Project Overview

– Funding: DOE $200,000, Cost share $50,008
– Overall Project Performance Dates 1/1/2022 - 3/31/2023
– Project Participants
  • FIPR Institute, Florida Polytechnic University
  • Pacific Northwest National Laboratory
    – Dr. Tatiana Levitskaia
  • Florida International University
    – Dr. Yelena Katsenovich
  • Oak Ridge National Laboratory
    – Dr. Costas Tsouris
  • The Mosaic Company
Project Overview

– Overall Project Objectives

• The primary objective of this project is to design a research plan for developing and integrating a series of concentration, recovery, extraction and separation technologies for mass production of rare earth metals (REM) using phosphoric acid sludge as the Rare Earth Element (REE) resource.
  – Initial Effort: Y, Nd, Gd, Dy, Sm, and Pr
  – Scope Addition: Leaching and recovery of Eu, Tb, and Lu
  – Exploratory research evaluating the potential recovery of Mn, Sr, V, and Ti.
Technology Background

• FIPR Institute research since 2010 identified phosphate as the most significant unconventional REE resources
  o Y, Sc and HREE accounting for 50% of the total REE in phosphate
  o Much of the US demand for many critical REEs could be met by recovery from phosphate mining wastes

<table>
<thead>
<tr>
<th>Waste product</th>
<th>Production tons/y</th>
<th>Average REE, ppm</th>
<th>Recoverable REE, tons/year</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>∑</td>
</tr>
<tr>
<td>Acid sludge</td>
<td>450,000</td>
<td>2654</td>
<td>1100</td>
</tr>
<tr>
<td>Waste clay</td>
<td>20 million</td>
<td>290</td>
<td>5800</td>
</tr>
<tr>
<td>Phosphogypsum</td>
<td>20 million</td>
<td>170</td>
<td>3400</td>
</tr>
<tr>
<td>Flotation tails</td>
<td>3.9 million</td>
<td>200</td>
<td>780</td>
</tr>
</tbody>
</table>
Technology Background

- Conceptual overall processing flowsheet based on 9-year FIPR Institute research under CMI and PNNL’s expertise in solvent extraction and ion exchange
Technology Background

• Prior technology development efforts
  o FIPR Institute’s 9-year research under CMI
  o PNNL’s in separation

• Technical and/or economic advantages
  o Recovery of high value phosphoric acid
  o Selective separation of HREE from LREE
  o High selectivity of the solvent extraction scheme
  o Environmentally friendly processing

• Demonstration Site – New Wales of Mosaic
  o Largest REE feed source
  o Adjacent to infrastructures
  o Support of disadvantaged community
REE recovery from leachate

- Innovative solvent extraction with diglycolamide (DGA)
- Has been previously evaluated for separation of dissolved used nuclear fuel: **new to phosphate processing**
- Organic solvent formulation
  - Diluent: Kerosene-like mixture of high alkanes (ExxonMobil)
  - Extractant: DGA
  - Solvent modifier: Exxal™ (ExxonMobil) primary alcohol C8 - C13 mixture
- Scrub: 1 – 2 M nitric acid to remove residual metals co-extracted with REE
- Stripping: dilute nitric acid to recover REE
Technical Approach/Project Scope

- Maximize P recovery to improve overall economics
- Achieve REE leaching recovery to 90% or higher
- Recover U and Th in separate products
- Optimize solvent extraction to separate HREE from LREE
  - Achieve two types of final products with high purity
- Oxalate precipitation and calcination to produce mixed REO
- Advanced ion exchange to produce individual or group REMs
- Recover additional commodity critical metals: Mn, other
- Minimize overall waste volume
- Reduce environmental impact
- Provide equitable employment opportunity to local communities
Progress Current Status of Project - Sample Characterization

- SEM showed a higher fraction of small-size particles in fresh sludge samples compared to aged sludge samples.
- EDS elemental maps indicated higher enrichment in Dy, Y and Tb in the fresh sample.
- Both SEM/EDS and XRD suggested that fresh sludge is more amorphous and is a better feedstock for REE.
Progress Current Status of Project - Sample Characterization

