Technology Development and Integration for Volume Production of High Purity Rare Earth Metals from Phosphate Processing

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Patrick Zhang

FIPR Institute, Florida Polytechnic University

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Project Overview

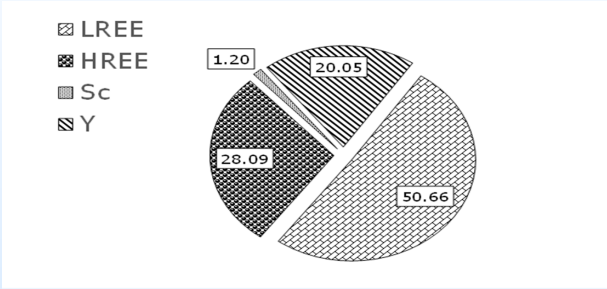
- Funding: DOE $200,000, Cost share $50,008
- Overall Project Performance Dates 1/1/2022 - 3/31/2023
- Project Participants
  - FIPR Institute, Florida Polytechnic University
  - Pacific Northwest National Laboratory
    - **Dr. Tatiana Levitskaia**
  - Florida International University
    - **Dr. Yelena 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
  - Y, Sc and HREE accounting for 50% of the total REE in phosphate

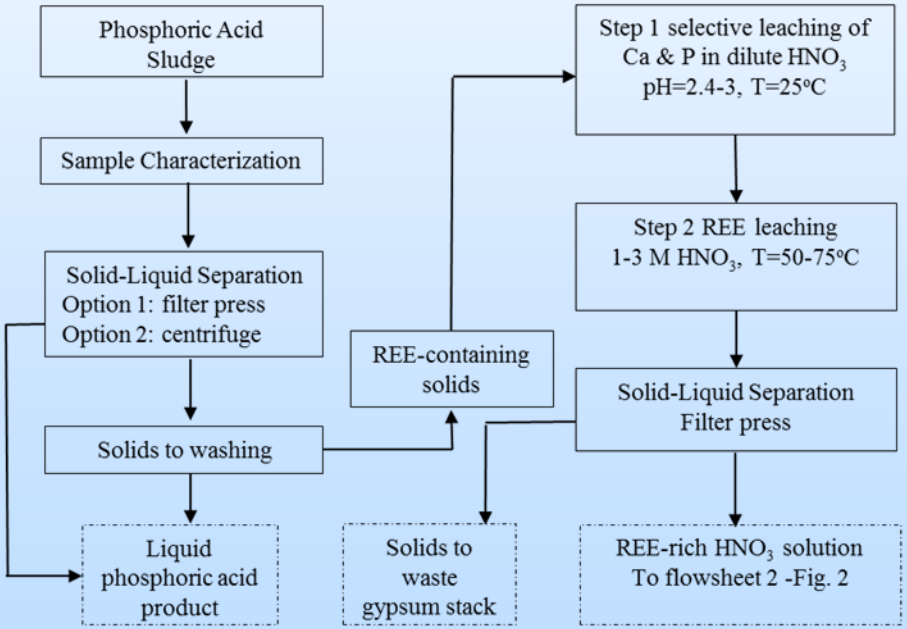


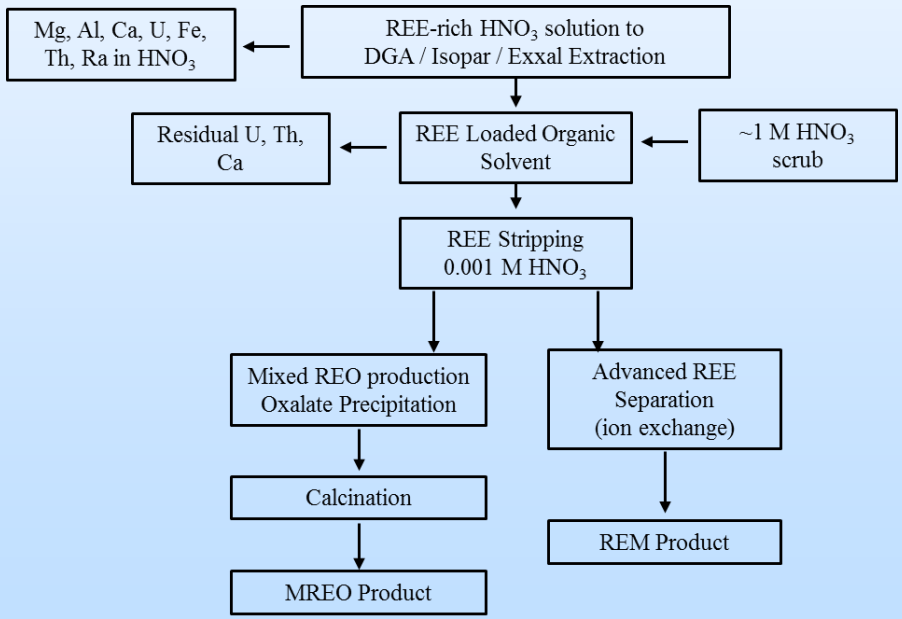
  - Much of the US demand for many critical REEs could be met by recovery from phosphate mining wastes

