Annual Project Report (2024-2025)

Project: Investigating methods to improve efficiency of resource recovery during thermal treatment of phosphate acid sludge

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Abstract:

This project investigates innovative strategies to enhance the efficiency of resource recovery during thermal treatment of phosphate acid sludge, focusing on the interplay between speciation, composition, and recoverability of phosphorus and REEs. The first stage involved a **comprehensive literature review** of phosphorus mining and waste management practices, emphasizing major global producers such as China, the United States, Morocco, Russia, and Tunisia. Data from the Florida Industrial and Phosphate Research Institute (FIPR) highlighted the underexplored potential of acid sludge and phosphogypsum among 54 documented waste streams, with only a fraction of studies targeting recovery strategies. This gap underscores the urgent need for systematic evaluation of waste valorization pathways. Second stage includes experimental work progressed through **sequential extraction** tests, beginning with phosphorus as a model element. Results demonstrated that a significant fraction of phosphorus in acid sludge is readily extractable, confirming the feasibility of recovery under mild conditions. Parallel sequential extraction of REEs revealed concentration profiles across different operational steps, with recovery rates varying according to mineral phase associations. These results illustrate the heterogeneous binding environments of REEs, informing process optimization for selective leaching. The understanding of REE speciation was from a **complementary X-ray diffraction (XRD) analysis** to monitor mineralogical changes during stepwise extraction and treatment. This characterization provided insights into the transformation of crystalline phases and their influence on the availability of phosphorus and REEs. Together, these findings strengthen mechanistic understanding of how acid sludge mineralogy governs recovery efficiency. A critical advancement was achieved through **hydrothermal treatment trials**, where preliminary results indicated promising REE recovery. This pathway, combined with the use of cost-effective adsorbents, offers dual benefits: (i) lowering the conductivity and contaminant levels of lime-treated process waters, and (ii) concentrating valuable resources for downstream recovery. Such integrated approaches align with circular economy principles, simultaneously mitigating waste burdens and generating new value streams.

Overall, this project demonstrates significant progress toward the dual goals of waste minimization and resource recovery in phosphorus mining industries. By integrating literature insights, extraction experiments, mineralogical analysis, and hydrothermal recovery techniques, it lays the groundwork for scalable processes that enhance sustainability. The outcomes not only contribute to improved phosphorus circularity but

also open pathways for recovering critical materials such as REEs, positioning this research at the nexus of environmental stewardship and resource security.

1. Background:

Phosphorus, primarily as soil phosphate minerals, is vital for living organisms' biochemical energy processes. It is mined using sulfuric acid to produce phosphoric acid, crucial for fertilizer production and widespread agricultural applications. The U.S. phosphorus industry, notably in Florida, is geologically positioned for accessible, concentrated deposits. Phosphate has significant economic importance in Florida, yet its environmental impact has not been comprehensively estimated and addressed [1]. During mining processes, different waste streams are produced (Table 1). There are four types of waste products that are distinguishable and potentially be further reused for useful elements recovery, such as elemental P and rare earth element (REE). Acid sludge is generated during the production of phosphoric acid, it contains high REE and phosphate (PO_4^{3-}) because the naturally high amount of REE in phosphate ores. Waste clay is the by-product during the washing and refining of phosphate rock [2]. Phosphogypsum, which is usually considered as the dominant waste product (> 20 million tons /year), is the by-product of the acid extraction process. Flotation tail is generated during the flotation process which is used to separate phosphate minerals from non-phosphate material. Although acid sludge and phosphogypsum are both by-products of the mining process, acid sludge is produced during the purification of phosphoric acid, and its composition is complicated with a vast variety of substances such as unreacted acid, heavy metals, and other impurities. On the other hand, the main composition of phosphogypsum is $CaSO_4$ (usually with dihydrate).

Table 1. Summary of recovery efficiency of REE in different waste products of mining process (adapted from FIPR boarding meeting).

Waste product	Million tons/yr	Sum of REE, ppm	Recoverable REE, tons/yr
Acid sludge	~0.5	2654	1100
Waste clay	> 20	290	5800
Phosphogypsum	> 20	170	3400
Flotation tail	~ 3.9	200	780

Compared with other waste products, acid sludge contains a significant amount of REE and PO_4^{3-}, which could be a promising source for resource recovery. In addition, the radioactivity level in acid sludge is generally considered to be lower than that of phosphogypsum, where the radionuclides are more concentrated due to the nature of the chemical reactions involved. Currently, various methods to recover REE from acid sludge and elemental phosphorus have been proposed, such as sequential extraction [3] , thermal treatment, plasma treatment [4]. Thermal treatment is considered in the

proposed work because of its high extraction efficiency and its complete destruction of complicated matrix [5]. However, its environmental impact and its economic benefits should be further discussed to have a comprehensive understanding of its usability in resource recovery and reclamation of mining industry.

