

U.S. Department of Energy, Office of Fossil Energy

DOE Award: DE-FE0026927

January 1, 2018 – December 31, 2019

Recovery of Rare Earth Elements (REEs) from Coal Mine Drainage, Phase 2

Project Summary Report

Principal Investigator:

Paul Ziemkiewicz, PhD

Director, West Virginia Water Research Institute

West Virginia University

pziemkie@mail.wvu.edu

304-293-6958

*Handwritten signature: P. Ziemkiewicz
27 Mar 2020*

Submitted by:

Paul Ziemkiewicz, PhD

Director, West Virginia Water Research Institute

Submission Date:

March 31, 2020

West Virginia University Research Corporation

DUNS Number: 191510239

886 Chestnut Ridge Road, PO Box 6845

Morgantown, WV 26506-6845

WVU Team Members

Virginia Polytechnic Institute and State University

Rockwell Automation

Acknowledgment: "This material is based upon work supported by the Department of Energy National Energy Technology Laboratory under Award Number DE-FE0026927."

Disclaimer: "This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof."

Contents

Executive Summary	3
Summary of Phase 1 Tasks and Results	3
Phase 1 of DE-FE-0026927 included three primary tasks:	3
Task 1	3
Task 2	3
Task 3	3
Summary of Phase 2 Tasks and Results	3
Description of the Project	4
Methods	4
Objectives/Results	4
Potential Impact: Benefits and Outcomes	5
Accomplishments	6
Task 1.0 Project Management and Planning	6
Task 2.0 Split Sampling	7
Task 3.0 Bench-Scale REE Extraction System	8
Subtask 3.1 Final System Design	8
Subtask 3.2 Instrumentation Package	10
Subtask 3.3 Equipment Procurement	16
Subtask 3.4 Sample Procurement / Feedstock Sourcing	18
Subtask 3.5 Environmental Health and Safety	19
Task 4.0 Initial System Testing Plans	20
Subtask 4.1 Operating Test Plan	20
Subtask 4.2 Sampling Plan	21
Subtask 4.3 Analytical Plan	21
Subtask 4.4 System Plans	22
Task 5.0 System Construction and Installation	23
Subtask 5.1 Construction	23
Subtask 5.2 Shakedown Tests	30
Subtask 5.3 Exploratory Testing	34
Task 6.0 Parametric Systems Testing	40
Task 7.0 Validation Testing	48
Task 8.0 System Design Optimization	55
Task 9.0 System Decommissioning	63
Task 10.0 Techno-Economic Analysis	63
Task 11.0 Resource/Reserve Characterization	68
Task 12.0 Environmental, Health, and Safety Assessment	72
Task 13.0 Commercialization Plan	74
Subtask 13.1 Technology Commercialization	74
Subtask 13.2 Resource Ownership and Control	76
Subtask 13.3 Intellectual Property and Other Legal Barriers	78
Task 14.0 Outreach and Communication	78
References	79
Products	83
Participants and Other Collaborating Organizations	83
Changes/Problems	83
Special Reporting Requirements	83

Budgetary Information	84
Milestone Status Report	85
Acknowledgements	85
Appendices	86
Appendix A: Resource and Reserve Report Documentation	86
Appendix B: Legal Ownership and Control Report	86

Executive Summary

This project is the second of a two-phase research program. The following summarizes the strategies and results of both phases.

Summary of Phase 1 Tasks and Results

Phase 1 of DE-FE-0026927 included three primary tasks:

1. Identify whether acid mine drainage could be an important feedstock for rare earth production.
2. Identify a scheme for producing a 2% purity REE concentrate.
3. Estimate the economics of producing commercial rare earth feedstock from acid mine drainage.

Task 1

Approximately 3,300 cubic feet of acid mine drainage (AMD) are produced by Appalachian coal mines every second. Responsible parties, including the coal industry and state agencies, are obliged to treat this effluent in accordance with the Federal Clean Water Act. In Phase 1, we found that acid forming coal spoils, tailings, and underground mines act as heap leach reactors, where the sulfuric acid produced through pyrite oxidation leaches metals, including rare earth elements (REE) from the surrounding shales and delivers them to AMD treatment plants; there they are captured while clean water is discharged via a permitted outlet. Conventional AMD treatment captures nearly 100% of REEs and concentrates them by a factor of 2,000x. On average ($n=74$), AMD precipitates have a total REE (TREE) concentration of 635 ppm (g/t) on an elemental, dry weight basis with a 95% confidence interval of 549 to 724 and a population range of 103 to 1,628 g/t. Our mean value exceeds many REE ores that are currently in offshore production. Actinides are present in very low concentrations: Th+U averaged 14.7 g/t on a dry weight basis. Post-processing waste would consist of acidified AMD precipitates which would simply be fed into an existing AMD treatment plant for neutralization and disposal via the existing, permitted facility. Ongoing AMD production in the Appalachian Coal Basin generates about 800 tons of TREE per year. The ratio of heavy rare earth elements (HREEs) to TREE is, per USDOE supplied definitions, 47%.

Task 2

Batch laboratory studies were used to obtain metallurgical data and cost factors for generating a 2% TREE product from AMD precipitates. Laboratory experiments indicated nearly 100% extraction of REE from AMD solids under acid leaching and re-precipitation as pH was adjusted upward. Solvent extraction was then used to separate TREE from the $\text{Fe}(\text{OH})_3$ matrix. After solvent extraction, the ratio of the REE to major ions has achieved more than 6% constantly in multiple attempts, which is far more than the Phase 1 target, 2%. To further improve extraction selectivity and yield, various types and concentration of acids have been explored, and pH adjustment is being refined to identify points where REEs more clearly separate from $\text{Fe}(\text{OH})_3$.

Task 3

A feasibility study was conducted on a greenfield REE recovery plant treating AMD solids. The results indicate that under current REE prices, typical AMD solids have a REE basket price of \$388/kg and an in-situ value of \$250/ton. The feasibility study further indicated that an \$80 million investment is needed to construct a centralized 2,100-ton-per-day processing plant. This plant has a payback period of 2.5 years and a 27% rate of return. Small, modular plants may also serve as an attractive alternative.

Summary of Phase 2 Tasks and Results

The primary project objective of this phase was to demonstrate the technical and economic feasibility of extracting a 2% purity TREE product from AMD precipitates. The secondary objective included identification of process improvements and incorporation into a final design. Sub-objectives included:

1. Develop a testing plan and a chemical hygiene plan for mini-pilot plant operation in the WVU High Bay research facility.
2. Design, construct, and operate our REE recovery system while optimizing system design parameters.
3. Assess capital and operating costs based on the following criteria:
 - a. System REE recovery,
 - b. Concentrate purity,
 - c. Reagent recycle rates and losses, and
 - d. Overall consumable costs.
4. Prepare a techno-economic analysis (TEA) based on the above criteria.
5. Prepare a Technology Development and Commercialization Assessment based on the results of the proposed Phase 2 testing and TEA.

Description of the Project

Phase 1 research identified a two-step refining train that will produce a 2% TREE product. It includes acid leaching of AMD precipitate feed followed by solvent extraction (SX). In Phase 2, a mini-pilot system was developed and installed that was capable of batch mode operation with sufficient storage capacity to feed an aqueous, enriched REE liquor to a mini-pilot SX plant operating in continuous mode at a feed rate capable of producing 3 g/hour 2% TREE. Important process variables included feed rate, extractant makeup, flowsheet configuration, and stripping conditions. Operating parameters were optimized through a feedback-capable SCADA system that was configured to the SX mini-pilot plant.

Methods

Three AMD precipitate sources were selected from the Phase 1 samples. They represent the regional range of compositions. They were dissolved in the acid leach tank under conditions identified in Phase 1. Enriched liquor was then fed into the SX unit. This configuration ensured that the final product exceeded the 2% purity criterion, including a heavy and light REE separation. Both aqueous and solid residues were sampled at each stage to assess recovery rates and separation efficiencies of REE from gangue metals: Fe, Al, and Mn. The acid leaching process was optimized to minimize residence time and maximize gangue metal separation. The SX process was optimized to maximize REE recovery and purity. It was also optimized to minimize extractant loss and reagent consumption. Results formed the basis for the TEA and the Technology Development and Commercialization plan.

Objectives/Results

Following is a summary of the objectives and ensuing results for Phase 2 of the research program:

1. Develop a testing plan and a chemical hygiene plan (CHP) for mini-pilot plant operation in the WVU High Bay research facility. A CHP was developed and approved by WVU's Office of Environmental Health and Safety.
2. Design, construct, and operate our REE recovery system while optimizing system design parameters. The Rare Earth Extraction Facility (REEF) was commissioned on July 18, 2018. It incorporates acid leaching, solvent extraction, and precipitation processes to form an integrated process train. It allowed the research team to develop continuous processes for extraction of high grade REE concentrates from solid AMD precipitates (AMDp) and pre-concentrates.
3. Assess capital and operating costs based on the following criteria:
 - a. System REE Recovery: Recoveries were generally in the range of 30-60% with HREEs consistently showing a significantly higher recovery than light rare earth elements (LREEs). In some cases, the recovery of HREEs approached 70% through solvent extraction.
 - b. Concentrate Purity: Product grades of >90% exceeded the 2% target per FOA DE-0001202.

- c. Reagent Recycle rates and losses: through both task-specific parametric testing as well as a continuous 104-hour validation test run, reagent consumption rates were carefully measured and tracked.
 - d. Overall consumable costs: the processing of raw sludge resulted in high consumable costs, particularly leaching acid and stripping acid. Together, these two items accounted for a majority of the overall consumable costs.
4. Prepare a techno-economic analysis (TEA) based on the above criteria.
- The techno-economic analysis showed that the overall economic viability is strongly influenced by the feed grade entering the acid leach tanks. A simple sensitivity analysis suggested that increasing the feed grade to approximately 1% produced an exceedingly favorable economic outcome. The upstream concentration process developed by the research team in a separate DOE-funded effort (DE-FE31524) offers a comprehensive solution to the issues of both dispersion of sources and feedstock grade. Most significantly, the upstream concentrator will increase the grade of the ALSX feed by rejecting iron and aluminum during the standard water treatment process. Increased feedstock grade will drastically reduce the acid requirement and increase the maximum haulage distance to a central processing facility (>200 miles). These factors will substantially reduce processing costs while simultaneously increasing the quantity of feedstock, meeting the economic thresholds. If widely implemented across the Appalachian region, the pre-concentration plants will ensure a consistent and reliable supply of feedstock for ALSX operations.
5. Prepare a Technology Development and Commercialization Assessment based on the results of the proposed Phase 2 testing.
- This task produced a scenario evaluation model (SEM) that integrates both database information on known AMDp reserves (identified under DE-FE26444) and the TEA model developed in the current project. The SEM includes a robust user interface and facilitates the assessment of various feed arrangements for a centralized ALSX processing unit. The SEM was designed to evaluate the three scenarios described in the SOPO, namely a large centralized ALSX facility receiving feed from all sites in a regional AMDp database (n = 143), a regional ALSX facility receiving feed from up to six sites, and a limiting case where the plant was only fed by a single site. It was concluded that a central processing facility serving pre-concentration units within a roughly 200-mile radius would produce high grade Mixed Rare Earth Oxides (MREO) at commercially attractive costs.

Potential Impact: Benefits and Outcomes

The project identified a new, domestic source of REE that will be easily extracted, operate on already permitted sites, and produce negligible actinides or other waste materials. AMD precipitates could be recovered immediately. Our technology largely consists of off-the-shelf components already used in hydrometallurgy so technology deployment time would be minimal. Production of at least 800 t TREE/year from the northern and central Appalachian coal basins is feasible. This is sufficient for current U.S. defense industry needs but only 5% of domestic demand. Nonetheless, it could support a \$300 MM/year domestic industry. AMD is treated at sites that already have access, a local workforce, infrastructure, and are under permit. Benefits would include national security, economic development in depressed Appalachian communities, and an additional revenue stream for the coal industry. Monetization of AMD treatment would incentivize recovery efforts to restore watersheds impaired by pre-law discharges.

Prior studies by the project team have shown that AMD is a promising feedstock for domestic Rare Earth Element and Critical Mineral (REE/CM) production. AMD is a pollutant generated by many coal and other types of mines and is treated in compliance with federal and state clean water regulations to adjust pH and remove metal ions of Fe, Al, and Mn. Specifically, these prior studies have included: (1) a

regional survey assessing the content, distribution, and form of REE/CM in AMD and the related treatment byproducts (DE-FE0026444); (2) the design, development, and testing of a bench-scale process to extract, purify, and concentrate REE/CM from AMD treatment byproducts (DE-FE0026927); and (3) the development and testing of a novel method to preconcentrate REE/CM from raw AMD (DE-FE0031524). These results are summarized in the project interim and final reports.

Altogether, these studies have clearly demonstrated that AMD is a viable domestic source of REE/CM. For example, results from DE-FE0026444 have shown that AMD discharges in the Northern and Central Appalachian basin have the potential to produce about 1,000 tons per year of REE/CM oxides. Moreover, recent results from DE-FE0026927 have shown that the team's unique extraction and concentration technology has the potential to produce high grade REE concentrates, consistently within 50% to 80% rare earth oxide (REO) purity. Equally important, the program has demonstrated a pathway to potentially incentivize the treatment of AMD. Current industry practices focus on compliance-based treatment that is designed to minimize cost. The prospect of new REE/CM revenue streams has the potential to change this paradigm and greatly improve the environmental outcomes for many coal mining districts while creating new jobs supporting a domestic supply chain for REE/CM.

Most of the testing and development to date has been conducted at the laboratory or small bench-scale. While this work is a necessary part of technology development, continued scale-up and system optimization is needed to commercialize the various technology components.

[Accomplishments](#)

[Task 1.0 Project Management and Planning](#)

[Approach](#)

This task shall include all work elements required to maintain and revise the Project Management Plan and to manage and report on activities in accordance with the plan. It shall also include the necessary activities to ensure coordination and planning of the project with the Department of Energy/National Energy Technology Laboratory (DOE/NETL) and other project participants. These shall include, but are not limited to, the submission and approval of required National Environmental Policy Act (NEPA) documentation.

[Overview](#)

Project management functions were preformed to ensure that the project team executed all tasks and subtasks to completion and maintained consistent communications while working towards project objectives. WVU managed and directed the project in accordance with a Project Management Plan to meet all technical, schedule, and budget objectives and requirements. WVU coordinated activities in order to effectively accomplish the work, ensuring that project plans, results, and decisions were appropriately documented, and that project reporting and briefing requirements were satisfied. Additionally, bi-weekly meetings were held throughout the course of the project to monitor researcher progress and allow for collaborative understanding.

[Results and Discussion](#)

In addition to the completed NEPA statement, the project was undertaken under a chemical hygiene plan as approved by WVU's Environmental Health and Safety Office. Following is a list of external reports and publications and presentations prepared by the project team.

[Task Completion Status](#)

100% complete.

Task 2.0 Split Sampling

Approach

The Recipient will provide NETL with a single sample that reflects the highest achieved REE concentration generated during conduct of project effort. The quantity of material to be provided to NETL shall be no less than 5 grams. Material Safety Data Sheets (MSDS) are required to accompany material supplied to NETL. NETL reserves the right for DOE/NETL employees or its agents to witness the sampling and splitting. Results of any analysis arranged by DOE/NETL will be documented in a Publicly Releasable Report accessible on the NETL website.

Overview

A split sample per the above specifications was shipped to NETL on February 12, 2020. The AMDp sample was from the WVDEP's Royal Scott AMD treatment plant. It was subjected to WVU's ALSX process for purification. Table 1 summarizes its chemical composition. Note the sample, on an oxide basis consisted of 93% Mixed Rare Earth Oxides (MREO). The grade of the split sample exceeded the project target of 2% MREO.

Table 1. Analytical results for the split sample supplied to NETL.

		Analysis Date	191217 DOE Split Sample ETD-50 solid 19'3180			
Lab ID						
Al	mg/kg	12/17/19	643.8			
Ca	mg/kg	12/17/19	<			
Co	mg/kg	12/17/19	<			
Fe	mg/kg	12/17/19	<			
Mg	mg/kg	12/17/19	<			
Mn	mg/kg	12/17/19	<			
Ni	mg/kg	12/17/19	<			
S	mg/kg	12/17/19	<			
Si	mg/kg	12/17/19	<			
Zn	mg/kg	12/17/19	<			
			643.8			
			metal		oxide	
Y	mg/kg	12/18/19	350,188.8	43%	0.875	400,437
La	mg/kg	12/18/19	3,465.5	0%	0.853	4,064
Ce	mg/kg	12/18/19	44,231.5	5%	0.814	54,333
Pr	mg/kg	12/18/19	8,728.4	1%	0.828	10,545
Nd	mg/kg	12/18/19	51,755.6	6%	0.857	60,367
Sm	mg/kg	12/18/19	55,814.8	7%	0.862	64,724
Eu	mg/kg	12/18/19	18,558.6	2%	0.864	21,489
Gd	mg/kg	12/18/19	115,561.5	14%	0.868	133,199
Tb	mg/kg	12/18/19	17,387.1	2%	0.850	20,450
Dy	mg/kg	12/18/19	79,847.2	10%	0.871	91,640
Ho	mg/kg	12/18/19	13,119.6	2%	0.873	15,029
Er	mg/kg	12/18/19	30,134.3	4%	0.875	34,458
Tm	mg/kg	12/18/19	3,410.8	0%	0.876	3,895
Yb	mg/kg	12/18/19	15,833.7	2%	0.878	18,030
Lu	mg/kg	12/18/19	1,971.3	0%	0.879	2,242
TREE			810,008.5	100%		934,903
HREE			77%			77%
Th	mg/kg	12/18/19	1.0			
U	mg/kg	12/18/19	0.2			

Results and Discussion

During the reporting period, two products assaying 86% and 87% Total Rare Earth Oxides (TREO) were produced from the ALSX system. The remaining products, after sampling, were retained as used to test various refining approaches.

Task Completion Status

100% complete.

Task 3.0 Bench-Scale REE Extraction System

Subtask 3.1 Final System Design

Approach

The Recipient will utilize the system design package submitted to DOE/NETL at the end of Phase 1 to complete the detailed engineering design of the bench-scale REE extraction system for its construction

in the WVU National Research Center for Coal and Energy (NRCCE) High Bay Research Facility. The Recipient will conduct a final design review to identify opportunities for process intensification and ensure the bench-scale system design will meet the specific Phase 2 objectives noted in Section A above. After the final design review, the Recipient will make any additional modifications to the system design after proposed modifications review with the DOE/NETL Project Officer.

The Recipient will also determine what changes are needed to the NRCCE High Bay to accommodate the bench-scale REE extraction system and identify and complete any construction permits needed.

The Recipient will provide the following documents to the DOE/NETL Project Officer for review and comment before starting procurement or construction activities: (1) final flowsheet and associated drawings; (2) final vendor selection for key equipment; (3) facilities selection and list of required modifications; (4) waste management plan suitable for flowsheet and facilities; and (5) final engineering/construction/vendor drawings.

Overview

A bench-scale REE extraction system was designed and approved for installation. Although equipment changes were made to the acid leaching and filtration portions of the system, the fundamental design system remained unchanged throughout the duration of the project. Also, changes were made to the High Bay area of the NRCCE to accommodate both the acid leaching and solvent extraction portions of the system.

Results and Discussion

After the Phase 1 design package was reviewed to ensure that the system specifications were adequate for the overall project objectives, equipment procurement began and, while minor modifications to vendor selection and equipment sizing were made, no major modifications were identified or implemented immediately. During the actual procurement, some minor modifications were made about vendor selection and equipment sizing. Also, numerous meetings with the WVU facilities management team took place to ensure the High Bay infrastructure would accommodate the ALSX system. Several changes to the facility were completed or initiated during the reporting period to provide an optimal working environment for the bench-scale plant, such as clearing out old equipment, designating a ventilation area, installing new electrical circuits, and installing a working sink.

The only major modification to the final system design was introduced during Q3 as described under Task 5 below. The initial pan filter was deemed inadequate to effectively separate pregnant leach solution (PLS) from residual solids. To overcome this issue, a two-stage filtration circuit including the pan filter and plate and frame filter press was evaluated as an effective alternative and subsequently implemented. A block flow diagram representing the Final system design is shown in Figure 1.

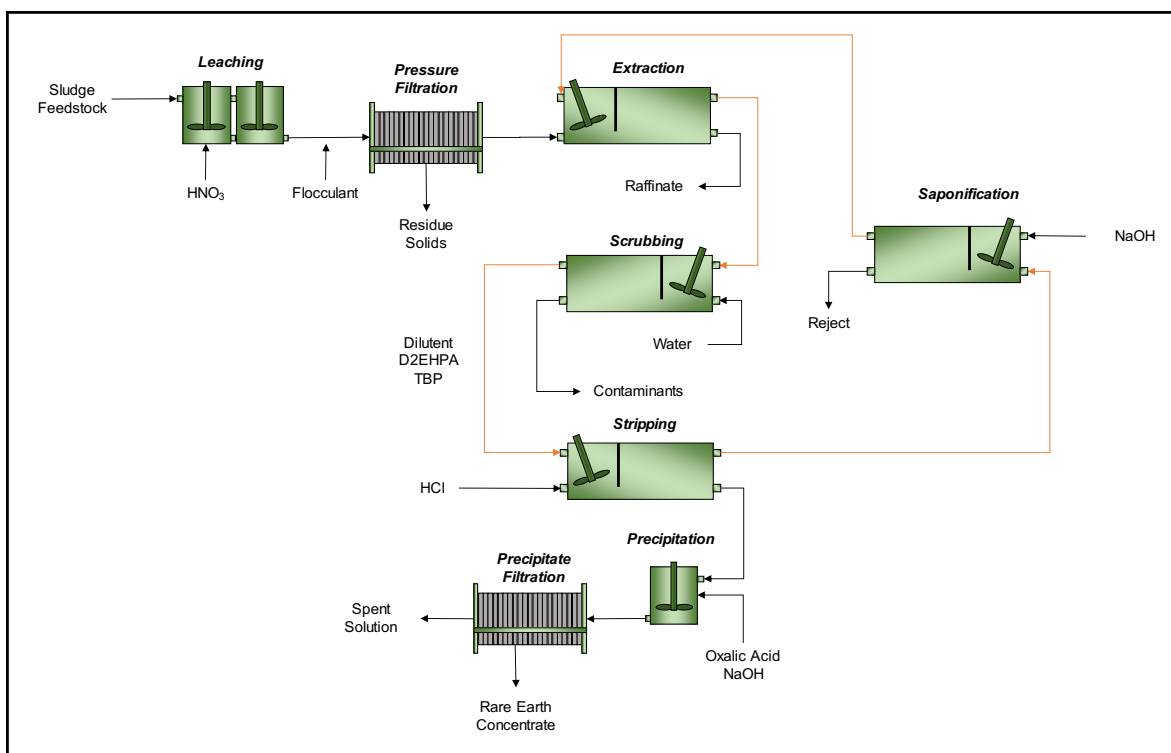


Figure 1. Final System Design.

Subtask 3.2 Instrumentation Package

Approach

After the process flowsheet is finalized, the Recipient will design an instrumentation and control package to be integrated into the SX bench-scale system. This package will provide real-time measurements of pump and mixer motor conditions, pH measurements, select ion concentrations, and other operating variables. These values will be logged in an archival data format and used for feedback loop control of the bench-scale REE extraction system.

Overview

In coordination with Rockwell Automation, instrumentation and control mechanisms were installed and tested in order to gather real-time measurements.

Results and Discussion

Rockwell Automation was selected as the sub-recipient to provide the system instrumentation package. After the initial meetings discussing project goals and instrumentation needs, Rockwell Automation staff implemented installation of the process controls.

During this time, an initial exploratory test was completed to determine whether the electrical current from the mixing unit (i.e., a surrogate for mixer torque) could be used as a proxy for monitoring the organic to aqueous (O:A) ratio in real time. Thus, amperage and, hence, mixer torque would be used for monitoring and possibly controlling the mixing O:A ratio in the individual mixing units.

Results from this experiment are shown in Figure 2. The data indicate that when the O:A ratio is approximately 1:1 the mixer will draw maximum current and generate maximum torque. We found that this information can be used to control the mixer O:A ratio (i.e., the phase ratio in the actual unit, including internal recycle); however, it will not be useful in controlling the advance ratio (i.e., the overall phase ratio set by the feed pumps). This mixing ratio control can be accomplished by installing a pump

between the mixer and settler to recycle the primary fluid back to the mixer as needed. This approach will be advantageous for two reasons. First, prior data has shown that a mixer O:A ratio of 1:1 produces an ideal chemical environment for efficient mass transfer. Second, this control will provide steady mixing conditions, whereas manual control may introduce variability and thus less reliable operation of the SX plant. As a result, from this test, miniature peristaltic pumps were evaluated for use in the recycle lines between the mixing and settling units.

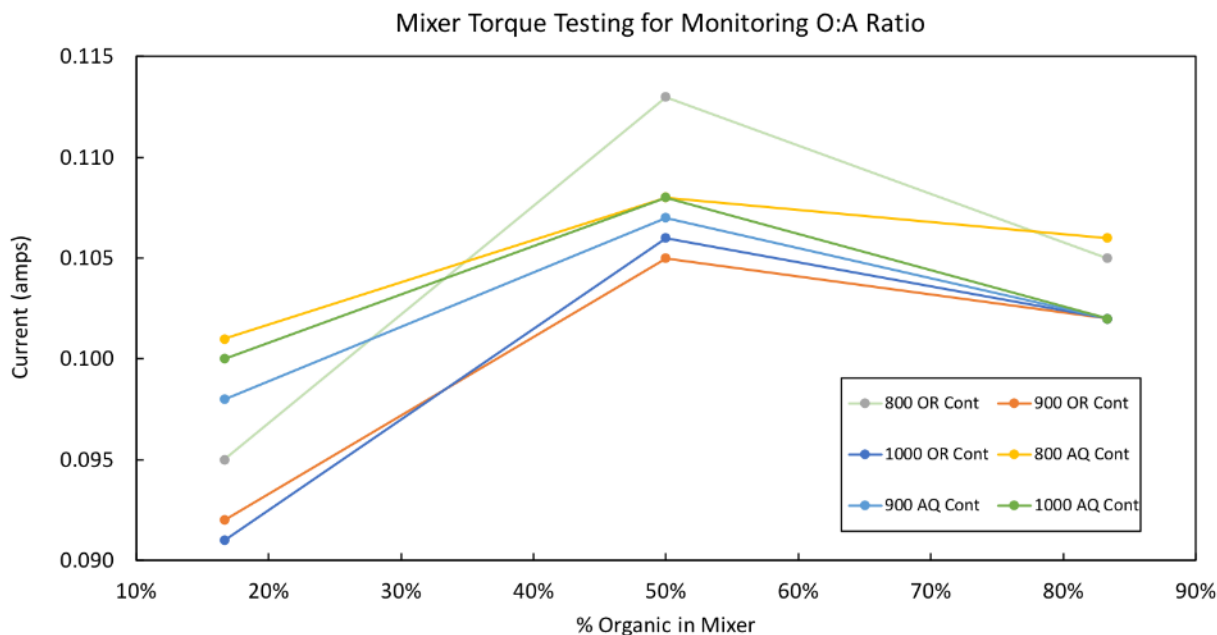


Figure 2. Results from mixer torque testing.

Following this test in Q4 and Q5, Rockwell Automation completed a significant portion of the automation package installation. Figure 3 shows some of the installed components including:

- A. Instrumentation Cabinet
- B. pH Transmitter
- C. pH Probe
- D. Radar Level Tank Sensor
- E. Rack-Mounted Server
- F. Recirculation Pumps
- G. Variable Frequency Drives
- H. Torque Sensor

All sensors used in the system are directly connected to the instrumentation cabinet. This cabinet converts analog signals to digital and then sends this information to the rack-mounted server. Finally, the server compiles, stores and analyzes all data.

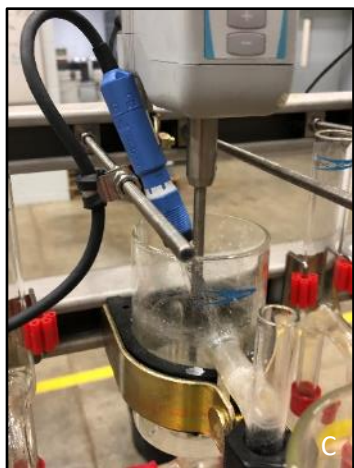




Figure 3. Automation equipment installed.

The design and installation of this automated SX plant was conducted in parallel with the parametric testing (Task 6) to allow for progress in both areas of research in a timely manner. For the automation portion of this project, the instrumentation and control equipment were installed on a ten-unit sub-set of mixer-settlers of the ALSX system.

Included in the system is a series of recirculation pumps and variable frequency drives that eliminate manual valves, which control the mixer O:A ratios by recycling fluid from the settler back to the mixer. Analog control of this parameter had proven to be challenging in shakedown and parametric testing.

A total of ten pumps will activate when the respective torque sensor detects a change in power-draw from the mixers. This change indicates a shift in viscosity of the fluid in the mixer has occurred; therefore, the O:A ratio in the mixers may require adjustment. As a result, the pumps will increase the flow of organic or aqueous to ensure the flow rates of organic and aqueous solutions in the mixers are consistent with the desired mixing O:A ratio.

Alongside the previously installed components, safety locks were programmed into the system to stop the plant when a chemical tank level exceeds preset limits (empty/full). Additionally, the program alerts operators when waste tanks are almost full or when feed tanks are almost empty before forcing a system shutdown. The sequence of operations and the control narrative were also programmed into the instrumentation equipment. Data entry screens and operational graphics were implemented to allow operators control of the equipment and set inputs for the automation package. Historian software was also installed in the server to collect and archive data that the system produces. Figure 4 shows some of the human-machine interface screens.

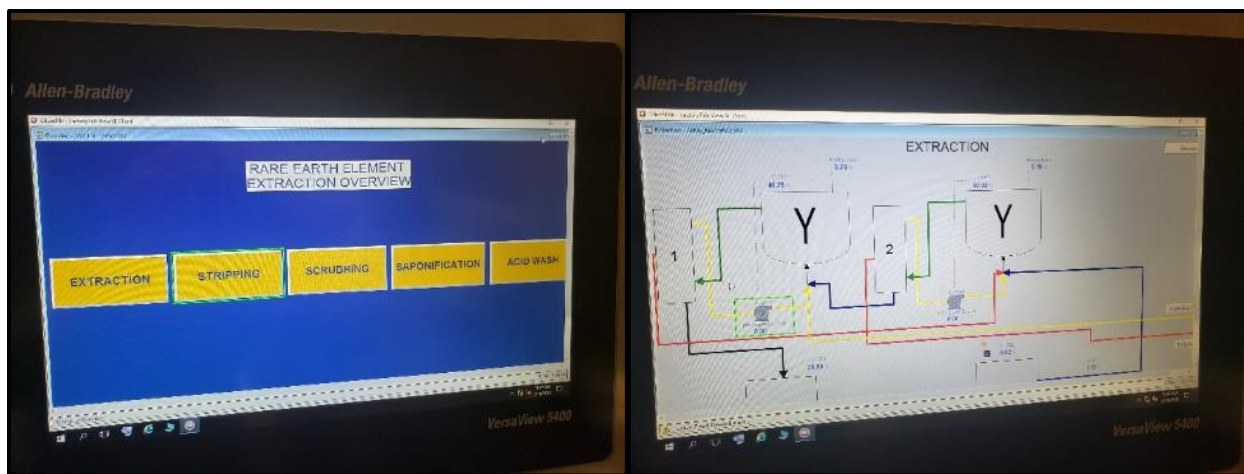


Figure 4. Human-machine interface screens used in ALSX control.