Waste product	**Production tons/y**	**Average REE, ppm**	**Recoverable REE, tons/year**						
			∑	Y	Nd	Gd	Sm	Dy	Py
Acid sludge	450,000	2654	1100	262	172	41	24	22	16
Waste clay	20 million	290	5800	1200	1080	300	120	140	60
Phosphogypsum	20 million	170	3400	700	600	60	100	100	120
Flotation tails	3.9 million	200	780	140	156	16	20	20	23

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

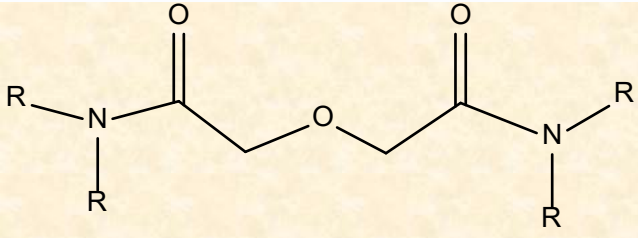




Technology Background

- Prior technology development efforts
  - FIPR Institute's 9-year research under CMI
  - PNNL's in separation
- Technical and/or economic advantages
  - Recovery of high value phosphoric acid
  - Selective separation of HREE from LREE
  - High selectivity of the solvent extraction scheme
  - Environmentally friendly processing
- Demonstration Site – New Wales of Mosaic
  - Largest REE feed source
  - Adjacent to infrastructures
  - Support of disadvantaged community

Technology Background



TODGA: R=octyl
T2EHDGA: R=2-ethyhexyl

REE recovery from leachate

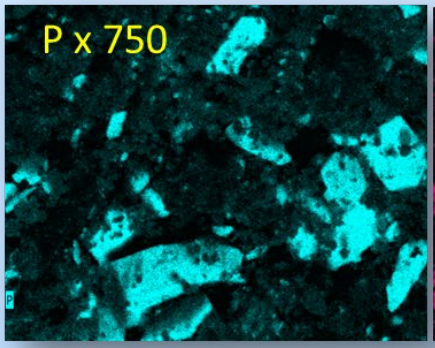
- Innovative solvent extraction with diglycolamide (DGA)
  - Has been previously evaluated for separation of dissolved used nuclear fuel: **new to phosphate processing**
    - Organic solvent formulation
      - Diluent: Kerosene-like mixture of high alkanes (ExxonMobil)
      - Extractant: DGA
      - 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

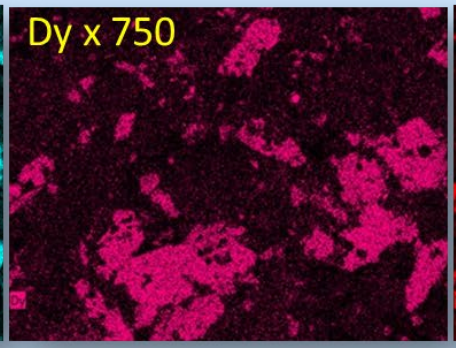
Technical Approach/Project Scope

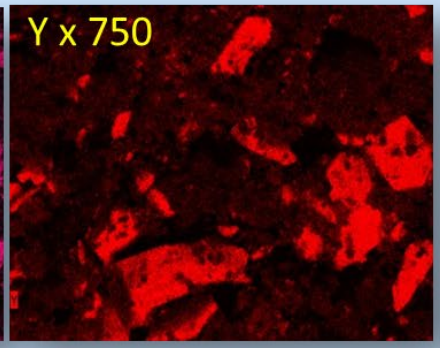
- Maximize P recovery to improve overall economics
- Achieve REE leaching recovery to 90% or higher
- Recover U and Th in separate products
- Optimize solvent extraction to separate HREE from LREE
  - Achieve two types of final products with high purity
- Oxalate precipitation and calcination to produce 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

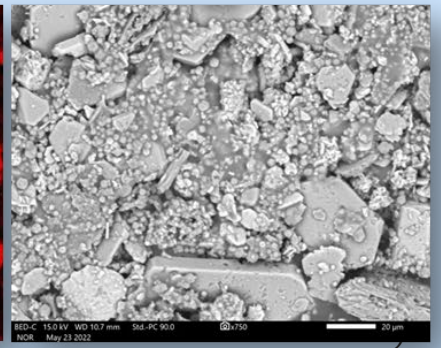
Progress Current Status of Project - Sample Characterization

