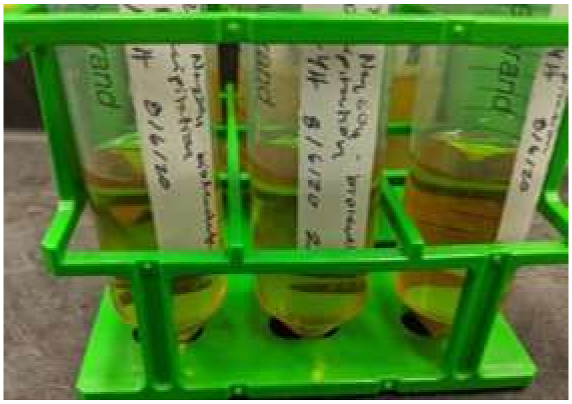

Figure 8: Hasler, A., 2020. Sodium Sulfate Precipitation Reaction

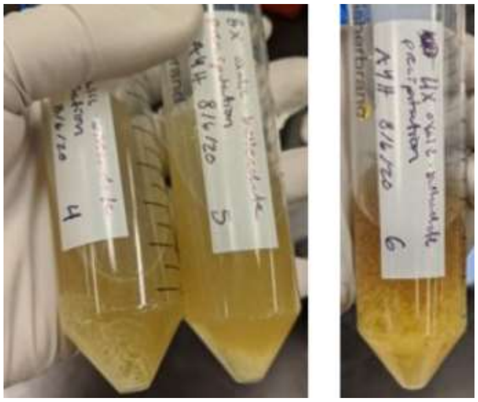

Figure 9: Hasler, A., 2020. Oxalic Acid Precipitation Reactions

Figure 10: Hasler, A., 2020 Precipitant Filter Post-Drying

Top Row Sodium Sulfate L to R: 4x, 8x, 12x

Bottom Row Oxalic Acid L to R: 4x, 8x, 12x

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