2. Objectives

Our overall objectives are 1) conduct a comprehensive literature review on phosphorus mining wastes, with a focus on acid sludge and phosphogypsum, to identify knowledge gaps and recovery opportunities 2) quantify recoverability of phosphorus and rare earth elements (REEs) from acid sludge through sequential extraction techniques, establishing recovery efficiencies and binding environments 3) characterize mineralogical transformations during stepwise treatment using X-ray diffraction (XRD), linking phase changes to resource availability 4) evaluate hydrothermal treatment as a recovery pathway, testing its ability to mobilize REEs and phosphorus while reducing contaminant load 5) develop cost-effective strategies for processing water treatment, applying adsorbents to lower conductivity and remove contaminants from lime-neutralized wastewater 6) Integrate findings with standardized leaching assessment protocols (e.g., EPA Method 1313 LEAF framework) to evaluate environmental risks and guide sustainable waste valorization. And finally, 7) strengthen cross-project synergies, connecting phosphate mining waste research with parallel work to establish a unified framework for zero-waste resource recovery. *Objectives 4 to objectives 7 are on-going efforts in the second year of current project.*

3. Methodology:

For Objective 1. Literature Review on Phosphorus Mining Wastes

A comprehensive literature review was conducted to assess the current state of knowledge on solid wastes generated from phosphorus fertilizer production, particularly acid sludge and phosphogypsum. Databases including Web of Science, Scopus, and Compendex, along with technical reports from the Florida Industrial and Phosphate Research Institute (FIPR), were systematically searched using keywords such as “phosphogypsum,” “acid sludge,” “phosphoric acid production,” and “rare earth recovery.” Studies were screened for inclusion if they provided explicit waste characterization and reported recovery or recycling outcomes. Each selected study was coded by waste type, treatment strategy, and extraction efficiency. Statistical analysis of reported data allowed identification of research gaps, including the limited attention given to acid sludge compared with phosphogypsum.

For Objective 2. Sequential Extraction of Phosphorus and Rare Earth Elements

Sequential extraction experiments were designed following protocols adapted from Tessier-type fractionation and recent environmental geochemistry studies. Acid sludge samples were subjected to a five-step extraction scheme to operationally separate: (i) exchangeable, (ii) carbonate-bound, (iii) Fe/Mn oxide-bound, (iv) organic/sulfide-bound,

and (v) residual fractions. Each step involved agitation with the prescribed extractant at controlled solid-to-liquid ratios (1:20 w/v) under ambient laboratory conditions. Supernatants were separated by centrifugation and analyzed by ICP-OES and ICP-MS to quantify phosphorus and rare earth elements (REEs). Mass balances were verified against total digestion values, and recovery rates (%) were calculated for each element across fractions.

For Objective 3. XRD Characterization of Stepwise Mineral Speciation

To evaluate mineralogical transformations during sequential extraction, solid residues collected after each fractionation step were oven-dried at ≤40 °C to avoid structural alteration. Samples were finely ground and analyzed using powder X-ray diffraction (XRD) with Cu Kα radiation across a 5–70° 2θ range. Phase identification was performed using standard databases, and semi-quantitative analysis was conducted through Rietveld refinement. Changes in crystalline phases, such as calcium sulfate, phosphate minerals, and REE-bearing phases, were tracked stepwise. These results were compared with sequential extraction data to establish correlations between mineral phase stability and element recoverability.