After equipment installation, the research team conducted shakedown experiments to evaluate the feasibility of implementing an automatic control scheme that will control the O:A mixing ratio of each individual mixing unit. This control feature will vary the volumetric flow rate of the recycle feed at each mixer to obtain a 1:1 ratio inside the mixing chamber. The initial shakedown testing showed the torque sensors in the initial design did not accurately locate the optimum range for O:A ratios. More specifically, the mixer torque shakedown tests indicated the algorithm would arrive at a local minimum when using the training data set versus finding the optimum global minimum. As a result, additional sensors are needed to properly monitor system performance.

Concurrently, the shakedown testing also provided real-time data that is stored in the onsite server. This preliminary data was used to help shape the analysis, reporting, and presentation of the resulting data for future tests. As expected, complications with the preliminary programming and hardware performance, such as motor failure and level sensor failure, were also observed and corrected throughout the testing regime. Furthermore, parametric testing showed that the automation components provided substantial control over the flow rates of the organic and aqueous phases when compared to the manually-operated system. The incoming flows are precisely measured and consistent advance O:A ratios are produced when the flow rates are changed. This precision and control overflow is critical to consistent REE recovery as the technology advances to the next Technology Readiness Level (TRL).

Following some additional minor system modifications to mitigate sensor performance issues, two production runs were successfully completed using the automated SX plant. These runs resulted in the highest grade REO (87%) acquired from the overall SX processes to date. Table 2 shows the final precipitated product generated from the automated SX unit.

Table 2. MREO product obtained from first Auto SX plant run.

Analyte	Acid-Wash Product Assay	Acid-Wash Product Mass	Oxide Ratio	Oxide Based Assay	Oxide Product Mass
Mass (g)	1.0198				
Major Ions	(mg/kg)	(g)		(mg/kg)	(g)
Al	18,810.69	0.02	0.53	35,531.30	0.04
Ca	964.42	0.00	0.71	1,350.19	0.00
Co	15.49	0.00	0.79	19.69	0.00
Fe	-	-	0.70	-	-
Mg	-	-	0.60	-	-
Mn	47.92	0.00	0.77	61.85	0.00
Ni	-	-	0.79	-	-
Si	491.92	0.00	0.47	1,054.12	0.00
S	-	-	0.33	-	-
Zn	31.85	0.00	0.80	39.64	0.00
REEs	(mg/kg)	(g)			(g)
Sc	-	-	0.65	-	-
Y	346,792.84	0.35	0.87	396,553.86	0.40
La	1,603.66	0.00	0.85	1,880.73	0.00
Ce	34,004.49	0.03	0.81	41,770.29	0.04
Pr	7,644.01	0.01	0.83	9,235.27	0.01
Nd	41,663.02	0.04	0.86	48,595.30	0.05
Sm	36,711.95	0.04	0.86	42,571.80	0.04
Eu	16,592.65	0.02	0.86	19,212.88	0.02
Gd	116,235.10	0.12	0.87	133,975.28	0.14
Tb	18,735.59	0.02	0.85	22,036.39	0.02
Dy	82,817.97	0.08	0.87	95,049.54	0.10
Ho	13,560.00	0.01	0.87	15,533.20	0.02
Er	29,979.13	0.03	0.87	34,280.81	0.03
Tm	2,816.85	0.00	0.88	3,217.04	0.00
Yb	9,848.25	0.01	0.88	11,214.17	0.01
Lu	1,071.78	0.00	0.88	1,218.79	0.00
Actinides	(mg/kg)	(g)			(g)
Th	-	-	0.94	-	-
U	1.02	0.00	0.91	1.12	0.00
Summary	mg/kg	(%)		mg/kg	(%)
TMM	20,362	2%		38,057	4%
TREE	760,077	76%		876,345	88%
TACT	1	0%		1	0%
Total Ions	780,441	78%		914,403	91%
REE Distribution					
TREE	760,077	76%		876,345	88%
LREE	138,220	18%		163,266	19%
HREE	621,858	82%		713,079	81%
CREE	506,602	67%		581,448	66%
Residual					
Unaccounted Ions	219,559	22%		85,597	9%

Subtask 3.3 Equipment Procurement

Approach

The Recipient will purchase major equipment items after the completion of Subtasks 3.1 and 3.2. The Recipient will develop and implement staged delivery of major equipment items for shakedown testing of smaller sub-systems prior to construction of the entire bench-scale system.

Overview

Equipment procurement began immediately with most pieces of equipment purchased, received, and installed by the second quarter. Additional purchases were made later when the pan-filter was deemed inadequate for the system design and a plate and frame filter press was procured during the third quarter.

Results and Discussion

During the first and second quarters, all major equipment items for the ALSX and ancillary operations were ordered, received, and installed except for the 470mm plate and frame filter press that was ordered in the third quarter. As described under Task 3.1 above, a plate and frame filter press was added to the circuit design to overcome filtration issues caused by the inadequate pan filter. As such, a 150-mm laboratory-scale filter press and a 470mm filter press were purchased and delivered in the fourth quarter. Table 3 lists the major components and whether they were “received,” or “installed.”

Table 3. List of major plant components and procurement status.

Line Item	Description	Vendor	Quantity	Status
1	Leaching			
1.1	Agitated Leach Tanks with Mixers	Titan Manufacturing	2	Installed
1.2	Sandpiper Leach Transfer Pump	Cole Parmer	1	Installed
1.3	Rubber Covered Chemflour Tubing 10'	Cole Parmer	4	Installed
1.4	Tygon 2375 Ultra Chemical Resistant Tubing	Cole Parmer	100	Installed
2	Solid/Liquid Separation			
2.1	4' X 4' Pan Filter	Titan Manufacturing	1	Installed
2.2	Sandpiper Leach Transfer Pump	Cole Parmer	1	Installed
3	Solvent Extraction/Stripping			
3.1	100 Mixer-Settlers +4 Pump Package	SX Kinetics	1	Installed
3.2	Tables for SX Units	Uline	13	Installed
3.3	Peristaltic Pump for Acid/Base Addition	Cole Parmer	6	Installed
3.4	3/8" ID Masterflex Tygon Tubing X 50'	Cole Parmer	1	Installed
3.5	D2EHPA Extractant per Gram	Sigma Aldrich	20200	Received
3.6	Organic - Kerosene Diluent per Liter	Univar	83	Received
4	Precipitation			
4.1	10 Gallon Open Top Tank with Lid	US Plastics	1	Installed
4.2	Precipitation Tank Mixer	IKA	1	Installed
4.3	10 "Pressure Filter	Titan Manufacturing	1	Installed
4.4	Peristaltic Pump	Cole Parmer	2	Installed
5	Storage			
5.1	10 Gallon Open Top Tank with Lid	US Plastics	1	Installed
5.2	30 Gallon Open Top Tank with Lid	US Plastics	1	Installed
5.3	Tailings Storage Container	Uline	1	Installed
5.4	55 Gal Full Drain Cone Tank	National Tank Outlet	2	Installed
5.5	55 Gal Full Drain Cone Tank Stand	National Tank Outlet	2	Installed
5.6	250 ml Glass Sample Jars	Cole Parmer	24	Installed
5.7	55 Gallon Lined Opent Top Steel Drum	Uline	20	Installed
5.8	Sandpiper Leach Transfer Pump	Cole Parmer	1	Installed
6	Safety			
6.1	18 X 18 X 22" Poly Corrosive Cabinet	Uline	2	Installed
6.2	36 X 23 X 36" Poly Corrosive Cabinet	Uline	1	Installed
6.3	43 X 18 X 44" Flammable Cabinet	Uline	1	Installed
6.4	Gloves/Glases/Facemasks/Aprons/etc.	Cole Parmer	1	Installed
7	Lab Equipment			
7.1	Ohaus Laboratory Balance	Cole Parmer	1	Installed
7.2	Ohaus Floor Balance	Cole Parmer	1	Installed
7.3	Mettler Toledo pH Meter with Data Logging	Cole Parmer	3	Installed
7.4	Binder Gravity Convection Oven	Cole Parmer	1	Installed

Subtask 3.4 Sample Procurement / Feedstock Sourcing

Approach

To demonstrate system robustness and assess a range of regional feedstock REE composition variations, the Recipient will obtain sufficient quantities from at least three (3) AMDp feedstocks for the ten (10) week test program of the bench-scale REE extraction system. The three (3) feedstocks will be from the Omega, DLM, and Royal Scott sites. These feedstocks will be delivered to the WVU research facility in 55-gallon drums, which will then be catalogued, analyzed, and appropriately stored prior to testing.

Overview

Feedstock for the ALSX plant was collected from Omega, Royal Scott, and DLM sites during the third and fourth quarters of this project.

Results and Discussion

During the third and fourth quarters, a contract was issued for the acquisition of feedstock for the ALSX plant. This contract provided ten 55-gallon drums of AMDp from each of the three sites to be evaluated in this project. Ten drums of Omega sludge were received at the ALSX facility by the third quarter with the rest from Royal Scott and DLM arriving in the fourth quarter. Various photos from the sampling exercise are shown in Figure 5 while the final delivered samples are shown in Figure 6. Thus, all feedstock for the ALSX plant was acquired by the end of the fourth quarter.



Figure 5. Recovery of sludge samples from the Omega site.



Figure 6. Drums of Omega sludge for use as feedstock to the ALSX plant.

Subtask 3.5 Environmental Health and Safety

Approach

The Recipient will work with WVU Environmental Health and Safety personnel to develop a detailed chemical hygiene and waste management plan specially addressing the bench-scale REE extraction plant. The chemical hygiene plan will describe all engineering controls, personal protective equipment requirements, standard operating procedures, and waste handling procedures needed to ensure safe operation of the facility throughout the duration of the project.

A major focus of the chemical hygiene plan will be safe handling of strong acids in the bench-scale REE extraction system. The Recipient will also include laboratory safety training, hazardous waste management training, and secondary containment and spill and response protocols in the plan.

Overview

A Chemical Hygiene Plan was developed and approved by WVU Environmental Health and Safety that contains all relevant information pertaining to preparing, operating, and maintaining the ALSX system in the High Bay of the NRCCE. Alterations were made over the course of the project as ideal operating conditions and parameters were identified as well as when additional pieces of equipment were installed in the system.

Results and Discussion

During the first quarter, an initial Environmental Health and Safety (EHS) Chemical Hygiene Plan (CHP) was developed and reviewed by the WVU EHS team. After approval in the second quarter, this plan was placed in the laboratory facility and reviewed by all personnel working in the laboratory area. This initial plan is the basis of the more comprehensive EHS package that will follow this project through scale-up to the next TRL or commercial development of the technology. As such, this document was expected to be modified and augmented as the project identifies new reagents and procedures. For example, the CHP was modified to include the addition of the plate and frame filter press. Further updates to the CHP were implemented as needed.

Task Completion Status

100% complete.

Task 4.0 Initial System Testing Plans

Approach

Starting with the preliminary testing plan documents, the Recipient will develop an operating plan, a sampling plan, and an analytical plan to be used during all bench-scale REE extraction system testing. At a minimum, these plans will include test procedures, specific sampling and analytical procedures, and American Society for Testing and Materials (ASTM) standards that laboratory personnel will use to operate the bench-scale REE extraction system. The Recipient will submit the final system testing plan to the DOE/NETL Project Officer for review and comments before starting system testing.

Subtask 4.1 Operating Test Plan

Approach

The Recipient will utilize the following general overall testing plan and procedure.

Each test series will be designed to be completed over a five (5) day working period, using a single eight (8) hour operating shift per day. The series will begin by using batch-wise acid leaching to produce approximately 55 gallons of pregnant leach solution. Leaching will be conducted in a specialized acid-resistant leach vessel and agitation will be supplied by an industrial scale mixer outfitted with a titanium or other corrosion-resistant impeller. Leaching will be conducted using the general protocols and parameters developed during the laboratory-scale testing, including ambient temperature, solid to liquid ratio of about 1:1, and pH range of about 2 to 3.5. After leaching, additional caustic adjustment will be performed as needed, and the leach slurry will then be transferred to a laboratory filter for solid-liquid separation. The final leach solution will be split into lots of approximately 5 to 10 gallons for daily SX testing, and the solid residue will be retained for analysis.

After solid-liquid separation, the pregnant leach solution will be fed into the continuous solvent extraction and solvent stripping unit using peristaltic feed pumps. Regardless of scale, solvent extraction units are designed to operate continuously 24 hours a day, seven days a week to ensure phase continuity between the aqueous and organic fractions. Any interruption to production can cause a phase inversion, which must be purged from the system after restart. Since this purge can take several hours to complete, the Recipient will work with the solvent extraction equipment vendor to develop a standard idling protocol to limit daily startup time.

During testing, the organic fractions will be recirculated within the system. The raffinate will be stored in a 275-gallon (or other appropriate size) tote bin, and the stripped aqueous solution will be stored in a final product container. After the test run is complete, the REEs in the stripped aqueous solution will be precipitated with oxalic acid, and the final product will be separated from the liquid fraction using the original pan filter. Both the raffinate and the unloaded aqueous solution will be recirculated back to their respective places in the circuit for future tests.

Overview

The operating plan was regularly reviewed and updated as the project developed. Although some experiments required slightly different procedures, the fundamental operating plan remained intact and was carefully followed during testing.

Results and Discussion

The vendor-supplied operating manual for the SX system served as the basis for the operating plan. This manual describes installation, start-up, shut-down, cleaning, and operating instructions. Furthermore, as new procedures and operational schemes were developed, the operating plan was updated to reflect those additional developments. Additionally, the system was operated in conjunction with exploratory tests to identify optimum running states and generate feedstock for laboratory testing. Finally, an

overall validation run was performed to evaluate different feedstocks and the results defined an overall operating condition.

Subtask 4.2 Sampling Plan

Approach

The Recipient will develop and utilize a sampling plan which contains the following elements. Samples will be obtained from the following points when a complete extraction system mass balance is needed:

1. The raw AMDp entering the leach reactor (solid phase)
2. The pregnant leach liquor after solids removal, also denoted the SX feed (liquid phase)
3. The solid residue filtered from the leach liquor (solid phase)
4. The raffinate leaving the SX-extraction unit (liquid phase)
5. The stripped solution leaving the SX-stripping unit, also denoted the SX product (liquid phase)
6. The final dilute aqueous after precipitation and filtration (liquid phase)
7. The final REE concentrate (solid phase)
8. The pregnant leach liquor after leaching but before caustic adjustment
9. Any solid residue after leaching but before caustic adjustment

Sampling protocols will utilize the appropriate ASTM or accepted industrial standards such as full stream cuts for designated time intervals. The Recipient will collect samples at designated time increments, with a nominal time increment of one hour. The Recipient will store all aqueous samples in suitable size polypropylene sample containers for shipment to the analytical laboratory. The Recipient will filter and dry solid samples overnight in a laboratory oven or desiccator prior to storage and shipment.

Overview

The sampling plan was consistently and thoroughly reviewed each quarter to ensure it met the current needs of the project. No changes occurred over the duration of the project.

Results and Discussion

The initial sampling plan was regularly reviewed, but no changes were made.

Subtask 4.3 Analytical Plan

Approach

The Recipient will analyze aqueous and solid samples for REEs, major gangue metal concentrations, and other beneficial or deleterious elements as determined through testing. REE aqueous concentrations will be determined using inductively coupled plasma-mass spectrometry (ICP-MS). AMDp samples will be digested by sodium peroxide (Na_2O_2) fusion and re-dissolution in hydrochloric acid. This method appears to be comparable with the United States Environmental Protection Agency's (USEPA's) total digestion method 3052 (microwave digestion) for total REEs. Resulting aqueous analysis will then be undertaken using ICP-MS. Major ions such as iron (Fe) and aluminum (Al) will be determined by inductively coupled plasma-optical emission spectrometry (ICP-OES).

The Recipient will specify an analytical method(s) for scandium that will be used on aqueous and solid samples.

Overview

The analytical plan devised and implemented was carried out by laboratories at WVU and Virginia Tech. Caution and care were exercised to limit discrepancies between labs.

Results and Discussion

The Recipient used resources at the WVU/NRCCE analytical laboratory to carry out its analytical plan. By the end of the second quarter, additional equipment was acquired and training was undertaken to

ensure the plan's success. Sample validation was also undertaken by comparing acid digestion methods against commercial laboratory results to ensure sample accuracy and precision.

While the standard analytical procedures used at WVU continued to include either sodium peroxide fusion or strong acid digestion followed by ICP-MS finish, in order to expedite sample analysis for the work conducted at Virginia Tech, several on-campus laboratories were evaluated during the third quarter. Unfortunately, the Virginia Tech facilities do not have the instruments and environmental controls needed to perform sodium peroxide fusion or digestions with large quantities of hydrofluoric acid (HF). Alternatively, researchers at Virginia Tech analyzed 11 different microwave-assisted digestion procedures to determine which produced the best results, most comparable with the WVU analytical results. The tests were repeated for three different sludge samples, and the methods evaluated in this study included acid digestion using nitric acid, aqua regia, moderate hydrofluoric acid, and combined alkaline/acid digestions. To validate the data obtained from this method, a comparative study was conducted by analyzing a representative split of Omega sludge using the preferred procedures at both the WVU and VT analytical labs. Figure 7 shows the results from this study. The WVU procedure (sodium peroxide fusion) does not produce a scandium assay and shows a notably lower yttrium analysis relative to the VT procedure. Alternatively, the VT data shows notably lower concentrations of La-, Ce-, and Nd-light REEs typically associated with difficult-to-digest mineral species.

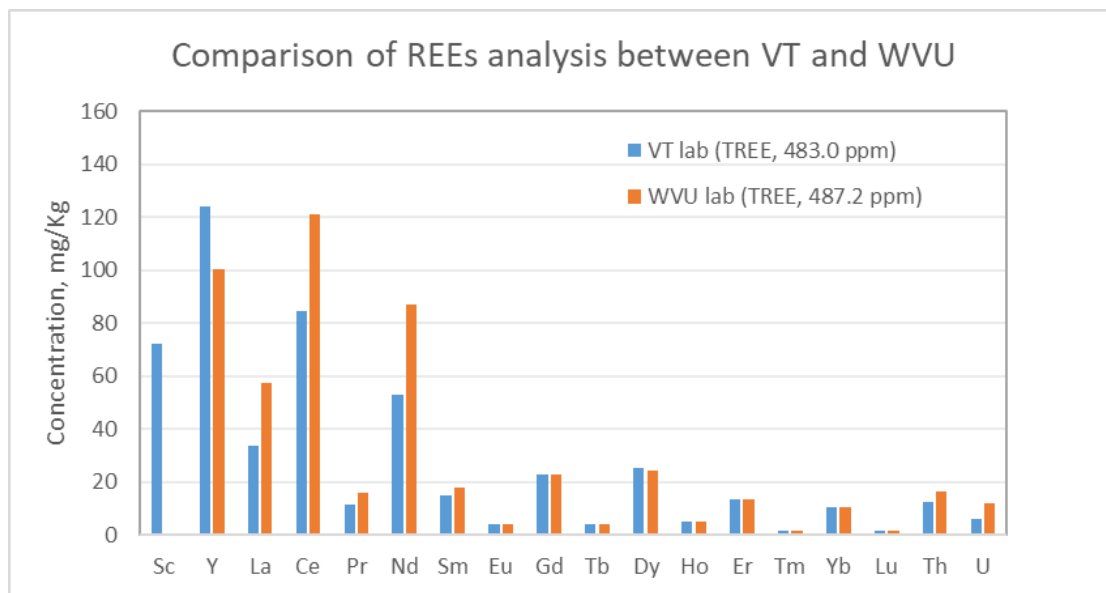


Figure 7. Rare earth elemental concentration analyzed by VT lab and WVU lab for Omega sludge.

Given the discrepancies in these data sets, care must be exercised when comparing results from different groups; however, the results are sufficient for standard day-to-day test work. Going forward, the WVU facility will be used for all detailed analyses, while the VT facility will only be used for quick analysis of the VT experimental work. Overall, the availability of both laboratories will help to reduce the load on any single laboratory and reduce turnaround times.

Subtask 4.4 System Plans

Approach

The Recipient will provide a working document covering the operations, sampling, and analytical testing plans for the ALSX system.

Overview

The finalized system plans were generated after the initial system shakedown and testing.

Results and Discussion

System plans for the ALSX system include detailed process flowsheets, process and instrumentation diagram (P&ID) drawings, and facility layout drawings. Together, these specify the operations, sampling points, and testing scheme for the overall ALSX system. The facility layout is shown in Figure 8 below.

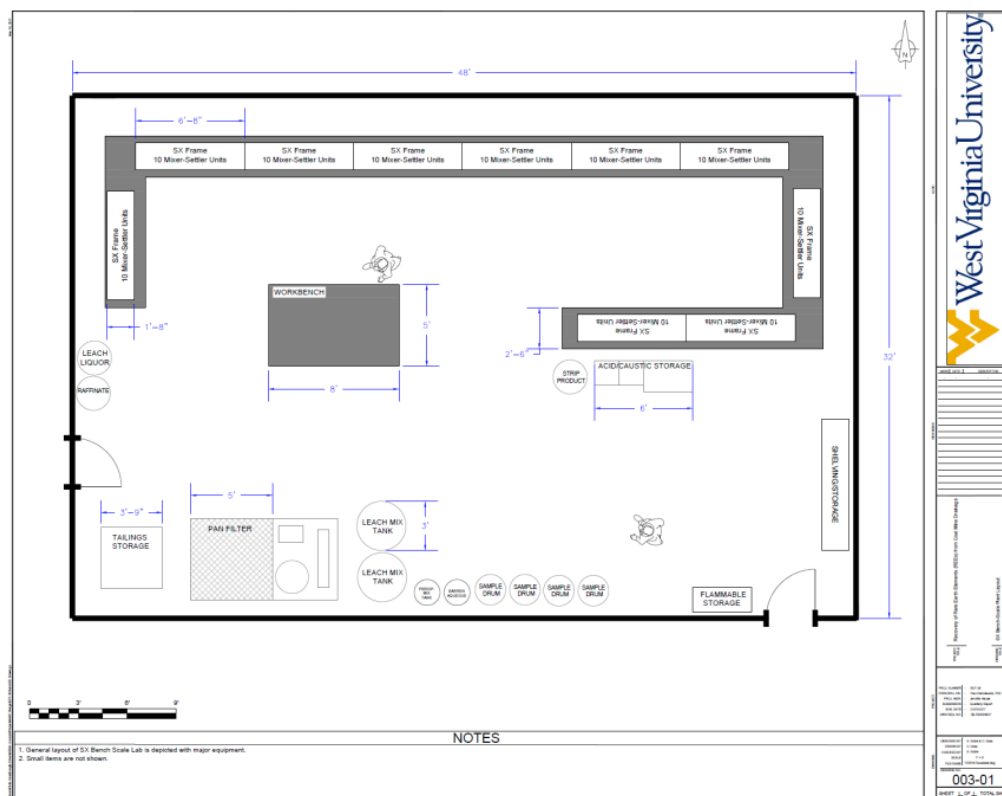


Figure 8. Facility layout diagram.

Task Completion Status

100% complete.

Task 5.0 System Construction and Installation

Subtask 5.1 Construction

Approach

The Recipient will start building modifications, equipment installation, and other construction activities after the completion of Subtask 3.1. Since many of the large items will be purchased as turn-key packages, the Recipient will work with product vendors during startup to ensure all equipment is installed to vendor specifications. The Recipient will also determine if on-site visits are needed from key equipment providers during either the installation or start-up. The Recipient will also conduct a final safety review after construction is completed but before testing is started.

Overview

After the equipment for the ALSX system was ordered and received in the first and second quarters, it was immediately unboxed and installed in the High Bay area of the NRCCE. Once installation was complete, additional site modifications and adjustments were made to improve operational efficiency.

Results and Discussion

Upon the project award, efforts were made to clear the NRCCE High Bay facility and prepare for the delivery and installation of the ALSX system. At the time, the High Bay facility was being used to store old equipment from prior university projects. This effort required coordination with multiple project managers to facilitate the decommissioning of the existing projects located in the High Bay. Figure 9 shows the initial condition of the NRCCE High Bay at the start of the project.



Figure 9. NRCCE High-Bay at the beginning of the project.

After clearing the testing facility, tables and work benches were assembled to support the SX system frames and arranged to provide a clear view of all the SX units by the operators. The tables were oriented in a manner comparable to the proposed layout that was submitted within the design package; however, some modifications were required due to existing infrastructure within the High Bay.

After delivery of the SX-system, the individual racks (10 mixer-settler per rack) were unboxed, inspected, and placed on the support tables. During delivery, the glassware in one rack was broken, and this unit was returned to the vendor for replacement. The 100 overhead mixing units were delivered with the mixer-settler glassware, but due to shipping constraints, they were not installed on the racks upon delivery. Each mixer thus required installation on the appropriate support structure. Figure 10 shows

several pictures of the delivery and assembly of the SX system. Figure 11 shows a close-up of one mixer settler after installing the overhead mixer.



Figure 10. Select pictures of delivery and installation of the SX system. Top left: boxes of mixer-settler racks after delivery. Top right: mixer-settlers racks installed on support tables. Bottom-left: close-up of one run of mixer-settlers. Bottom right: glassware broken during delivery.



Figure 11. Close-up of single mixer-settler unit.

Each mixer-settler unit is comprised of 3 separate pieces of glass all connected by chemically resistant Tygon tubing. The *mixer* piece is located at the back of the system directly under the overhead stirrer. This unit is where the mass transfer occurs between phases (aqueous and organic). The *settler* piece is the large cylindrical glass located directly in front of the mixer. This glass unit allows the two phases to separate before advancing to the next unit. Lastly, the *aqueous over-flow weir*, located to the left of the mixer, is used to adjust the position of the aqueous-organic interface within the settler based on the density of each phase.

A workbench was placed in the center of the SX layout to provide a working surface for maintenance and sampling duties. For example, the workbench provided a useful surface for the assembly of the peristaltic pump drives and pump heads. In a similar manner, once the system began operation this area was instrumental in organizing samples and mixing reagents used in the SX process. Figure 12 shows the overall layout of the entire SX bench-scale plant.



Figure 12. Layout of SX system.

While the solvent extraction portion of the system was delivered and installed, the leaching components of the project were being manufactured and shipped. Upon delivery, the leaching area was located under the fume hood station in the NRCCE High Bay as shown in Figure 13. This area housed the leach tanks, pan filter/vacuum receiver, and other miscellaneous equipment.



Figure 13. Image of existing fume hood to ventilate the leaching operations.

Finally, a deep-frame, restaurant-style sink was purchased and installed in the High-Bay. This sink was used as a general area to clean storage vessels and maintain overall cleanliness of components. Next to the sink, a safety shower and eyewash station are available for emergencies as described in the chemical hygiene plan. Figure 14 shows the sink and safety shower area.



Figure 14. Image showing wash-down sink and safety shower.

Proceeding from the laboratory findings from the third quarter, a 470mm plate and frame filter press was procured and delivered to the ALSX facility during the current reporting period. Upon receipt, the instrument was properly installed following the manufacturers recommended guidelines. Figure 15 shows the installed plate and frame filter.



Figure 15. 470mm Plate and Frame Filter Press.

In addition to the electrical work, other construction and installation activities were needed to bring the leaching area to an operational status. For example, casters were added to the mixing tanks to increase their mobility and the paddles of the leach tank were replaced with a larger mixing prop to provide better stirring and agitation. Additional site modifications to the facility included enclosing the fume hood with plastic sheeting and installing 230V power for the mixing and filtration equipment. Additionally, the original fume hood area did not contain adequate lighting to ensure proper operation and worker safety. Several lights were thus mounted within the fume hood to assist in this regard.

Subtask 5.2 Shakedown Tests

Approach

After completion of Subtask 5.1, the Recipient will conduct a series of shakedown tests to identify and resolve operational issues that may arise during the detailed system testing. Specific objectives of Subtask 5.2 include: (1) verify vendor specifications on capacity and power; (2) ensure the sufficiency of various ancillary equipment and utilities; and (3) identify the operational limits to be used in detailed system testing.

After shakedown testing is completed, the Recipient will modify the operational and sampling plan as required and submit the revised operational and sampling plan to the DOE/NETL Project Officer for review and comments before starting any further testing (Subtask 5.3, Task 6.0, and Task 7.0).

Overview

Shakedown tests were carried out to investigate the integrity of the SX system and search for potential problems and solutions regarding the use of AMDp as a feedstock before parametric testing began. Initial shakedown tests using water and organics showed physical weak points in the system which were subsequently fixed. Unfortunately, the equipment in initial leach process design could not produce PLS at all due to filtration difficulties with the pan filter. The following tests investigated mitigation strategies and potential replacements for the pan filter. The use of flocculants and coagulants was investigated further in Subtask 5.3 and finally a 470mm filter press was selected as an appropriate replacement for the pan filter.

Results and Discussion

Hydrostatic Test Run and Operational Integrity

After installation, shakedown testing was performed on the solvent extraction units. This testing was primarily conducted to confirm the operational viability of the system. Furthermore, the results of the shakedown testing led to the acquisition of operating knowledge regarding system functions. Two tests were conducted during the second quarter of the project: a hydrostatic test and a kerosene/water test. First, all the SX mixer-settler units were subjected to a hydrostatic test to ensure no leaks were present. During this test, all 100 SX units were filled with water, and the mixing units as well as a peristaltic feed pump were operated for forty-eight hours. During this test, two glass settler units were found to have a rough surface on the face of the threaded coupling that is used to attach the interconnected hoses. These units were subsequently replaced by the manufacturer. Additionally, several hose clamps were installed in areas where small drips were observed during the testing procedure. Figure 16 shows an installed hose clamp and threaded coupling of a settler unit.

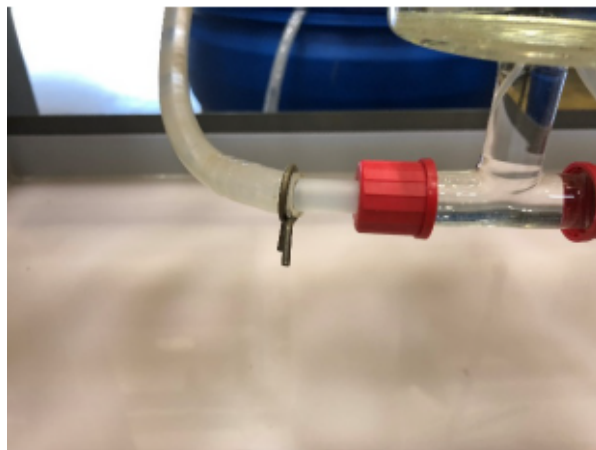


Figure 16. Threaded hose coupling with hose clamp.

Following the water-only test, a second shakedown test was conducted using water and kerosene to represent the aqueous and organic phase, respectively. During this test, a single rack of 10 mixer-settlers was configured to represent an extraction, scrubbing, stripping and saponification circuit. In addition to testing the structural integrity of the SX components, this test also provided a means to evaluate various organic to aqueous (O:A) ratios in the mixer-settler units. The O:A ratio is a critical operating parameter that influences the SX efficiency and the product quality that can be produced. Typically, the ideal O:A ratio is determined from parametric batch testing; however, different ratios are often desired for different parts of the SX circuit. For example, an O:A ratio of 1:1 may be desired in the extraction stage; however, a higher ratio of 10:1 or even 50:1 may be desired in the stripping stage.

In the continuous ALSX system, the O:A ratio is defined by two quantities: the advance ratio and the mixing ratio. The advance ratio is simply defined by the rate at which the two phases enter and leave the system. This value can be controlled by the feed pumps for the organic and the various aqueous components. Alternatively, the mixing ratio is the actual O:A ratio in a specific mixer-settler. This value can be controlled by modifying the amount of organic or aqueous that is recycled back to the same mixer.

To achieve a certain mixing ratio, a recycle stream from the settler may be used to adjust the O:A ratio in each individual mixer cell. This recycle stream (organic for extraction and aqueous for other stages) permits even mixing within the chambers while preserving the desired advance ratio for the stage. This two-pronged approach to O:A ratio control allows better regulation of the concentration of metals within each stage. Figure 17 shows a single mixer-settler unit with the individual flow ports labeled to indicate the recycling path options.

