Fiscal Year 2022/2023 Annual Report

Florida Industrial and Phosphate Research Institute

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Financial Information is included at the end of this report

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Jun Kim, Ph.D., Assistant Professor

Derek Henderson, Ph.D., Assistant Professor

Xiaofan (Caleb) Xu, Ph.D., Assistant Professor

Executive Director's Message – Dr. Terry Parker

FIPR has transformed itself from a standalone, state-funded research center to a university research institute that is fully embedded within Florida Polytechnic University. FIPR's core funding is a small fraction of the Florida state severance tax on phosphate rock product, which provides between $1.2M and $1.5M in support for research operations; multiple research grants and testing services provide important augmentation to these funds. As a research institute, FIPR has continued to focus on four critical areas that are consistent with its statutory mission:

- Minerals processing / rare earth elements (REE's)
- Phosphogypsum (PG) stacks and PG utilization
- Water, including process / industrial wastewater
- Phosphatic clay

In order to augment operations in these areas and to bring new ideas and viewpoints to FIPR, the University has created a strong alignment between the Environmental Engineering Department and FIPR. This partnership brings the inherent strength of the environmental engineering department in water and water quality to FIPR. A critical area for the phosphate industry in the future is water with problems ranging from managing process water to very broad effects of the industry on water in the environment.

FIPR is an internationally recognized institution of excellence in the global phosphate realm and has been leveraging this expertise to gain prominence in addressing the needs of our nation's security and economic independence based on efforts that support domestic production of critical rare earth elements. FIPR continues to be a unique contributor to the United States' efforts to ensure a domestic supply chain of these materials. This role was formalized 10 years ago as it became a founding member of the Critical Material Institute. FIPR has maintained its presence in this effort over the last decade. At this time, the effort has expanded into other grant opportunities where FIPR is looking to develop methods to exploit Florida's vast phosphate resources to meet the challenges of ensuring a domestic supply of critical rare earth elements. FIPR's ongoing efforts in the Critical Materials Institute and within other federally funded grants is a clear indication of our federal government's acknowledgement of FIPR's unique capabilities.

Since its creation in 2013, the USDOE's Critical Materials Institute has consistently supported FIPR's research in exploring the viability of phosphate deposits as a potential source of a domestic supply of rare earth elements. The 10-year funding program, with FIPR as a founding member, has made great progress in developing methods of REE extraction from all phosphate processing streams. The Critical Materials Institute has been renewed at the federal level, and FIPR remains a vital and active part of this national effort.

Significant progress has also been made toward realizing the capability to economically separate phosphate from dolomite in the vast high-magnesium phosphate pebble resources in Florida. FIPR's pilot plant at Mosaic's South Pasture facility has demonstrated that this recovery can be accomplished. This will greatly expand Florida's phosphate reserves well into the future. FIPR is investigating how to apply this technology so that the economics are favorable to the overall industry

The goal of finding high-volume uses for phosphogypsum was also addressed with the development of a novel road base technology through FIPR's Smart Road research project. The technology demonstrated load bearing strengths with Phosophgypsum as a road base that exceeded the state's standards with competitive economics to conventional methods. FIPR's intent is to identify pathways for using this material as a way of limiting, and potentially decreasing the amount of phosphogypsum stacked in Florida. To move this forward, we will continue to test the material as a road base, and work with the phosphate industry as a partner to identify regulatory barriers to adopting this as a roadbase.

Seamless integration of FIPR's efforts and capabilities with those of Florida Poly has made great strides during the past year. FIPR directorial staff served on committees to select the University's Environmental Engineering faculty. Environmental Engineering faculty have embarked upon new phosphate research projects that draw upon their individual areas of expertise with FIPR's support.

FIPR's laboratory services capabilities continue to be recognized by industry as providing high-quality, high-value results. This business center's activity has continued to be robust in its service to industry and academia. FIPR laboratory instrumentation will also be employed to enhance Florida Poly faculty research moving forward. FIPR and Florida Poly look forward to enhancing these partnerships as the University grows well into the future.

I am pleased to present this report of the Institute's activities and accomplishments during the 2022-2023 fiscal year and look forward to the challenges and achievements to come in the year ahead.

Summary of Core FIPR Activities (Contributed by Dr. Patrick Zhang, A. Medley)

Recovery of Critical Materials from Phosphate

CMI Phase II

FIPR is one of the founding members of the Critical Materials Institute (CMI) and has secured about $2 million CMI funding during Phases I and II for research on recovery of critical rare earth elements (REE) from byproducts and wastes generated during phosphate mining and processing. On July 1, 2023, CMI Phase II officially concluded and began its new phase. FIPR's achievements under CMI Phase II reached a new level during the current year by meeting all the milestones and filling two provisional patents. In a patent titled System and Method for Recovery of Rare Earth Elements and Phosphate from Byproduct Materials (US patent 63/465,121, May 9, 2023), FIPR disclosed a physical treatment method that can enhance REE leaching from phosphate byproducts achieving higher recovery with reduced leaching time and acid consumption. The other innovation involves thermal cracking of REE in phosphoric acid sludge achieving over 95% REE recovery while recovering the phosphate as high-value elemental phosphorus. (System and Method for Recovery of Rare Earth Elements and Phosphate from Phosphoric Acid Sludge, US patent 63/466,858, May 26, 2023).

CMI 2023 Phosphate Workshop

As a Florida Poly News post summarized, “Research scientists and industry leaders from across the country converged at Florida Polytechnic University to learn about research around rare earth element (REE) extraction at the CMI 2023 Phosphate Workshop”. FIPR organized this workshop to present our recent developments in collaboration with national labs in REE recovery from phosphate and to seek technical input from experts in the field. This two-day event also featured presentations by three technology companies on separation and purification of REE metals in the forefront of technology development by US scientists.

Workshop participants engaging in discussion with an industry representative during coffee break.

Successful REE Project Funded by US Department of Energy (DOE)

In collaboration with Pacific Northwest National Laboratory (PNNL), Oak Ridge National Laboratory (ORNL), Florida International University and Mosaic, FIPR Institute successfully concluded a new REE recovery project funded by the DOE (DE-FE0032123, 01/01/2022 to 09/30/2023). The project was titled “Technology Development and Integration for Volume Production of High Purity Rare Earth Metals from Phosphate Processing”. The research team developed a promising processing flowsheet (Figure 1) for production of high purity mixed rare earth oxide and rare earth metals. Considering this achievement, we are collaborating with the team members and preparing a new ($2-3 million) grant proposal for continuous testing of the processing technology to bring it one step closer to commercialization. The proposal is titled Optimization of Continuous Process Flowsheet Towards Mass Production of High-Purity REE from a Phosphate Mining Byproduct.