For Objective 4. Hydrothermal Treatment for Resource Recovery

For hydrothermal recovery trials, phosphogypsum (PG) and acid sludge (AS) were used as feedstocks. Initially, 2 g of PG or 4 g of AS were suspended in 20 mL (PG) or 40 mL (AS) of deionized water, respectively, and shaken for 1 h to obtain a homogeneous slurry. Following equilibration, a 1 g aliquot of the solid fraction was separated and subjected to acid leaching tests. The solids were contacted with 10 mL of HCl solutions at graded concentrations (0.1, 0.2, 0.5, 0.7, and 1.0 M), with shaking maintained for 1 h to evaluate the influence of acid strength on solubilization of phosphorus and rare earth elements (REEs). Subsequently, the solid–liquid mixtures were transferred to Teflon-lined stainless-steel hydrothermal reactors and placed in a programmable furnace. Hydrothermal reactions were conducted at 150 °C for 3 h under autogenous pressure conditions. After cooling, samples were centrifuged to separate the liquid and solid fractions. The supernatants were collected for elemental analysis of phosphorus and REEs by ICP-OES/MS, while the solid residues were retained for mineralogical characterization. This stepwise approach allowed the integration of pre-leaching, hydrothermal mobilization, and post-treatment characterization, thereby providing systematic insights into recovery efficiencies under variable acid strengths and hydrothermal conditions. Solid residues were characterized by XRD to identify mineralogical transformations induced by hydrothermal conditions. Preliminary results demonstrated promising recovery of REEs and provided insights into treatment conditions that maximize resource yield.

4. Results:

4.1 Literature review:

From over 100 collected papers, the literature review highlights the predominance of phosphogypsum as the most studied solid waste stream in the phosphate fertilizer industry, representing 57.1% of reviewed studies. In contrast, other byproducts such as clay (2%), tailings (10.2%), concentrates (4.1%), and acid sludge (4.1%) received considerably less attention, despite their potential resource value. Collectively, "other" wastes accounted for 22.5% of reviewed efforts. This distribution underscores ***a strong research bias toward phosphogypsum management***, while more challenging streams like acid sludge remain understudied (**Figure 1**).

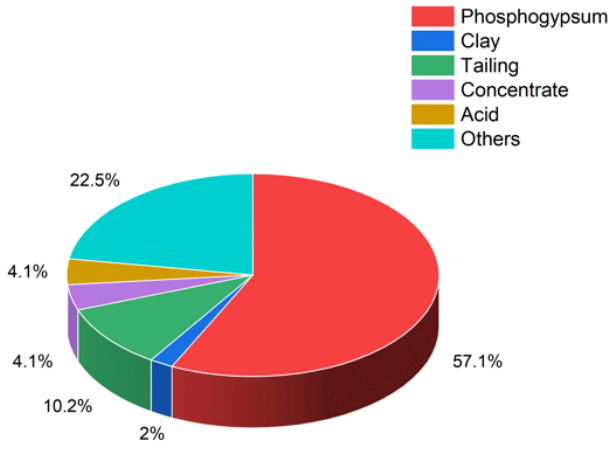


Figure 1. Distribution o[illegible]rature. Phosphogypsum dominates research attention (57.1%), while other streams such as clay, tailings, concentrates, and acid sludge remain underexplored.

Global analysis of production data from the Florida Industrial and Phosphate Research Institute (FIPR) indicates that major phosphoric acid producers include China (9530 × 10^3 tons P_2O_5), USA (7877 × 10^3 tons P_2O_5), Morocco (2770 × 10^3 tons P_2O_5), Russia (2322 × 10^3 tons P_2O_5), and Tunisia (1430 × 10^3 tons P_2O_5). These countries generate the largest quantities of secondary wastes, implying that successful valorization strategies in these regions could have significant global impact (**Figure 2**).

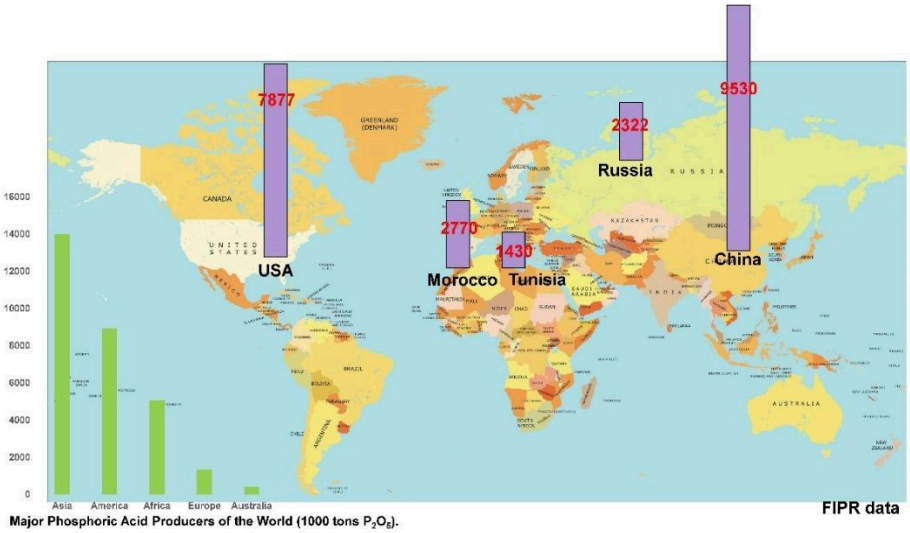


Figure 2. Global production of phosphoric acid by country (FIPR data) – China, USA, Morocco, Russia, and Tunisia represent the largest producers and therefore the largest generators of secondary wastes.