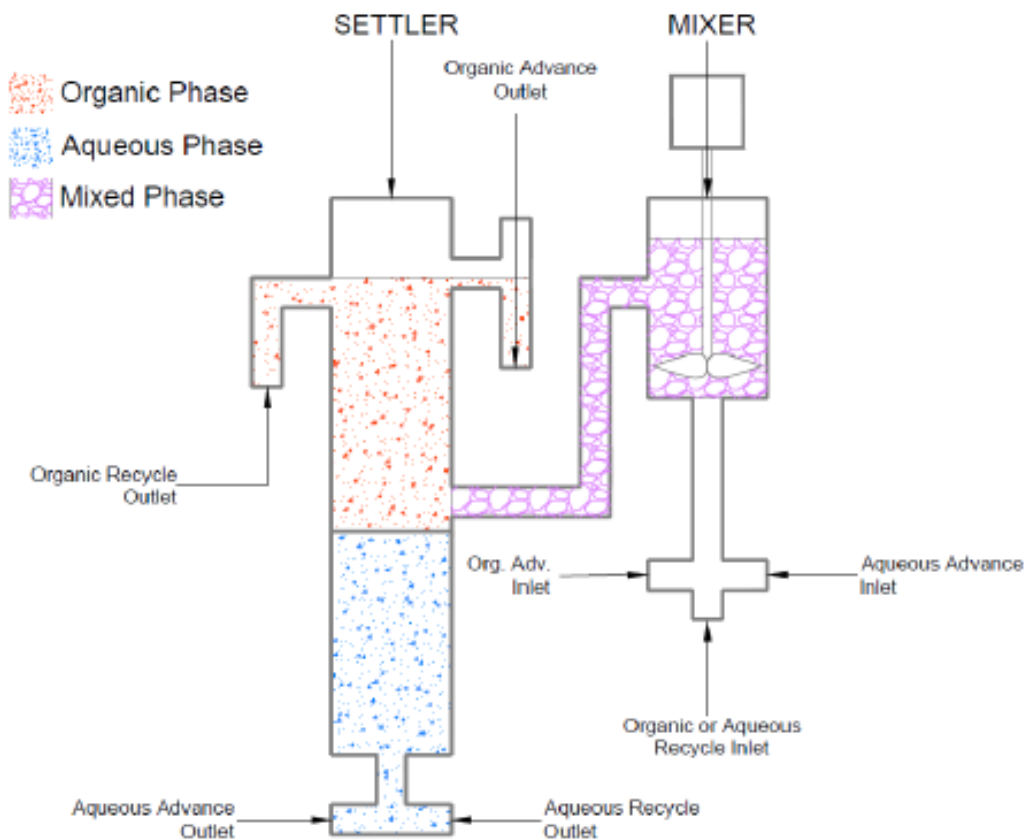


Figure 17. Generic mixer-settler unit after (Webster, 2018).

During this shakedown testing series, operators evaluated both methods for controlling the O:A ratio, and simple calibration charts were developed to assist in setting pump speeds and other flow variables.

Problems with Solid Gel Formation and PLS Filtration

With the completion of Subtask 5.1, the ALSX system was commissioned and shakedown tests were initiated. The initial efforts focused on the operation and optimization of the acid leaching (AL) plant to generate sufficient PLS for the SX system. During this startup testing, three separate attempts were made to create PLS to feed the SX system. During all three attempts, one overarching problem arose in the process; namely, the effective filtration of the PLS slurry. This issue was observed while using two different sludge feedstocks, namely Omega and DLM.

During the initial experimental trials, approximately 30 gallons of wet Omega sludge was first loaded into the leach tanks and leached with nitric acid. Following this leach reaction, the pH of the mixture was adjusted upward to approximately 2.5 using both NaOH and $\text{Ca}(\text{OH})_2$. During the first trial, the pH was raised using NaOH and, after this step, the material in the leaching tank formed a gelatinous paste. This gel was extremely difficult to handle and could not be transferred by pumping alone. Moreover, the gel did not respond to vacuum filtration, as the pan filter was unable to remove any liquid from the material.

Initially, the experimental team suspected that the sodium in the NaOH was the primary culprit in the gel formation. To test this hypothesis, a second trial was performed in a similar manner, except $\text{Ca}(\text{OH})_2$ rather than NaOH was used to raise the pH. Unfortunately, the PLS once again formed a consistent gelatinous substance that could not be transferred to the filter via pumping. As a result, the pH was dropped back down using nitric acid, and the mixture once again became liquid. This mixture was then pumped to the vacuum pan filter where it eventually bonded to the filter cloth, as shown in Figure 18. Even at the lower pH, the PLS could not be filtered.



Figure 18. Unfilterable gelatinous PLS on vacuum pan filters.

Initially, the issue with gel formation was suspected to be a unique characteristic of the Omega AMDp. To test this hypothesis, an additional shakedown test was performed with the DLM feedstock, which has a distinct elemental composition notably different than the Omega material. In this test, approximately 30 gallons of DLM sludge were mixed with an equal mass of water in the leaching tank using the same procedure described above. Next, the pH was lowered to the leaching point, and the PLS was once again directly pumped onto the vacuum filter before pH adjustment. Once again, the PLS was unable to pass through the vacuum filter using the polypropylene filter media. Additionally, coarser media was stacked on top of the pan filter. However, the additional layers of filter cloth did not alleviate the issue.

Given these unforeseen setbacks, this PLS sample was further evaluated in the laboratory using a small pressure filter. During these tests, the pH of the initial PLS was raised to different set points and the filtration rate of the resultant precipitate was qualitatively evaluated. The results suggested that at a pH of 2.7, small colloids, less than 11 microns formed, and these initial coagula inhibited filtration.

This shakedown test led to several conclusions. First, the pH of the PLS affects the ability of the solution to be filtered. Mechanistically, this result is most likely due to the surface charge of the particles in solutions as well as the size of the initial coagula. Next, while many of the solutions were capable of being filtered on a small scale, we were unable to accurately scale-up the filtering process properly using the laboratory experiments from Phase 1. As a result, the active surface area and bed depth of the precipitate after filtering were not sufficient in sizing the pan filter.

Process Design Revisions

Due to these unforeseen difficulties in PLS filtration, an extensive laboratory-scale testing regime was planned and implemented to identify potential solutions. Several research groups and members of the project team were directed to this challenge, and the experimental trials focused on three potential solution paths: (1) modifications to the filtration process design/approach; (2) the addition of filtration aids/chemical additives, and (3) modifications to the filtration equipment. The initial objectives of this test were to identify an overall pathway that minimized gel formation and improve filtration kinetics. After identifying a suitable process, the second objective was to evaluate and optimize specific process parameters.

In addition to the changes in processing steps and chemical addition, the most critical change evaluated the use of alternative filtration equipment in the ALSX process. After meeting with numerous vendors, a plate-and-frame filter press was identified as the optimal choice for filtering PLS residue. Based on this finding, a 150 mm laboratory-scale plate and frame filter press was purchased for further evaluation.

Subsequent tests with the laboratory-scale 150 mm plate and frame (P&F) press evaluated the operational capability of this style filtration device. Figure 19 shows the laboratory P&F and the resulting filtrate and filter cake. During the initial testing, multiple feedstocks and pH points were evaluated to confirm proper filtration media selection. The successful implementation of this device led to the purchase and installation of a much larger, 470mm filter press for use in the ALSX facility.

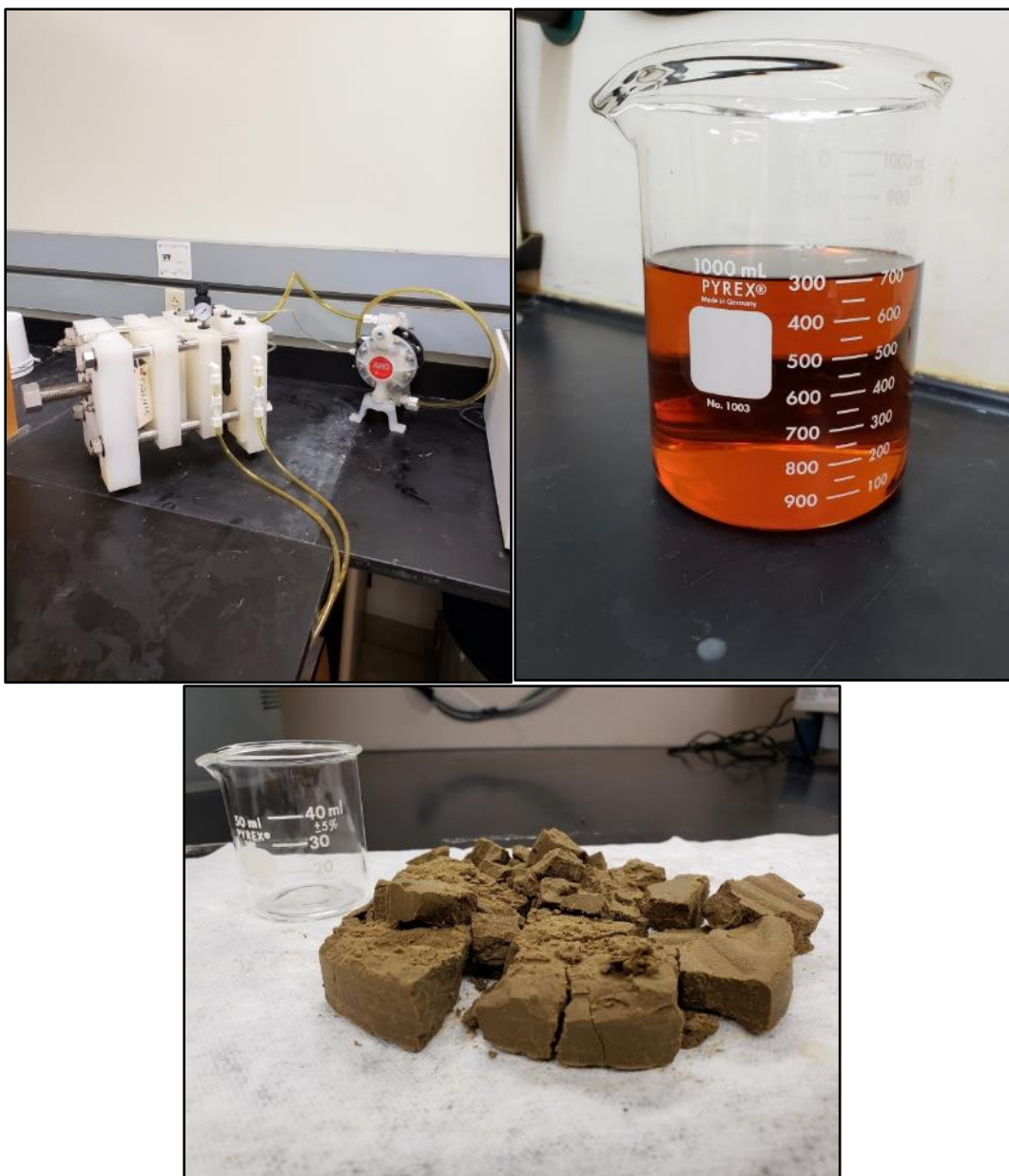


Figure 19. Laboratory scale P&F filter along with the clear filtered solution and filter cake.

Following purchase and installation, shakedown tests were performed to determine the operational requirements for successfully producing filtered PLS for the SX Plant.

Subtask 5.3 Exploratory Testing

Approach

Concurrent with Subtask 5.2 and Task 6.0, the Recipient will conduct a select number of laboratory-scale and bench-scale exploratory tests to identify novel processing routes or reagent mixtures not tested during Phase 1. This Subtask will align with the existing flowsheet design, and specific items may include but are not limited to: (1) novel leaching methods, such as AMD recirculated leaching or countercurrent leaching; (2) novel metal recovery/removal methods, such as electrocoagulation or electroplating; (3) novel flowsheet configurations, such as the addition of a scrub circuit, or inter-vessel organic recirculation; and (4) novel reagent mixtures for leaching and solvent extraction. The Recipient will

utilize the results from these exploratory tests to design an optimized commercial-scale process to reduce system costs while increasing REE recovery and selectivity.

Overview

Exploratory testing underwent several campaigns that evaluated different conditions affecting the ALSX system and its subsequent oxalic acid precipitation process. Notable experimental campaigns include AMDp characterization, crud mitigation, and leaching optimization that led to successful runs with the SX system and produced a MREO product that met the project requirements.

Results and Discussion

Sludge Characterization and REE Speciation

While prior efforts in Phase 1 focused on empirical methods for improving process performance, efforts in the current phase refocused this approach to include a more fundamental assessment. For the case of leaching, better knowledge of the REE speciation and morphology in sludge material would provide insight into more cost efficient and productive leaching methods. These characterization efforts focused on identifying the particle size distribution and the microstructure of the sludge materials as both properties have considerable influence on the kinetics and efficiency of the leaching process. To evaluate the influence of particle size on REE partitioning, sieve analysis was performed on three types of AMDp. For each AMDp and size fraction, the sample was desiccated at 107° C in an oven and digested using a standard microwave assisted NaOH and HNO₃ digestion procedure. Tables 4, 5, and 6 give the REE-by-size analysis for Omega, DLM and Royal Scott sludges. As seen, the REE distributions for Omega and DLM are bimodal while that of Royal Scott are mostly within the <63-micron size fraction.

Table 4. REE-by-size Analysis for Omega AMDp Sample.

Size Class (microns)	Mass Distribution (w.t. %)	REE Content (g/t)	REE Distribution (w.t. %)
< 63	35%	501.13	38%
63~300	8%	239.3	22%
>300	57%	184.2	40%

Table 5. REE-by-size Analysis for DLM AMDp Sample.

Size Class (microns)	Mass Distribution (w.t. %)	REE Content (g/t)	REE Distribution (w.t. %)
< 38	28%	1192.4	25%
38~63	1%	908.92	1%
63~106	2%	1100.7	1%
106~212	4%	1297.3	4%
212~300	3%	1164.2	2%
300~500	8%	1333.8	8%
500~850	14%	1176.1	13%
>850	40%	1486.2	46%

Table 6. REE-by-size Analysis for Royal Scott AMDp Sample.

Size Class (microns)	Mass Distribution	REE Content (g/t)
< 63	More than 99% of particles are <63 micron	1480.3
>63	A few particles in this fraction	147.6

Following particle size analysis, mineralogical and microstructure analyses were conducted using XRD and SEM/EDS at the Nanoscale Characterization and Fabrication Laboratory, Virginia Tech. Initial

microscopic studies were conducted using the +212-micron fraction of the DLM sample to determine the macroscopic of the larger particles. Figure 20 shows a close-up image of the coarse particles. The image indicates that this sample was composed of two different particle microstructures. Some particles clearly show a naturally crystalline, layered structure, while others are aggregates of smaller particles.

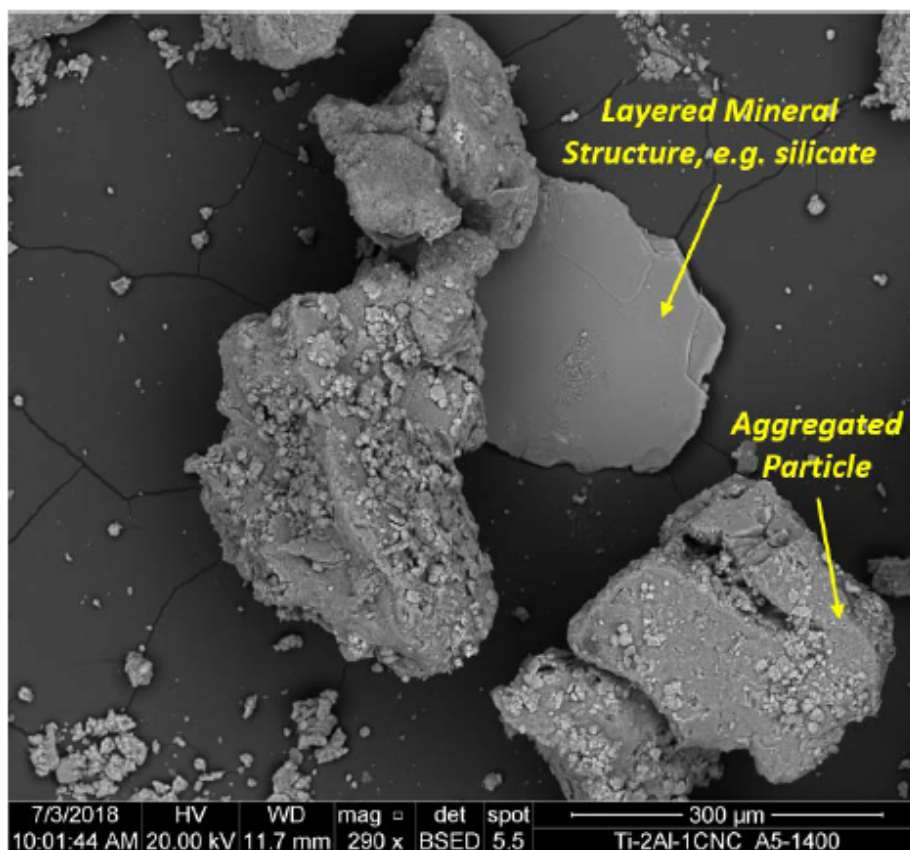


Figure 20. A closer macro structural view of Coarse Particles from DLM AMDp with size +212 micron.

SEM was further used to assess the fine microstructure of the sludge particles <20 microns, and EDS was used to determine the chemical compositions of specific points. The EDS Spectra generally showed the following trends:

- DLM Sludge: mostly pyrite, Mg, and Al-bearing minerals are present.
- Royal Scott Sludge: carbonate, Mg, Al, Si, and Fe bearing oxides or sulfates are present.
- Omega Sludge: Al, Fe silicate, and carbonates are present.

In order to evaluate the speciation and distribution of REEs in the AMDp sample, a chemical sequential extraction procedure based on Tessier et al. (1979) and Novikov et al. (2009) was applied on a representative wet sludge sample from the primary sample lot. The detailed protocol is also described in a previous publication: Iwatsuki et al. (2017). Table 7 provides the experimental procedure, including the detailed chemical makeup of the leach solutions. Results from the sequential extraction tests for DLM, Royal Scott, and Omega sludge samples are summarized in Table 8. Figures 21, 22, and 23 give the rare earth element concentrations in the ion exchangeable, carbonate, iron and manganese oxides, organic, and crystalline fractions for DLM, Omega, and Royal Scott AMDp samples. Since only a small fraction of Royal Scott AMDp was in the +63-micron range, and this size fraction had low REE content, only the -63-micron size fraction was tested.

In all three materials, REE occurrence in the ion exchangeable and the organic fractions were negligible while the REEs were predominantly distributed across the carbonate, iron/manganese oxides, and crystalline phases. This data show that the majority of the REEs occur in the fine sludge fraction within the iron/manganese oxides and carbonates. This data may be useful in improving and optimizing the leaching process, as additives that increase the solubility of these components may greatly improve leaching recovery at lower acid costs.

Table 7. REE chemical sequential extraction procedure.

Tessier et al. (1979) and Novikov et al. (2009)			
Step	Speciation Form	Selection of Chemical	Condition
S1	Ion Exchangeable	40 mL 1 mol CaCl ₂ (pH=7)	7h at 25 °C
S2	Bound to Carbonates	40 mL 1 mol NH ₄ acetate + acetic acid (pH=4.8)	12h at 25 °C
S3	Bound to Iron and Manganese Oxides	40 mL 0.04 mol NH ₂ OH·HCl + acetic acid (pH=2)	8h at 95 °C
S4	Organic Matters	40 mL 2 mol NaOH (pH=10)	12h at 85 °C
Residue	Acid Extractable	Microwave assisted NaOH+HNO ₃ Digestion	

Table 8. Summary table for chemical speciation distributions for DLM, Omega, and Royal Scott sludge samples.

Step	Speciation Form	DLM		Omega		Royal Scott
		+63 micron	-63 micron	+63 micron	-63 micron	-63 micron
S1	Ion Exchangeable	0.05	0.07	0.04	0.08	0.38
S2	Bound to Carbonates	50.73	64.08	13.73	22.59	35.41
S3	Bound to Iron and Manganese Oxides	48.21	34.89	44.65	52.44	62.82
S4	Organic Matters	0.71	0.43	0.05	0.02	0.06
Residue	Acid Extractable	0.31	0.54	41.52	24.86	1.33
Total		100	100	100	100	100

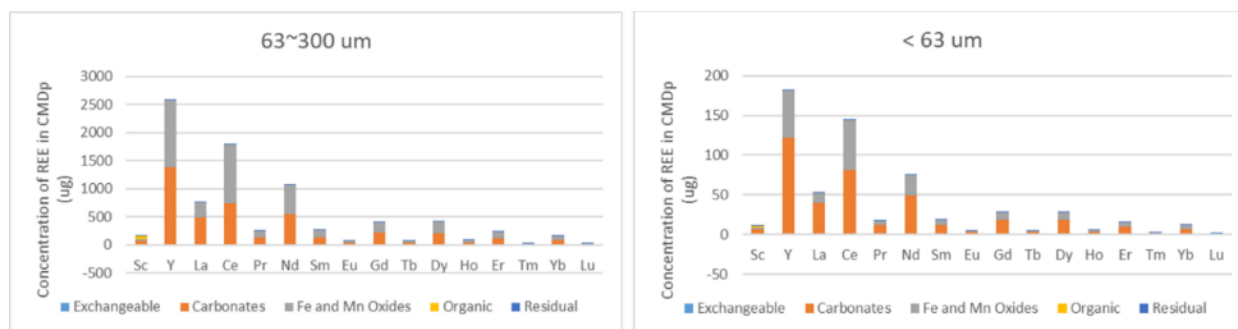


Figure 21. Rare earth elemental concentration in exchangeable, carbonates, iron and manganese oxides, organic, and crystalline materials for DLM AMDp with size fractions -63 and +63 micron.

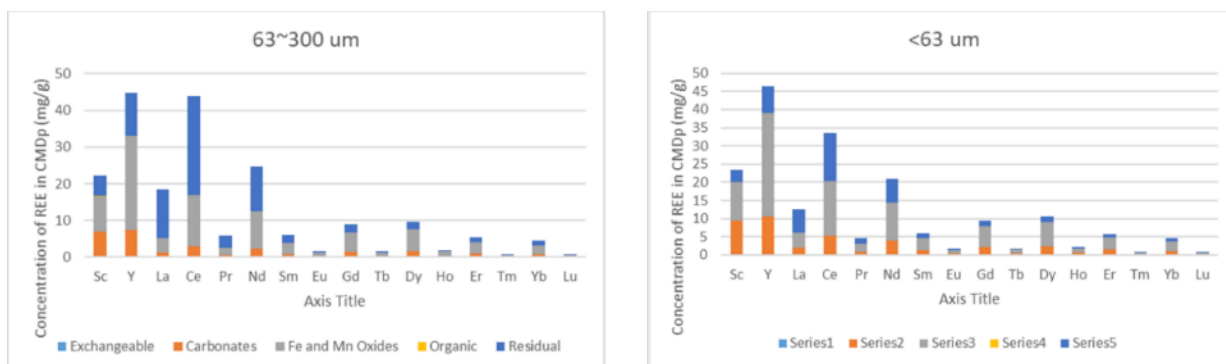


Figure 22. Rare earth elemental concentration in exchangeable, carbonates, iron and manganese oxides, organic, and crystalline materials for Omega AMDp with size fractions -63 and +63 micron.

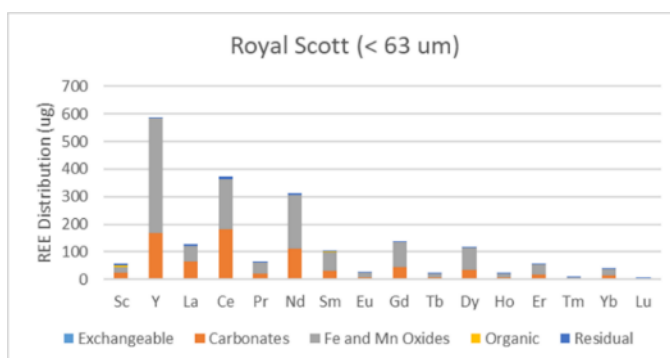


Figure 23. Rare earth elemental concentration in exchangeable, carbonates, iron and manganese oxides, organic, and crystalline materials for Royal Scott AMDp with size fractions -63 micron.

Leaching Optimization

Based on the findings from the REE characterization work, several methods were evaluated to improve leach recovery while maximizing leach selectivity and minimizing leaching cost. Efforts focused on two approaches utilizing various leaching additives: (1) dispersive liberation + ion exchange and (2) increased iron oxide solubility. All tests were conducted at the laboratory scale (approximately 0.5 to 1 L) using the Omega sludge sample. Overall, changes showed that leaching additives may enhance leachability in some conditions, but the most viable economic route will likely be simple acid leaching with no additives.

PLS Preparation Using Flocculants and Coagulants

In order to mitigate crud formation in the SX circuit, a clear PLS free of particulate material is required. In this task, particulate removal using sequential coagulation and flocculation was evaluated. Two chemicals, AQ200 and AQ590, were provided by Aquamark, and used as the coagulant and flocculent, respectively. Parameters studied include coagulant and flocculent dosage, mixing speed, and retention time.

Phase Disengagement

This test was used to determine the time needed to disengage the organic phase from the aqueous phase after mixing. Data from this test can be used to evaluate different diluents, determine whether an organic-continuous or aqueous-continuous mixture is ideal, and ultimately minimize organic losses during the SX process. Detailed procedures for the phase disengagement test were provided by the SX vendor. After fully mixing a solution with an O:A ratio of 1:1 for two minutes, the impeller is stopped, and the disengagement of the phases is visually recorded until full disengagement is achieved. By plotting percent disengagement versus time, a linear model was fit and used to analyze the rate of

disengagement. The process is then repeated for different diluents, evaluating both aqueous and organic-continuous conditions.

The diluents evaluated in this test include kerosene, which was used extensively in prior studies, as well as three specialty diluents, namely Elixore 205, Elixore 230 and Elixore 250 (supplied by Total Special Fluids, Inc. – Houston, TX).

In total, eight experimental conditions were tested: the four diluents in both aqueous-continuous and organic-continuous conditions. Each test iteration was video-recorded and later analyzed using video editing software to identify the 25 and 75 disengagement times. Linear fits were then constructed for these two data points. In addition, some tests were repeated to verify the experimental approach.

The full disengagement times (extrapolated from the linear fit) are then summarized in Figure 24. This data does show that kerosene has the quickest disengagement, with just over 20 seconds in the aqueous-continuous mixture and approximately 50 seconds in the organic-continuous mixture. Elixore 205 performs similarly in the aqueous continuous mixture and performs better than kerosene in the organic continuous mixture. Alternatively, Elixore 230 consistently showed the longest disengagement times, exceeding 100 seconds in some cases. Nevertheless, these disengagement times are substantially lower than the retention time in the bench-scale settler, which is estimated to be 7 minutes in normal operating conditions. Thus, this data confirms that settling rates of all diluents are sufficient to ensure proper operation in the SX system. Elixore 205 was selected for its similar properties to kerosene without the aromatic characteristics of kerosene.

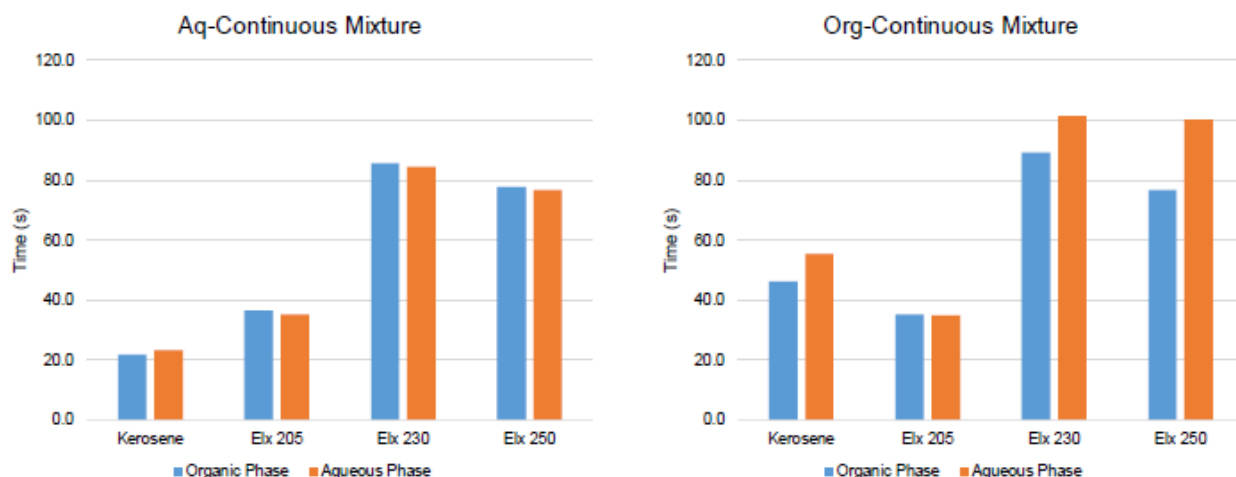


Figure 24. Full Disengagement times for four diluents in a sludge PLS.

Oxalic Acid Precipitation

In order to transfer the REEs from strip solution to a MREO, they must be precipitated out of the solution using oxalic acid. The first oxalic acid precipitation tests were performed with a synthetic strip solution/leachate containing four specific rare earth elements (Sc, Y, Nd, and Dy) and two gangue elements (Fe, Mg). The purpose of these tests was to begin characterizing the robustness of the oxalic acid precipitation process with respect to the concentration and distribution of common gangue elements. Subsequent tests used real strip solutions from the ALSX system including both chloride and nitrate media. Results showed the optimal path to optimize REE recovery and gangue rejection.

Task Completion Status

100% complete.

Task 6.0 Parametric Systems Testing

Approach

The Recipient will use the results from Subtasks 5.2 and 5.3 to generate a detailed test matrix using a statistical experimental design. The Recipient will conduct parametric systems tests over an eight (8) hour operating shift, with each experimental condition constituting a single shift. Experiments will be blocked by week and repeated to assess experimental error while mitigating the influence of covariates, such as AMDp heterogeneity and ambient environmental conditions. The Recipient will then conduct a 24-hour test as a final confirmation of system and process robustness.

The Recipient will repeat the entire experimental design for each of the three (3) AMDp sources, to prove the robustness of the system and to determine the specific experimental parameters needed for each feedstock.

The Recipient will analyze REE concentrate precipitates generated from these tests with Scanning Electron Microscopy and X-Ray Diffraction to determine the form and structure of the REEs in the final product.

The Recipient will then use a response surface methodology to analyze the results from the parametric systems, and identify the optimal conditions leading to the highest recovery and selectivity. Initial efforts will focus on technical success criteria (i.e. grade, mass recovery, and separation efficiency). The Recipient will later integrate economic factors (i.e. operating costs, value-based recovery) into the performance objectives as testing continues.

The Recipient will analyze, at a minimum, the following process variables for their effect on REE extraction efficiency and purity: (1) the influence of SX extractant type and concentration; (2) the influence of SX solvent type and ratio; (3) the influence of extracting and stripping acid type and pH; and (4) the number of extracting and stripping stages needed to reach the target purity level. The Recipient will also investigate pathways to remove non-target impurities and optimize the process with regards to separation efficiency, solvent recycling, and waste minimization.

Overview

Initial runs through the SX system with Omega and DLM AMDp produced significant amounts of crud that made tracking the flow of REE and system optimization significantly difficult, but MREO products were still created albeit with varying results. Fortunately, Royal Scott AMDp produced a negligible to no crud during its initial run and was selected for all future parametric tests. The results from these tests improved the researchers' fundamental understanding of the SX system and AMDp as a source of REE. Results include the selection of different scrubbing agents, the addition of an acid wash segment, and the differences between different stripping agents. Future tests evaluated the steady-state condition of the system as well as time to reach steady-state. Lastly, parametric tests investigated the precipitation process that transfers the REEs from the stripping solution produced by the SX system into a MREO product.