Mineral forms of REE and their distribution in phosphate sludge: XRD analysis

- Monazite $M(PO_4, SiO_4)$, 20-30% of total REE
  - Dominant constituents: light lanthanides (La – Gd), and Th (some U)
- Xenotime $MPO_4$, ~30% of total REE
  - Dominant constituents: Y, heavy lanthanides (Tb – Lu), and U (some Th)
- Calcium substitution in phosphate crystals, ~40% of total REE
Progress and Current Status of Project
- Leaching Studies

- Screened leaching conditions and identified near optimal conditions for REE leaching from fresh sludge
  - 5M nitric acid
  - 70°C
  - Solid to liquid ratio: 3:7

- Over 90% REE leaching recovery achieved

<table>
<thead>
<tr>
<th>Product</th>
<th>REE recovery (%)</th>
<th>Total REE (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Final leachate</td>
<td>88.85</td>
<td>407.00</td>
</tr>
<tr>
<td>Residue washing water</td>
<td>5.12</td>
<td>21.24</td>
</tr>
<tr>
<td>Residue</td>
<td>6.03</td>
<td>141.78</td>
</tr>
<tr>
<td>Sludge feed (weighted average)</td>
<td>100.00</td>
<td>1159.57</td>
</tr>
</tbody>
</table>

Product
REE recovery (%)
Total REE (ppm)
Progress and Current Status of Project - Promising REE Extraction Results

- Tested solvent formulation
  - Diluent: Exxsol D80 (ExxonMobil)
  - Solvent modifier: 1 M Exxal C8 (ExxonMobil)
  - Extractant: 0.1 M TODGA

- Extraction efficiency increases from light to heavy REE
  - Selective separation of unwanted La and Ce is feasible
  - Near 100% extraction of heavy REEs: leachate matrix does not pose interference
Progress and Current Status of Project

- Promising REE Extraction Results

- U and Th are not extracted
- Scrub allows separation of unwanted La and Ce
- Easy stripping of REE from the loaded extraction organic phase with dilute HNO$_3$ or tap water
- REE purity in the striping product solution is >99%
- Oxalate precipitation of REE from the strip in progress
  - Preliminary results indicate >95% recovery in the MREOxide product
Progress and Current Status of Project - Promising REE Extraction Results

<table>
<thead>
<tr>
<th></th>
<th>Y</th>
<th>La</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Tb</th>
<th>Dy</th>
<th>Ho</th>
<th>Er</th>
<th>Tm</th>
<th>Yb</th>
<th>Lu</th>
<th>Th</th>
<th>U</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leached in 2 steps</td>
<td>89%</td>
<td>83%</td>
<td>83%</td>
<td>83%</td>
<td>83%</td>
<td>84%</td>
<td>84%</td>
<td>85%</td>
<td>87%</td>
<td>89%</td>
<td>90%</td>
<td>90%</td>
<td>94%</td>
<td>90%</td>
<td>86%</td>
<td>76%</td>
<td>84%</td>
</tr>
<tr>
<td>Extracted in 1 step</td>
<td>100%</td>
<td>63%</td>
<td>84%</td>
<td>94%</td>
<td>99%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>Scrubed in 1 step</td>
<td>0%</td>
<td>74%</td>
<td>40%</td>
<td>22%</td>
<td>9%</td>
<td>0%</td>
<td>0%</td>
<td>1%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Striped in 2 steps</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
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<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>n/a</td>
<td>n/a</td>
<td></td>
</tr>
</tbody>
</table>

REE content in strip, ppm
|             | 46.7 | 21.4 | 41.3 | 6.7 | 28.2 | 6.4 | 1.8 | 10.4 | 1.3 | 6.8 | 1.3 | 2.2 | 0.13 | 0.41 | 0.06 | 0 | 0 |
Progress and Current Status of Project - Promising REE Extraction Results

Recovery of Critical Metals from Liquid Sludge Fraction

- Liquid fraction of phosphate sludge contains:
  - About 2/3 of total Tm (0.84 ppm), Yb (6.8 ppm), and Lu (1.4 ppm)
  - >90% of total Mn (450 ppm)
- Work in progress to develop flowsheet for their recovery
- Solvent composition
  - Diluent: Exxsol D80 (ExxonMobil)
  - Extractant: 0.1 M TODGA
  - Solvent modifier: bis(2-ethylhexyl) phosphoric acid
- Aqueous feed: liquid sludge fraction + solid sludge H₂O wash solution
  - Preliminary results indicate >95% recovery REE
  - Testing of Mn recovery in progress
Progress and Current Status