Analysis of recycling focus within the literature shows that the majority of studies targeted rare earth element (REE) recovery (~80%), followed by elemental extractions (~20%), with phosphorus recovery representing only a negligible share. When considering process efficiency, studies reported variable extraction efficiencies depending on both waste type and recovery strategy. Acid sludge treatments showed wide variability, while ion exchange methods produced higher and more consistent recovery efficiencies compared to thermal treatments (**Figure 3**).

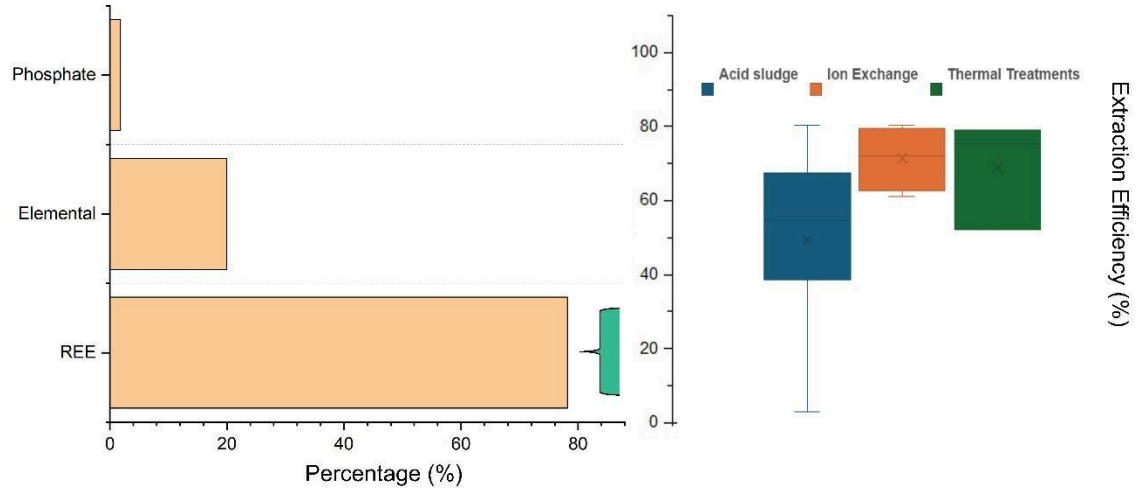


Figure 3. Recycling focus and reported extraction efficiencies from the literature, REE recovery dominates the literature (~80%), while phosphorus recovery is rarely targeted;

efficiency varies by method, with ion exchange (n = 9) generally outperforming thermal treatments (n = 3), acid treatment (n = 30) with the most various efficiency.

Together, these results reveal two major gaps: (i) a disproportionate focus on phosphogypsum compared with other waste streams such as acid sludge, and (ii) limited attention to phosphorus recovery relative to REEs, despite phosphorus being the primary nutrient product. These gaps highlight the need for systematic evaluation of acid sludge valorization through both sequential extraction and hydrothermal recovery, as targeted in this project.

4.2 Sequential extraction and speciation understanding of REE and P in different solid wastes.

Sequential extraction provided insights into the binding environments and recovery potential of rare earth elements (REEs), phosphorus (P), and associated radioactive elements such as uranium (U) in multiple phosphate waste streams, including acid sludge, phosphogypsum, flotation tailings, concentrates, and waste clay.

Rare Earth Elements (REEs)