Results and Discussion

Analysis of Acid Leaching System

Initial full-scale SX runs were completed for each feedstock to establish a baseline for all operating conditions. The tests were conducted on DLM, Omega, and Royal Scott AMDp. Throughout this testing, multiple obstacles were encountered; nevertheless, the testing runs were completed and REE products were produced from all three feedstocks. Remarkably, all three feedstocks produced REE products during the initial testing regime that well exceeded the overall goal of a 2% MREO. Each step of the full-scale testing will be described in further detail below.

First, the acid leaching process was used on the AMDp to create a pregnant leach solution (PLS). In this process, the AMDp is combined with water and nitric acid to produce a solution with a very low pH. After filtration, the pH is again adjusted to reject as many gangue metals as possible. Finally, this product is filtered to remove any fines that may be harmful to the solvent extraction process.

Analysis of Solvent Extraction System

Next, a total of 20 mixer-setters were set up to perform four solvent extraction operations. Five units were dedicated to each operation and the unit was operated in eight-hour shifts over the course of a week or until the PLS was exhausted. All advance O:A ratios were maintained constantly between the different test runs and mixer O:A ratios were maintained at between 1.5:1 and 1:1.5. Results from these baseline tests will be used to evaluate the effects of parametric changes as the testing and optimization of the SX circuit proceeds.

During these initial parametric tests, two of the feedstocks (DLM and Omega) caused considerable third-phase formation as seen in Figure 25. This third phase, also called crud, causes significant problems in the SX circuit as noted by Ritcey (1980). Some of the issues encountered during the initial testing runs included difficulties in obtaining mass balances, organic loss to the aqueous streams, and blockages in the SX system. Unfortunately, the generation of crud makes parametric testing with these feedstocks difficult to impossible to complete. These two feedstocks (DLM and Omega) underwent further exploratory testing to generate a feedstock that will allow the SX plant to operate at steady-state.



Figure 25. Picture of SX units running three different feedstocks.

*Notice the crud (third phase) formation in the DLM and Omega SX units.

In contrast, the Royal Scott feedstock did not produce a detrimental quantity of crud. When the PLS of these three feedstocks is compared, it was evident that the Fe content in the Royal Scott PLS was considerably lower than in the other two. The current hypothesis is that Fe will reach a Limiting Organic Concentration (LOC) where the Fe will start to precipitate and create a nucleus that allows for crud formation (Chiarizia et al., 2007). As a result, the Royal Scott PLS was used exclusively for parametric testing and optimization of the SX circuits.

After each baseline parametric test, the strip raffinate was subjected to a precipitation procedure to collect the REEs concentrated through the ALSX process. This multi-step procedure involved precipitating the REEs from the HCl solution using oxalic acid as documented by Chi (1999). After precipitation, the solid precipitate is subjected to a series of washing and drying steps to convert the oxalates to oxides. Results from the DLM and Omega feedstocks are shown in Table 9.

Table 9. Results of REE precipitation from SX strip solution.

DLM REO Product			Omega REO Product		
Element	(mg/kg)	Element (mg/kg)	Element (mg/kg)	Element (mg/kg)	Element (mg/kg)
Sc	740.45	Al	17,596.31	Sc	-
Y	423,961.42	Ca	670.85	Y	211,688.90
La	5,578.77	Co	34.46	La	9,405.20
Ce	108,052.37	Fe	59,229.92	Ce	49,675.33
Pr	8,218.83	Mg	104.41	Pr	6,984.96
Nd	39,093.42	Mn	294.21	Nd	33,959.51
Sm	19,149.20	Na	-	Sm	14,461.78
Eu	6,025.82	Si	2,785.19	Eu	4,330.29
Gd	37,269.40	SO4	-	Gd	26,422.43
Tb	10,983.59	Cl	-	Tb	5,864.41
Dy	73,637.85	TMM	80,715.35	Dy	38,232.28
Ho	14,861.22	% MM Ox	8.1%	Ho	7,864.76
Er	38,392.18	%Tot ions	9.1%	Er	23,549.63
Tm	3,786.34			Tm	3,484.45
Yb	11,007.34	Th	0.09	Yb	18,696.47
Lu	1,021.88	U	-	Lu	2,380.85
TREO	801,780.09	Th+U	0.09	TREO	457,001.23
Total Oxides			Total Oxides	701,641.83	70.2%
Unaccounted			Unaccounted	298,358.17	29.8%
LREE			LREE	118,817.06	26.0%
HREE			HREE	338,184.17	74.0%
TREE			TREE	457,001.23	45.7%
TMM			TMM	244,640.25	24.5%
T_Th+U			TAc	0.35	0.0%

The DLM and Omega feedstocks both generated a product well above the 2% target, despite the crud formation that caused operational problems. As shown above, DLM and Omega produced a rare earth oxide product in excess of 80% and 45%, respectively. The large variation in grade between the two assays can primarily be attributed to the composition of the gangue metals in the stripped raffinate. While oxalic acid precipitation rejects iron and most aluminum, it has an affinity for Ca.

Eight subsequent batches of PLS were created using the Royal Scott feedstock. Of the eight batches, six were used for parametric testing in the ALSX unit and two were used in the Automated ALSX (Auto-ALSX) system. The analytical analysis of the PLS created during the quarter is shown in Table 10.

Table 10. Analytical results from leaching operations.

PLS Sample	1	2	3	4	5	6	7	8
Run #	Run # 2/3	Run # 2/3	Run #4	Run #5 Auto Shakedown	Run #6	AUTO Run #1	Run #7	Run #8
Major Ions (mg/L)								
Al	2,548.01	2,490.35	2,561.80	2,556.16	2,443.44	2,457.54	2,299.95	2,655.74
Ca	598.30	590.10	668.71	658.34	615.89	660.57	603.87	758.57
Co	20.08	19.21	20.08	20.86	20.30	19.29	18.43	24.89
Fe	3.90	5.45	6.10	4.98	7.02	5.28	4.33	4.94
Mg	2,071.69	1,982.83	1,937.21	2,184.34	2,101.03	2,202.42	2,064.72	2,581.44
Mn	691.66	622.20	645.44	664.38	644.42	644.25	614.37	679.19
Na	10,116.54	9,619.27	8,097.32	8,718.67	9,453.17	9,785.50	9,014.34	10,355.42
Ni							38.63	51.12
Si	59.19	82.46	106.41	76.11	69.16	85.06	94.50	61.21
Zn							85.24	108.73
SO4	1,172.00	1,179.83	935.00	1,065.75	1,006.20	1,104.99	949.17	1,094.84
Cl	4.77	8.67	4.97	4.57	3.14	3.89	4.27	4.54
REEs / Actinides (µg/L)								
Sc	127.18	91.17	144.21	119.30	133.92	112.77	93.43	113.50
Y	14,805.39	10,748.95	11,482.10	12,620.21	11,683.39	11,702.61	10,171.71	14,849.10
La	3,163.87	2,220.82	2,321.16	2,597.98	2,393.31	2,411.48	2,146.30	2,992.17
Ce	8,912.46	6,467.22	6,549.26	7,360.81	6,680.00	6,712.39	6,051.86	8,455.00
Pr	1,411.37	1,051.55	1,240.97	1,225.70	1,087.63	1,095.09	974.16	1,387.55
Nd	7,151.18	5,448.04	5,543.47	6,189.49	5,632.09	5,590.97	5,160.64	7,150.53
Sm	2,286.26	1,777.17	1,787.70	1,990.08	1,771.62	1,778.91	1,652.04	2,318.60
Eu	588.83	446.71	541.77	517.42	441.54	446.87	438.39	589.41
Gd	3,376.57	2,567.93	2,656.87	2,941.66	2,601.94	2,589.76	2,415.11	3,466.47
Tb	508.30	386.66	484.26	463.20	390.87	398.19	363.14	568.14
Dy	2,843.46	2,102.36	2,169.98	2,428.03	2,120.66	2,125.61	1,995.76	2,854.13
Ho	512.74	384.89	471.44	451.58	383.79	387.90	354.92	508.17
Er	1,330.97	982.57	1,210.79	1,160.30	968.18	983.77	908.26	1,332.29
Tm	167.03	126.85	151.07	145.15	119.13	122.44	112.90	162.08
Yb	910.54	673.66	820.36	789.42	667.08	673.33	638.35	886.45
Lu	132.15	98.67	123.16	114.69	96.44	96.66	91.79	127.32
Th	<0.007	0.92	1.42	0.73	<0.007	0.06	<0.007	<0.007
U	263.53	243.30	321.02	277.17	288.76	271.92	199.37	293.34
TOTALS								
TREE	48,228.30	35,575.21	37,698.57	41,115.01	37,171.58	37,228.74	33,568.76	47,760.89
HREE	24,714.33	18,163.71	19,714.23	21,233.54	19,165.39	19,193.04	17,145.37	24,867.64
LREE	23,513.98	17,411.51	17,984.34	19,881.47	18,006.19	18,035.70	16,423.39	22,893.25
CREE	25,897.16	19,132.71	20,221.58	22,218.34	20,268.55	20,264.26	18,129.65	26,011.30

During baseline testing, the researchers observed that a portion of the organic was reporting to the saponification raffinate and not recycling back to the organic tank. A literature review indicated that other REE SX processes utilized an additional stage to separate the organic and aqueous phases as indicated by Ritcey and Wong (1985). As a result, an additional circuit, "Acid Wash," was implemented directly after the saponification stage. This addition resolved the misreporting of the organic phase to the aqueous raffinate tank. Furthermore, the concentration of saponification reagent was changed from 2 M sodium hydroxide to 2 M ammonium hydroxide. The combination of reagent substitution and the additional stage greatly improved the recovery of organic to the organic recycle tank.

Parametric SX runs were completed for 6 of the PLS batches using a modified ALSX flowsheet. In this operating scheme, 5 units were dedicated to each operation, except for the new operation located at the end of the SX run termed "Acid Wash," which used three mixer-settlers. Parametric tests were conducted under the same conditions as the previous parametric tests.

Analysis of Precipitation System

Precipitation Testing

During solvent extraction, the REEs are concentrated in the stripped raffinate. In order to convert the REEs from ion form to oxides, a precipitation procedure is required.

Using this procedure, a 61.8% MREO product was generated. This was accomplished by adding anhydrous oxalic acid to stripped concentrate. Next, the pH of the solution was upwardly adjusted with 50% NaOH. After precipitation, the solid and liquid fractions were separated. The precipitated solid consisted of REEs oxalates and other major ions. To convert the oxalates to oxides, the solid portion was calcined at 750 degrees Celsius. This step upgraded the grade of the solid from 5.8% to 10.7% REEs on a dry whole metal basis. Furthermore, the major contaminant in the REE oxide product was Ca.

To further concentrate the REO product, a water washing step was proposed to remove additional contaminants. After successive washes using DI water, the Ca remained a major contaminant. Next, an acid wash step was proposed to further reduce the concentration of Ca. This wash was accomplished by placing the REO product in 1 L of DI water and adding nitric acid, dropwise. At this stage the solution was again filtered and dried. The resulting grade of the washing steps successfully increased the REO concentration from 10.6% to 32.9% and 52.9%.

Finally, the analysis of the Acid-Wash product was used to convert the whole metal analysis to an oxide basis. Table 11 shows the oxide conversion calculations. As shown, the final grade of the REO product is estimated to contain 62% rare earth oxides. However, a significant portion of the REO product (23%) contains ions that are not accounted for. This omission is concerning, and further testing is proposed to evaluate the source of this error. As a result, future testing during the next quarter will focus on parametric testing of the precipitation module to identify an optimal precipitation procedure.

Table 11. Metal to oxide conversion calculations.

Analyte	Acid-Wash Product Assay	Acid-Wash Product Mass	Oxide Ratio	Oxide Based Assay	Oxide Product Mass
Mass (g)	13.8				
Major Ions	(mg/kg)	(g)		(mg/kg)	(g)
Al	12,216.35	0.17	0.53	23,075.34	0.32
Ca	76,539.70	1.06	0.71	107,155.58	1.48
Co	2.83	0.00	0.79	3.60	0.00
Fe	747.72	0.01	0.70	1,068.17	0.01
Mg	84.87	0.00	0.60	141.46	0.00
Mn	13,946.67	0.19	0.77	18,003.88	0.25
Ni	-	-	0.79	-	-
Si	673.15	0.01	0.47	1,442.47	0.02
S	-	-	0.33	-	-
Zn	-	-	0.80	-	-
REEs	(mg/kg)	(g)			(g)
Sc	-	-	0.65	-	-
Y	173,857.99	2.40	0.87	198,804.73	2.74
La	24,773.21	0.34	0.85	29,053.37	0.40
Ce	95,649.61	1.32	0.81	117,493.66	1.62
Pr	14,605.79	0.20	0.83	17,646.29	0.24
Nd	74,810.91	1.03	0.86	87,258.65	1.20
Sm	25,531.83	0.35	0.86	29,607.14	0.41
Eu	6,595.16	0.09	0.86	7,636.64	0.11
Gd	36,883.24	0.51	0.87	42,512.48	0.59
Tb	6,018.63	0.08	0.85	7,078.98	0.10
Dy	33,200.82	0.46	0.87	38,104.32	0.53
Ho	6,098.79	0.08	0.87	6,986.26	0.10
Er	16,236.05	0.22	0.87	18,565.75	0.26
Tm	2,152.52	0.03	0.88	2,458.33	0.03
Yb	11,866.55	0.16	0.88	13,512.39	0.19
Lu	1,652.33	0.02	0.88	1,878.97	0.03
Actinides	(mg/kg)	(g)			(g)
Th	53.45	0.00	0.94	57.13	0.00
U	39.80	0.00	0.91	43.81	0.00
Summary	mg/kg	(%)		mg/kg	(%)
TMM	104,211	10%		150,890	15%
TREE	529,933	53%		618,598	62%
TACT	93	0%		101	0%
Total Ions	634,238	63%		769,589	77%
REE Distribution					
TREE	529,933	53%		618,598	62%
LREE	241,967	46%		288,696	47%
HREE	287,967	54%		329,902	53%
CREE	294,484	56%		338,883	55%
Residual					
Unaccounted Ions	365,762	37%		230,411	23%

The results from multiple precipitations indicated there were additional parameters that have a major impact on REE product quality that were unforeseen during initial planning. While the majority of the test work has focused on SX parameters, it was discovered that the precipitation stage has a much greater impact on overall grade of the REO product. As a result, several parameters were explored.

Effect of pH adjustment reagent

At the first stage of precipitation, a precipitation reagent is used in conjunction with NaOH to raise the pH of the strip solution. At this point, rare earth oxalates and other compounds precipitate from solution. Previously, many of the products acquired after the initial precipitation required a consecutive stage consisting of a water wash to remove sodium salts from the precipitate. As a result, ammonium hydroxide was used in place of the sodium hydroxide. The resulting oxalate precipitate was of a higher-

grade REE grade and virtually devoid of sodium salts. Additionally, it was shown that the water wash step was no longer required before calcination.

Furthermore, another beneficial factor of using ammonium hydroxide was observed. Previously, when using NaOH as the pH adjustment reagent, the time to bring the pH up to the desired level would often exceed several hours. This was caused by elevated temperatures, often in excess of 80 degrees Celsius, observed in the stripping solution after the addition of NaOH. In fact, several tests were conducted in an ice bath to minimize the amount of time required to precipitate the REE oxalates. Alternatively, the use of NH_4OH did not increase the temperature of the sample to a degree that required external cooling methods.

Effect of Calcination Temperature

Previously, the calcination of the rare earth oxalates was conducted in accordance with literature research as described by many authors including Chi and Xu, 1999 and Hoogerstraete et al., 2014 with the results shown in Table 11 previously.

Unfortunately, this total accounting for ions seldom exceeded 77%. This anomaly indicated that the metals were not fully oxidized. As a result, a thermogravimetric analysis (TGA) was used to explore the optimal calcination temperature. Figure 26 is representative of results from the TGA.

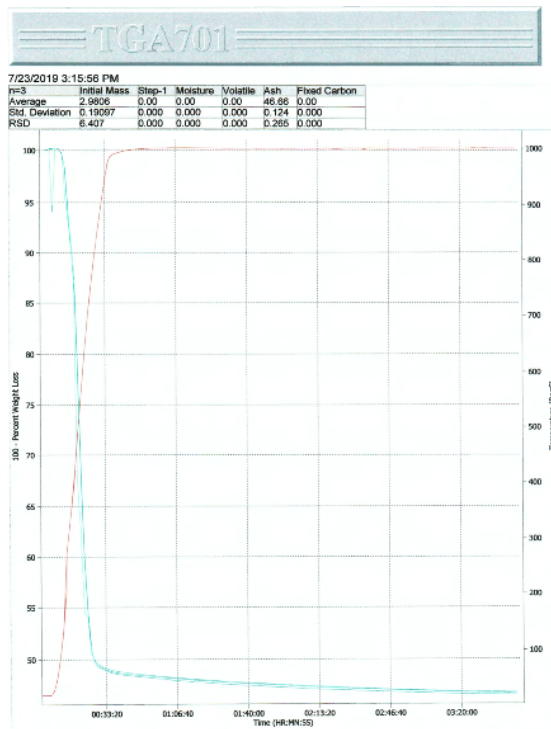


Figure 26. Example of TGA results for optimal calcination temperature.

Results of this testing indicated that the previous calcination temperature of 750 degrees Celsius was too low. By increasing the temperature to 1000 degrees Celsius, a more thorough accounting of the REO product ions was achieved. This is shown in Table 12. Additionally, these results indicated that a more thorough analysis of the calcination process is required for optimization.

Additionally, Table 12 also shows the most concentrated REO product achieved during parametric testing. This was accomplished by using mild acid scrubbing to remove the majority of the calcium while sacrificing some of the less desirable LREEs. The result from parametric test #5 also had a very high

distribution of the HREEs in the final product. Figure 27 shows the overall product distribution of the 86% MREO product.

Given that this is the highest-grade product achieved to date, a sample has been retained for submittal to DOE. Pending the production of any higher-grade products, this sample will be submitted at the end of the project.

Table 12. 86% REO product calcined at 1000 degrees C.

Analyte	Acid-Wash Product Assay	Acid-Wash Product Mass	Oxide Ratio	Oxide Based Assay	Oxide Product Mass
Mass (g)	4.1722				
Major Ions	(mg/kg)	(g)		(mg/kg)	(g)
Al	16,835.85	0.07	0.53	31,801.06	0.13
Ca	3,615.45	0.02	0.71	5,061.63	0.02
Co	2.55	0.00	0.79	3.25	0.00
Fe	-	-	0.70	-	-
Mg	-	-	0.60	-	-
Mn	91.70	0.00	0.77	118.38	0.00
Ni	60.84	0.00	0.79	77.42	0.00
Si	594.70	0.00	0.47	1,274.36	0.01
S	-	-	0.33	-	-
Zn	92.80	0.00	0.80	115.52	0.00
REEs	(mg/kg)	(g)			(g)
Sc	-	-	0.65	-	-
Y	310,291.64	1.29	0.87	354,815.13	1.48
La	7,133.98	0.03	0.85	8,366.55	0.03
Ce	58,018.95	0.24	0.81	71,269.06	0.30
Pr	11,020.15	0.05	0.83	13,314.23	0.06
Nd	57,362.05	0.24	0.86	66,906.48	0.28
Sm	50,838.91	0.21	0.86	58,953.66	0.25
Eu	16,188.93	0.07	0.86	18,745.41	0.08
Gd	96,221.55	0.40	0.87	110,907.19	0.46
Tb	14,442.38	0.06	0.85	16,986.82	0.07
Dy	68,636.82	0.29	0.87	78,773.95	0.33
Ho	11,893.90	0.05	0.87	13,624.65	0.06
Er	25,420.02	0.11	0.87	29,067.52	0.12
Tm	2,492.58	0.01	0.88	2,846.70	0.01
Yb	9,364.32	0.04	0.88	10,663.12	0.04
Lu	1,140.74	0.00	0.88	1,297.21	0.01
Actinides	(mg/kg)	(g)			(g)
Th	-	-	0.94	-	-
U	-	-	0.91	-	-
Summary	mg/kg	(%)		mg/kg	(%)
TMM	21,294	2%		38,452	4%
TREE	740,467	74%		856,538	86%
TACT	-	0%		-	0%
Total Ions	761,761	76%		894,989	89%
REE Distribution					
TREE	740,467	74%		856,538	86%
LREE	200,563	27%		237,555	28%
HREE	539,904	73%		618,982	72%
CREE	466,922	63%		536,228	63%
Residual					
Unaccounted Ions	238,239	24%		105,011	11%

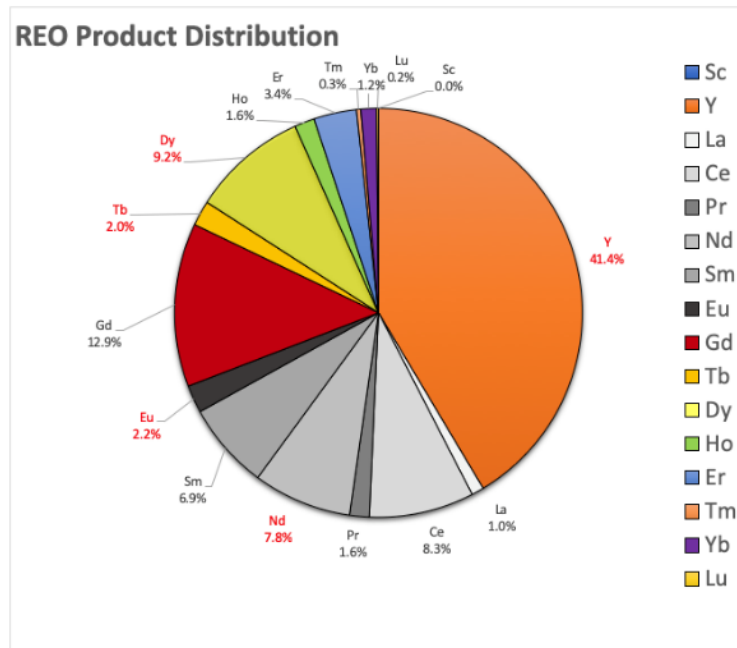


Figure 27. Distribution of REEs in 86% MREO product.

Task Completion Status

100% complete.

Task 7.0 Validation Testing

Approach

After completion of Task 6.0, the Recipient will repeat a select number of experimental runs to validate the complete bench-scale REE extraction system performance. The Recipient will repeat these tests at least three (3) times, and retain the product generated during these tests to fulfill the Task 2.0 requirement, which is provide split samples to NETL. The Recipient will also collect enough feed, product, and intermediate samples during the validation tests to construct a fully closed system mass balance that will be used in Tasks 8.0, 10.0, and 13.0.

Overview

Three validation test runs were completed over a continuous run period of 104 hours. Data showed considerable agreement between the three test runs, particularly with respect to extraction recovery, stripping recovery, and gangue rejection. The first test was found to exhibit the best overall performance. Recovery values for this test included: Extraction 100% (extracted to organic), Scrubbing: 79.8% (retained in organic), Stripping: 31.92% (stripped to aqueous), Saponification: 82.34% (retained in organic), and acid wash: 99.97% (retained in organic), suggesting an overall recovery of 46% to the strip solution and 37% to the scrub solution. The results vary widely element to element, with HREEs generally having higher recovery values to the strip solution (67.3%), with the LREE having much higher recovery to the scrub solution (up to 91%). Results also show a notable deportment of HREEs to the saponification product, as high as 73% in one test.

Results and Discussion

The validation test was conducted by first generating a large quantity of pregnant leach solution (PLS) to ensure continuous plant operation for 104 hours in total. For the validation test, Royal Scott was selected as the feed solution, and the leaching conditions matched those used in the parametric test

series described under Task 6. The PLS was sampled five times over the course of the run to monitor any changes. No significant changes were observed, and the mean ICP-MS assay values for REES and major metals are displayed in Figure 28.

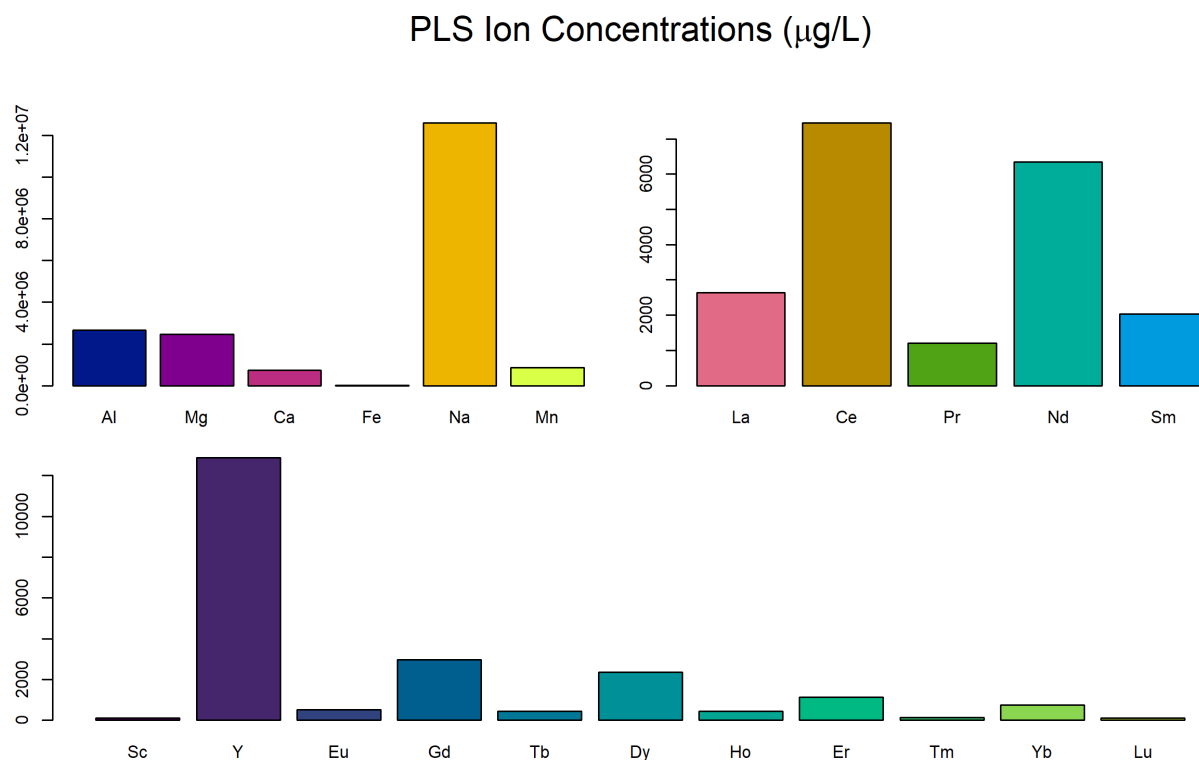


Figure 28. Mean PLS ion concentrations for the validation test.

Like the parametric tests, the SX circuit in the validation tests was configured to include three to five mixer settlers in each stage and the optimal chemical conditions. These values were selected based on the cumulative knowledge gained during parametric testing.

During the course of the test, samples were taken in one-hour intervals for the first 24 hours, and then in two-hour intervals for the rest of the duration of the test. At each time interval, samples were taken of the organic and aqueous outputs of the extraction, scrubbing, stripping, saponification, and acid wash stages. Samples were also taken from the organic diluent feed tank, making 11 samples for each time step.

After running the test, aqueous samples were sent directly for ICP-MS analysis, and organic samples underwent microwave digestion so that the contents of the organic liquid could be dissolved in an aqueous solution for ICP-MS. The concentrations were then plotted over time to determine when the plant was at steady state, and the data was split into three intervals to constitute three test runs for comparative purposes. Element concentrations were averaged over each interval. Average TREE, LREE, HREE, and gangue plots for each test are included in this section.

Figures 29 and 30 show the observed concentrations for REEs and major gangue metals from the first of the three validation test runs. Overall, results showed considerable agreement between the test runs, verifying the operability and robustness of the ALSX system.

With regard to the REEs, the tests confirm the potential to effectively extract REEs into the organic phase. In all three tests, the aqueous output from the extraction stage (i.e. the raffinate) had non-

detectable REE concentrations but moderate gangue concentrations, particularly Na, Al and Mg. Some LREEs were extracted in the scrubbing stage; however, the largest REE concentration (particularly HREE concentration) consistently appeared in the stripping stage. The majority of the gangue elements were rejected into raffinate; however, Al tended to persist through to the final strip solution. Earlier testing in Task 5.3 showed that oxalic acid has relatively high selectivity of REEs over Al, and thus, high grade products are anticipated from this test. The concentrations in the saponification stage output were subject to the highest variability, likely owing the soap formation that precluded the ability to routinely recover a representative sample. The aqueous concentration data also suggests that very little REE mass was lost in the acid washing stage.

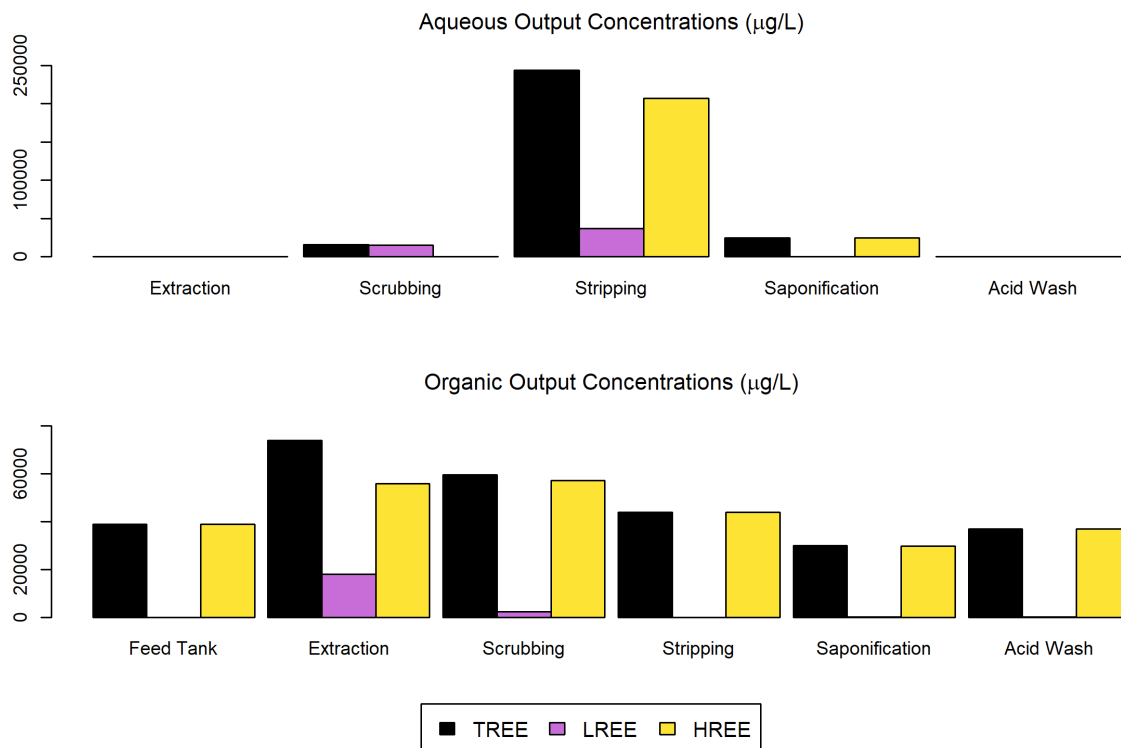


Figure 29. Mean TREE concentrations found in first validation test.