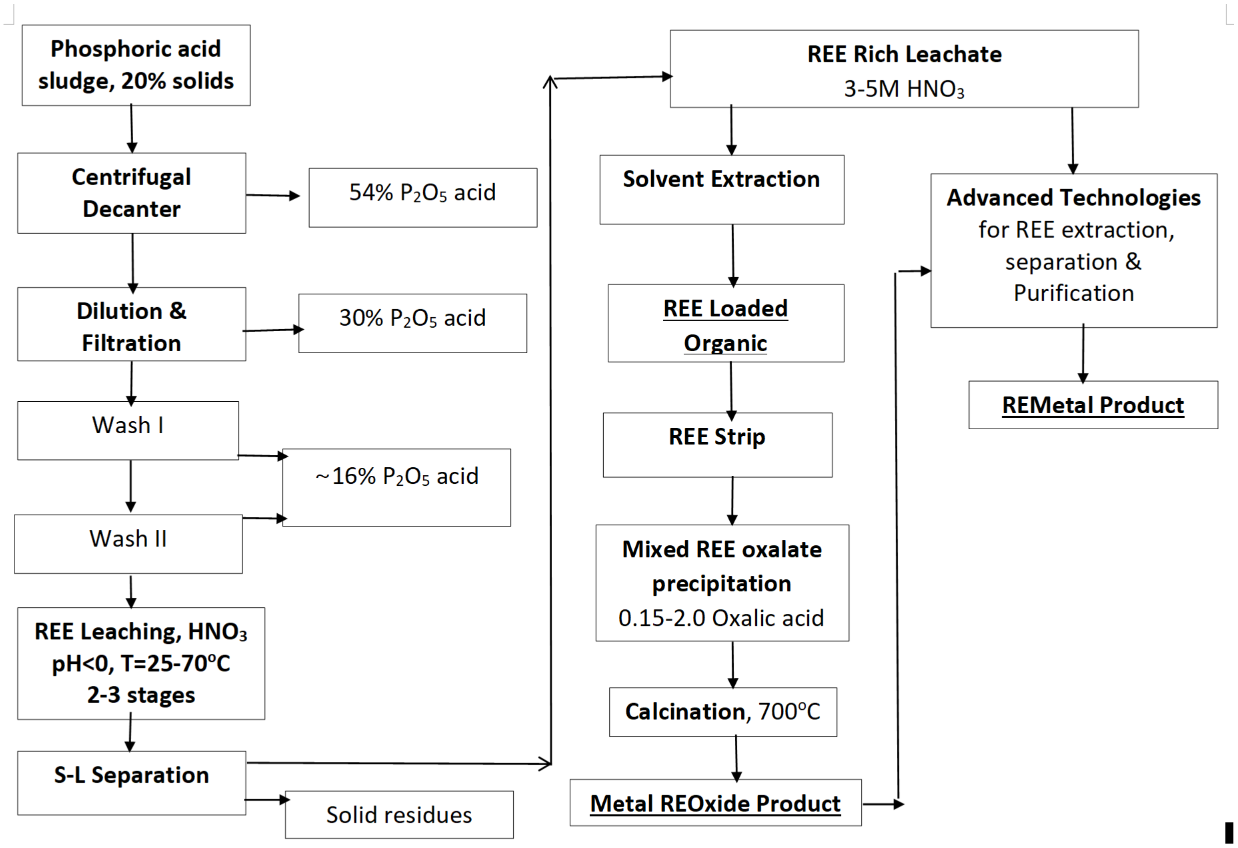


Figure 1. Overall processing flowsheet developed by FIPR and collaborators for production of high-purity MREO and REE metals using phosphoric acid sludge as feedstock.

CMI Phase III

FIPR led a five-member team in submitting a proposal to compete for CMI Phase III projects and succeeded in securing funding for the proposal in the amount of about $800K ($250K for FIPR) per year, likely for 5 years. The project is titled “Total Utilization of Phosphogypsum Waste for Production of REEs, Fertilizers, and Construction Materials”. Team members include Rutgers University, PNNL, ORNL, FIU and Florida Poly. The research project is designed to integrate recovery of critical elements into total utilization of the huge amount of PG generated from phosphoric acid manufacturing with five major objectives:

1. Reduce radionuclides in PG thus removing a hurdle to its use
2. Maximize REE leaching recovery from PG
3. Develop technologies for REE extraction from the PG leachate and production of mixed rare earth oxide/salt or individual rare earth metals (MREO/MRES/REMs)
4. Combine PG use with significant CO_2 sequestration.
5. Produce low-cost cement and concrete using PG as raw material with dramatic reduction in carbon footprint compared to the current commercial operations.

Collaboration with CF Technologies

FIPR collaborated with CF Technologies, a technology startup, in securing a research grant under DOE’s Small Business Innovation Research (SBIR) program to evaluate CF Technologies’ supercritical fluid process for extracting and purifying REEs using leachate from phosphate byproducts and wastes. The project demonstrated the feasibility of supercritical extraction technology. Preliminary economic analysis shows profitable scenarios using phosphoric acid sludge as feedstock, as shown in the table below.

• Acid Sludge tons/yr	50,000	400,000
• Extractor Diameter (m)	0.15	0.2
• Capital Cost Estimate	$1.3 M	$2.4M
• Operating Rate (hrs/yr)	2000	8000
• Operating Cost ($/yr)	$0.7M	$4.2M
• Annual Revenue ($/yr)	$1.6M	$13M
• Net ($/yr)	$0.9M	$8.8M
• Payback (yr)	<2	<1

Phosphogypsum Research

PG Use for Road Construction

In collaboration with Madrid Engineering, FIPR research produced an innovative road base composition and method of construction. The road base mixture incorporates varying quantities of by-product phosphogypsum (PG) from phosphate fertilizer production, sand, clayey sand and CONSOLID additive. The resultant mixtures impart strength and resilience properties into the road base when compared to traditional road construction methods. Additionally, the mix also has been demonstrated to be hydrophobic, thus improving moisture resistance and long-term durability under wet conditions.

Extensive PG Characterization

Recently, Mosaic undertook a major effort to establish a database of PG characteristics both chemically and physically. Lots of samples were collected under that effort, including many core samples from different depths and horizontal directions in a stack, fresh PG from the pan filter, and PG samples from different acid plants. FIPR participated in that program and analyzed numerous samples for rare earths and heavy metals, physical properties, and SEM/EDS maps. The information generated from this program can serve as a useful guide for developing methods for REE extraction, reduction of radioactivity, and PG purification for different uses.

Technology Development for Reducing Radioactivity in PG

As discussed above, removal of radionuclides from PG is a research component of the CMI Phase III project. Since PG contains a low concentration of radium-226 in a complex matrix, it is extremely challenging to develop an economically feasible process for reducing the radioactivity level to meet the current regulatory limit. During this year, FIPR ran radioactivity analysis of sieved fractions from three PG samples. Results indicate that a large portion of radionuclides may be eliminated from PG by removing a small fraction of material within a certain size range using physical methods.

Research to Improve Phosphate Industry Efficiency

Packed Column Jig (PCJ) for Removing Dolomite

Since late 2021, FIPR has conducted several pilot testing campaigns to demonstrate the feasibility of PCJ for removing dolomite from high-Mg phosphate pebbles achieving encouraging results. Based on the test results, operating parameters, mass balance information and equipment prices, KEMWorks Technology Inc (a Lakeland-based engineering firm) conducted a feasibility study on a PCJ plant, which shows rapid return on investment for commercialization of this technology. KEMWorks summarized the main conclusions of the study as follows: “The operating cost for this process is estimated to be ≈$20 per short ton of product material. The economics of the process will be predominately dependent on the values assigned to the low-quality pebble feed and the higher quality product. With current rock prices around $300/mt, this project becomes very economically attractive.” Compared to flotation process for dolomite removal from dolomitic phosphate pebbles, PCJ has the following advantages:

- “Operating Cost – the Jig Column Process had a significantly lower operating cost
- Capital Cost – the Jig Column Process had a significantly lower (≈24%) capital cost
- Phosphate Recovery – the Jig Column Process recovery was at least comparable, if not better.”

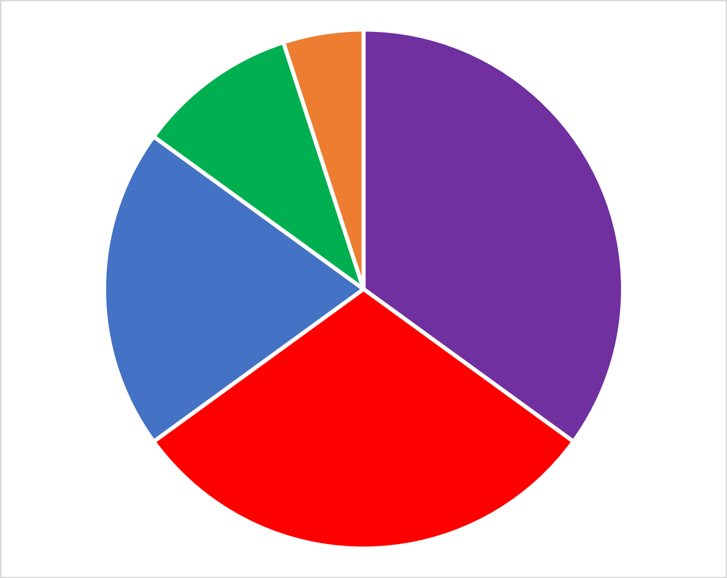
Considering these encouraging results and the market potential for PCJ, FIPR filed a provisional PCJ-based patent (System and Method for Separating Carbonaceous and Siliceous Materials from Phosphate Via Gravity Separation, US Patent 63/468,413, May 23, 2023).

Recovery of Phosphate from PG

A recent PG characterization study showed that a small fraction of PG contains as high as 15% P_2O_5. This fraction is quite easy to separate from the bulk PG. With some minor treatment, this fraction could be used as a feed for phosphoric acid manufacturing, since it contains low concentrations of minor elements (Mg, Fe, and Al). FIPR is investigating strategies for utilizing this phosphate resource within the acid plant before PG is pumped into the stack that is subject to environmental regulations.

FIPR Laboratory 2022-2023 AR

The FIPR analytical and metallurgical testing laboratories play a vital role in both our internal research programs and key research projects funded by the federal government and industries In addition, these labs provide quality analytical, testing and consulting services to external research institutions, engineering firms and industrial companies. The FIPR labs have developed specialized capability for tests associated with phosphate chemistry. This capability includes specific processes and analytical methods such as flotation, grinding, screening, particle size analysis, solvent extraction, thermal analysis, colorimetric testing, optical emission spectroscopy and mass spectroscopy. The combination of state-of-the-art instrumentation with a laboratory staff dedicated to providing impeccable quality standards has led to industrial recognition of the FIPR analytical lab as a leader in phosphate-related analyses.