Work in progress:
Evaluation of combined flowsheet for REE and critical metal recovery from phosphate sludge
Progress and Current Status of Project
- Major Accomplishments

• Demonstrated feasibility of proposed technical approaches ahead of schedule and beyond expectations
• Recovery of critical metals per added scope is feasible
• Generated broad interest in recovering critical elements from phosphate processing
• Mobilized a competent team of collaborators for commercial demonstration
Progress and Current Status of Project - Synergistic collaboration

- Developed synergistic collaboration among team members thus ensuring project success
  - PNNL’s solvent extraction guiding REE leaching
  - FIU sample characterization shed light on chemistry
  - FIPR Institute providing 9-year CMI experiences and industrial perspectives
  - Communities (local media, government agencies, industries, chamber of commerce) recognizing a significant mission
Progress and Current Status of Project – Blueprint of a Demonstration Plant

- Versatile in REE feedstocks, leaching type, and product variety
- Using phosphoric acid sludge as the “home” REE feedstock
- Production capacity: 900 to 1100 tons REM per year
Plans for future testing/development/commercialization – Current Project

- Batch scale experiments for production of REE products from solvent extraction concentrate
- Exploration of Mn extraction
- Completion of overall flowsheet for commercial production with complete mass balance and equipment selection
Plans for future testing/development/commercialization – Next Project(s)

• Aspire for a Phase 1 grant from DE-FOA-0002618, Rare Earth Element Demonstration Facility
• Establish a REE demonstration/production facility in Polk county, central Florida using phosphoric acid sludge as the main REE feedstock
• Rationales
  o The sludge is high in REE (over 2000 ppm), easy to access, and unregulated
  o Polk county, a disadvantaged community bearing a century-long environmental impact by phosphate mining, can use a revenue from REE recovery for economic development
Outreach and Workforce Development Efforts or Achievements

Outreach

• Bartow Chamber of Commerce
• Polk County Economic Council
• Local channels of NBC, ABC, CBS, and Fox News
• Local newspaper, the Ledger

Workforce Development

• Three Florida Polytechnic University undergraduate students trained in lab skills
• One FIU research associate working on the project
• One PNNL graduate student working on the project
Summary

• REE leaching from phosphoric acid sludge was optimized after maximized recovery of P
• A novel solvent extraction system was developed for selective separation of HREE from LREE
• An integrated processing flowsheet was developed for commercial production of REO/REM using an unconventional feedstock.
• The process is feasible both technically and economically, and is ready for demonstration
• Phosphate mining wastes/byproducts are viable resources for critical elements, sufficient to meet the entire US demand
Appendix

- These slides will not be discussed during the presentation but are mandatory.
<table>
<thead>
<tr>
<th>Task</th>
<th>ACTIVITY</th>
<th>PERCENT COMPLETE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Task 1</td>
<td>Project Management Plan</td>
<td>100%</td>
</tr>
<tr>
<td>Task 2</td>
<td>Teaming plan with at least two commitment letters</td>
<td>100%</td>
</tr>
<tr>
<td>Task 3</td>
<td>REE feedstock resource characterization data, including chemical/physical/mineralogical properties, Eu, Tb, Lu, Mn, Sr, Ti, V, and Ti, quantities required for Phase 2</td>
<td>100%</td>
</tr>
<tr>
<td>Task 3</td>
<td>REE feedstock pre-treatment and REE leaching data including Eu, Tb and Lu</td>
<td>60%</td>
</tr>
<tr>
<td>Task 4</td>
<td>Method(s) for REE extraction from leaching solution</td>
<td>75%</td>
</tr>
<tr>
<td>Task 5</td>
<td>Technologies for advanced REE separation</td>
<td>80%</td>
</tr>
<tr>
<td>Task 2 - 5</td>
<td>Complete and detailed Technical Research plan with processing flowsheet for producing MREO/REM</td>
<td>80%</td>
</tr>
</tbody>
</table>