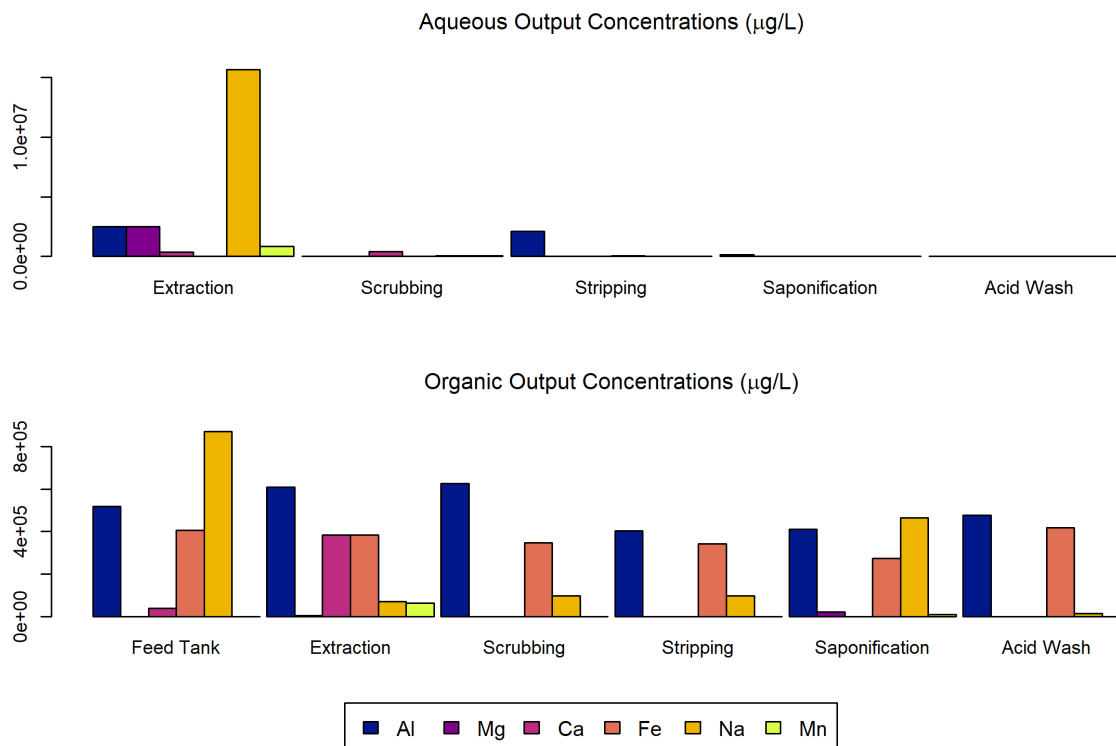


Figure 30. Mean Gangue concentrations found in first validation test.

For each of the three data sets, a mass balance was conducted by adjusting each assay under a conservation of mass flow rate constraint while minimizing the sum of squared percent deviation from the observed values. After the mass balance, recovery of each element to each aqueous output was calculated. TREE, LREE, and HREE recoveries are displayed in Table 13 below, while Table 14 shows similar data for select major metals. In these cases, unit recovery values have been defined as the following:

- Extraction: Mass fraction in the PLS that is extracted to the organic phase
- Scrubbing: Mass fraction in the loaded organic that is retained in the organic through scrubbing
- Stripping: Mass fraction in the scrubbed organic that is extracted to the strip solution
- Saponification: Mass fraction in the stripped organic that is retained in the organic
- Acid Wash: Mass fraction in the saponified organic that is retained in the organic

Table 13. Mass Balanced Recovery Values for REEs Derived from Validation Testing.

Stage	Test 1			Test 2			Test 3		
	LREE	HREE	TREE	LREE	HREE	TREE	LREE	HREE	TREE
Extraction	99.94	99.96	99.95	100.00	99.98	99.99	100.00	99.99	99.99
Scrubbing	18.47	99.26	79.78	8.76	98.64	79.49	14.72	99.08	79.40
Stripping	100	27.89	31.92	88.72	9.92	11.78	99.72	20.65	24.07
Saponification	ND	82.34	82.34	15.95	66.22	66.07	5.42	73.33	73.32
Acid Wash	ND	99.97	99.97	97.85	99.97	99.97	ND	99.99	99.99

ND: Not detected. Values in the feed stream were determined to be below <1ppt.

Table 14. Mass Balanced Recovery Values for Gangue Elements Derived from Validation Testing.

Stage	Test 1			Test 2			Test 3		
	Al	Ca	Fe	Al	Ca	Fe	Al	Ca	Fe
Extraction	9.09	52.78	91.97	5.40	55.48	52.01	7.75	60.80	86.05
Scrubbing	98.87	2.18	99.95	98.99	0	99.95	100.00	3.23	99.96
Stripping	31.89	38.16	1.51	13.31	ND	0.58	21.73	24.87	1.57
Saponification	94.59	100.00	99.86	93.41	ND	99.78	90.54	100.00	99.66
Acid Wash	98.99	42.95	99.99	99.08	ND	100.00	100.00	0.00	99.99

During the solvent extraction validation tests, two buckets of strip solution were generated and stored. Each bucket was later treated with oxalic acid using the optimal batch-wise precipitation and calcination process developed under Task 6. The full elemental analysis for these products is shown in Tables 15 and 16. Together, the products represent more than 7.7 grams of grade mixed rare earth product with TREO assays of 91.25% and 60.41%, respectively. The 91.25% product represents the highest-grade product produced from this study. The products are notably concentrated in HREE, particularly Y and Gd.

Table 15. Elemental Analysis MREO Product Generated from Validation Test 191113.

191113 Ox CAL PRECIP	Product Assay	Precipitate Mass	Oxide Ratio	Oxide Based Assay	Oxide Product Mass
Analyte					
Mass (g)	2.1122				
Major Ions	mg/Kg	g		mg/Kg	g
Al	22,780.71	0.05	0.53	42,982.47	0.09
Ca	-	-	0.71	-	-
Co	7.35	0.00	0.79	9.31	0.00
Fe	41.96	0.00	0.70	59.94	0.00
Mg	-	-	0.60	-	-
Mn	99.18	0.00	0.77	128.81	0.00
Ni	125.01	0.00	0.47	265.97	0.00
Si	278.18	0.00	0.33	842.95	0.00
Zn	29.10	0.00	0.80	36.38	0.00
S	200.42	0.00	0.33	607.32	0.00
REEs					
Sc	-	-	0.65	-	-
Y	306,374.36	0.65	0.87	352,154.44	0.74
La	386.64	0.00	0.85	454.87	0.00
Ce	28,321.44	0.06	0.81	34,964.74	0.07
Pr	7,350.41	0.02	0.83	8,855.91	0.02
Nd	39,947.15	0.08	0.86	46,450.17	0.10
Sm	63,160.99	0.13	0.86	73,443.02	0.16
Eu	20,159.15	0.04	0.86	23,440.87	0.05
Gd	118,876.50	0.25	0.87	136,639.66	0.29
Tb	18,004.02	0.04	0.85	21,181.20	0.04
Dy	77,185.18	0.16	0.87	88,718.60	0.19
Ho	12,874.00	0.03	0.87	14,797.70	0.03
Er	29,894.69	0.06	0.87	34,361.71	0.07
Tm	3,912.24	0.01	0.88	4,445.73	0.01
Yb	21,478.76	0.05	0.88	24,407.68	0.05
Lu	2,840.83	0.01	0.88	3,228.22	0.01
Actinides					
Th	-	-	0.94	-	-
U	1.59	-	0.91	-	-
Summary	mg/Kg	% of Product Mass		mg/Kg	% of Product Mass
TMM	23,561.90	2.36		44,933.15	4.49
TREE	750,766.37	75.08		867,544.53	86.75
TACT	1.59	0.00		0.00	0.00
Total Ions	774,329.86	77.43		912,477.67	91.25
REE Distribution	mg/Kg	% of TREE		mg/Kg	% of TREE
TREE	750,766.37			867,544.53	
LREE	159,325.78	21.22		187,609.59	21.63
HREE	591,440.59	78.78		679,934.94	78.37
CREE	441,510.71	58.81		508,504.41	58.61
Residual					
Unaccounted Ions	225,670.14	22.57		87,522.33	8.75

Table 16. Elemental Analysis MREO Product Generated from Validation Test 191114.

191114 Ox CAL PRECIP	Product Assay	Precipitate Mass	Oxide Ratio	Oxide Based Assay	Oxide Product Mass
Analyte					
Mass (g)	5.6311				
Major Ions	mg/Kg	g		mg/Kg	g
Al	12,296.92	0.03	0.53	23,201.74	0.05
Ca	214,633.21	-	0.71	-	-
Co	1.79	0.00	0.79	2.26	0.00
Fe	173.11	0.00	0.70	247.29	0.00
Mg	<	-	0.60	-	-
Mn	56.61	0.00	0.77	73.52	0.00
Ni	324.98	0.00	0.47	691.44	0.00
Si	368.30	0.00	0.33	1,116.05	0.00
Zn	46.50	0.00	0.80	58.12	0.00
S	212.89	0.00	0.33	645.12	0.00
REEs					
Sc	-	-	0.65	-	-
Y	131,336.19	0.28	0.87	150,961.14	0.32
La	9,585.87	0.02	0.85	11,277.49	0.02
Ce	81,272.73	0.17	0.81	100,336.70	0.21
Pr	14,395.16	0.03	0.83	17,343.56	0.04
Nd	76,288.59	0.16	0.86	88,707.67	0.19
Sm	38,285.99	0.08	0.86	44,518.59	0.09
Eu	10,800.62	0.02	0.86	12,558.86	0.03
Gd	64,067.31	0.14	0.87	73,640.59	0.16
Tb	8,255.40	0.02	0.85	9,712.24	0.02
Dy	33,945.44	0.07	0.87	39,017.74	0.08
Ho	5,365.63	0.01	0.87	6,167.39	0.01
Er	11,276.40	0.02	0.87	12,961.38	0.03
Tm	1,312.58	0.00	0.88	1,491.57	0.00
Yb	7,265.80	0.02	0.88	8,256.59	0.02
Lu	1,005.24	0.00	0.88	1,142.32	0.00
Actinides					
Th	-	-	0.94	-	-
U	1.59	-	0.91	-	-
Summary	mg/Kg	% of Product Mass		mg/Kg	% of Product Mass
TMM	228,114.30	22.81		26,035.56	2.60
TREE	494,458.94	49.45		578,093.82	57.81
TACT	1.59	0.00		0.00	0.00
Total Ions	722,574.83	72.26		604,129.38	60.41
REE Distribution	mg/Kg	% of TREE		mg/Kg	% of TREE
TREE	494,458.94			578,093.82	
LREE	230,628.95	46.64		274,742.87	47.53
HREE	263,829.99	53.36		303,350.95	52.47
CREE	249,825.62	50.53		288,398.79	49.89
Residual	mg/Kg	% of Product Mass		mg/Kg	% of Product Mass
Unaccounted Ions	277,425.17	27.74		395,870.62	39.59

Task Completion Status

100% complete.

Task 8.0 System Design Optimization

Approach

The Recipient will use the data obtained during the parametric (Task 6.0) and validation testing (Task 7.0) campaigns to generate detailed process models using standard mineral-industry approaches. The Recipient will integrate these models into an in-house or commercial process flowsheet simulation software to evaluate flowsheet alternatives and investigate options for flowsheet reduction/intensification.

The Recipient will also use a linear circuit analysis approach to perform an overall system analysis to evaluate unit sensitivity and uncertainty propagation within the circuit. The Recipient will use this analysis to identify how each separation unit contributes to overall recovery and selectivity; and to specify sub-systems that strongly influence overall system performance.

Overview

Several techniques were deployed to model and optimize process performance. These techniques assisted in the interpretation of the laboratory data and in the development of the techno-economic analysis (TEA).

Results and Discussion

Several modeling tools were developed during the project and used to analyze the process performance, namely:

1. Material flow balance for TEA
2. Steady state estimation by autoregressive Bayesian process modeling
3. Oxalic acid consumption modeling by solution chemistry
4. SX Circuit Sensitivity analysis

The development and utilization of these tools is described in further detail below.

Material Flow Balance Tool

To assess the steady-state circuit performance for a commercial implementation of the project technology, an Excel-based mass balancing routine was developed and deployed. A screenshot of this tool is shown in Figure 31. This spreadsheet is integrated into the TEA worksheet described under Tasks 10 and 13 to ensure that the downstream capital and operating costs are directly influenced by the technical parameters influence material flow.

The material balances were largely based on the experimental data described in earlier parts of the report. This experimental data was used to determine the unit-by-unit component recovery values for each relevant unit operation in the circuit. From this data, the total material balance was then determined using a direct calculation approach known as Linear Circuit Analysis (see: Noble and Luttrell, 2014). In this method, all process streams are solved analytically a priori, and as a result, no spreadsheet iteration is needed despite the prominence of recycle loops. The direct solution ensures that the steady-state mass balance condition (i.e. process input = process output) is met for all individual process modules and the circuit as a whole. For example, given the circuit configuration shown below, the recovery to the MREO product can be directly calculated from the component recoveries by the following equation:

where P1 is the leaching recovery, P2 is the SX extraction recovery, P3 is the retention through the scrubbing stage, P4 is the stripping recovery, P5 is the precipitation recovery, P6 is the retention through the saponification stage, and P7 is the recycle of raffinate. Note acid washing was not included, since experimental data repeatedly showed no metal loss through this stage.



Steady state estimation by Autoregressive Bayesian Inference

Modeling a pilot SX system is complicated, since SX systems require long retention times and complex recirculating loops (Baird 1991). Frequently, elemental concentrations are plotted over time, and steady state is determined by eye. However, this subjective characterization of the data can lead to problems in performance comparisons. One individual may pick a different steady state concentration than another, and, therefore, it is entirely possible different individuals come to different conclusions based on the same data.

To mitigate this issue, an objective means of determining steady state was developed and evaluated during this project. Unfortunately, resource restrictions and computation requirements limited the full application of this method for the complete data set; however, the method was evaluated on a subset of the validation data collected under Task 7.

The model used to quantify steady state is an autoregressive (AR) time series model. An AR model makes future states dependent on past states (Shumway 2017). For example, an AR model for REE concentrations in an SX plant makes a future concentration dependent on the concentration from the prior time step. To illustrate the method, an example of an AR time series, which includes the addition of a constant value (μ), and random perturbations and noise (ϵ) is:

$$y_t = \phi y_{t-1} + \mu + \epsilon$$

where t is a discrete time step index in one-hour intervals. Examples of this model are shown in Figure 32 below. If $|\phi| < 1$ the behavior of the model is predictable, as illustrated in Figure 32, and the steady state can be calculated as:

$$\frac{\mu}{1 - \phi}$$

An important converse to the previous statement, if $|\phi| \geq 1$ the behavior is not predictable and the steady state equation is not valid. The *exploding* time series, shown as $y_t = 1.2y_{t-1} + 2$, does not converge to a steady state and exponentially increases over time with no limit.

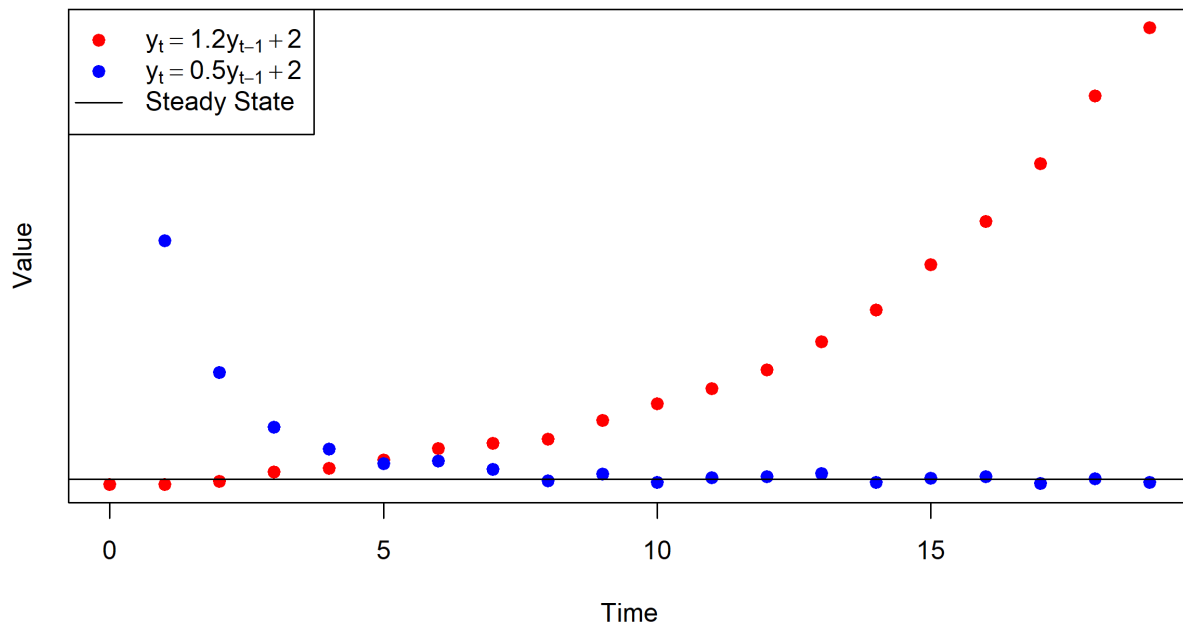


Figure 32. Example autoregressive processes.

When fitting this kind of model, a point estimate of ϕ is generated. However, if the value of ϕ is very close to 1.0, the validity of the steady state equation may be compromised. To quantify this uncertainty, Bayesian inference may be applied. Bayesian inference is a statistical method where probability distributions of all unknown model parameters are fully quantified (Hoff 2009). Using Bayesian inference, a probability distribution of the value of possible ϕ are determined rather than a single point estimate. When applied to this problem, a Bayesian inference approach can be used to:

1. Inspect the distribution of the value of ϕ , to infer if steady state is predictable
2. Stipulate a prior distribution of ϕ which forces $-1 < \phi < 1$ to ensure the steady state equation is valid for steady state calculations
3. Generate random samples of ϕ and μ , which are, in turn, used to generate a probability distribution of the steady state concentration (Carlin, Gelfand, and Smith 1992; Hastings 1970)

Once steady state is known for all elements at each sampling point, a complete mass balance of the circuit can be rigorously determined with no arbitrary assumptions.

Figures 33 and 34 show how this technique can be applied to the current problem. Figure 33 shows time series data from one of the process streams in the stripping circuit during one of the detailed parametric tests. In this example, samples were taken once per hour following a process parameter change for a total of 43 hours. Using the steps outlined, the distribution of ϕ is first built. The data collected and the distribution of ϕ , given this data, are shown as the two plots in Figure 33.

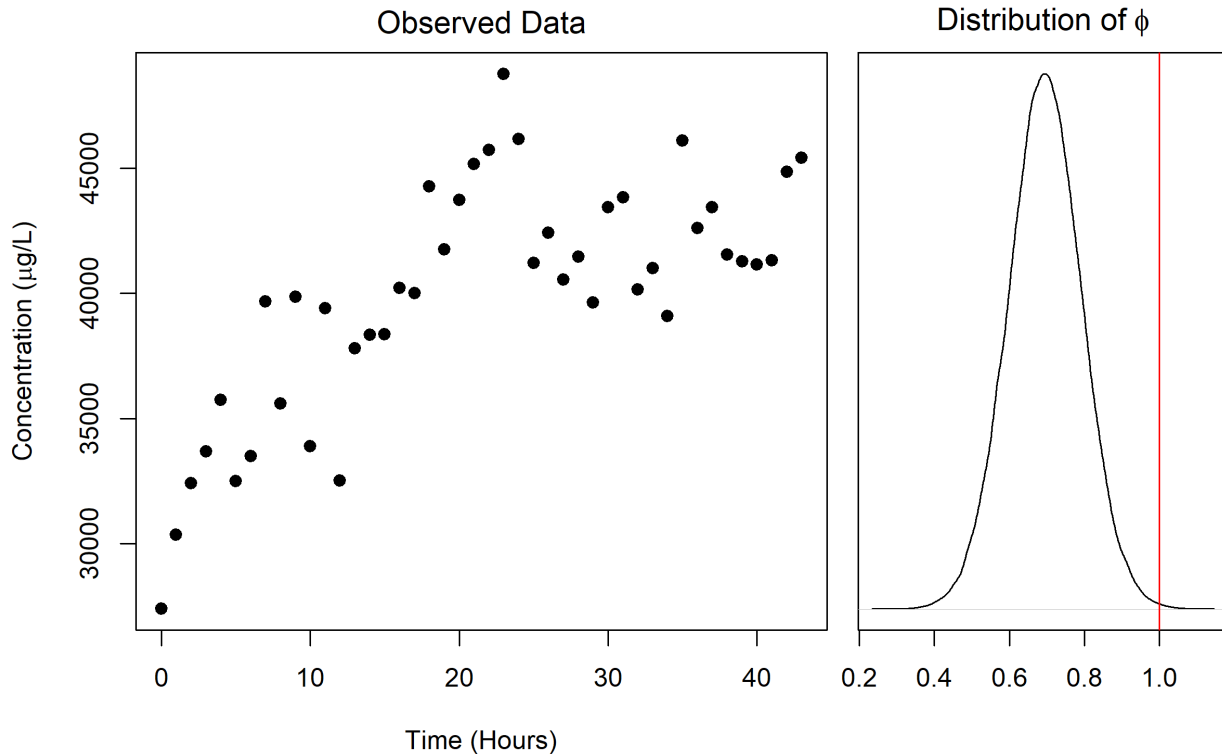


Figure 33. Plot of data and distribution of ϕ .

The probability that $|\phi| \geq 1$ is 0.119%. While the value is small, it does indicate some non-zero possibility that the calculation of steady state is not valid. However, based on the actual value, one can be fairly confident that $|\phi| < 1$. Thus, the model was refit while forcing $|\phi| < 1$ using a prior distribution. Samples of μ and ϕ were then produced and used to calculate the distribution of steady state, shown in the plots in Figure 34.

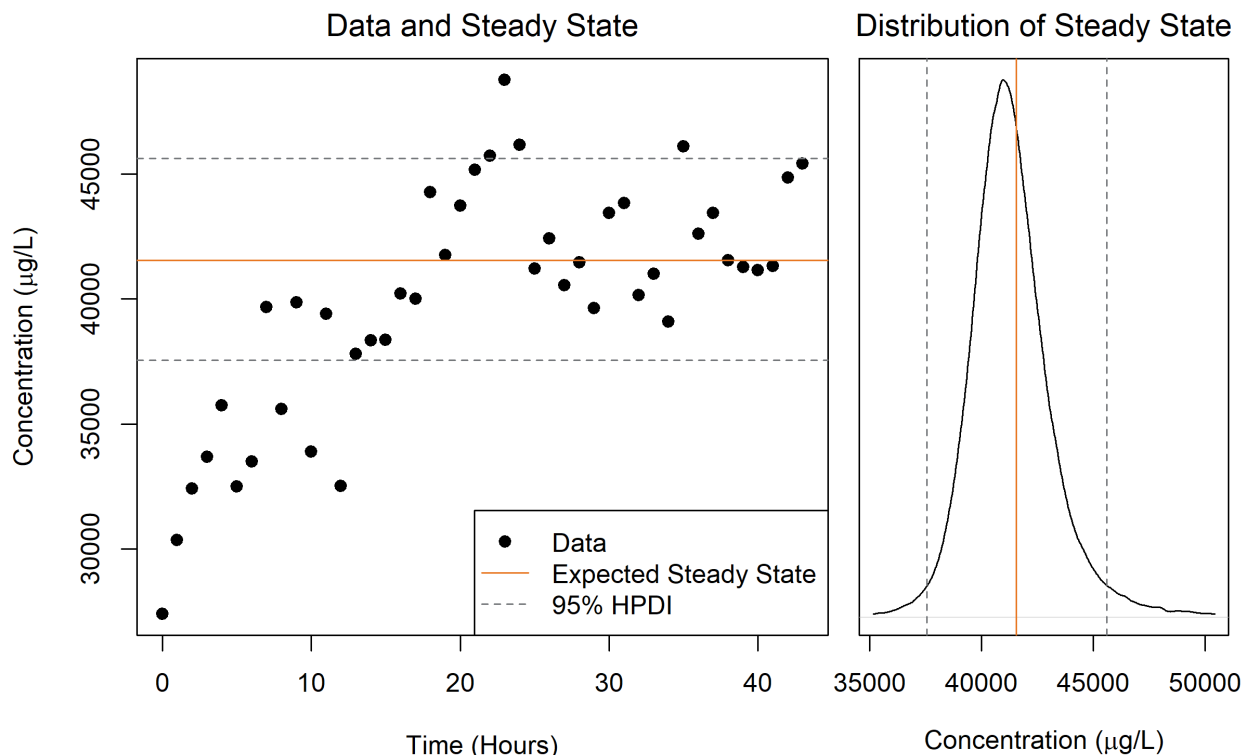


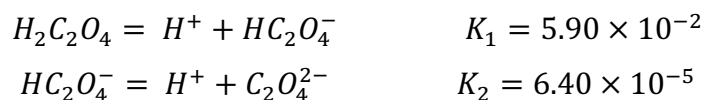
Figure 34. Plot of data with distribution of steady state.

In conclusion, a robust, objective, sensible method for determining steady state concentrations was produced. For the data used with this method so far, all sampling points had a $> 90\%$ chance that $|\phi| < 1$, good evidence the entire system is at steady state and predictable. This model can be improved to account for conservation of mass between stages, and it is a good foundation for future models. Most importantly, the model is useful for objective verification of steady state. Unfortunately, one significant drawback of using this method is the intensive computation time. In its current state, the code used to make these inferences is inefficient and it was not feasible to use for all the elements in the full validation test.

Oxalic Acid Consumption Modeling by Solution Chemistry

The ALSX process uses oxalic acid to precipitate rare earth oxides from the loaded strip solution leaving SX. To evaluate the oxalic acid dosage as well as the precipitation efficiency, a solution chemistry model was developed using literature data on REE thermodynamics. The approach employed in this model has been thoroughly described by Chi and Xu (1999), and the key points are summarized here.

To properly optimize the pH for oxalic acid precipitation, the first step of the model calculation is to determine the distribution of the oxalic acid species. Oxalic acid dissociates to H^+ and the oxalate ion per the two-step dissociation reaction given by:



Given these intermediate oxalate products, the total concentration of oxalic acid containing species is given by:

$$[H_2C_2O_4]T = [HC_2O_4^-] + [C_2O_4^{2-}] + [H_2C_2O_4]_{aq}$$

Moreover, the fractional speciation of the products is given by:

$$\begin{aligned}\varphi_0 &= \frac{[C_2O_4^{2-}]}{[H_2C_2O_4]T} = \frac{K_1K_2}{[H^+]^2 + K_1[H^+] + K_1K_2} \\ \varphi_1 &= \frac{[HC_2O_4^-]}{[H_2C_2O_4]T} = \frac{K_1[H^+]}{[H^+]^2 + K_1[H^+] + K_1K_2} \\ \varphi_2 &= \frac{[H_2C_2O_4]S}{[H_2C_2O_4]T} = \frac{[H^+]^2}{[H^+]^2 + K_1[H^+] + K_1K_2}\end{aligned}$$

where $\varphi_0 + \varphi_1 + \varphi_2 = 1$. Given these relationships, the fractional speciation of oxalic acid can be readily calculated based on the solution pH value. The results of this calculation are shown for a range of pH values in Figure 35.

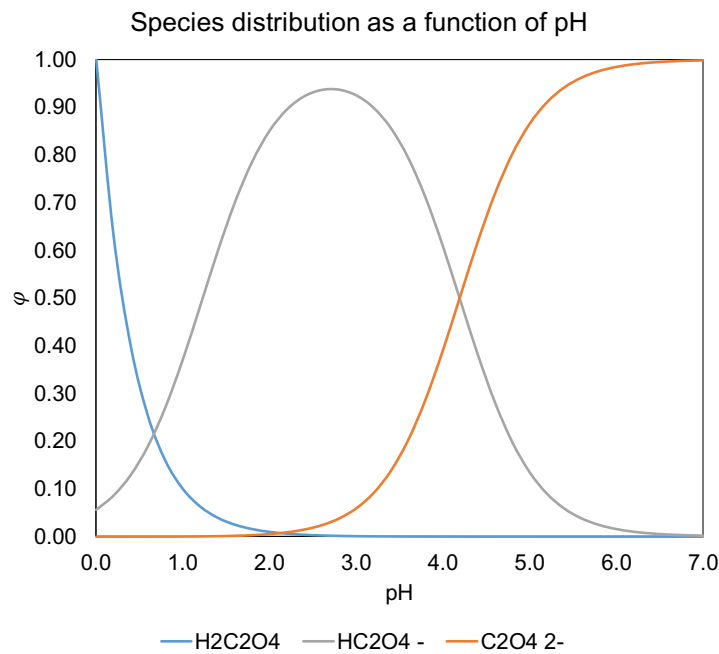
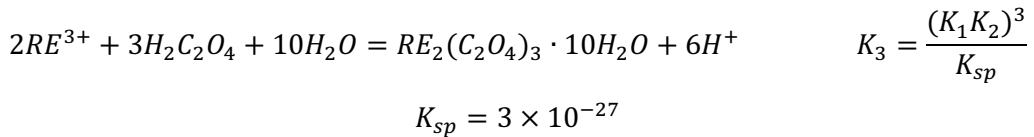


Figure 35. Species distribution for the dissociation of oxalic acid in water.

The precipitation of rare earth elements (RE^{3+}) by oxalic acid is given by:



Given this reaction, the amount of oxalic acid needed to precipitate REEs can be calculated by summing three independent components. Details on these parameters are given in Chi and Xu (1999).

- 1) Stoichiometric dosage of oxalic acid (H_p):

$$H_p = \frac{3}{2}(C_{RE} - [RE^{3+}])K_{sp}$$

- 2) Excess oxalic acid needed to ensure a complete precipitation (H_e):

$$H_E = \frac{[H^+]^2 + K_1[H^+] + K_1K_2}{K_1K_2} \sqrt[3]{\frac{K_{sp}}{[RE^{3+}]^2}}$$

3) Oxalic acid consumed by Non-RE contaminants (H_I):

$$H_I = H_{IP} + H_{IC}$$

where H_{IP} is the amount of oxalic acid needed to precipitate non-RE contaminants

$$H_{IP} = [Ca^{2+}]_T - \frac{K_{sp}^{Ca^{2+}}}{[L]}$$

and H_{IC} is the amount of oxalic acid that complexes with non-RE contaminants.

$$H_{IC} = \frac{([H^+]^2 + K_1[H^+] + K_1K_2)[Ca^{2+}]_TK_{sp}[L]}{[H^+]^2 + K_1[H^+] + K_1K_2 + K_1K_2K_{sp}[L]}$$

In these equations, calcium is used as an indicative contaminant ion; however, other contaminants may include Al, Fe, Mg, as well as other major and minor metals.

Given these three components, the total consumption of oxalic acid H_T can be readily determined by:

$$H_T = H_P + H_E + H_I$$

Lastly, the oxalic acid efficiency (OAE) can be determined by:

$$OAE = \frac{H_P}{H_P + H_E + H_I} \times 100$$

These equations have been implemented into an Excel spreadsheet to streamline the model calculations. A screenshot of the Excel interface is shown in Figure 36. This tool was later employed to support the TEA and other experimental activities.