🟪 35% = Phosphate Analysis Big 6 (P_2O_5, Insol, MgO, Al_2O_3, Fe_2O_3, CaO)
🟥 30% = Individual Metal Analysis (Cd, Co, Ni, Cu, Zn, Au, Ag, Li, Na, Mn)
🟦 20% = Rare Earth Elements + Th and U
🟩 10% = Water Analysis (P_2O_5, MgO, Al_2O_3, Fe_2O_3, CaO, SO_4, F, TDS, pH, ORP, DO, Conductivity)
🟧 5% = Particle Size Analysis, Sample Preparation

Categorization of Laboratory Services Analyses (Source: FIPR Institute Analytical Laboratory).

In Fiscal Year 2022-2023, the FIPR Institute laboratories provided analytical services to fourteen (14) different entities in multiple work efforts totaling more than $113,000. Laboratory Services has had an increase in internal research and analysis of Rare Earth Elements and Lithium recovery from the last fiscal year. FIPR analytical laboratory equipment includes: ICP-OES, ICP-MS, Lachat QuickChem P_2O_5 analyzer, Astoria Pacific rAPID-T water analyzer, Horiba Particle Size Distribution Analyzer, and Orion pH/ISE meters.

The FIPR laboratories have worked closely with Florida Polytechnic's Environmental Engineering program supplying them with samples and analyses. The FIPR Institute looks forward to collaborating with them even more on several of their research projects.

Environmental Engineering Projects

Application of biochar to phosphorus control in phosphogypsum process water treatment

Principal Investigator: Dr. Xiaofan (Caleb) Xu, xxu@floridapoly.edu

Abstract: As a byproduct of phosphate mining, phosphogypsum (PG) is usually managed in large stacks due to its weak radioactivity. The process water stored at the PG stacks poses a risk of leakage, potentially contaminating nearby surface water and groundwater. Of particular concern is the presence of elevated levels of nitrogen and phosphorus in the process water, which can lead to water eutrophication. Compared to nitrogen, is recognized as the limiting nutrient in freshwater bodies, contributing to harmful algae blooms (HABs). Nevertheless, research on phosphorus control in PG process water treatment has been limited, with most related technologies remaining at the lab scale due to economic feasibility constraints. Biochar, a form of black carbon derived from biomass sources, has gained prominence in wastewater treatment as an effective and cost-efficient adsorbent, owing to its porous structure. This study employed biochar in the treatment of PG process water to mitigate HABs through phosphorus management, and evaluated the technological performance and life-cycle environmental impacts of biochar relative to its phosphorus management capability. Three commercial biochar products of varying particle sizes—medium (>25 mesh), small (26-50 mesh), and powder (<50 mesh)—were mechanically mixed with two process water samples provided by the Mosaic Company. The mixture comprised 5g of biochar and 100mL of the sample, maintained at a constant temperature of 22 ℃. Over a span of five days, phosphate concentration in the six groups was monitored, with removal efficiency peaking at 33% to 41% within three days. It's worth noting that the low pH in the process water was identified as a limiting factor affecting biochar performance. To comprehensively evaluate the environmental impacts, a life cycle assessment (LCA) was conducted using SimaPro PhD software for the biochar application in PG process water treatment. Three different end-of-life (EOL) strategies were considered, including landfill, incineration, and composting. Coal-based granular activated carbon (GAC) with thermal regeneration was used as a benchmark for comparison. Six categories of environmental impacts were assessed using the Tool for Reduction and Assessment of Chemicals and Other Environmental Impacts (TRACI) v2.1 developed by the US EPA. Notably, biochar exhibited fewer environmental impacts compared to GAC. Among the various strategies considered, biochar with a composting EOL approach was found to be the most sustainable option, yielding the lowest impacts in eutrophication potential, global warming potential, and human toxicity.

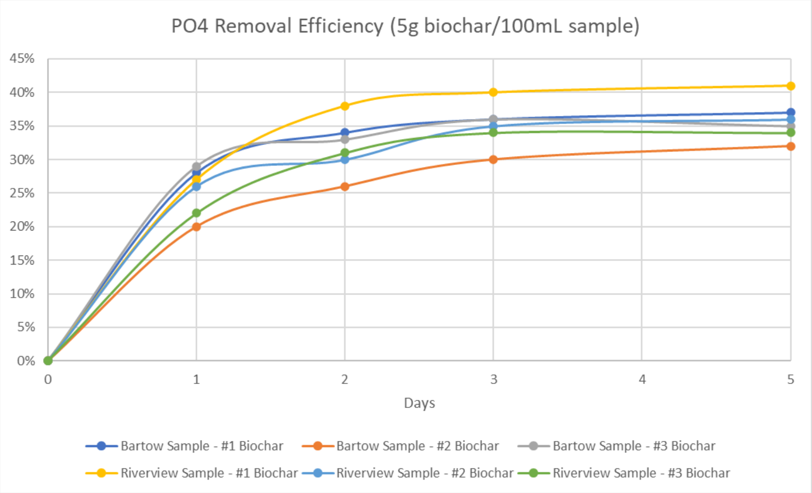


Figure 1. Phosphate removal efficiency of three biochar products for two process water samples.

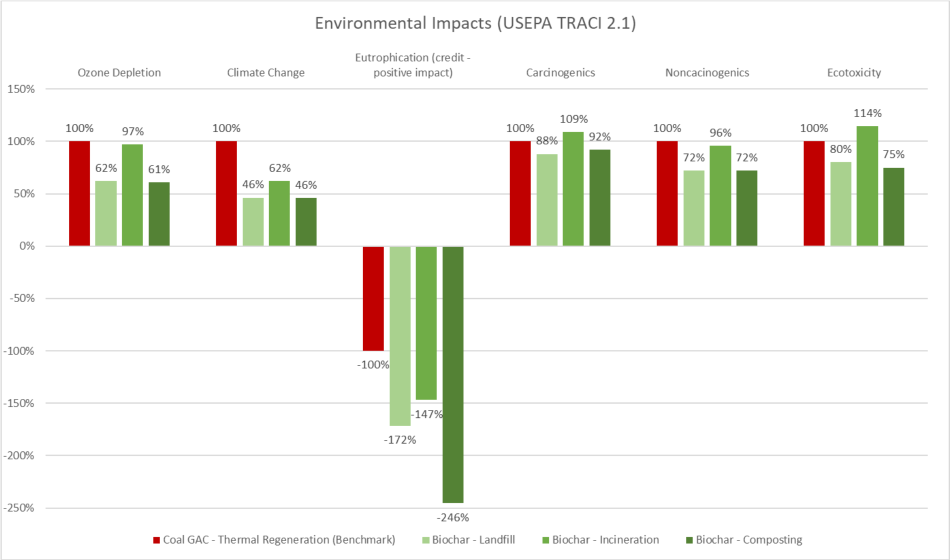


Figure 2. Environmental Impacts of biochar and with different strategies relative to process water treatment.

GAC EOL

Purification of Phosphoric Acid Manufacturing Process Water with Recovery of Critical Materials via Ion-selective Capacitive Deionization

Jun Kim[1], **Patrick Zhang**[2]

[1]Dept. of Environmental Engineering, Florida Polytechnic University
[2]Florida Industrial and Phosphate Research Institute, Florida Polytechnic University

I. INTRODUCTION

Every year, the United States consumes more than 20 million tons of phosphate rock mainly for producing fertilizers. Phosphoric acid is also used in everything from food and cosmetics to animal feed and electronics. During the phosphate mining process, the production of highly saline process water with phosphate ion (PO_4^{3-}) is inevitable. Meanwhile, the process water contains an appreciable amount of critical rare earth elements (REEs), such as Y, Dy, Gd, Pr, and Nd[1]. The extraction of REEs has great potential economic benefits when properly recovered from the process water. Membrane capacitive deionization (MCDI) is an ion-selective electrochemical water treatment process for various hazardous contaminants and targeted elements using microporous carbon electrodes and ion-exchange membranes[2]. Kim et al. demonstrated a higher adsorption rate of multi-valent cations and anions, thus MCDI can be further used for resource recovery, especially for trivalent REEs (3+) and phosphate (3-) ions.

II. MATERIALS AND METHODS

A. MCDI reactor

In this study, the membrane capacitive deionization (MCDI) reactor is composed of supercapacitor carbon supercapacitor electrodes on titanium (Ti) substrates, a cation and anion exchange membrane (CEM and

AEM) with a spacer in-between. DC 1.2V is applied for electrosorption and reversed-voltage (DC -1.2V) is for complete discharge and electrode regeneration.

B. Measurement

A UV-Vis spectrophotometer (Agilent, Cary 60) and a quadrupole inductively coupled plasma - mass spectrometry (ICP-MS, PerkinElmer, NexION 350X) is utilized for the analysis of water samples.

C. Ion-selectivity

The performance of the MCDI is under evaluation in a flow-through cell using binary electrolyte solutions. The total ion adsorption capacity of the electrode remains the same with and without the nanocomposite coating. However, the MCDI reactor can demonstrates selectiv-electrosorption towards trivalent cations and anions over the monovalent cations and anions, respectively.