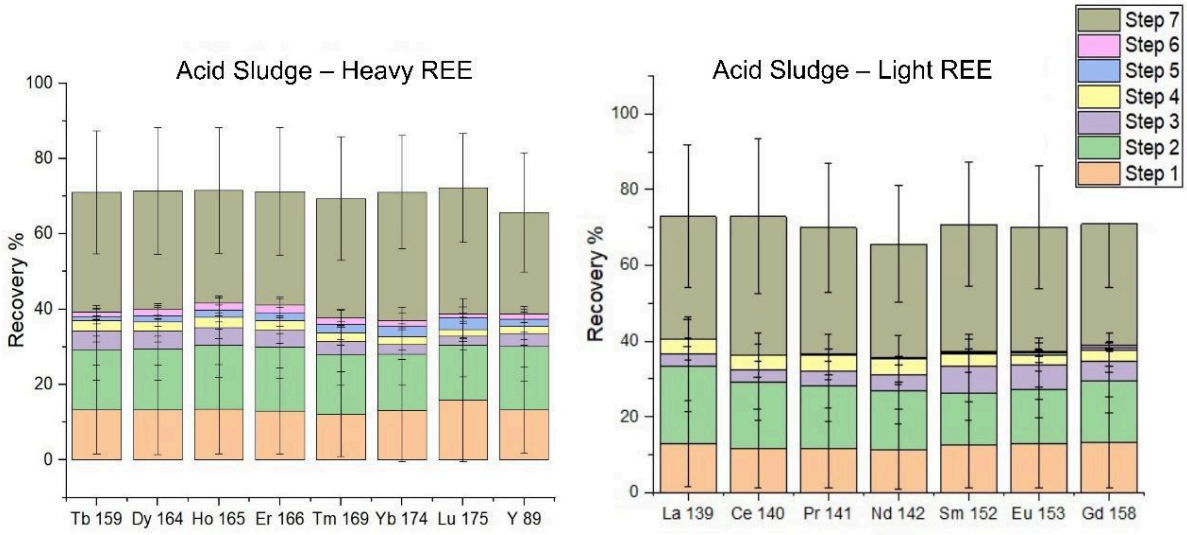


Figure 4. Recovery of heavy and light REEs from acid sludge during sequential extraction. Stepwise recovery profiles reveal high overall extractability (>60%) across both light and heavy REEs.

Acid sludge exhibited the highest REE concentrations, with 1091 ppm light REEs and 458 ppm heavy REEs. Recovery was distributed across multiple extraction steps, with the majority associated with moderately extractable fractions. For heavy REEs (e.g., Dy, Ho, Er, Yb), recoveries typically exceeded 60–70%, while light REEs (e.g., La, Ce, Nd, Sm) followed a similar trend, indicating their association with relatively labile mineral phases (**Figure 4**). Phosphogypsum contained significantly lower REE concentrations (108 ppm light REEs; 40 ppm heavy REEs), and recoveries were lower and less evenly

distributed across extraction steps, with most REEs sequestered in more resistant fractions (**Figure 5**).

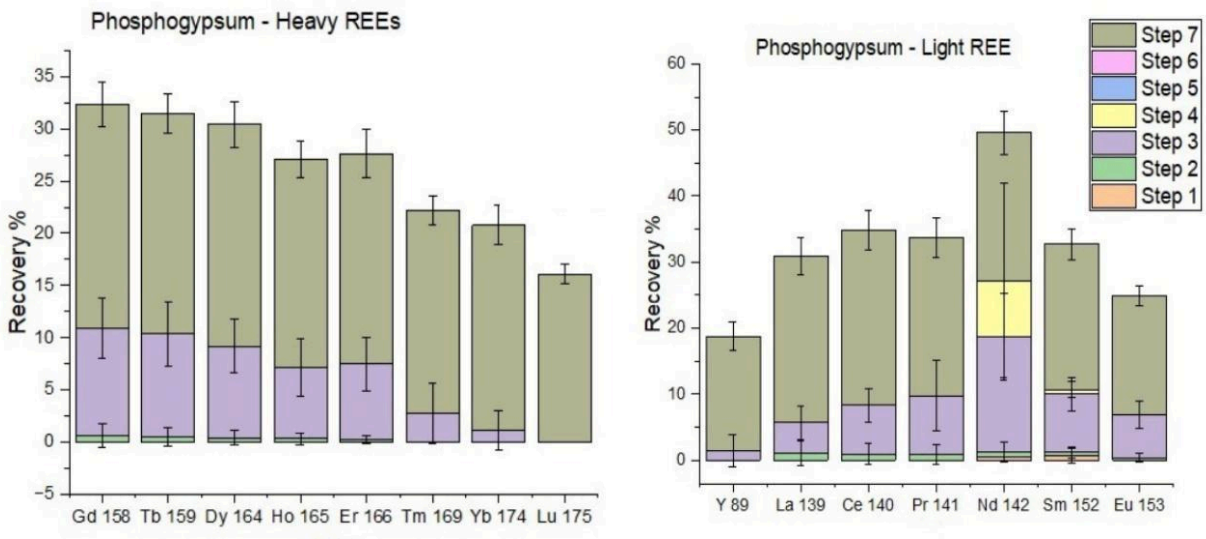


Figure 5. Recovery of heavy and light REEs from phosphogypsum during sequential extraction.