Oxalic Acid Dosage Calculator Based on Theoretical Calculations			
pH:	1.5		
[Initial REE]:	6.00E-03	mole/dm ³ or M or mol/L	
[Final REE]:	1.00E-05	mole/dm ³ or M or mol/L	
[Ca ²⁺]:	0.00E+00	mole/dm ³ or M or mol/L	
[Al ³⁺]:	0.00E+00	mole/dm ³ or M or mol/L	
[Fe ³⁺]:	0.00E+00	mole/dm ³ or M or mol/L	
[Mg ²⁺]:	0.00E+00	mole/dm ³ or M or mol/L	
Run			
Calculated Oxalic Acid Dosage			
REE consumption:			
H _P (stoichiometric dosage)	8.99E-03		
H _E (excess dosage)	2.36E-03		
Impurities consumption:			
H _{IP} (stoichiometric dosage)	-6.31E-03		
H _{IC} (excess dosage)	0.00E+00		
H _I (Total consumption)	-6.31E-03		
Final Total Oxalic Acid consumption			
Total oxalic acid consumption:	0.0050	mole/dm ³ or M or mol/L	
Oxalic acid efficiency (OAE):	1.78E+02	%	
Oxalic dosage	0.45	g/L	

Unit Conversion		
TREE	Concentration, ppm or mg/L	mol/L
Y	38.35	4.31E-04
La	47.18	3.40E-04
Ce	129.17	9.22E-04
Pr	21.14	1.50E-04
Nd	109.92	7.62E-04
Sm	30.86	2.05E-04
Eu	6.93	4.56E-05
Gd	37.92	2.41E-04
Tb	3.01	1.89E-05
Dy	10.46	6.44E-05
Ho	1.54	9.35E-06
Er	2.84	1.70E-05
Tm	0.24	1.42E-06
Yb	0.84	4.87E-06
Lu	0.10	5.52E-07
TREE	440.48	3.21E-03
Ca	4252.00	1.06E-01

Figure 36. Screenshot of oxalic acid consumption estimator.

SX Circuit Sensitivity Analysis

Circuit sensitivity analysis is an extension of linear circuit analysis that can be used to evaluate unit sensitivity and uncertainty propagation within the circuit (Lucay et al., 2012; Noble and Luttrell, 2014;

Amini and Noble 2017; Amini and Noble 2019). This approach can be used to identify how each separation unit contributes to overall recovery and selectivity; and the method can specify sub-systems that strongly influence overall system performance. For the current project, circuit sensitivity analysis was applied to the SX circuit. First, an analytical circuit solution for the total recovery through SX was produced using linear circuit analysis:

$$R_{SX} = \frac{P1 * P2 * P3}{P1 * P2 * P3 * P4 * P5 - P1 * P2 * P4 * P5 + 1}$$

where P1 is the extraction recovery, P2 is the scrubbing recovery, P3 is the stripping recovery, and P4 is the saponification recovery, and P5 is the acid wash recovery.

After deriving the equation, the model can be manipulated to evaluate the relative influence of certain input parameters. Care must be exercised in interpreting the result, as the assumption of linearity is not wholly valid for SX; however, general trends can be observed. Figure 37 illustrates this sensitivity analysis by showing the SX recovery as a function of individual stage recovery in a simple one-variable-at-a-time analysis. The data show the relatively high impact of extraction, scrubbing, and stripping with respect to the overall system recovery. Saponification has a relatively low impact, and acid washing was not included, since the experimental data consistently showed no losses in this stage.

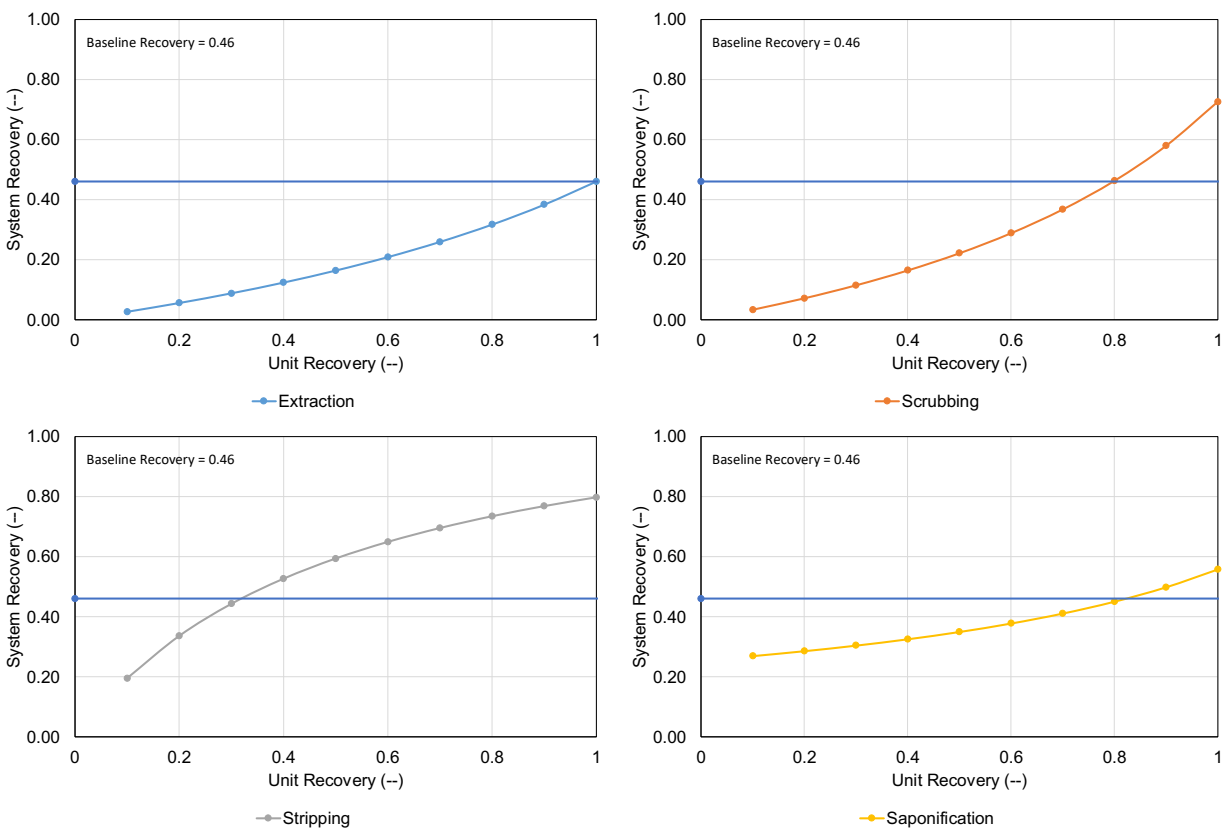


Figure 37. Linear Sensitivity Analysis of Solvent Extraction System.

The baseline recovery shown in Figure 38 below is relatively low relative to expectations. As shown in the plot, this result is primarily due to poor stripping, which may be counteracted by better optimization of the stripping acid and the O:A ratio in that stage. As an alternative, one option for the commercial implementation may be to recycle all or part of the scrub solution back to the circuit feed. This action would increase recovery; however, it may also cause a large buildup of gangue metals. To evaluate the

potential benefit of this alternative, another sensitivity analysis was conducted whereby the system recovery was determined as a function of the fraction of the scrub solution recycled to the circuit feed. This result shows that the final recovery could be increased from 46% to 73% assuming other recovery values stay consistent. This result is favorable, but further analysis and testing is needed to confirm the viability.

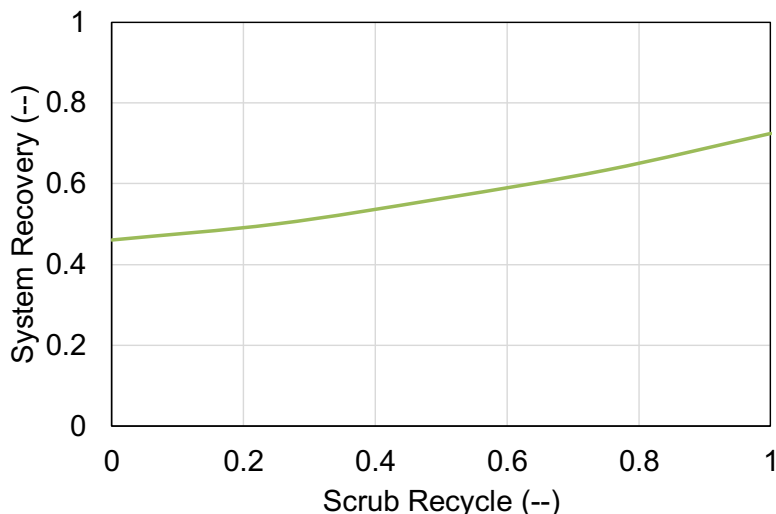


Figure 38. Linear sensitivity analysis showing system recovery as a function of scrub solution recycle.

Task Completion Status

100% complete.

Task 9.0 System Decommissioning

Approach

After the conclusion of all testing campaigns (Tasks 5.0, 6.0, and 7.0) the Recipient will decommission the system in the following manner. All residual solutions, including organic and extractant, will be drained from the SX plant and disposed according to University waste handling protocols. The glass mixer-settler units will be acid washed, and any remaining wear parts or other waste will be landfilled. After final cleaning and decommissioning, the unit will either be stored in a suitable location at WVU until disposition of property is agreed with DOE at the end of the project performance period.

Overview

This task is unnecessary since the equipment will be continually used in future DOE projects.

Results and Discussion

As of this past quarter, it was determined that system decommissioning will not occur at the end of this project due to continued use of the system in DE-FE0031834.

Task Completion Status

N/A

Task 10.0 Techno-Economic Analysis

Approach

The Recipient will use the experimental and system design optimization results from Tasks 6.0, 7.0 and 8.0 to perform a techno-economic analysis (TEA) of the AMDp REE extraction technology. The TEA will report costs and performance at the existing scale and project those costs to the next design scale

and/or a commercial implementation using standard scaling factors and itemized costs as appropriate. All analyses will use guidelines and assumptions provided by NETL, and results will be presented in accordance with NI 43-101 reporting standards for disclosing mineral projects. At a minimum, the TEA will include: a clear statement of the assumptions; cash forecasts on an annual basis; a discussion of potential Net Present Value and Internal Rate of Return; a summary of the tax structure imposed; and a sensitivity analysis with respect to grade, price, and other significant input factors.

The Recipient will also incorporate stochastic pricing models (e.g., geometric Brownian motion or mean-reverting models such as the Hull-White-Vasicek model) into the TEA to account for the high variability in REE prices. The Recipient will use the stochastic pricing model to rigorously determine the effect of REE price volatility on the economic optimum configuration of the AMDp REE extraction technology.

Overview

In this task, a techno-economic analysis was used to evaluate the economic viability of extracting REEs from AMD-based feedstocks using the technology developed in this project. The methodology utilized in this study incorporated a power law scaling function for capital cost estimation and itemized operating cost estimates for consumables, power, and labor. Other overhead and miscellaneous costs were estimated using standard chemical engineering costing criteria. The economic model was constrained by the financial and operational assumption as prescribed in the NETL document *Guidance for Development of Techno-Economic Analyses for DOE/NETL's Feasibility of Recovering Rare Earth Elements Program*¹. Results from this analysis include comparative economic indicators for both processing methods as well as sensitivity analyses for the pre-concentrate approach developed in this project. Overall, this assessment showed that moderate pre-concentration of AMD to 1.5 to 2.0% will be needed to support economic viability.

Results and Discussion

To assess the economic feasibility and future commercial viability of the technology developed in this project, a detailed techno-economic evaluation was conducted. The primary input data for this analysis consisted of experimental testing conducted at both the bench-scale and small pilot-scale as well as cost models for capital, labor, consumables, and power. Key output metrics included REE production cost (\$/kg), 20-year project NPV, rate of return, and payback period. By convention, all analyses were conducted using a fixed plant feed rate of 125 TPD.

To facilitate this analysis, a spreadsheet-based techno-economic analysis spreadsheet was developed and updated as new data was produced. This software integrates both technical factors (e.g., process feed rates, unit recovery values, reagent consumption rates, scale-up criteria, etc.) and economic factors (e.g., process capital costs, reagent costs, finance and tax structure, etc.), while outputting key economic indicators, such as project net present value (NPV), internal rate of return (IRR), and capital payback period. Per DOE guidelines, the tool makes use of the Microsoft Excel Spreadsheet software. The software contains no locked or hidden cells; however, it does extensively use “named ranges” to carry values between sheets. Nevertheless, the “open” nature of the software ensures that all of the calculation steps can be readily traced by an experienced Excel user.

Several technical and economic assumptions were required to complete the analysis in this report section. Many of the economic assumptions, including those regarding the financing structure, escalation rates, tax calculations, and operating period have been supplied by National Energy Technology Laboratory (NETL) in the *Guidance for Development of Techno-Economic Analyses* document. Key economic assumptions utilized in this study include:

¹ Available: < <https://netl.doe.gov/sites/default/files/netl-file/Rare-Earth-Element-TEA-Guidance.pdf> >

- All amounts are in US dollars.
- The total operational period for the plant is 20 years.
- The plant feed rate is fixed at 175 metric tons per day
- The feedstock grade for each case reflects laboratory analyses from material sampled during this study.
- Inflation has been applied to sales revenue and operating costs using a fixed rate of 3%.
- Capital costs are spread over a period not to exceed three years, and the allocation between those three years is 10%, 60%, and 30% for years one through three, respectively. Thus, the total analysis period (capital purchase plus operating) is not to exceed 23 years.
- During the capital expenditure period, capital costs escalate at a constant rate of 3.6%.
- The project is debt financed for 50% of the total overnight capital requirement. The remaining 50% is financed by equity.
- The debt repayment terms include: 6% interest rate, 10-year loan period, and no grace period on debt repayment. The repayment uses a standard amortization schedule with constant payments throughout the payoff period.
- Working capital is not included in this estimate and will instead be borne by the operating entity at no cost to the project.
- The combined federal and local tax rate is fixed at 26%. This value is lower than the one required in the NETL guidance document; however, it reflects a recent reduction in corporate tax rates.
- All capital is depreciable, using a 150% declining balance depreciation schedule over 20 years. The depreciation method was NOT changed to straight line when conditions favored the switch.
- The mineral depletion rate for REEs is 14%. Depletion is charged at the appropriate rate times the net sales revenue after deducting royalties and any severance tax, provided that the total amount calculated by depletion rates does not exceed 50% of the taxable income before depletion.
- The plant is part of a larger commercial entity with sufficient revenue to offset negative taxable income. Thus, losses are not carried forward and are instead calculated as a “negative tax” that indicates the reduction in tax burden required for overall entity.
- The land and mineral rights are leased, and royalties will be paid to the landowner.
- Royalties are charged at standard rate of 4% of total sales revenue.
- The plant operation schedule is fixed at eight (8) hours per shift, three (3) shifts per day, 340 operational days per year.
- Equipment costs were determined by scale-factor analysis. Installation costs were determined by an overall Lang factor.
- Reagents, consumables, power, and labor were determined by itemized cost analysis.
- Other operating costs, including maintenance and supply, QA/QC, sales, administration, property tax, insurance, and plant overhead were all calculated using proportional factors.

In the TEA model, capital costs were estimated using scale models derived from the CostMine Mine and Mill Equipment Cost guide (2016). In addition to the base equipment price, installation and other costs were determined using modular cost factors, as specified in Gentry and O’Neil 1984.

Operating costs were estimated using an itemized assessment of the various labor and consumable requirements. These costs have been subdivided into fixed, variable, and operating expense categories; a revenue estimate was determined using the simplified REE metal price values provided by NETL that roughly reflect 2016/2017 market values. These REE prices are slightly depressed when compared to values from the past decade; however, scandium prices are still strong in this scenario. Stochastic pricing models were investigated; however, given the current stage of process development, they were not

found to be useful in influencing optimal processing routes, particularly since individual elemental separations were not included in this study.

The TEA was used to evaluate various production scenarios including different feedstock types, feed rates, feed grade values, SX configurations, and operational scenarios. Unfortunately, none of the scenarios processing raw sludge were able to produce favorable economic outputs. The combination of low feed grade, low SX recovery particularly in the stripping stage, and very high acid leaching consumption prompted high operating costs and subsequently negative NPV values. To evaluate potential pathways for further optimization and improvement, a detailed cost assessment was conducted using relevant data from the validation test run. Key assumptions in this specific analysis include:

- Royal Scott feed profile: 933 ppm TREE @175 TPD
- Net acid consumption: 1180 kg/t
- Leaching % solids: 5%
- Average haulage = 25 miles @ \$0.20/t-mile
- SX System Parameters matching those used in validation test

The total CAPEX for this scenario was \$35.6 million, including base equipment, installation, and a 20% contingency. The distribution of capital costs trends is largely driven by the leaching circuit, which accounts for approximately 85% of the total equipment cost. In addition, operating expenses exceeded cash revenues by an order of magnitude. The breakdown of these operating costs is shown below in Figure 39. As shown, chemical consumption in the leaching and SX circuits constitute a majority of the operating costs.

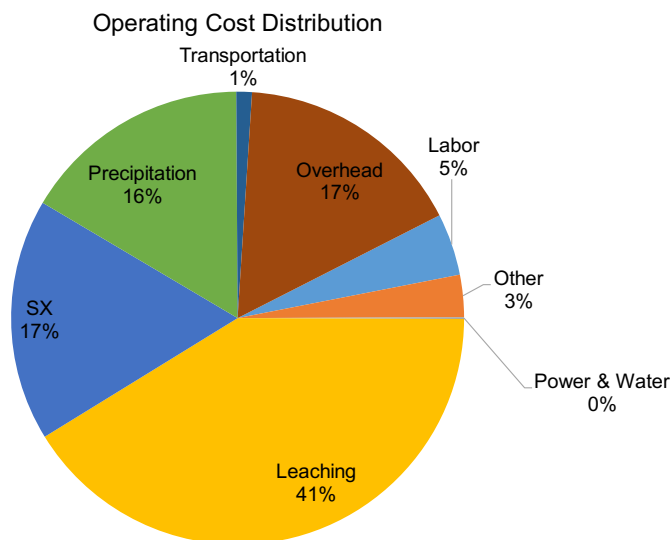


Figure 39. Distribution operating costs for TEA analysis.

To evaluate potential alternative approaches that are economically viable, individual sensitivity analyses were used to evaluate the influence of feed grade on acid costs and shipping costs. Since the AMDp reserve at individual sites is quite limited, increased feed grade may allow larger shipping distances and thus allow a larger reserve base to feed a centralized plant. Figure 40(a) shows the maximum possible acid dose required to keep the total acid cost below an economic threshold of \$100/kg as a function of REE feed grade and leaching recovery. As shown, raw sludge can only be processed in a cost-effective manner if the maximum acid dose is on the order of 100 to 150 kg/t. This breakeven value is much

higher than the acid consumption found during pilot testing, which was as high as 1100 kg/t in some cases. Even with substantial acid recycle from SX, the acid costs are likely to be prohibitive unless the feed grade is improved. Figure 40(b) shows a similar analysis whereby the maximum haulage distance needed to keep the total shipping cost below 5% of the feedstock contained value (CV) has been determined as a function of feed grade and feed moisture. For raw sludge (0.6% REE, 50-80% moisture), the maximum haulage distance is almost negligible—less than 10-15 miles.

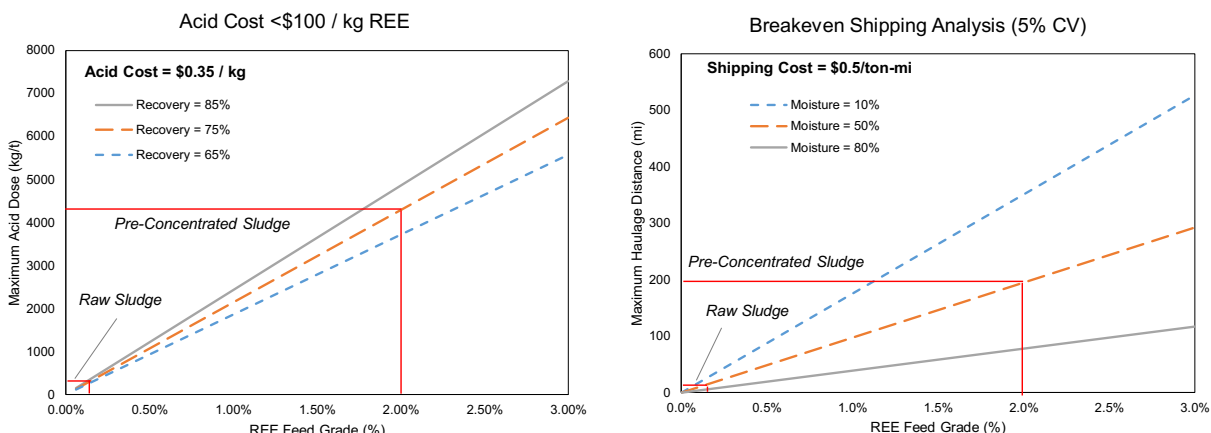


Figure 40. Sensitivity analyses showing maximum acid dose as a function of sludge feed grade and leaching recovery (left, a) and breakeven shipping distance as a function of feed grade and moisture (right, b).

Unfortunately, traditional compliance-based treatment of AMD tends to push both the sludge acid consumption and the sludge moisture to unfavorable values. Many AMD treatment operators tend to overdose lime addition to avoid non-compliant discharges. This practice leaves large quantities of unreacted lime in the final precipitate, and this base must be fully consumed during the acid leaching step of our process at a significant cost to the REE producer. Moreover, traditional sludge drying cells are ineffective at reducing sludge moisture, and many of the sludge samples evaluated in our prior studies have values exceeding 80-90%. Both of these issues are problematic for commercialization as they reduce the number of viable sludge sites that meet thresholds for economic viability. Sludge samples that do not meet the economic thresholds are considered *stranded resources* and are not considered relevant to a regional production scenario. When taken together these results indicate that the hypothetical plant described above may have difficulty identifying a sufficient quantity of raw sludge feedstock that meet these criteria. A reduction in total plant throughput will inevitably lead to a proportional reduction in economic outcomes.

As a more comprehensive sensitivity analysis, Figure 41 shows the influence of AMDp feed grade and a REE price multiplier on the overall project NPV. The point where the curves cross \$0 NPV may be considered the cutoff grade for this particular implementation of the ALSX technology. As shown below, for current prices (1x multiplier), the cutoff grade is approximately 1.0 to 1.5% implying that some pre-concentration is needed to produce an economically viable operation.

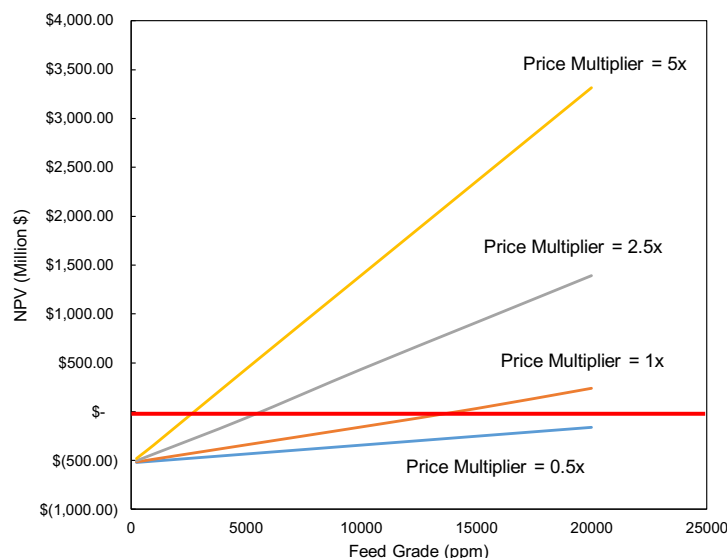


Figure 41. Sensitivity analysis showing price the influence of REE prices and AMDp feed grade on project NPV.

As part of another DOE funded study (DE-FE31524) such a pre-concentration unit was developed and tested. TREE grades between 1 and 5% were achieved in small scale testing. Figure 40 shows the impact that this pre-concentrated sludge has on the economic thresholds for the technical parameters. In short, this upstream concentration process offers a comprehensive solution to both acid consumption and maximum haulage issues. Most significantly, the upstream concentrator will increase the grade of the ALSX feed by rejecting iron and aluminum during the standard water treatment process. Figure 40(a) and Figure 40(b) show the drastic influence that the increased feedstock grade will have on maximum acid dose (>4,000 kg/t) and maximum haulage distance (increased to >200 miles). In addition to the simple grade increase, the upstream concentrator will provide better pH control technology to mitigate the acid consumption issues associated with overdosed lime addition; moreover, the use of geotubes or other advanced passive dewatering technologies will assist in reducing product moisture. All of these factors will substantially reduce processing costs, while simultaneously increasing the quantity of feedstock meeting the economic thresholds. If widely implemented across the Appalachian region, the pre-concentration plants will ensure consistent and reliable supply of feedstock for ALSX operations. Further details on the techno-economic assessment of this technology are given in Task 13.

Task Completion Status

100% complete.

Task 11.0 Resource/Reserve Characterization Approach

The Recipient will use data from Phase 1 to generate a model that predicts AMDp REE content from raw water characteristics. The Recipient will refine this model during Phase 2 and combine it with other REE databases to produce grade-tonnage curves typical for mineral industry exploration studies.

The Recipient will also use the experimental data from Tasks 6.0 and 7.0 and the results from Task 10.0 to identify an economic cut-off grade, which can then be used to determine from which sources of AMDp REEs can be economically extracted.

Overview

Data from Phase 1 of this project as well as raw data from another DOE project (DE-FE0026444) were synthesized to estimate the total REE resource available in the AMD and AMDp present in the Appalachian coal basin. Results for AMD show that for influent samples with a pH <4, the average TREE concentration was 371 ug/L, while for samples with a pH >4, the average concentration was only 88 ug/L. Thus, the influent pH has a strong influence on the overall REE concentration; however, pH alone cannot explain all of the variance in the dataset. A five factor least squares analysis showed that the concentration of Mn, Al, Si, and Mg were also strongly correlated to TREE concentration. Lastly, a regional flow rate estimate showed that the total amount of REEs produced from AMD can vary between 771 and 3,400 tons per annum.

Regarding AMDp, results showed that traditional AMD treatment captured approximately 78% of the TREES, leaving a precipitate with an average concentration of 724 g/ton. Both the Northern and Central Appalachian basins contained similar distributions of REEs with a total of resource of 340 tons stored at the 141 sites sampled in the DE-FE0026444 study. While this analysis cannot quantify the basin-wide REE inventory, it does strongly suggest that AMD is a much more viable long-term resource.

Results and Discussion

Detailed results and discussion from this task have been published in two comprehensive peer reviewed studies. These papers are included in Appendix A, and key details are reproduced here for convenience.

In the initial study as part of Phase 1, nine Northern Appalachian coal mine sites with AMD outflows were chosen for detailed sampling. Both aqueous AMD and solid AMDp samples were collected over periods of between four and 17 months, depending on the sampling site. At each site, both the influent and effluent aqueous streams as well as AMDp samples were collected to obtain a complete mass balance around the treatment process. The aqueous and precipitate samples were then analyzed for REE and major metal content using ICP-MS. The results were aggregated and used to assess the major trends and factors controlling the content and distribution of REEs in both AMD and AMDp.

During the DE-FE0026444 study, sampling was conducted in two campaigns. The initial campaign consisted of a regional survey of 141 AMD discharges and formed the basis for estimating the REE resource available in surface AMDp storage cells and the annual REE production rate (flux) based on AMD generation. A subsequent, intensive sampling campaign focused on potentially attractive sites based on either surface sludge resource or REE flux. A maximum of ten AMDp samples were taken on each site, and the total number of samples collected between both campaigns was 185 for AMD and 623 for AMDp. Approximately 30% of the samples were taken from the Central Appalachian basin (CAPP), while the remaining 70% were recovered from the Northern Appalachian basin (NAPP). The aqueous and precipitate samples were then analyzed for REE and major metal content using ICP-MS. Statistical analyses were conducted to assess variation between the basins and to identify principle factors correlated to increased REE content.

Figure 42 shows the distribution of REE concentrations in the AMD influent samples for CAPP and NAPP samples as box and whisker plots. Average concentrations for the CAPP and NAPP basins were determined to be 228 µg/L and 305 µg/L, respectively; however, this data also shows that the REE content in raw AMD can vary by several orders of magnitude. To better understand the mechanisms causing this large range, the research team assessed the correlation between aqueous REE concentration and other independent parameters. Initial graphical analyses showed that neither total flow nor raw water pH were sufficient to predict the REE content of AMD. Thus, a partial least squares analysis was conducted to include major metal concentrations in the prediction. Results from this analysis indicate that five factors can explain over 75% of the variance in concentration of TREES in the

AMD dataset. These factors, in order of importance, include the Mn concentration, Al concentration, raw water pH, Si concentration, and Mg concentration.

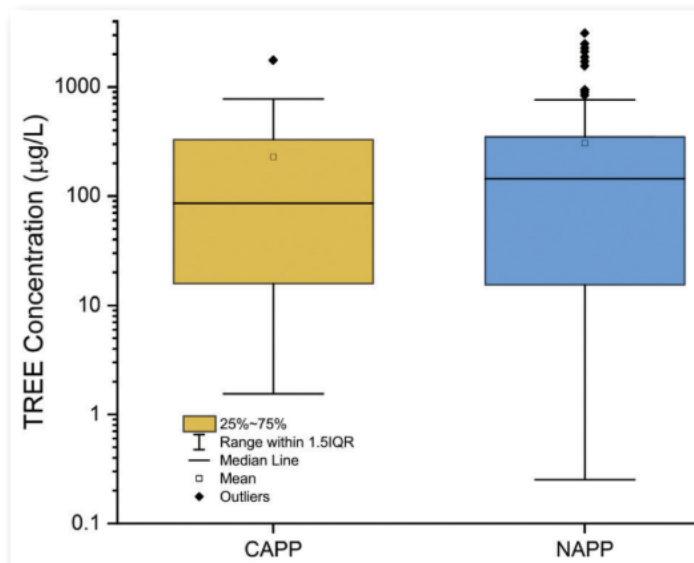


Figure 42. Distribution of total REEs in raw AMD samples.

Similar to Figure 42, Figure 43 shows the distribution of REE concentrations in the AMDp influent samples for CAPP and NAPP samples as box and whisker plots. AMDp followed a similar trend with respect to total concentration; CAPP averaged 669 g/t, while NAPP averaged 750 g/t – a difference of 81 g/t between the basins. Overall, the precision of the AMDp is much higher than that of the AMD samples, which may be attributed to the larger sample size.

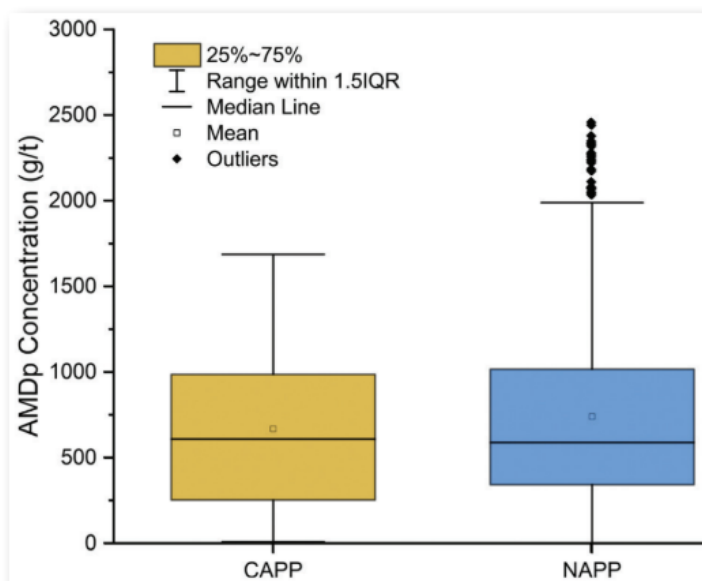


Figure 43. Distribution of total REEs in raw AMDp samples.

During sampling, estimates for the mass of REEs contained in individual storage cells was calculated using the cell volumetrics, the measured REE content on a dry-weight basis, the measured moisture content sample, and the measured sludge density according to:

$$REE\ Mass = Area * Depth * (1 - MoistureContent) * REE\ Content_{DWB} * Density$$

For the volumetric calculations, additional geographic data was collected on the location, size, and depth of each AMDp storage cell during the on-site sampling campaign. Afterwards, where applicable, these dimensions were confirmed using geospatial software and satellite imagery. In cases where depth data was not available, it was estimated based on the overall cell dimensions, not to exceed 10 feet. The moisture content of each AMDp samples was determined by full desiccation and reported with the REE analysis by SGS Canada Inc. Lastly, an average sludge density was determined to be 2.2 g/cc (95% confidence interval = 2.04 to 2.19) based on gravimetric analysis of 21 representative samples from the population. This value was used in calculations for all sites.