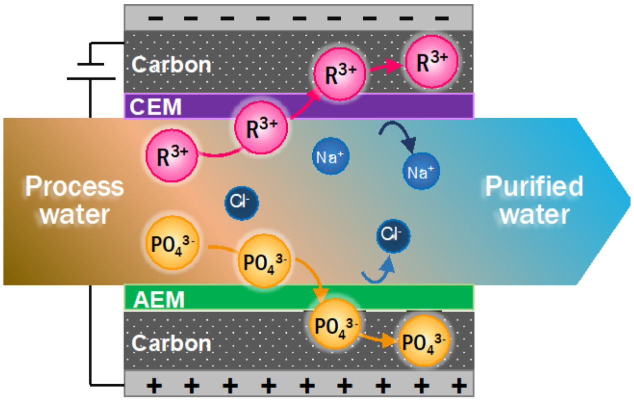


Figure 1: Membrane capacitive deionization process diagram

D. Performance Evaluation

Total amount of target (T) ions adsorbed (meq) during electrosorption can be calculated by

$$q_T = \int_0^{t_{ad}} Q \sum \left(C_{i,inf} - C_{i,eff} \right) dt$$

Selectivity for the target (T) ions (Nd^{3+}, PO_4^{3-}) over the competing (C) ions (Na^+, Cl^-) can be written as

$$Selectivity_t = \frac{q_{T,t}}{q_{T,c}} \Big/ \frac{C_{in,t}}{C_{in,c}}$$

ACKNOWLEDGEMENTS

This research is part of the Florida Industrial and Phosphate Research (FIPR) Institute projects.

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2. Kim et al., “Selective Removal of Calcium Ions from Water Using Target-ion Specific Capacitive Deionization”, Water Research, 160, 445-453, 2019.

[Supporting Information]

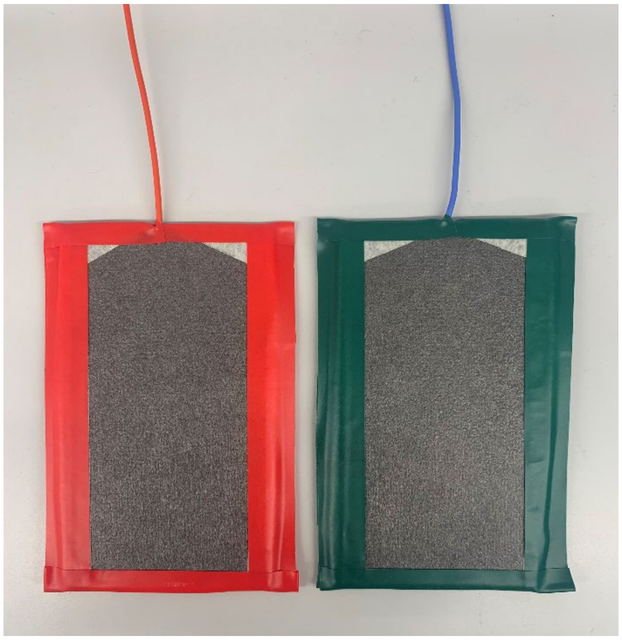
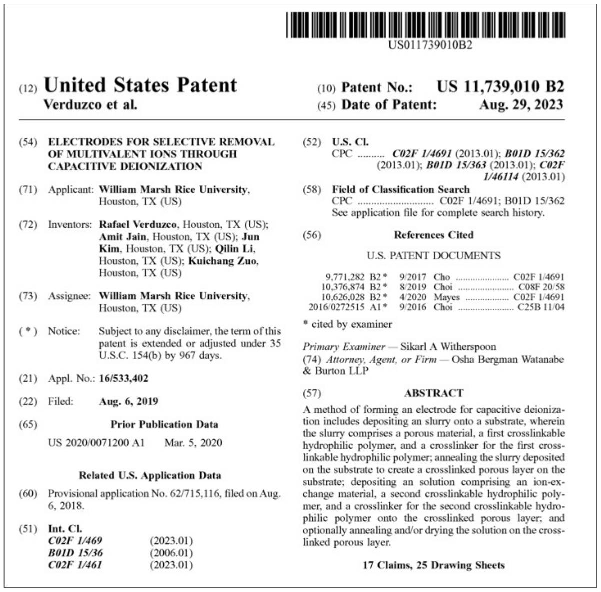


Figure S1. Electrosorption test-set up

Figure S2. Supercapacitor electrodes

[Technological Advantages]

- High-selectivity
- Regeneratable electrodes
- Easily scalable
- Easy operation & maintenance
- No pressure-driven process
- No chemical usage (hazardous waste)
- Patented process (US 11,739,010)



US011739010B2

(12) **United States Patent**
Verduzco et al.

(10) **Patent No.: US 11,739,010 B2**
(45) **Date of Patent: Aug. 29, 2023**

(54) **ELECTRODES FOR SELECTIVE REMOVAL OF MULTIVALENT IONS THROUGH CAPACITIVE DEIONIZATION**

(71) Applicant: **William Marsh Rice University**, Houston, TX (US)

(72) Inventors: **Rafael Verduzco**, Houston, TX (US); **Amit Jain**, Houston, TX (US); **Jun Kim**, Houston, TX (US); **Qilin Li**, Houston, TX (US); **Kuichang Zuo**, Houston, TX (US)

(73) Assignee: **William Marsh Rice University**, Houston, TX (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 967 days.

(21) Appl. No.: **16/533,402**

(22) Filed: **Aug. 6, 2019**

(65) **Prior Publication Data**

US 2020/0071200 A1 Mar. 5, 2020

Related U.S. Application Data

(60) Provisional application No. 62/715,116, filed on Aug. 6, 2018.

(51) **Int. Cl.**
C02F 1/469 (2023.01)
B01D 15/36 (2006.01)
C02F 1/461 (2023.01)

(52) **U.S. Cl.**
CPC ***C02F 1/4691*** (2013.01); ***B01D 15/362*** (2013.01); ***B01D 15/363*** (2013.01); ***C02F 1/46114*** (2013.01)

(58) **Field of Classification Search**
CPC C02F 1/4691; B01D 15/362
See application file for complete search history.

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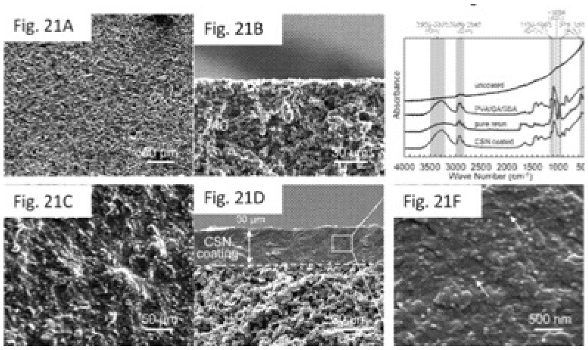
* cited by examiner

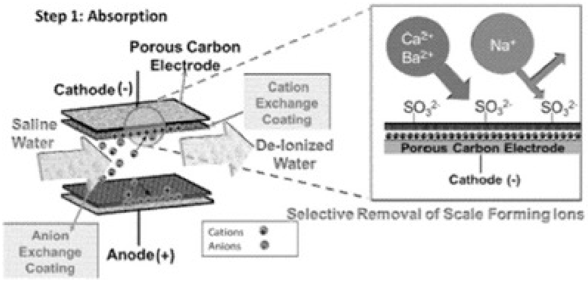
Primary Examiner — Sikarl A Witherspoon
(74) *Attorney, Agent, or Firm* — Osha Bergman Watanabe & Burton LLP

(57) **ABSTRACT**

A method of forming an electrode for capacitive deionization includes depositing an slurry onto a substrate, wherein the slurry comprises a porous material, a first crosslinkable hydrophilic polymer, and a crosslinker for the first crosslinkable hydrophilic polymer; annealing the slurry deposited on the substrate to create a crosslinked porous layer on the substrate; depositing an solution comprising an ion-exchange material, a second crosslinkable hydrophilic polymer, and a crosslinker for the second crosslinkable hydrophilic polymer onto the crosslinked porous layer; and optionally annealing and/or drying the solution on the crosslinked porous layer.

17 Claims, 25 Drawing Sheets





Phosphogypsum Road Base and REE/RN Extraction Research

Derek Henderson, Florida Polytechnic University

Introduction

PG road base:

The use of existing phosphogypsum (PG) stack material as a road base material has been considered by various entities, however, the long-term performance of a road constructed with a PG road base under simulated road loading and environmental conditions is not well understood. The selection of a binder-PG-additive mixture, tested under simulated environmental conditions, will be an important component of successful PG road base implementation. Furthermore, the monitoring of synthetic stormwater runoff from a PG based test road will likely be necessary for public and regulatory acceptance and will reveal what, if any, mitigation systems may be needed for stormwater runoff management of a PG based road.