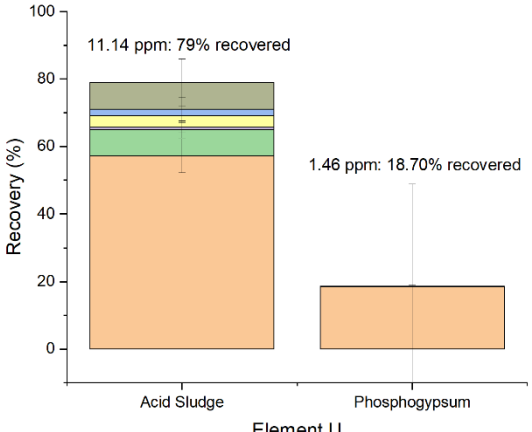
Comparative analysis confirmed that acid sludge is the richest and most recoverable REE source among tested waste streams, followed by waste clay and concentrate, with flotation tailings being negligible (**Table 2**).

Table 2. Concentrations of light REEs, heavy REEs, Th, and U in different phosphate wastes. Acid sludge is enriched in both REEs and U, while waste clay shows notable U enrichment.

	Light REE (ppm)	Heavy REE (ppm)	Th 232 (ppm)	U 238 (ppm)
Flotation Tail	0.78	0.01	0.00	0.00
Concentrate	176.82	90.21	3.47	52.14
Phosphogypsum	108.00	40.18	0.20	11.49
Acid Sludge	1091.07	457.89	7.14	85.77
Waste Clay	219.72	99.72	8.83	148.12

Uranium (U)

Uranium was also detected, with acid sludge containing 85.8 ppm U and waste clay containing 148 ppm U (**Figure 6**). Recovery tests revealed high mobilization potential for U from



acid sludge (79%), in contrast to low recovery from phosphogypsum (18.7%). While REEs represent valuable resources, uranium poses an environmental risk factor requiring strict management during valorization efforts.

Phosphorus (P)

Figure 6. Uranium recovery from acid sludge and phosphogypsum.

Phosphorus content varied widely across waste streams (**Figure 7**). Acid sludge contained the highest concentration (104,600 ppm; 104.6% by mass equivalence), followed by concentrate (82,285 ppm), waste clay (45,241 ppm), and phosphogypsum (7,904 ppm). Recovery efficiencies exceeded 100% for some wastes (e.g., flotation tailing at 654%, phosphogypsum at 135%), likely due to measurement variability and secondary phase dissolution during extraction. Acid sludge demonstrated both high concentration and efficient recovery, reinforcing its potential as a dual source of P and REEs.

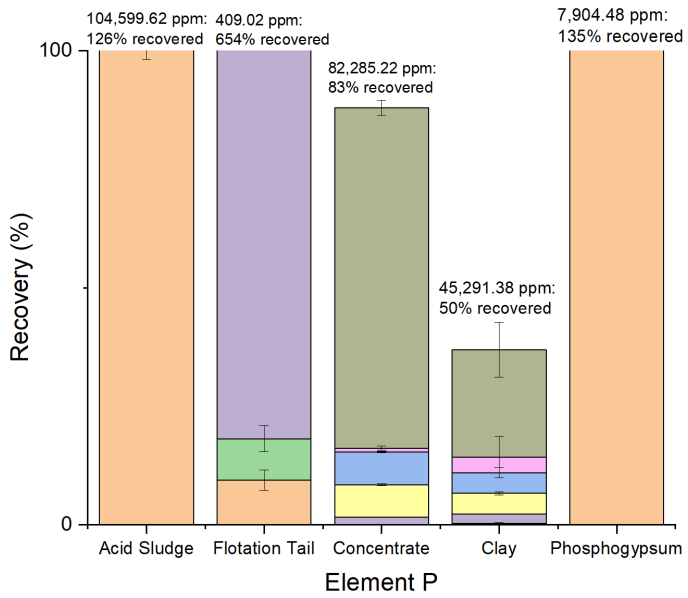


Figure 7. Phosphorus concentrations and recovery efficiencies in different phosphate wastes.

Table 3. Phosphorus content in different phosphate wastes. Acid sludge contains the highest P concentrations, followed by concentrate and waste clay.