By compiling the assay and tonnage data from all AMDp samples, a grade recovery curve was generated for the 141 sites evaluated in the study (Figure 44). The purpose of this exercise it to show how a minimal cut-off grade could impact the AMDp reserve base. For example, if a cut-off grade of 1000 g/t is applied to this data, this would leave approximately 86 tons of REEs with an overall average grade of approximately 1,400 g/t. The grade-tonnage model graphically represents the available resource should a cut-off grade be applied for economic reasons. From this plot, it can be seen that a low cut-off grade will be required for AMDp to provide a considerable mass of REEs. However, the mass of AMDp does not fluctuate linearly with the TREE mass.

This finding indicates that a processing cut-off grade may exclude a significant portion of AMDp currently stockpiled; but at the same time, it will not exclude the majority of REEs contained in the AMDp resource. As a result, not all AMD sites are equal candidates for REE feedstock production. While this is indicative of the AMDp produced during conventional AMD treatment, our results suggest that integration of AMD treatment and REE recovery would produce a superior feedstock for REE beneficiation.

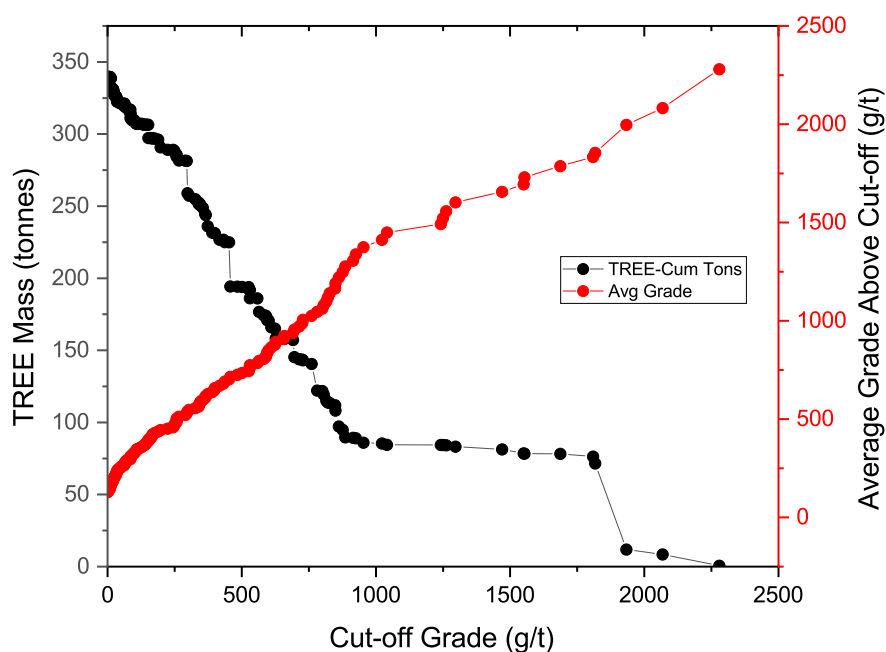


Figure 44. Grade-tonnage curves indicating resource mass and average grade given a processing cut-off level.

Prior to NETL's current REE research initiative, regionally meaningful REE load estimates from AMD were practically nonexistent due to the complexity of flow interactions, large seasonal variations, and the temporal nature of the effluent constituents. As a result, we compiled AMD outfall datasets from over 150 sites to estimate the regional REE production from known AMD sources. Flow data are drawn from datasets compiled by the West Virginia Water Research Institute, Pennsylvania Abandoned Mine Land Department, West Virginia Department of Environmental Protection, and various studies from others.

In all, this regional estimate compasses over 1,100 unique AMD outlets, predominately in the NAPP region and indicated that the regional AMD flow rate is approximately 94,700 L/sec. Consequently, this estimate may be considered conservative in relation to the actual flow rate. Previously, Stewart et al., 2016 provided a regional flow estimate of 417,448 L/sec. By comparison, the methods used by Stewart could lead to overestimation of the true quantity of AMD due to the incorrect assumption that all coal mining leads to the generation of AMD and neglecting the spatial reduction of multi-seam extraction, which is common in Central Appalachia (CAPP). Given these complexities, an accurate and precise determination of AMD flowrate for the Appalachian basin would require a more extensive study well beyond the scope of this research. Nevertheless, for the purpose of the current study, both Stewart's methodology and the authors' methodology were used to estimate the high and low AMD flow rate values, respectively. In addition, the REE content of this AMD was assumed to be the average for the NAPP values shown in Table 17. Given these inputs, the estimated REE production from AMD was determined to be between 771 to 3,400 tons of REEs per year. The high variance in the two estimated production rates indicates that further exploration of the resource is required to identify an economically feasible process to extract REEs from AMD.

Table 17. Low and high regional flow rate estimates.

Regional AMD Flow Estimate	Units	Low¹	High²
PA	(L/s)	51,401	-
WV	(L/s)	24,095	-
OH	(L/s)	18,900	-
MD	(L/s)	317	-
TOTAL	(L/s)	94,712	417,448
TREE Concentration (mg/L)	(mg/L)	0.258	0.258
TREE Load	(ton/yr)	771	3,400

1 Regional flow estimates based on proprietary AMD studies

2 Regional flow estimate by Stewart et.al.

Task Completion Status

100% complete.

Task 12.0 Environmental, Health, and Safety Assessment

Approach

Environmental and waste management have been primary considerations in the system design from the onset of the project. AMDp is currently an environmental liability for many companies and utilization of this waste could prompt significant economic and environmental benefits. The bulk of generated waste will be identical to conventional coal-derived AMD sludge which is recognized as non-hazardous per USEPA Method 1311 (TCLP). On the other hand, rejects produced during ALSX will require separate testing and perhaps, handling. To date, the small-scale tests conducted during Phases 1 and 2 did not generate enough leach residue to permit detailed characterization tests.

Overview

Solid leaching residues were analyzed for environmental compliance using EPA 1311 TCLP analysis. The results indicate that all of the tested parameters fall below the maximum allowable concentration by at least two orders of magnitude.

To assess and identify waste disposal options for the leach residue/acidified AMDp, will be conducted on this material during follow-up studies to the extent that sufficient masses of waste product are generated and tested to determine the leachability of toxic metals/organic compounds in solid residuals. If found to be non-toxic, the proposed disposal route in a commercial system will be to re-introduce the solids into the AMD treatment system's lime mixing tank to neutralize the material prior to disposal per current AMDp handling protocols at the treatment facility.

Results and Discussion

The predominant solid waste stream from this process will be identical to conventionally-produced AMD sludge: Transition metal hydroxides. Low volumes of waste generated during ALSX will include SX precipitates. They will also resemble AMD sludge in every respect other than pH which can be easily adjusted. SX residues, depending on the organic (e.g. Elixor 206) recovery efficiencies to be achieved during continuous operations may require special handling. No other reagents will be added other than acids and bases which, also, are easily neutralized. However, the extent of environmental risk associated with these streams cannot be assessed until large scale, continuous pilot-scale operations yield sufficient materials for characterization and toxicity testing (Table 18).

Table 18. Results of residual solid TCLP Testing.

ETD 50 - Results of residual solid TCLP testing

Parameter	Units	PQL	Organic / Inorganic	Results			Maximum Allowable Concentration
				Omega	DLM	Royal Scot	
Arsenic	mg/L	0.03	I	ND	ND	ND	5
Barium	mg/L	0.05	I	0.64	ND	0.84	100
Cadmium	mg/L	0.02	I	ND	ND	ND	1
Chromium	mg/L	0.03	I	ND	ND	ND	5
Lead	mg/L	0.03	I	ND	0.08	ND	5
Selenium	mg/L	0.04	I	ND	ND	ND	1
Silver	mg/L	0.03	I	ND	ND	ND	5
Mercury	ug/L	1.00	I	ND	ND	ND	200
Chlordane (Technical)	ug/L	1.00	O	ND	ND	ND	30
Endrin	ug/L	0.20	O	ND	ND	ND	20
Heptachlor	ug/L	0.10	O	ND	ND	ND	8
Heptachlor epoxide	ug/L	0.10	O	ND	ND	ND	8
Methoxychlor	ug/L	1.00	O	ND	ND	ND	10,000
Toxaphene	ug/L	2.00	O	ND	ND	ND	500
gamma-BHC (Lindane)	ug/L	0.10	O	ND	ND	ND	400
1,1-Dichloroethene	ug/L	50.00	O	ND	ND	ND	700
1,2-Dichloroethane	ug/L	50.00	O	ND	ND	ND	500
2-Butanone (MEK)	ug/L	100.00	O	ND	ND	ND	200,000
Benzene	ug/L	50.00	O	ND	ND	ND	500
Carbon tetrachloride	ug/L	50.00	O	ND	ND	ND	500
Chlorobenzene	ug/L	50.00	O	ND	ND	ND	100,000
Chloroform	ug/L	50.00	O	ND	ND	ND	6,000
Tetrachloroethene	ug/L	50.00	O	ND	ND	ND	700
Trichloroethene	ug/L	50.00	O	ND	ND	ND	500
Vinyl chloride	ug/L	50.00	O	ND	ND	ND	200
1,4-Dichlorobenzene	ug/L	500.00	O	ND	ND	ND	7,500
2,4,5-Trichlorophenol	ug/L	5,000.00	O	ND	ND	ND	400,000
2,4,6-Trichlorophenol	ug/L	100.00	O	ND	ND	ND	2,000
2,4-Dinitrotoluene	ug/L	100.00	O	ND	ND	ND	130
2-Methylphenol(o-Cresol)	ug/L	2,000.00	O	ND	ND	ND	200,000
3&4-Methylphenol(m&p Cresol)	ug/L	2,000.00	O	ND	ND	ND	200,000
Hexachloro-1,3-butadiene	ug/L	100.00	O	ND	ND	ND	500
Hexachlorobenzene	ug/L	100.00	O	ND	ND	ND	130
Hexachloroethane	ug/L	200.00	O	ND	ND	ND	3,000
Nitrobenzene	ug/L	100.00	O	ND	ND	ND	2,000
Pentachlorophenol	ug/L	5,000.00	O	ND	ND	ND	100,000
Pyridine	ug/L	250.00	O	ND	ND	ND	5,000

PQL = Practical Quantitation Limit

ND = Non-Detect

Task Completion Status

100% complete.

Task 13.0 Commercialization Plan

Subtask 13.1 Technology Commercialization

Approach

The Recipient will prepare a commercialization plan for developing REE recovery from an AMD resource material. The plan will consist of scaling up the technology developed in Phase 2 to a technically- and commercially-viable venture. The Recipient's commercialization strategy will consist of three (3) options.

1. The Recipient will prepare a REE extraction facility plan for a site-specific location having a large, known quantity of highly-concentrated resource material (AMDp) feeding a processing facility. The processing facility design will be integrated into an existing AMD treatment operation.
2. The Recipient will prepare a REE extraction facility plan to be located in a local area where there would be several AMDp resources feeding a larger REE extraction operation facility. The REE resources would be similar but would likely have different REE concentrations. The REE feedstocks will be transported to the facility by vacuum trucks.
3. The Recipient will prepare a REE extraction facility plan larger in size than either options 1 or 2 and will be in a regional coal basin with many sources of AMDp feedstocks that can supply this centralized REE extraction facility.

The Recipient will model the economics of each option and attempt to optimize each one. The Recipient will compile the results from the optimization evaluation into a TEA and develop the operational size capacity for a commercialization plan.

Overview

Results from the initial commercialization assessment suggested that neither of the three scenarios identified in the original SOPO produced attractive long-term economic returns needed for commercialization. The high costs associated with processing low grade, high moisture AMDp as well as the relatively small reserve volume strongly suggested that a commercial strategy solely focused on the processing of AMDp would not be successful. Integrating work from a separate DOE project (DE-FE0031524), the research team investigated an alternative strategy whereby pre-concentrated AMD is processed using the same project technology developed in the current effort. The findings suggest that this hybrid approach is superior to the AMDp-only production scenarios. This approach was then assessed in detail under this task.

Moreover, a formal commercialization assessment commissioned by the research team and conducted by a third party concluded that: “The potential market opportunity is attractive with the rare earth elements market expected to increase to over \$20 billion by 2024. However, further demonstration of technical- and economic-feasibility at commercial-scale will be critical to market success.” In addition, the report recommended that the team move forward to find a commercial partner. Nevertheless, given the findings in Task 10 and Task 11, the team did not exercise this option.

Results and Discussion

Initial efforts under this task produced a scenario evaluation model (SEM) that integrates both database information on known AMDp reserves (identified under DE-FE26444) and the TEA model developed in the current project. The SEM includes a robust user interface and facilitates the assessment of various feed arrangements for a centralized ALSX processing unit. The SEM was designed to evaluate the three scenarios described in the SOPO; namely, a large centralized ALSX facility receiving feed from all sites in the database (n = 143), a regional ALSX facility receiving feed from up to six sites, and a limiting case where the plant was only fed by a single site. For the scenarios evaluated in this study, the central facility was assumed to be located in Monongalia County, West Virginia, at an existing treatment site south of Morgantown. To estimate realistic haulage costs, Google Earth was used to estimate the over-the-road haulage distance between this central facility and each site in the database. Grade and estimated reserve values were also integrated for each database entry.

Screenshots of the model interface are shown in Figure 45. Initial results from the model suggested that even under favorable processing costs and rare earth prices, positive NPVs were only obtained when the feed moisture was kept at a relatively low value (40%) and the operating period was very short (3 years). Even in these cases, NPV values were not exceptionally high, usually on the order of \$500,000 to

\$1,000,000. The largest contributing factor to these poor results was the relatively low reserve size for AMDp-based resources, as has been explained in Task 11.

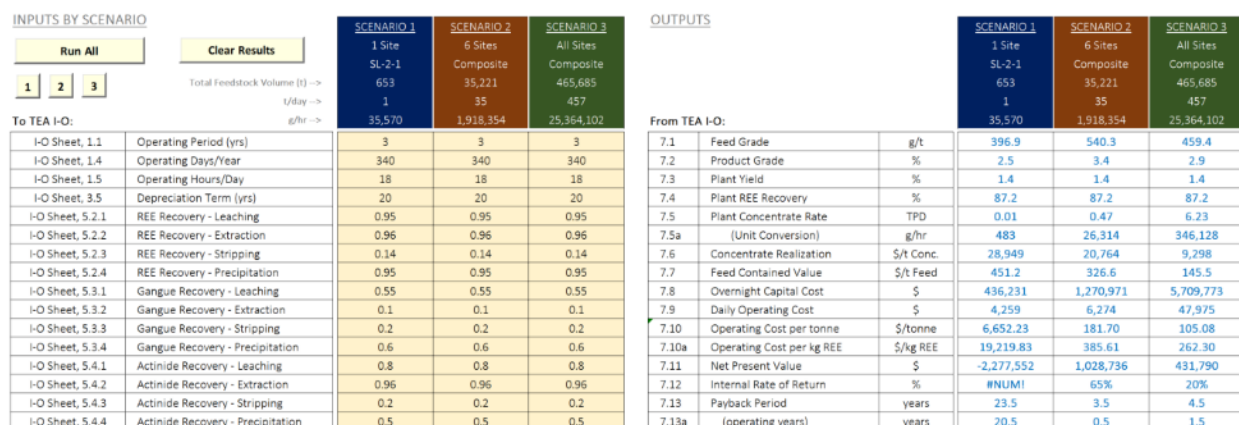
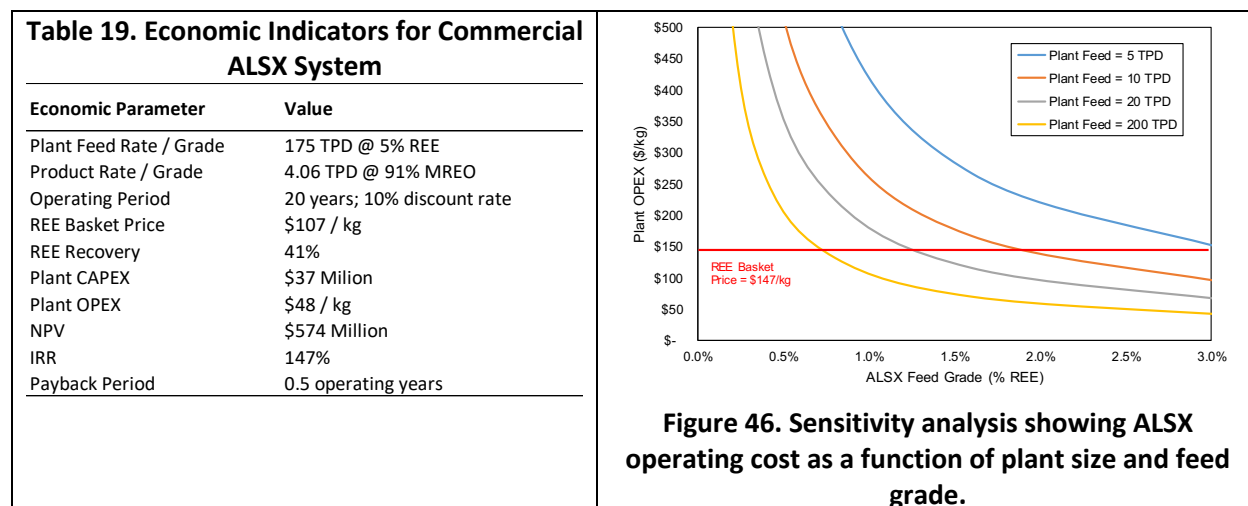


Figure 45. Screenshot of AMDp Scenario Evaluation Model.

Through work conducted under DE-FE31524, an alternative production scenario whereby raw AMD is first pre-concentrated using a proprietary low-cost method was evaluated. Following the on-site pre-concentration step, the material is further processed (either on site or remotely) using the ALSX technology developed under this project. To investigate the economic viability of processing pre-concentrates of the upstream concentration through ALSX, a techno-economic analysis (TEA) was conducted under project DE-FE31524. Pertinent results from that analysis are reproduced here. Table 19 shows the summary economic indicators, while Figure 46 shows a sensitivity analysis with respect to plant size and plant feed grade. Further details may be found in the final report for DE-FE31524.

Following the success in this financial analysis, the research team commissioned a third party to conduct a detailed commercialization assessment regarding the viability of the project technology, which has been provided to DOE.



Subtask 13.2 Resource Ownership and Control Approach

The Recipient will assess the issues of severed property estates (common practice in West Virginia and Pennsylvania); multiple ownership interests as those relate to ownership and control of in-place minerals, their extraction, transportation, preparation for sale, further transportation and ultimate sale;

and the issues of superior and subordinate property rights that exist under multiple split estates for their possible impact on a commercialization plan for the REE extraction technology being developed in Phase 2.

The Recipient will also evaluate the issue of severed minerals becoming personal property once extracted from the deposit, along with the related issue of abandonment and what the applicable law of the controlling jurisdiction reveals about the topic. The Recipient will review Pennsylvania and West Virginia state laws addressing these relevant property rights, potential competing interests to those rights, and liability issues; and perform an assessment of precedential case law in Pennsylvania and West Virginia. The Recipient will supplement this work as needed with a review of subject matter treatises and other published works, and an analysis of case law for other similar issues as well as an analysis of case law in other similarly-situated jurisdictions that may provide guidance and insight to the resolution of Pennsylvania and West Virginia property rights and liability issues.

The review will include an assessment of issues regarding determining the ownership of REEs, with regard, as noted above to both real and personal property aspects, that may be recovered from: (a) naturally occurring deposits in isolation and in association with the extraction of coal seams and immediate strata above and below such seams which activities result in byproducts, including AMDp; (b) active and inactive coal preparation and processing facilities including treatment ponds and related structures actively treated and monitored for effluent discharges and from which AMDp is removed; (c) the effluent discharges themselves at such active and inactive coal preparation and processing facilities; (d) active and inactive refuse disposal sites including treatment ponds and related structures actively treated for effluent discharges and from which structures AMDp is removed; (e) facilities of any of the type that may be under the control of a bankruptcy trustee; (f) facilities of any type that may be under the control of any state or federal agency as a result of permit and/or bond forfeitures; (g) facilities that are fully reclaimed and no longer inspected; and (h) any other sources identified during Task 13.0.

The Recipient's review will include an up-to date assessment and summary of any legislative actions taken or being contemplated by other state jurisdictions or by the federal government to address the above listed issues.

The Recipient will also review regulatory requirements, and environmental, health, and safety issues associated with REE capture and extraction and any resulting disposal required of chemicals or the residue of any REE capture and extraction process.

Overview

A legal ownership and control analysis was prepared by the law firm Dinsmore and Shohl LLC. The executive summary of the report is included below. A full copy of the report is included as Appendix B.

Results and Discussion

Executive Summary – Ownership and Control

Various arguments can be made regarding who owns rare earth elements ("REEs"). Due to the lack of any prior litigation or legislation addressing ownership, who owns REEs and what regulations the extraction of REEs are subject to are currently questions with no definitive answers. With regard to ownership, while many may perceive that the desire to develop REEs domestically will result in perhaps a "lawyer's relief act," one lesson from coalbed methane development is that business parties covering the range of potential "ownership interests" can, and often do, work out solutions where each party participates in the arrangement, and profits, expenses, and liabilities are agreed upon based on discussions, negotiations, and factual matters. Thus, while some surface owners, coal owners, and reclamation site owners, including government entities, may seek court involvement in litigating the issues, others will likely be willing to enter into agreements to allow for the development of REEs. Said

development, however, will still be subject to governmental regulations, the exact identity of which is currently unknown, especially as “waste products” from extraction methods may well, independently, be the subject of state and federal regulations. What is known, however, is that the federal government has become increasingly interested in the extraction of REEs over the past two years. Based upon such interest, we may soon have guidance regarding ownership of REEs and what regulations will govern their extraction.² Continuous monitoring in this realm is necessary to stay current with the state of REE ownership and the applicable regulations governing extraction. For now, what is left for analysis is what the courts have—and have not—said about what constitutes “minerals,” whether mine tailings are real or personal property, ownership according to that classification, and responsibility for byproducts of REE extraction.

Subtask 13.3 Intellectual Property and Other Legal Barriers

Approach

The Recipient will conduct a review of patentable and intellectual property (IP) specific to certain aspects of the selected technology for REE extraction and concentration and identify patentable and IP technologies. The Recipient will list them separately for consideration in the commercialization plan. The Recipient will also provide each applied technology with features to mitigate the effects of any adverse environmental conditions. The Recipient will identify and evaluate each potential environmental condition and develop a mitigation strategy for each environmental condition that is identified.

Overview

Throughout the project, the team consulted with the WVU Office of Technology Transfer concerning the protection and security of project IP.

Results and Discussion

A provisional patent for intellectual properties associated with PLS generation was submitted by WVU’s Office of Technology Transfer.

Task Completion Status

100% complete.

Task 14.0 Outreach and Communication

Approach

The Recipient will coordinate with the DOE Project Officer to identify and select conferences appropriate for disseminating project information and results. The Recipient will attend a maximum of two (2) external, non-DOE conferences/meetings during each calendar year. The Recipient will submit materials prepared as abstracts and presentations to the DOE Project Officer for review and comments prior to attending and presenting.

The Recipient will also coordinate with the DOE Project Officer to identify and select appropriate peer reviewed journals in which to publish project results. The Recipient will submit draft papers to the DOE Project Officer for review and comments prior to submission to peer reviewed journals.

Overview

The project team published two scientific papers, two PhD dissertations and one MS thesis. In addition, the project team made 37 public presentations, including testimony before the U.S. Senate Committee on Energy and Natural Resources (June 20, 2019).

² Of course, any legislative or executive guidance may still become the subject of litigation if the stakes warrant it. To date the legislative and executive guidance has taken the form of seeking to promote the development of REEs including allocation of funds, as discussed in Section VI of this Report.

Results and Discussion

The project team recognizes that public outreach assists USDOE/NETL's mission to develop a domestic supply chain around critical minerals and rare earth elements. The following summarizes our efforts.

Publications:

1. Vass, C., P. Ziemkiewicz, and A. Noble. (2019). "The occurrence and concentration of rare earth elements in acid mine drainage and treatment byproducts. Part 2: Regional survey of Northern and Central Appalachian coal basins." *Mining, Metallurgy & Exploration*.
2. Vass, C., P. Ziemkiewicz, and A. Noble. (2019). "The occurrence and concentration of rare earth elements in acid mine drainage and treatment byproducts. Part 1: Initial survey of the Northern Appalachian coal basin." *Mining, Metallurgy & Exploration*.
3. Vass, C., A Critical Assessment on the Resources and Extraction of Rare Earth Elements from Acid Mine Drainage, PhD Dissertation, Mining Engineering, West Virginia University, Summer 2019.
4. Ziemkiewicz, Paul. (2019). Pittsburgh Coal Conference. Pittsburgh, PA, September 5, 2019.
5. Ziemkiewicz, Paul. (2019). Council of Government Mining Attorneys. September 24, 2019.
6. Ren, Panpan, Recovery of rare earth elements from coal mine drainage sludge leachate. PhD Dissertation, Mechanical Engineering, West Virginia University, 2019.

Task Completion Status

100% complete.

References

- Amini, S. H., & Noble, A. (2017). Application of linear circuit analysis in the evaluation of mineral processing circuit design under uncertainty. *Minerals Engineering*, 102, 18-29.
- Amini, S. H., & Noble, A. (2019). Predicting and interpreting uncertainty propagation in separation circuits using functional unit evaluation. *Minerals Engineering*, 142, 105886.
- Arnold, D. C. (2015). Composition-driven structural phase transitions in rare-earth-doped bifeo3 ceramics: a review. *IEEE Transactions on Ultrasonics, Ferroelectrics, and Frequency Control*, 62(1), 21.
- B., S. M. (1990). Determination of trace lanthanides and yttrium in seawater by inductively coupled plasma mass spectrometry after preconcentration with solvent extraction and back-extraction. *Anal. Chem.*
- Bard, A. J., Parsons, R., & Jordan, J. (1985). *Standard potentials in aqueous solutions*.
- Bau, M. (1999). Scavenging of dissolved yttrium and rare earths by precipitating iron oxyhydroxide: experimental evidence for Ce oxidation, Y-Ho fractionation, and lanthanide tetrad effect. *Geochimica et Cosmochimica Acta*, 63(1), 11.
- Chen, X., Ren, P., Li, T., Trembly, J. P., & Liu, X. (2018). Zinc removal from model wastewater by electrocoagulation: Processing, kinetics and mechanism. *Chemical Engineering Journal*, 349, 358-367. doi:<https://doi.org/10.1016/j.cej.2018.05.099>
- Cheng, C. Y., Zhang, W., & Pranolo, Y. (2010). Separation of Cobalt and Zinc from Manganese, Magnesium, and Calcium using a Synergistic Solvent Extraction System Consisting of Versatic 10 and LIX 63. *Solvent Extraction and Ion Exchange*, 28(5), 17. doi:Solvent Extraction and Ion Exchange, Vol. 28, No. 5, September-October 2010: pp. 608–624
- Chi, R. A., & Xu, Z. G. (1999). A solution chemistry approach to the study of rare earth element precipitation by oxalic acid. *Metallurgical and materials transactions B*, 30(2), 189-195

- CostMine Division. Mine & Mill Equipment Costs, an Estimator's Guide. InfoMine, USA, 2016
- Ditze, A., & Kongolo, K. (1997). Recovery of scandium from magnesium, aluminum and iron scrap. *Hydrometallurgy*, 44(1-2), 179-184.
- Dupont, D., & Binnemans, K. (2015). Recycling of rare earths from NdFeB magnets using a combined leaching/extraction system based on the acidity and thermomorphism of the ionic liquid [Hbet][Tf2N]. doi:10.1039/C5GC00155B
- Feng, Y., Yang, L., Liu, J., & Logan, B. E. (2016). Electrochemical technologies for wastewater treatment and resource reclamation. doi:10.1039/C5EW00289C
- Gentry, D.W. and O'Neil, T.J., 1984. Mine Investment Analysis.
- Gergoric, M., Ekberg, C., Foreman, M. R. S. J., Steenari, B.-M., & Retegan, T. (2017). Characterization and Leaching of Neodymium Magnet Waste and Solvent Extraction of the Rare-Earth Elements Using TODGA. *Journal of Sustainable Metallurgy*, 3(3), 638-645. doi:10.1007/s40831-017-0122-8
- Goto, T., Kimura, T., Lawes, G., Ramirez, A. P., & Tokura, Y. (2004). Ferroelectricity and Giant Magnetocapacitance in Perovskite Rare-Earth Manganites. *Physical Review Letters*, 92(25), 257201. doi:10.1103/PhysRevLett.92.257201
- Haslam, M. (1999). *An investigation into the feasibility of extracting scandium from nickel laterite ores*. Paper presented at the In Proceeding of ALTA 1999 Nickel/Cobalt Pressure Leaching & Hydrometallurgy Forum.
- Hoogerstraete, T. V., Blanpain, B., Gerven, T. V., & Binnemans, K. (2014). From NdFeB magnets towards the rare-earth oxides: a recycling process consuming only oxalic acid. doi:10.1039/C4RA13787F
- Hoogerstraete, T. V., Wellens, S., Verachtert, K., & Binnemans, K. (2013). Removal of transition metals from rare earths by solvent extraction with an undiluted phosphonium ionic liquid: separations relevant to rare-earth magnet recycling. doi:10.1039/C3GC40198G
- Jordens, A., Cheng, Y. P., & Waters, K. E. (2013). A review of the beneficiation of rare earth element bearing minerals. *Minerals Engineering*, 41, 97-114. doi:https://doi.org/10.1016/j.mineng.2012.10.017
- Kim, D., Powell, L. E., Delmau, L. H., Peterson, E. S., Herchenroeder, J., & Bhawe, R. R. (2015). Selective Extraction of Rare Earth Elements from Permanent Magnet Scraps with Membrane Solvent Extraction. doi:10.1021/acs.est.5b01306
- Kim, E., & Osseo-Asare, K. (2012). Aqueous stability of thorium and rare earth metals in monazite hydrometallurgy: Eh–pH diagrams for the systems Th–, Ce–, La–, Nd– (PO4)–(SO4)–H2O at 25°C. *Hydrometallurgy*, 113-114, 67-78. doi:https://doi.org/10.1016/j.hydromet.2011.12.007
- Larsson, K., & Binnemans, K. (2014). Selective extraction of metals using ionic liquids for nickel metal hydride battery recycling. doi:10.1039/C3GC41930D
- Li, H., Guo, F., Zhang, Z., Li, D., & Wang, Z. (2006). A new hydrometallurgical process for extracting rare earths from apatite using solvent extraction with P350. *Journal of Alloys and Compounds*, 408-412, 995-998. doi:https://doi.org/10.1016/j.jallcom.2004.12.119
- Li, W., Guan, B., Yan, J., Zhang, N., Zhang, X., & Liu, X. (2016). Enhanced surface exchange activity and electrode performance of (La₂–2xSr_{2x})(Ni₁–xMnx)O₄+δ cathode for intermediate temperature solid oxide fuel cells. *Journal of Power Sources*, 318, 178-183. doi:https://doi.org/10.1016/j.jpowsour.2016.04.022
- Lucay, F., Mellado, M. E., Cisternas, L. A., & Gálvez, E. D. (2012). Sensitivity analysis of separation circuits. *International journal of mineral processing*, 110, 30-45.