REE/RN extraction:

Due to rapidly increasing demand for REE materials, their importance as critical materials, and their role in national security, securing domestic sources and processing methods of REEs is of great interest. Additionally, the processed PG may be used as an additional resource if radioactivity levels are sufficiently reduced, reducing liabilities related to phosphate production.

Research Goals

PG road base research goals:

Initial research goals of the PG road base study are the development and optimization of the road base test apparatus (RBTA) used to determine the long-term performance of PG road base. The design and development of the RBTA is currently underway with the construction of the steel frame currently in progress.

Following completion of the RBTA, an indoor asphalt surfaced, PG base test road will be examined for long term performance and durability under simulated road loading and environmental conditions. In addition, synthetic runoff samples will be collected and analyzed for indications of road degradation or material release. If necessary and feasible, mitigation systems will be designed and implemented into the RBTA. Methodology details can be found below.

The road base binder and mixture will be determined/improved by a series of cube tests of various binder-PG-additive mixtures and tested for compression strength by standard compression testing. In addition, prepared cube samples will be subjected to simulated environmental conditions such as extended contact with synthetic road runoff and high intensity UV. The synthetic road runoff used in these experiments will also be analyzed for water quality impacts as an indicator of material degradation or release.

REE and radionuclide extraction research goals:

Ionic liquids have gained some interest as a greener and recyclable alternative extraction solvent over concentrated, high temperature acids. The ionic liquid betainium bis(triflouromethylsulfonyl)imide, commonly referred to as [Hbet][Tf2N], was synthesized in lab and used an extraction solvent for REEs and RNs. REEs and RNs were quantified in the aqueous phase of the solvent mixture and low-strength acid used to strip the ionic liquid for reuse. Method details may be found below. The use of a group of more affordable and even greener solvents known as deep eutectic solvents may prove to provide similar results but at a more feasible cost based on further studies. Extraction of REE/RN from the insoluble clays are a potential study due to the high solubility of both phosphogypsum and acid sludge.

Rotary extraction was used to determine basic extraction characteristics of phosphogypsum as well as to create phosphogypsum nutrient extractions used in algal extraction experiments. Three conditions were selected for analysis: extraction kinetics, effect of solvent pH on extraction, and solid to solvent mass ratio. Method details are found below.

Following a series of solid-liquid and liquid-liquid REE and radionuclide extraction experiments, vegetative and algal extraction studies are already in progress to determine feasible plant species and ideal soil to PG ratios or phosphogypsum based nutrient solution for a hydroponic growth system which allow for rapid growth rates and high percentage of accumulation. These studies are of interest as a potential method to further isolate REE and RN from dissolved PG material found in liquid-liquid extraction. Although mass transfer from soil to plant is typically low, some species have been found to be high accumulators (Tyler 2004) which could then be processed for additional concentration through digestion or combustion and ash extraction. A column study of various plant species' potential for accumulation would be conducted for their feasibility as a viable extraction technology. The REE and RN mass stored in vegetative matter will be recovered using solid-liquid and liquid-liquid extraction methods on vegetative ash. This method potentially results in recovery of REE and/or RN while minimizing dissolution of PG which contributes to dissolved calcium and sulfate contamination. This study also examines the potential for accumulation of REE and RN by specific algal species. Although a pure phosphogypsum based nutrient solution has failed to support algal growth, possibly due to low pH of the nutrient solution, a commercial nutrient solution used with the rotary extraction method to extract REE/RN has successfully supported algal growth. Future research will include the comparison of initial REE/RN concentrations to post-growth concentrations to determine the biological assimilation of REE/RN and potential for remediation of contaminated process waters and extraction of critical materials.

Methodology

PG road base methodology:

The RBTA is currently designed as an eight by four-foot test bed enclosed within steel plating and supported by a steel tube frame to prevent any flexing of the test road during loading. The entire apparatus is suspended above a steel frame platform to allow for mechanical and sampling equipment to be located below the test road. The test road is designed to be as much as 12 inches of PG/binder road base with a two inch, cold applied asphalt surface.

Figure 1: Steel support frame for road base test apparatus

Long term performance of PG road base will be determined by fatigue testing in conjunction with simulated environmental conditions. Loading will be applied by a tire on a motorized track and adjustable by a series of hydraulic or mechanical presses located in the track system. Loading and fatigue will be measured through a combination of embedded strain gauges and loading cells. Deformation will be tracked with digital images and physical measurements of the road surface.

To better understand performance under typical road conditions, environmental conditions will be simulated by periodic application of synthetic stormwater road runoff through a series of sprayers. Road runoff will be recollected through a curb and gutters system for analysis. Infiltrated stormwater will be collected through an underdrain pipe system and an embedded “monitoring well”. Changes in moisture content of the road base will be analyzed using embedded moisture sensors.

Stormwater runoff and infiltrate will be analyzed to ensure there are no adverse environmental impacts. If potential environmental impacts are discovered, mitigation measures will be designed and, cost and scope permitting, implemented into the test apparatus.

Potential lanthanides and radionuclides will be analyzed using ICP-MS to determine if stormwater infiltrate has any potential to release heavy metals due to desorption or dissolution of PG material. Dissolved calcium will be analyzed using ICP-OES or ion chromatography as an indicator of dissolution of PG material which may lead to voids within the road base, road cracking, or road subsidence. Sulfate potentially released due to PG dissolution will be analyzed either through sulfate turbidity method using barium chloride or ion chromatography. All runoff samples will be analyzed for total suspended solids to determine if or to what extent solid particles are migrating from the road surface or road base using standard filtration and gravimetric determination. Samples will be analyzed for phosphate to determine potential for nutrient loading to receiving waters either by spectrometry or ion chromatography. Finally, the presence of polymers will be quantified by FTIR to determine potential degradation of the polymer binder. Particle emitters may be determined in future sampling by liquid scintillation counting, depending on equipment availability. Liquid scintillation would provide a sensitive and accurate method of determining particle emitters released either as dissolved ions or sorbed to other migrating solid particles.

Approximately 6000 pounds of phosphogypsum material has been secured through Mosaic for use in the road base testing and is currently stored on-site at Florida Polytechnic University. Approximately ten gallons of dry application Consolid polymer binder has been secured through FIPR for testing as a suitable binder material to increase the compression strength of the phosphogypsum and create a durable road base.

REE/RN extraction methodology:

Extraction experiments are already underway using various solid-liquid and liquid-liquid extraction methods. These methods include ionic liquid extraction, rotary leaching, vegetative extraction, and algal extraction. Liquid-liquid extractions are performed using a recyclable, synthesized, thermomorphic ionic and aqueous liquid solution. 50 mg of phosphogypsum or acid sludge were used for extraction with equal volumes of an aqueous nitrate solution and ionic liquid. The solution is heated to 50 degrees Celsius for one hour which creates a single-phase solvent. The solution is allowed to cool overnight which results in the solvent returning to a two-phase liquid (aqueous and ionic liquid) and partitions REE/RN and other dissolved ions between the resulting two phases. Recycling is done using a 1.5 M hydrochloric acid stripping process to extract REE/RN species from the ionic liquid phase.

Additional planned experiments include deep eutectic liquids and sonication extraction, as well as multi-step extraction processes aimed at further isolating REE/RN species of interest from common ions, particularly dissolved calcium and sulfate. For example, liquid-liquid extraction using thermomorphic liquids in combination with high REE aqueous solution produced from rotary leaching.

Rotary extraction was performed using a Thermofisher rotator with 15 mL centrifuge tubes for times ranging from 5 minutes to 108 hours with the same aqueous nitrate solution used with ionic liquid extraction at range of pH values from 1.0 to 11.0. The remaining planned experiment will examine the optimization of the solid phosphogypsum to solvent mass ratio.

Vegetative extraction, including algal extraction, will include flaming vegetative mass in a muffle furnace and using previously described extraction methods to preferentially extract REE/RN species. This is expected to provide isolated REE/RN species in solution at the expense of some extraction efficiency.

The isolated liquid extracts are examined for REE/RN using ICP-MS while dissolved calcium and sulfate are currently determined using ICP-OES. Future analysis of sulfate may be performed using ion chromatography depending on equipment availability.

Results:

Ionic Liquid Extraction of REE/RN

Concentrations of REE/RN were seen to range from 18.58 ppm from 50 mg of phosphogypsum to 25.91 ppm from 50 mg of acid sludge. Although some clarification is needed from the analytical lab, the sample volumes used for analysis were 1 mL when available. The phosphogypsum was analyzed for REE/RN and was determined to have 459.8 mg REE/RN per kg of phosphogypsum. This would equate to a mass of 22.99 mg of REE/RN for a 50 mg sample of phosphogypsum. This results in extraction efficiencies of 80.8% to 108.3% for phosphogypsum. There seems to be a large (unquantified) degree of variance between duplicate samples within the PG and acid sludge material, despite being dried and ground into a relatively fine powder. One current challenge is the isolation of REE/RN from other ions, particularly the calcium and sulfate dissolved from the phosphogypsum during extraction. The highest concentrations of these two ions are in the aqueous phase, which is also where the highest concentrations of REE/RN are found. Ionic liquid extraction was performed twice on the same samples in an attempt to separate the ions of interest, but no additional separation was observed. Although additional testing has been performed, only early results are presented here for brevity.