	P (ppm)	P (%)
Flotation Tail	409.02	0.41
Concentrate	82285.22	82.29
Phosphogypsum	7904.48	7.90
Acid Sludge	104599.62	104.60
Waste Clay	45241.38	45.24

Insoluble Fraction

Insoluble fractions (residues not extracted) varied by waste type, ranging from 0.54% in acid sludge to 98.5% in flotation tailings (**Table 3**). This indicates that acid sludge is highly reactive and extractable, whereas flotation tailings are chemically stable and unlikely to yield significant resources under the tested conditions.

Table 4. Insoluble fractions of phosphate waste. Acid sludge is highly soluble (<1%), while flotation tailings remain largely insoluble (>98%).

Solid Sample	Insoluble %
Flotation Tail	98.49
Concentrate	39.65
Phosphogypsum	14.83
Acid Sludge	0.54
Waste Clay	34.41

Mineralogical Characterization

As an on-going effort for the second-year task, X-ray diffraction (XRD) analysis further confirmed the presence of distinct crystalline phases, with acid sludge showing sharp diffraction peaks consistent with reactive mineral phases. These results support sequential extraction findings that acid sludge is dominated by labile and moderately bound species, favoring recovery of both REEs and P.

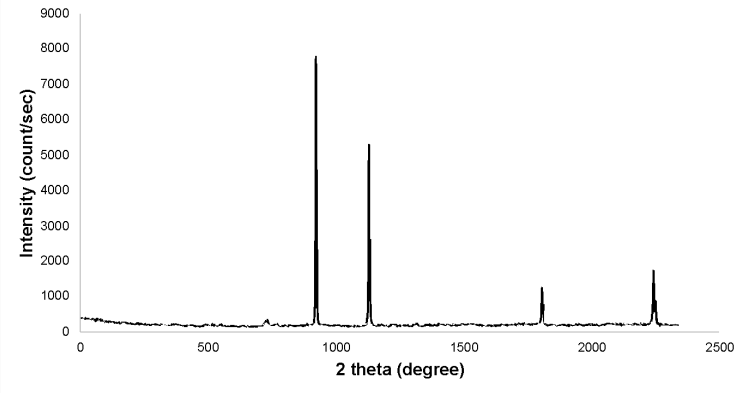


Figure 8. Representative XRD pattern of phosphate waste. Distinct crystalline peaks confirm mineral phases contributing to observed extraction behaviors.

4.3 REE extraction using hydrothermal treatment of solid mining waste

Hydrothermal treatment at 150 °C for 3 h using NaOH solutions of varying concentration (0.1–1.0 M) was applied to phosphogypsum (PG) and acid sludge (AS) to evaluate rare earth element (REE) recovery efficiency (**Figure 9**). For PG, both light and heavy REEs showed a strong dependence on NaOH concentration. Extraction efficiencies generally increased between 0.1 and 0.5 M NaOH, often reaching 40–60% recovery for elements such as Gd, Dy, and La. At higher concentrations (0.7–1.0 M), efficiency declined, likely due to the formation of insoluble hydroxide or carbonate precipitates that reincorporated REEs into solid phases. For AS, REE recovery was more stable across NaOH concentrations, with extraction efficiencies of 35–55% for both light and heavy REEs. The absence of a sharp concentration peak suggests that REEs in AS are present in more labile mineral phases (e.g., adsorbed or amorphous phases) that respond consistently to alkaline hydrothermal conditions. Importantly, while the recovery percentages of PG and AS appear similar, absolute REE concentrations in AS are significantly higher, making AS a more valuable feedstock overall.

The observed concentration-dependent recovery patterns highlight the dual role of NaOH during hydrothermal treatment. At low to moderate NaOH concentrations (0.2–0.5 M), hydroxide ions effectively disrupt mineral lattices (e.g., $CaSO_4$ or phosphate phases), releasing REEs into solution. At higher NaOH concentrations (> 0.7 M), supersaturation favors secondary precipitation (e.g., $REE(OH)_3$ or mixed hydroxides), which decreases apparent recovery efficiency. The relatively stable recovery profile in AS suggests that REEs are associated with less crystalline, more reactive matrices compared with the crystalline gypsum-dominated PG. These findings emphasize the importance of optimizing alkaline concentration during hydrothermal treatment. Moderate NaOH levels appear to balance mineral dissolution and prevent secondary precipitation, thereby maximizing recovery efficiency.