- 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

Product	REE recovery (%)	Total REE (ppm)
Final leachate	88.85	407.00
Residue washing water	5.12	21.24
Residue	6.03	141.78
Sludge feed (weighted average)	100.00	1159.57

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

	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Th	U
Leached in 2 steps	89%	83%	83%	83%	83%	84%	84%	85%	87%	89%	90%	90%	94%	90%	86%	76%	84%
Extracted in 1 step	100%	63%	84%	94%	99%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	0%	0%
Scrubed in 1 step	0%	74%	40%	22%	9%	0%	0%	1%	0%	0%	0%	0%	0%	0%	0%	n/a	n/a
Striped in 2 steps		100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	n/a	n/a
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 H_2O 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
  - The sludge is high in REE (over 2000 ppm), easy to access, and unregulated
  - 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

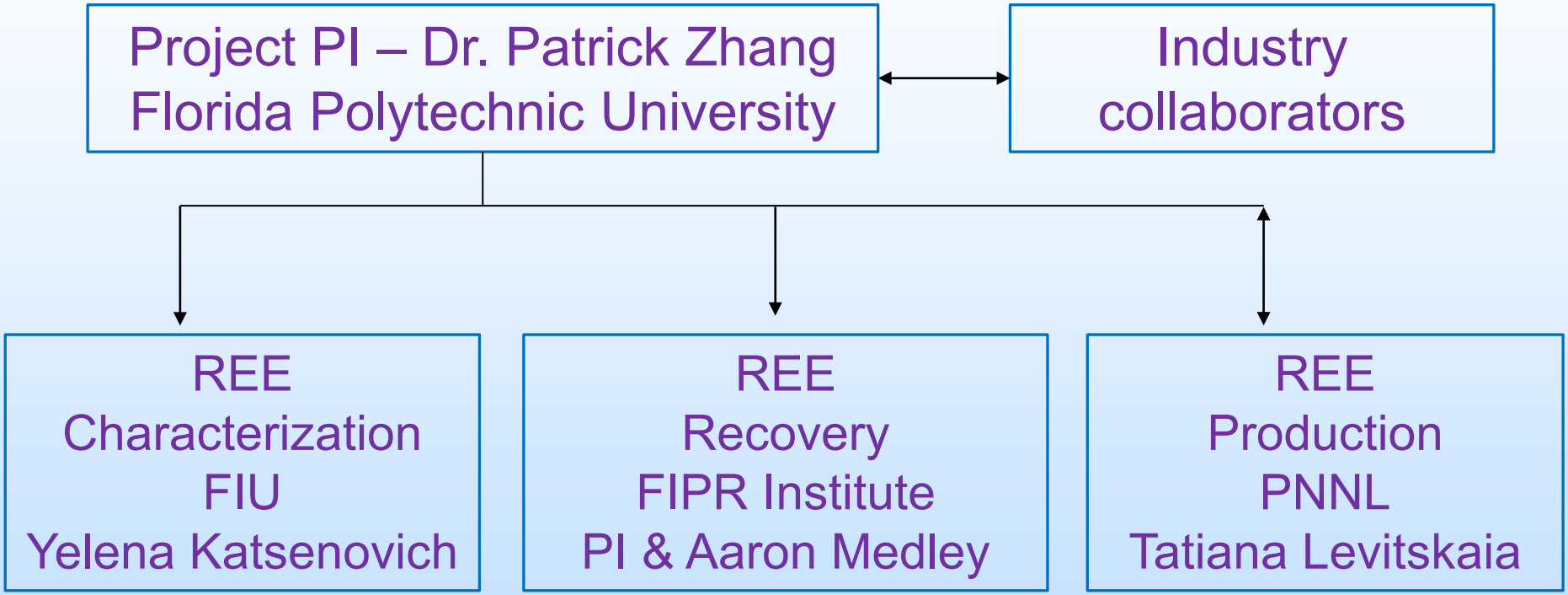
Summary

- 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.

Organization Chart



Gantt Chart

Task	ACTIVITY	PERCENT COMPLETE
Task 1	Project Management Plan	100%
Task 2	Teaming plan with at least two commitment letters	100%
Task 3	REE feedstock resource characterization data, including chemical/physical/mineralogical properties, Eu, Tb, Lu, Mn, Sr, Ti, V, and Ti, quantities required for Phase 2	100%
Task 3	REE feedstock pre-treatment and REE leaching data including Eu, Tb and Lu	60%
Task 4	Method(s) for REE extraction from leaching solution	75%
Task 5	Technologies for advanced REE separation	80%
Task 2 - 5	Complete and detailed Technical Research plan with processing flowsheet for producing MREO/REM	80%