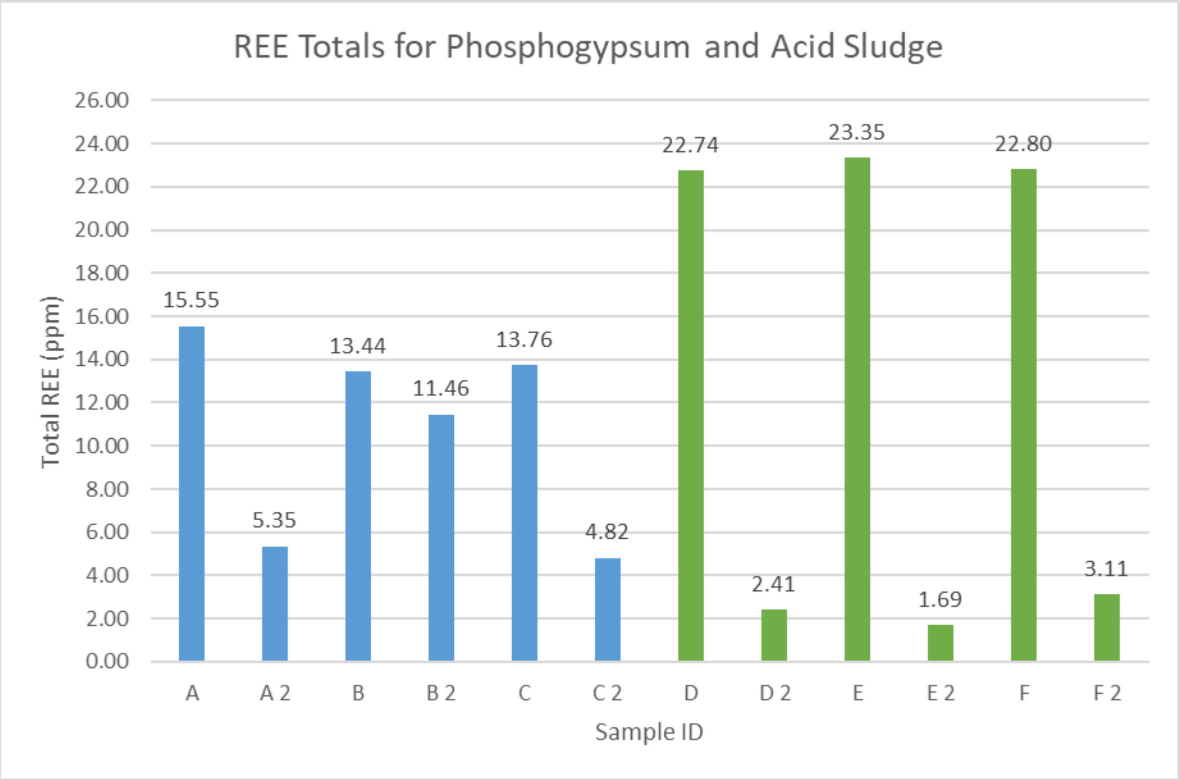


Figure 2: Total REE/RN concentrations for each sample of initial ionic liquid extraction from phosphogypsum and acid sludge experiments. Samples in green denote acid sludge. Each sample was tested for REEs in the aqueous solution and acid stripping solution.

Rotary extraction was used to optimize extraction times and pH values. The extraction times can be seen in Figure 3, below, truncated at 600 minutes for clarity.

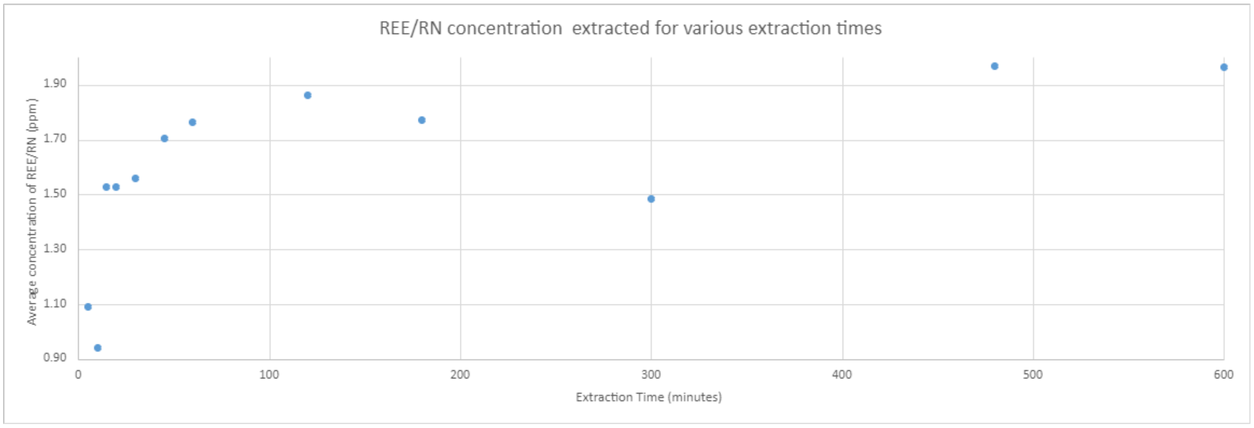


Figure 3: REE/RN average concentrations at extraction times from 5 minutes to 600 minutes.

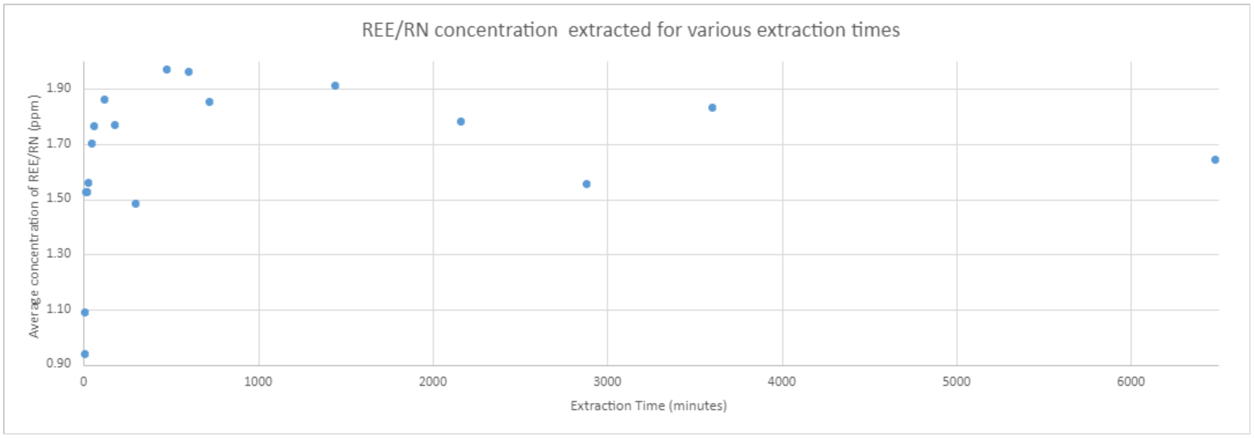


Figure 4: REE/RN average concentrations at extraction times from 5 minutes to 6480 minutes.

The maximum concentration of 1.97 ppm was observed at 480 minutes of extraction while a concentration of 1.86 ppm was seen at only 120 minutes of extraction time. It is noted that concentrations beyond 480 minutes did decrease in some cases. Additionally, the reported concentrations are averaged from duplicate samples.

pH ranging from 1 to 11 were extracted in duplicate for 120 minutes and 480 minutes. Results indicate that extraction done at 1 pH resulted in an average concentration of 1.49 for both extraction times. Concentrations dropped off quickly with an average concentration of 3.5 ppm at a pH of 2 and 120 minutes and 0.25 ppm at a pH of 2 and 480 minutes.