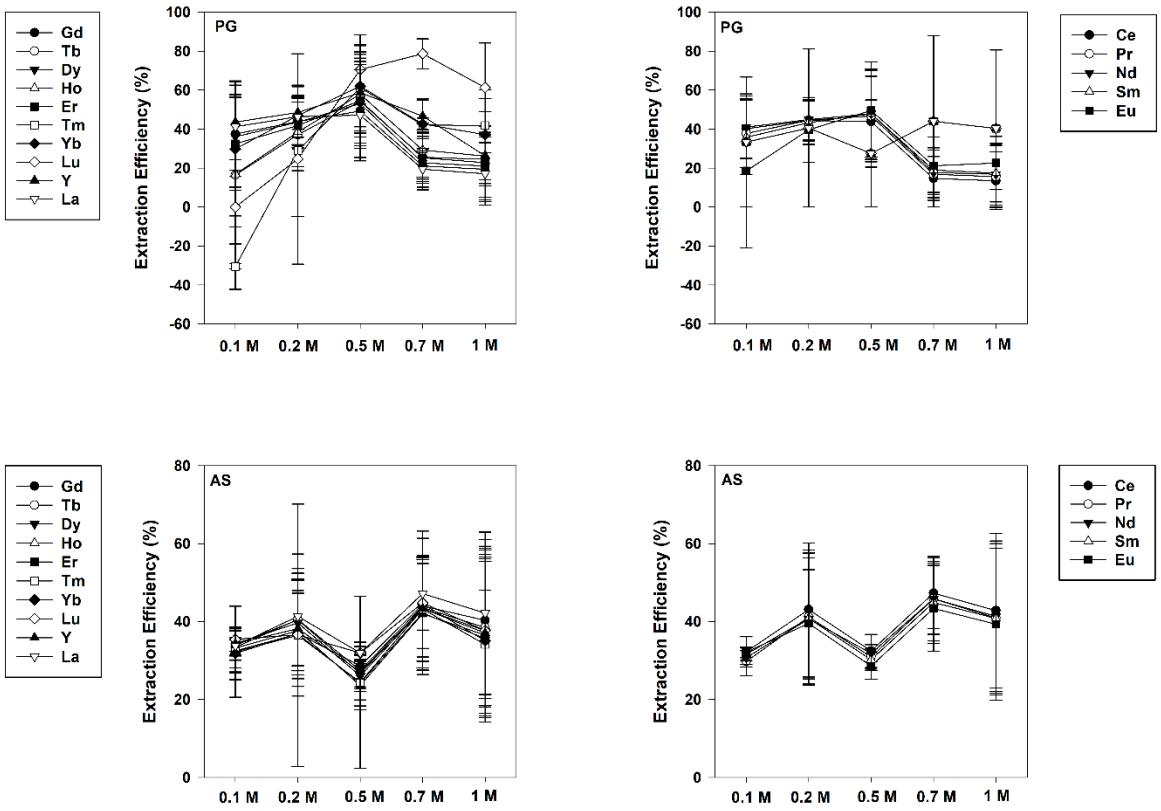


Figure 9. Hydrothermal extraction efficiency (%) of light and heavy REEs from phosphogypsum (PG) and acid sludge (AS) under varying NaOH concentrations (0.1–1.0 M, 150 °C, 3 h).

5. Future work and direction

Building on the sequential extraction and mineralogical analyses already conducted, the next phase of this project will focus on advanced X-ray diffraction (XRD) characterization to deepen understanding of mineralogical transformations during recovery processes. Detailed phase identification and quantification will allow stronger correlations between mineral structure, phosphorus availability, and rare earth element (REE) mobility, thereby refining strategies for selective extraction.

In parallel, future research will expand into **phosphorus mining wastewater treatment**, targeting the reduction of conductivity and emerging contaminants in lime-treated (neutralized) process waters. This will be achieved through the development and application of cost-effective adsorbent systems, building upon current expertise in biochar-based column studies and ongoing sponsored projects. Column-scale

experiments, informed by EPA Method 1413 (LEAF framework) and supported by analytical monitoring of TDS, DOM, and anionic surfactants, will provide a systematic evaluation of adsorbent performance under realistic operating conditions. These efforts will be synergistic with ongoing research on PFAS removal and destruction. Leveraging this expertise in adsorption, surface chemistry, and hydrothermal treatment, the project will extend to integrate phosphorus mining wastewater challenges with broader contaminant management strategies.

Ultimately, the future work is directed toward establishing a unified zero-waste resource recovery framework that simultaneously addresses resource recovery from mining waste (P and REEs) and contaminant mitigation (conductivity, DOM, PFAS, and other emerging pollutants). This dual focus will not only close material loops in phosphate mining operations but also advance scalable solutions for sustainable solid waste and wastewater management.

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