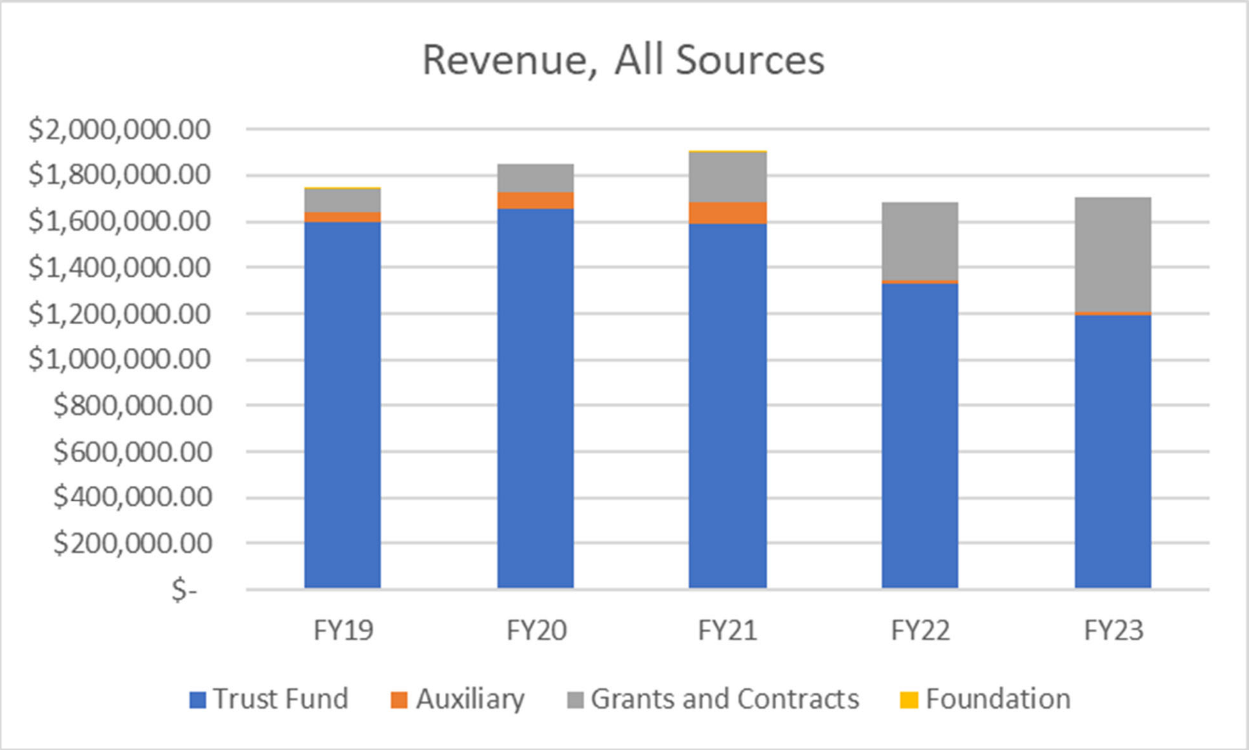
FIPR INSTITUTE
FLORIDA POLYTECHNIC UNIVERSITY

Fiscal Year 2022/2023 Financial Report

Florida Industrial and Phosphate Research Institute

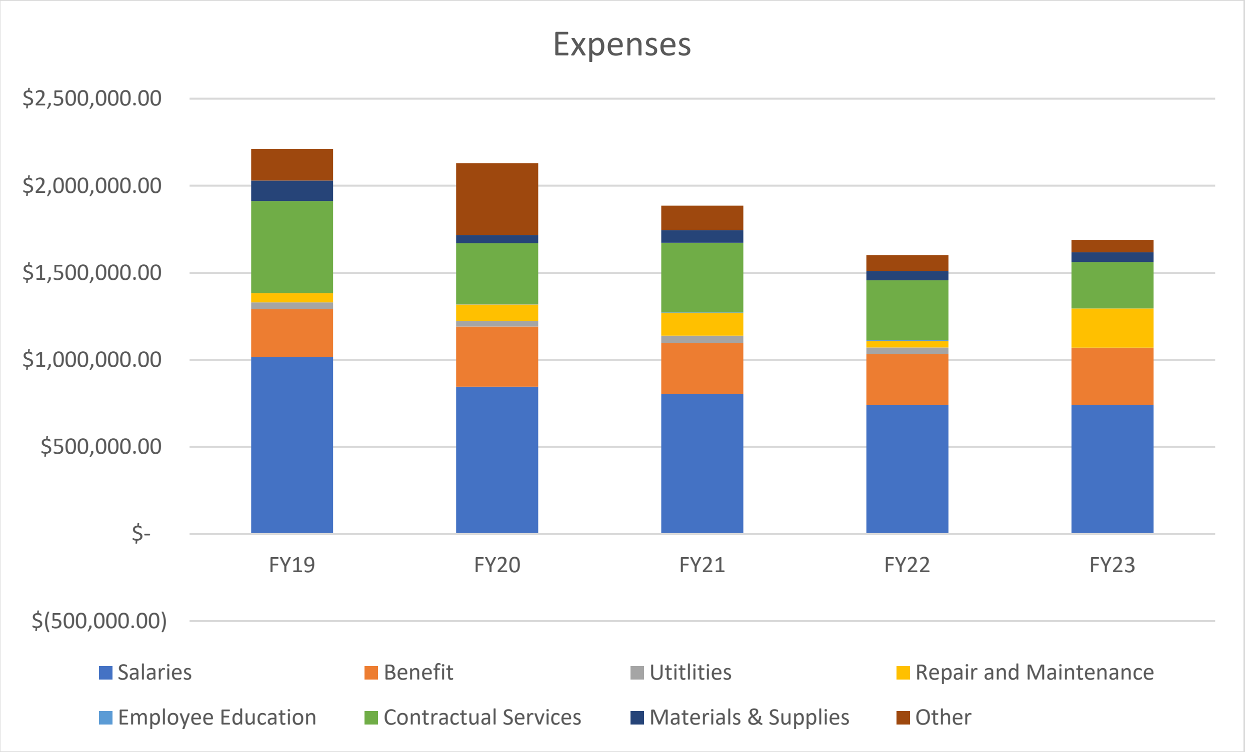
FIPR Institute revenue, all sources.

	FY19	FY20	FY21	FY22	FY23
Trust Fund	$ 1,598,967.65	$ 1,651,677.76	$ 1,591,279.81	$ 1,329,029.12	$ 1,193,160.53
Auxiliary	$ 43,559.69	$ 79,153.48	$ 90,776.68	$ 15,974.77	$ 16,015.48
Grants and Contracts	$ 97,580.55	$ 119,566.23	$ 217,188.10	$ 336,495.91	$ 498,624.38
Foundation	$ 209.60	$ -	$ 58.73		



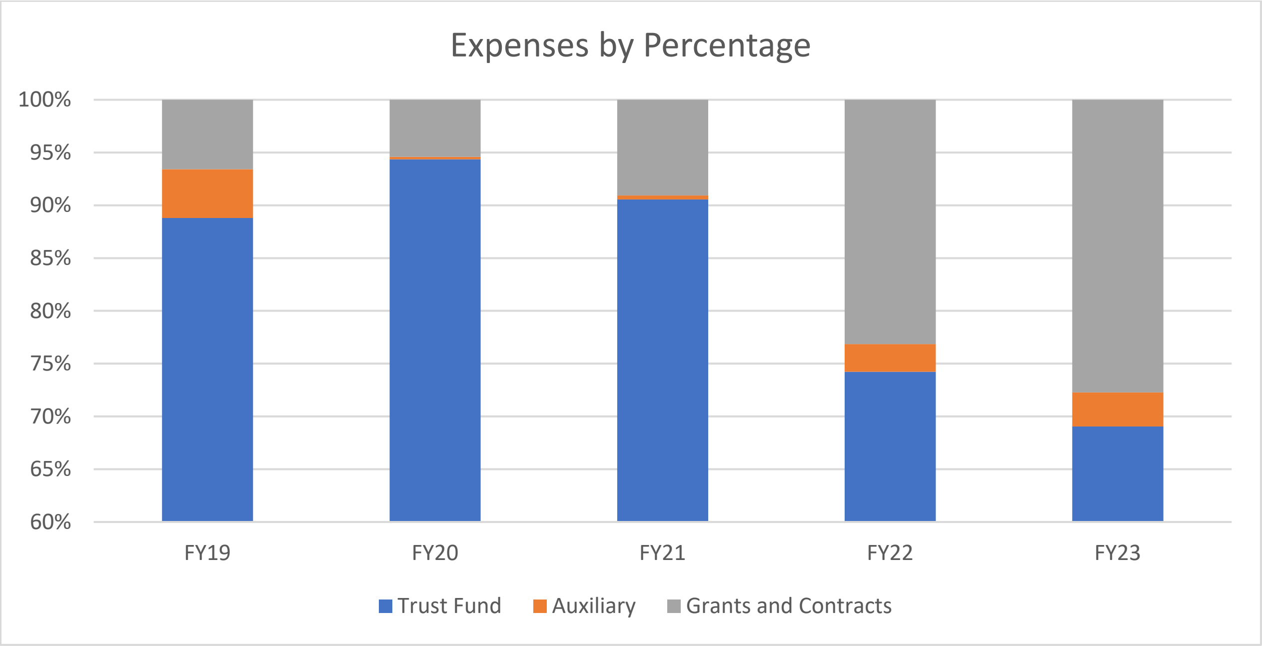
FIPR institution-wide expenses, listed in “typical” expense categories.

	FY19	FY20	FY21	FY22	FY23
Salaries	$1,014,884.84	$ 845,902.87	$ 804,142.42	$ 740,203.93	$ 741,775.92
Benefit	$ 277,306.26	$ 345,710.38	$ 293,034.45	$ 291,814.57	$ 325,123.85
Utilities	$ 37,348.82	$ 33,127.39	$ 41,904.56	$ 38,940.27	$ 2,725.16
Repair and Maintenance	$ 53,682.86	$ 93,009.39	$ 130,507.70	$ 36,107.78	$ 225,114.04
Employee Education	$ 1,422.00	$ 1,246.00	$ 2,418.76	$ 5,938.79	$ (3,464.00)
Contractual Services	$ 527,264.29	$ 350,764.74	$ 400,095.90	$ 343,569.02	$ 266,426.18
Materials & Supplies	$ 118,196.96	$ 47,442.08	$ 73,015.87	$ 54,510.76	$ 56,232.09
Other	$ 181,352.77	$ 412,254.09	$ 140,690.33	$ 90,269.03	$ 72,014.09



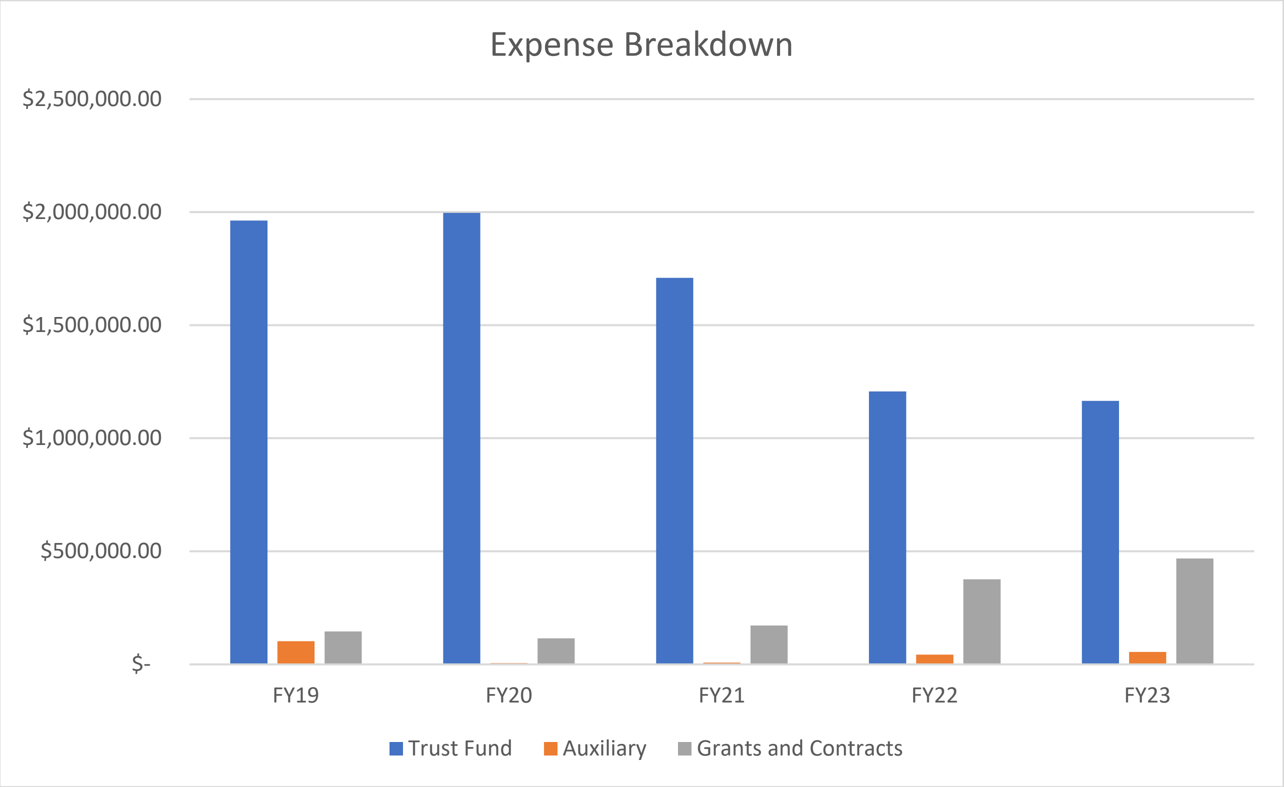
FIPR Institute expense percentages

	FY19	FY20	FY21	FY22	FY23
Trust Fund	89%	94%	91%	74%	69%
Auxiliary	5%	0%	0%	3%	3%
Grants and Contracts	7%	5%	9%	23%	28%



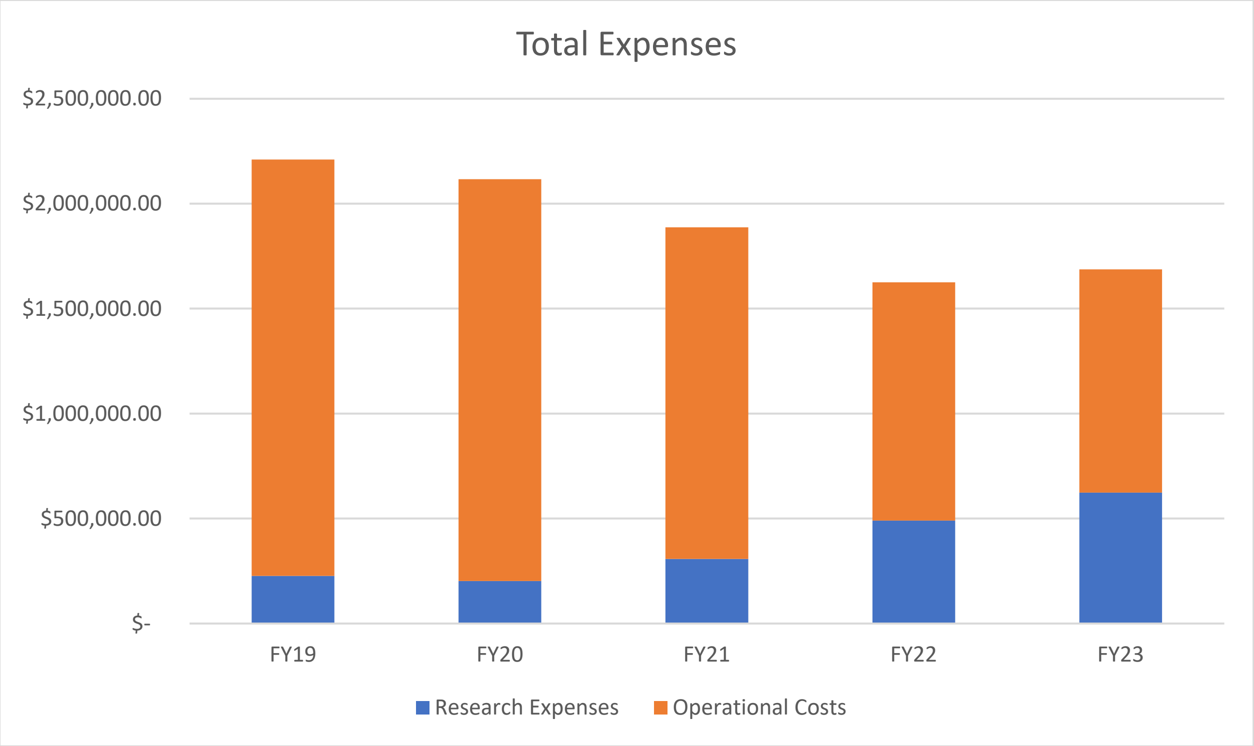
FIPR Institute expense break-down.

	FY19	FY20	FY21	FY22	FY23
Trust Fund	$ 1,962,502.42	$ 1,996,914.18	$ 1,709,131.73	$ 1,206,652.00	$ 1,164,881.41
Auxiliary	$ 102,168.32	$ 4,743.63	$ 6,938.52	$ 42,618.14	$ 54,458.76
Grants and Contracts	$ 145,202.73	$ 114,652.08	$ 171,140.92	$ 376,100.91	$ 467,767.32
Total	$ 2,209,873.47	$ 2,116,309.89	$ 1,887,211.17	$ 1,625,371.05	$ 1,687,107.49



FIPR Institute research expenses versus total expenses.

	FY19	FY20	FY21	FY22	FY23
Research Expenses	$ 226,563.13	$ 202,401.30	$ 307,364.28	$ 490,623.25	$ 623,399.07
Operational Costs	$1,983,310.34	$1,913,908.59	$1,579,846.89	$1,134,747.80	$1,063,708.42
Total Expenses	$2,209,873.47	$2,116,309.89	$1,887,211.17	$1,625,371.05	$1,687,107.49



FIPR Institute ending balances

	FY19	FY20	FY21	FY22	FY23
Trust Fund	$ 6,453,304.34	$ 6,108,067.92	$ 5,990,216.00	$6,112,593.33	$6,140,872.45
Auxiliary	$ 811,623.16	$ 753,014.53	$ 827,424.38	$ 836,852.69	$ 810,209.32