- Marie, C., Hiscox, B., & Nash, K. L. (2011). Characterization of HDEHP-lanthanide complexes formed in a non-polar organic phase using ^{31}P NMR and ESI-MS. doi:10.1039/C1DT11534K
- McCabe, W. L., & W, T. E. (1925). Graphical Design of Fractionating Columns -McCabe and Thiele. *Industrial and engineering chemistry*, 7.
- Mollah, M. Y. A. (2001). Electrocoagulation (EC) — science and applications. *Journal of Hazardous Materials*, 84(1), 13.
- Morgan, B., & Lahav, O. (2007). The effect of pH on the kinetics of spontaneous Fe (II) oxidation by O_2 in aqueous solution—basic principles and a simple heuristic description. *Chemosphere*, 68(11), 2080-2084. doi:[10.1016/j.chemosphere.2007.02.015](https://doi.org/10.1016/j.chemosphere.2007.02.015)
- Nepo, H. J. (2016). Electrocoagulation process in water treatment: A review of electrocoagulation modeling approaches. *Desalination*, 404, 21.
- Ning, P., Cao, H., Lin, X., & Zhang, Y. (2013). The crud formation during the long-term operation of the V (V) and Cr (VI) extraction. *Hydrometallurgy*, 137, 133-139. doi:[10.1016/j.hydromet.2013.05.001](https://doi.org/10.1016/j.hydromet.2013.05.001)
- Noble, A., & Luttrell, G. H. (2014). The matrix reduction algorithm for solving separation circuits. *Minerals Engineering*, 64, 97-108.
- PRAKASH, V. (2014). *ELECTROCHEMICAL RECOVERY OF RARE EARTH ELEMENTS FROM MAGNET SCRAP* - A THEORETICAL ANALYSIS. Paper presented at the 1st European Rare Earth Resources Conference.
- Preston, J. S. (1996). Recovery of REO from phosphoric acid byproduct_Part 1_Preston et al The-recovery-of-rare-earth-oxides-from-a-phosphoric-acid-by-product-Part-1-Leaching-of-rare-earth-values-and-recovery-of-a-mixed-rare-earth-oxide-by-solvent-extraction. *Hydrometallurgy*.
- REE - Rare Earth Elements - Metals, Minerals, Mining, Uses. (2018). Retrieved from <https://geology.com/articles/rare-earth-elements/>
- Reporter. (2019). Lynas and Blue Line MoU for rare earths separation. Retrieved from <https://www.miningmagazine.com/chemicals-reagents/news/1364528/lynas-and-blue-line-mou-for-rare-earths-separation>
- Riaño, S., & Binnemans, K. (2015). Extraction and separation of neodymium and dysprosium from used NdFeB magnets: an application of ionic liquids in solvent extraction towards the recycling of magnets. doi:10.1039/C5GC00230C
- Ritcey, G. M. (1980). Crud in solvent extraction processing—a review of causes and treatment. *Hydrometallurgy*, 5(2-3), 97-107. doi:[10.1016/0304-386X\(80\)90031-6](https://doi.org/10.1016/0304-386X(80)90031-6)
- Ritcey, G. M., & Wong, E. W. (1985). Influence of cations on crud formation in uranium circuits. *Hydrometallurgy*, 15(1), 55-61. doi:[10.1016/0304-386X\(85\)90066-0](https://doi.org/10.1016/0304-386X(85)90066-0)
- Rout, A., & Binnemans, K. (2013). Liquid–liquid extraction of europium(III) and other trivalent rare-earth ions using a non-fluorinated functionalized ionic liquid. doi:10.1039/C3DT52285G
- Rout, A., & Binnemans, K. (2014). Separation of rare earths from transition metals by liquid-liquid extraction from a molten salt hydrate to an ionic liquid phase. *Dalton Trans*, 43(8), 3186-3195. doi:10.1039/c3dt52541d
- Rout, A., Kotlarska, J., Dehaen, W., & Binnemans, K. (2013). Liquid–liquid extraction of neodymium(III) by dialkylphosphate ionic liquids from acidic medium: the importance of the ionic liquid cation. doi:10.1039/C3CP52218K
- Rout, A., Wellens, S., & Binnemans, K. (2013). Separation of rare earths and nickel by solvent extraction with two mutually immiscible ionic liquids. doi:10.1039/C3RA46261G

- Sadanandam, R., Singh, D. K., & Sharma, A. K. Use of operating line equations and operating parameters in solvent extraction system for the separation and purification of metal ions. In: Bhabha Atomic Research Centre, Mumbai, India.
- Separation Hydrometallurgy of Rare Earth Elements* | Jack Zhang | Springer. (2016).
- Singh, R. K., & Dhadke, P. M. (2003). Extraction and separation of scandium (III) from perchlorate media, by D2EHPA and PC-88A. *Bull Chem Technol Macedonia*, 22, 1-11.
- Skousen, J., Zipper, C., Rose, A., Ziemkiewicz, P., Nairn, R., McDonald, L., & Kleinmann, R. (2017). Review of Passive Systems for Acid Mine Drainage Treatment. *Mine Water and the Environment*, 36(1), 133-153. doi:10.1007/s10230-016-0417-1
- Stewart BW, Capo RC, Hedin BC, Hedin RS. (2016). Rare earth element resources in coal mine drainage and treatment precipitates in the Appalachian Basin, USA. *Int J Coal Geol* 2016;169:28–39. doi:10.1016/j.coal.2016.11.002.
- Survey, U. S. G. (2018). U.S. Mines Produced an Estimated \$75.2 Billion in Minerals During 2017. Retrieved from <https://www.usgs.gov/news/us-mines-produced-estimated-752-billion-minerals-during-2017>
- Tay, P. K. R., Manjula-Basavanna, A., & Joshi, N. S. (2018). Repurposing bacterial extracellular matrix for selective and differential abstraction of rare earth elements. doi:10.1039/C8GC01355A
- Vass, C. R., Noble, A., & Ziemkiewicz, P. F. (2019a). The Occurrence and Concentration of Rare Earth Elements in Acid Mine Drainage and Treatment By-products: Part 1—Initial Survey of the Northern Appalachian Coal Basin. *Mining, Metallurgy & Exploration*, 36(5), 903-916.
- Vass, C. R., Noble, A., & Ziemkiewicz, P. F. (2019b). The Occurrence and Concentration of Rare Earth Elements in Acid Mine Drainage and Treatment Byproducts. Part 2: Regional Survey of Northern and Central Appalachian Coal Basins. *Mining, Metallurgy & Exploration*, 36(5), 917-929.
- Wang, K., Adidharma, H., Radosz, M., Wan, P., Xu, X., Russell, C. K., . . . Yu, J. (2017). Recovery of rare earth elements with ionic liquids. doi:10.1039/C7GC02141K
- Wang, L., Huang, X., Yu, Y., Xiao, Y., Long, Z., & Cui, D. (2013). Eliminating ammonia emissions during rare earth separation through control of equilibrium acidity in a HEH(EHP)-Cl system. *Green Chemistry*, 15(7), 6. doi:10.1039/C3GC40470F
- Wang, W., & Cheng, C. Y. (2011). Separation and purification of scandium by solvent extraction and related technologies: a review. *Journal of Chemical Technology & Biotechnology*, 86(10), 1237-1246.
- Wikipedia. (2018a). Inductively coupled plasma atomic emission spectroscopy. Retrieved from https://en.wikipedia.org/wiki/Inductively_coupled_plasma_atomic_emission_spectroscopy
- Wikipedia. (2018b). Inductively coupled plasma mass spectrometry. Retrieved from https://en.wikipedia.org/wiki/Inductively_coupled_plasma_mass_spectrometry
- Xie, R.-J., Hirosaki, N., Li, Y., & Takeda, T. (2010). Rare-Earth Activated Nitride Phosphors: Synthesis, Luminescence and Applications. *Materials*, 3(6), 3777-3793. doi:10.3390/ma3063777
- Yan, H., Wang, L., Xiong, W., Li, B., Li, J., Earths, B. R. I. o. R., . . . Ltd, T. B. R. I. O. R. E. C. (2017). Rare Earth Based Hydrogen Storage Alloy and Application Thereof.
- Yasuda, K. (2016). Selective Formation of Rare-Earth–Nickel Alloys via Electrochemical Reactions in NaCl–KCl Molten Salt. *Journal of The Electrochemical Society*.
- Yu, J., & Liu, D. (2010). Extraction of magnesium from phosphoric acid using dinonylnaphthalene sulfonic acid. *Chemical Engineering Research and Design*, 88(5-6), 6.

Products

- Phase 1 summary report DE FE0026927
- Two journal papers have been published:
 - Vass, C. R., Noble, A., & Ziemkiewicz, P. F. (2019a). The Occurrence and Concentration of Rare Earth Elements in Acid Mine Drainage and Treatment By-products: Part 1—Initial Survey of the Northern Appalachian Coal Basin. *Mining, Metallurgy & Exploration*, 36(5), :3-916.
 - Vass, C. R., Noble, A., & Ziemkiewicz, P. F. (2019b). The Occurrence and Concentration of Rare Earth Elements in Acid Mine Drainage and Treatment Byproducts. Part 2: Regional Survey of Northern and Central Appalachian Coal Basins. *Mining, Metallurgy & Exploration*, 36(5), 917-929.

Participants and Other Collaborating Organizations

Table 20. Listing of Key Project Personnel.

Personnel	Role	Business Association	Primary Contact E-Mail
Paul Ziemkiewicz	PI	West Virginia University	Paul.Ziemkiewicz@mail.wvu.edu
Aaron Noble	Co-PI	Virginia Tech	aaron.noble@vt.edu
Xingbo Liu	Co-PI	West Virginia University	Xingbo.Liu@mail.wvu.edu
Qingqing Huang	Co-PI	West Virginia University	qingqing.huang@mail.wvu.edu
Chris Vass	Key Personnel	West Virginia University	crvass@mail.wvu.edu

Changes/Problems

N/A

Special Reporting Requirements

DOE requires delivery of county-specific and site-specific information on sources of coal and coal by-products/samples. Concentrations of REEs must be expressed as follows:

- REE concentrations in feedstock material should be expressed on both of the following bases: 1) REE elemental concentration on a dry mass/dry whole sample/dry whole coal basis; and 2) REE elemental concentration on a dry ash basis.
- REE concentrations in output products should be expressed on an elemental basis for comparison with the FOA objective to “approach 2% by weight total REE on a dry basis for solid material, as measured by elemental analysis.”

NETL intends to publicly post the site-specific sources of samples and the associated analytical results as <https://edx.netl.doe.gov/ree/>.

Budgetary Information

The SF-425 Federal Financial Report will be submitted by WVU's Sponsored Research Accounting (SRA) Office. All financial reports and official numbers are submitted through this office and will cover federal costs and recipient cost share incurred. Our Cost Plan/Status table can be found below in Table 21. Amounts contained within reflect internal adjustments currently making their way through WVU's financial systems.

Table 21. Cost Plan/Status Table.

Baseline Reporting Quarter	Budget Period 1															
	Q1		Q2		Q3		Q4		Q5		Q6		Q7		Q7	
	01/01/18 - 03/31/18		04/01/18 - 06/30/18		07/01/18 - 09/30/18		10/01/18 - 12/31/18		1/1/19 - 3/31/19		4/1/19 - 6/30/19		7/1/19 - 9/30/19		7/1/19 - 9/30/19	
	Q1	Cumulative Total	Q2	Cumulative Total	Q3	Cumulative Total	Q4	Cumulative Total	Q5	Cumulative Total	Q6	Cumulative Total	Q7	Cumulative Total	Q7	Cumulative Total
Baseline Cost Plan																
Federal Share	\$399,282	\$399,282	\$532,376	\$931,658	\$532,376	\$1,464,034	\$399,282	\$1,863,316	\$399,282	\$2,262,598	\$399,282	\$2,661,880	N/A	\$2,661,880	N/A	\$2,661,880
Non-Federal Share	\$0	\$0	\$30,000	\$30,000	\$30,000	\$60,000	\$160,000	\$220,000	\$300,375	\$520,375	\$208,000	\$728,375	N/A	\$728,375	N/A	\$728,375
Total Planned	\$399,282	\$399,282	\$562,376	\$961,658	\$562,376	\$1,524,034	\$559,282	\$2,083,316	\$699,657	\$2,782,973	\$607,282	\$3,390,255	N/A	\$3,390,255	N/A	\$3,390,255
Actual Incurred Cost																
Federal Share*	\$388,796	\$388,796	\$166,357	\$555,153	\$323,502	\$878,655	\$319,177	\$1,197,832	\$300,336	\$1,498,167	\$299,848	\$1,798,015	\$199,136	\$1,997,151	\$661,122	\$2,658,273
Non-Federal Share**	\$0	\$0	\$25,721	\$25,721	\$0	\$25,721	\$242,361	\$268,082	\$278,195	\$546,277	\$192,659	\$738,936	\$44,415	\$783,351	\$0	\$783,351
Total Incurred Costs	\$388,796	\$388,796	\$192,078	\$580,874	\$323,502	\$904,376	\$561,538	\$1,465,914	\$578,531	\$2,044,445	\$492,507	\$2,536,951	\$243,551	\$2,780,503	\$661,122	\$3,441,624
Variance																
Federal Share	\$10,486	\$10,486	\$366,019	\$376,505	\$208,874	\$585,379	\$80,105	\$665,484	\$98,946	\$764,431	\$99,434	\$863,865	N/A	\$664,729	N/A	\$3,607
Non-Federal Share	\$0	\$0	\$4,279	\$4,279	\$30,000	\$34,279	-\$82,361	-\$48,082	\$22,180	-\$25,902	\$15,341	-\$10,561	N/A	-\$54,976	N/A	-\$54,976
Total Variance	\$10,486	\$10,486	\$370,298	\$380,784	\$238,874	\$619,658	-\$2,256	\$617,402	\$121,126	\$738,528	\$114,775	\$853,304	N/A	\$609,752	N/A	-\$51,369

Milestone Status Report

Our Milestone Status Report is contained in Table 22 below.

Table 22. Milestone Status Report.

Milestone Title/Description	Verification Method	Planned Completion Date	Actual Completion Date	Percent Completed To date	Comments
Rockwell Automation instrumentation and controls incorporated into the REE system	Controls and sensors fully operational	11/15/19	5/31/19	100%	Complete.
System construction and installation completed and shakedown testing complete.	REE System operating parameters identified, limitations corrected	7/01/2018	7/1/2018	100%	Complete.
Techno-Economic Analysis Completed and multiple plant scales modeled	Cost and performance modeling completed	11/31/2019	7/1/19	100%	Complete.
Resource and Reserve Characterization refined from Phase 1 based on Phase 2 data and results.	Grade-tonnage curves generated, and economic cut-off grade identified	11/31/2019	8/30/19	100%	Complete.
Commercialization Plan to include resource ownership and control scenarios and evaluation of IP and other legal barriers	Commercialization TEA, resource ownership options, and IP/patent identified	11/31/2019	9/30/19	100%	Complete.

Acknowledgements

Aaron Noble, Chris Vass, Scott Koerner, Yan Wang, Daejin Kim, Wesley Edge, and Jessten Smith, Panpan Ren, Qinging Huang, Harry Finklea and Drew Bucy contributed to the development of this report.

Appendices

Appendix A: Resource and Reserve Report Documentation

Appendix B: Legal Ownership and Control Report

Appendix A: Resource and Reserve Report Documentation



The Occurrence and Concentration of Rare Earth Elements in Acid Mine Drainage and Treatment By-products: Part 1—Initial Survey of the Northern Appalachian Coal Basin

Christopher R. Vass¹ · Aaron Noble² · Paul F. Ziemkiewicz¹

Received: 25 February 2019 / Accepted: 6 June 2019
© Society for Mining, Metallurgy & Exploration Inc. 2019

Abstract

The conventional rare earth element (REE) industry has historically sought to develop ore deposits where geologic processes have produced mineralized zones with commercially attractive REE concentrations. These deposits are extremely uncommon, particularly in the USA. Given the criticality of these materials and the need for sustainable domestic supply, the current research seeks to leverage other autogenous processes that lead to concentrated REE resources. One such process is the generation of acid mine drainage (AMD). AMD is very common in many coal mining districts and results from the exposure and oxidation of pyrite during mining. During the generation and migration of AMD, liberated sulfuric acid mobilizes several metal ions including REEs. Treatment of AMD is required under U.S.C §1251, the Clean Water Act, and often consists of neutralization, oxidation, and metal hydroxide precipitation. To investigate the deportment of REEs during this process, a field sampling campaign was undertaken, whereby the concentration of REEs in AMD and AMD precipitates was measured directly. In the nine sites evaluated in this study, the REE concentrations of the precipitates varied from 29 to 1286 ppm with an average of 517 ppm among the sampled sites. The individual elements were enriched compared with the associated bulk Northern Appalachian (NAPP) coal material by factors ranging from 3 to 15. Furthermore, the distribution of REEs in all precipitate samples favored the heavy REEs (HREEs) when compared with traditional REE ores. This research represents the first part of multi-part research endeavor to characterize, classify, and determine the practicality of refining REEs from AMD and its by-products.

Keywords Acid mine drainage · Rare earth elements · Coal by-products

1 Introduction

Rare earth elements (REEs) occur in a wide variety of geologic formations; however, these occurrences rarely meet the necessary minimum cutoff limits to facilitate profitable extraction and refining. In cases where the ores do meet cutoff grade limits, the mineralization often contains significant concentrations of the actinides thorium and uranium. The mining and processing of these deposits often entail detrimental environmental consequences and higher operating costs owing to waste disposal and handling [1]. Given the scarcity of

geologic settings that lead to enriched REE deposits, more than 90% of REE production occurs in one country: China [2]. This near-monopoly creates a potential impairment for the USA and other countries where REEs are not readily produced. For example, during 2010 to 2012 rare earth crisis, China imposed reduced export quotas during a period of increased demand. This constrained market caused prices for many REEs to increase more than 100-fold, leading to shortages in downstream markets [3]. As the demand peaked during this period, almost \$6,000,000,000 of investment capital was raised by junior mining companies to secure additional REE resources outside of China. Unfortunately, by 2015, many of these companies entered bankruptcy or lost interest in REEs due to the lower prices. This event indicates the overall importance of REE supply on a local and global basis as well as the need to consider alternative resources [4].

Despite the increased investment, only two REE mines recently started production outside of China [5]. The Mount Weld deposit in Australia began production in 2013. The ore from Mt. Weld is processed in Malaysia by Lynas

✉ Christopher R. Vass
chris.vass@gmail.com

¹ West Virginia Water Research Institute, PO Box 6064,
Morgantown, WV 26506, USA

² Virginia Tech Mining and Minerals Engineering, Holden Hall 100,
Virginia Tech, 445 Old Turner Street, Blacksburg, VA 24061, USA

Corporation, whose operating permit has recently come under controversy concerning the disposal of radioactive waste [6]. The second operation, Mountain Pass located in the USA, has experienced instability in reaching full-scale production due to lower REE prices and the high distribution of light REEs (LREE) in the orebody [7].

Many industrial processes rely on REEs for their products including catalysts, metallurgy, petroleum refining, catalytic converters, ceramics, phosphors, magnets, and electronics. Currently, the USA consumes approximately 12,000 metric tons of REEs per year [8]. Of that, the Department of Defense uses less than 5%, or approximately 600 metric tons [9]. Future demand for individual REEs is difficult to predict due to the number of elements involved and variety of uses; however, given the increasing forecasted demand for green technologies and electronic devices, many researchers believe that demand for REEs will also increase [10, 11]. Specifically, supply concerns regarding the heavy REEs (HREE) are of primary concern because identifying economically feasible HREE-enriched deposits outside of China has been unsuccessful [12].

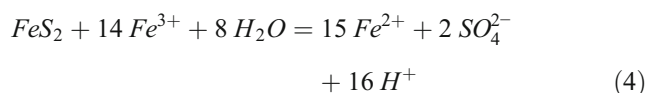
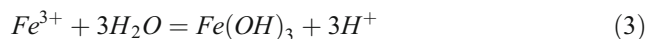
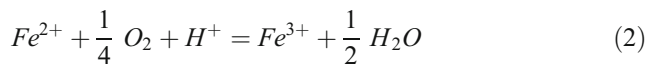
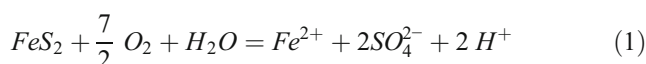
Given the disparity between current REE supply and future REE demand, many stakeholders including researchers, national governments, and private companies have attempted to identify alternative and unconventional REE resources. For example, by-products of phosphoric acid production have been identified as a potential alternative source of REE production [13–16]. Also, there has been an increased interest in recycling of REEs, further indicating the need for alternative REE supplies [17]. While the overall production volume of REEs may alleviate some criticality concerns of the REE supply, it will not successfully compensate for the projected increase in demand over the next several years [18].

The presence of REEs in coal has long been established by many researchers [19–22]. More recently, the classification of REEs as critical minerals by the USA has brought an increased interest in the availability of a domestic REE supply. Since 2014, the US Department of Energy has analyzed the economic feasibility of recovering rare earth elements from coal and coal by-products [23]. Most initial studies focused on the recovery of REEs from coal tailings (refuse) and coal fly ash [24].

In June 2015, researchers at West Virginia University found significant concentrations of REE in precipitates formed during acid mine drainage (AMD) treatment [25]. These findings formed the basis for a detailed study of REE occurrence in the northern (NAPP) and central (CAPP) Appalachian Coal Basin AMD and its by-products. Consequently, this research was developed to identify the grade and potential recovery of REEs from AMD and its by-products.

In the Appalachian Coal Basin, AMD constitutes one of the most significant and widespread water quality challenges.

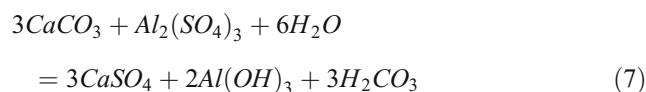
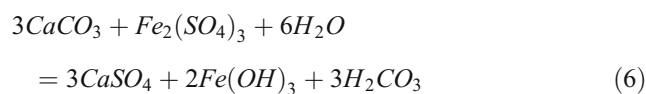
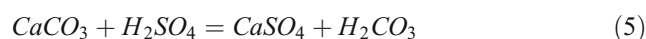
AMD occurs when pyrite-bearing mine spoil oxidizes after mining. It consists of acidity and a varied suite of metals such as iron, aluminum, and manganese as well as the dominant anion, sulfate. Mining exposes these sulfide minerals to weathering, and the increased mineral surface area then leads to elevated oxidation and leaching, resulting in AMD formation as follows [26]:



The detrimental effects of AMD are well-documented and include adverse impacts on nearby streams [27–30]. Over the last 50 years, researchers have extensively studied the factors controlling AMD and developed methods that predict the severity and extent of AMD based on mining practices and geological properties [28, 31].

Per Section 402 of the Clean Water Act, mine operators are obliged to treat AMD prior to discharge. This treatment often incorporates alkaline addition and oxidation to increase the pH and remove metal ions from solution [26, 30, 32, 33]. This method of treatment can be incorporated through the use of different processing systems, both active and passive, to maximize treatment efficiency, minimize cost, and ensure environmental compliance [29, 34].

As AMD is treated by alkaline addition, the dissolved metal ions precipitate as hydroxides (denoted AMD sludge, AMD precipitate, or AMDp) while clean water is discharged into the receiving stream as follows (when using $CaCO_3$ as the neutralizing agent) [35]:



The chemical and morphological characteristics of AMDp are unique to each treatment site and are a function of the composition of the AMD, type of neutralization chemical used, the amount of aeration, the extent of carbon dioxide release, and the configuration of the treatment system incorporated [26, 36]. Typically, AMDp is composed of an iron-rich sludge that can contain other metals and vary from granular to gelatinous in consistency [36]. Moreover, the AMDp

can contain fine to amorphous flocs that are greatly dependent on the treatment chemical used [37]. As a result, the AMDp from each mine site will vary as to the exact makeup of hydroxides, carbonates, and composition of metals. Lastly, this bulky and often moisture-rich sludge is difficult to handle and dispose of effectively. Alternative applications for this material could prove beneficial to the public and private entities liable for the treatment and disposal of AMD [38].

AMD chemistry represents the integration of reactions that occur on much smaller scales such as the pore water surrounding pyritic versus non-pyritic rock grains and localized oxidizing versus reducing environments. This integration occurs over the scale of mines that range in extent from hundreds of acres to 20 square miles or more as is the case of large, underground mines. AMD precipitate further integrates these variations in discharge chemistry by aggregating the dissolved metal loads over periods of months or years. The volume of mine drainage, either derived from surface or underground sources, changes seasonally according to the volume of infiltrating water; but, ionic composition fluctuates within narrow bounds at a given source. Thus, loads and concentrations vary inversely between the wet winter months and the dry late-summer to fall seasons.

While several prior studies have evaluated the partitioning and concentration of major AMD metals such as iron, aluminum, and manganese, few studies to date have evaluated the quality and quantity of REEs in AMD and AMD treatment by-products. Moreover, the lack of technical data on REEs in AMD limits the ability to answer key questions on the prospectivity (a predictive tool for choosing the location for further exploration efforts) of a potential REE resource derived from AMD. These questions include but are not limited to:

- What are the typical REE concentrations in AMD and what factors influence those concentrations?
- What is the size of the REE resource that can be realized from AMD in the Appalachian coal basin?
- What is the contained value of REEs in AMD and AMDp, and is this contained value sufficient to merit further study?
- What is the conceptual framework for the extraction and processing of these resources?
- What environmental, social, legal, and other intangible considerations must be resolved prior to resource development?

The objective of this manuscript is to evaluate the prospectivity of AMDp as an alternative source of REEs. The current technical literature lacks data from systemic studies that describe the content and quality of REEs in AMD and AMDp, and, as a result, few researchers have critically analyzed the value chain that can be derived from this current

waste stream. This manuscript will describe a prospecting study where nine AMD treatment sites were extensively sampled and analyzed to determine the variation among and within sites as well as the partitioning of REEs among the AMD, AMDp, and treated water streams. Following this initial characterization, a regional production model was developed and used to estimate the resource size and potential value of REEs from AMD. Lastly, the paper investigates the technical, environmental, and civil considerations that would accompany REE extraction from AMD.

2 Materials and Methods

To assist in assessing the prospectivity of REEs in AMD, nine Northern Appalachian coal mine sites with AMD outflows were chosen for detailed sampling that encompassed a variety of coal seams and mine types. Each of these sites employs active chemical treatment of the AMD to meet effluent limits. As a result, both AMD and AMDp were available for sampling. Figure 1 shows the location of these sites within the NAPP basin on a county level, while Table 1 shows the unique characteristics of each site.

Several classes of AMD were represented in the population of sampling sites. The two primary mine categories included underground and surface. The surface category included refuse storage areas and impoundments. Next, the mines were classified as either above or below drainage (a.k.a. flooded). Flooded mines that are located below drainage typically contained net-alkaline water in contrast to the net-acidic water commonly associated with AMD [39, 40]. This difference is caused by the restriction of pyrite oxidation under anoxic, flooded conditions and the gradual accumulation of the alkaline, bicarbonate ion buffer [41]. Under unflooded, oxidizing conditions, pyrite oxidation is unrestricted and acid generation may be controlled by either neutralizing minerals in the spoil or the eventual exhaustion of pyrite [42, 43]. This distinction is significant as the extent of acid generation is anticipated to influence REE loading.

Both aqueous AMD and solid AMDp samples were collected over periods of between four and 17 months, depending on the sampling site. Typically, both the influent and effluent aqueous streams were collected at the AMD treatment plant. Additionally, three AMDp samples were collected at the site during each visit.

The sampling interval was chosen based on the inherent variability, quality, or quantity of the AMDp produced at each site. For example, site AMD_7 was sampled frequently even though it had a low REE concentration in the AMDp because it had a high flux of AMD and was therefore a potentially high-volume producer of REEs. Likewise, site AMD_3 had the highest concentration of total rare earth elements (TREEs) in the population and was therefore intensively sampled.

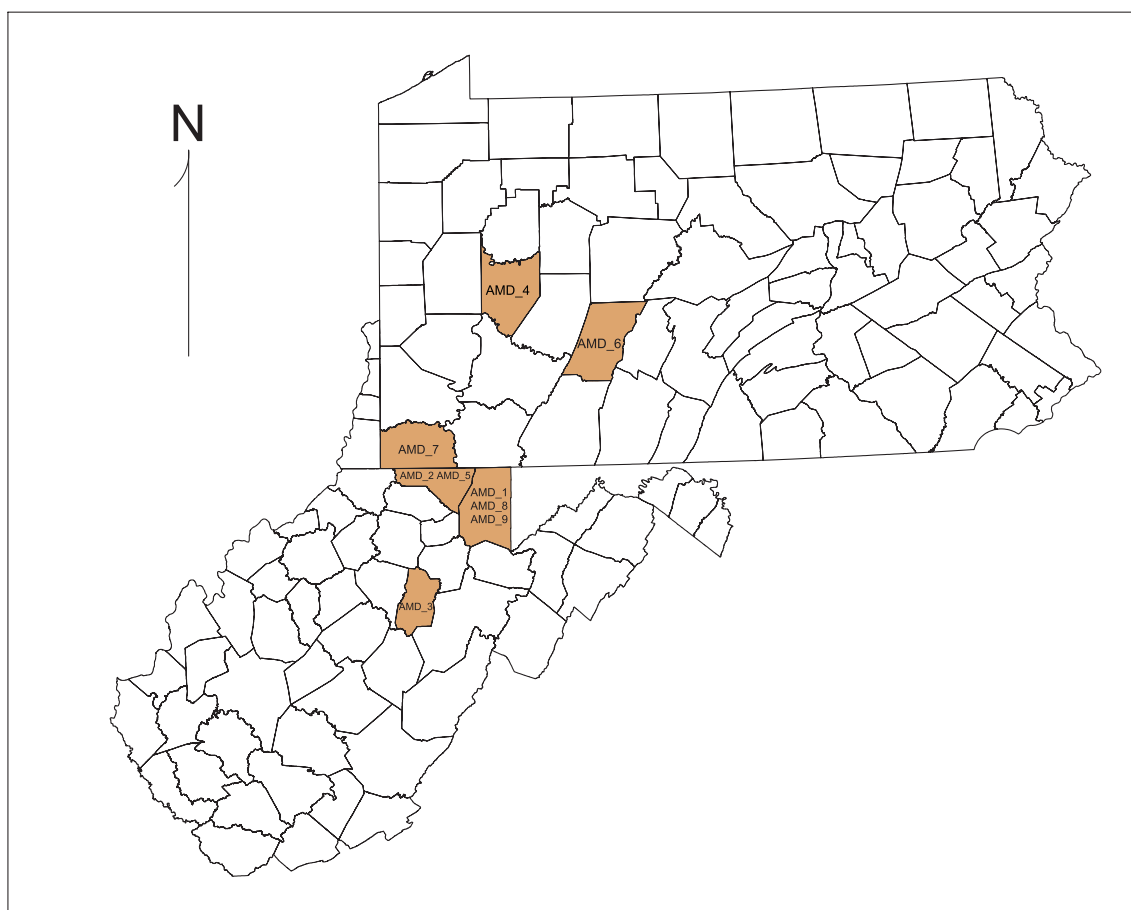


Fig. 1 County level location of the AMD sites evaluated

The collected aqueous and precipitate samples were then analyzed using ICP-MS for the REEs by TestAmerica Laboratories, Inc. and SGS Canada Inc., respectively. Both

laboratories are certified by their respective state/provincial agencies to undertake both aqueous and solid REE analysis. Additionally, West Virginia University's National Research

Table 1 AMD site topographic settings and characteristics

Site ID	State	County	Influent pH	Treatment chemical	Seam	Mine type	Flooded/above drainage
AMD_1	WV	Preston	2.73	Lime	Freeport	UG	Above drainage
AMD_2	WV	Monongahela	6.91	Lime	Pittsburgh	UG	Flooded
AMD_3	WV	Upshur	3.46	NaOH	Kittanning	SM	Above drainage
AMD_4	PA	Armstrong	3.17	Lime	Kittanning	SM/UG	Above drainage
AMD_5	WV	Monongahela	2.88	Lime	Freeport	UG	Above drainage
AMD_6	PA	Cambria	5.38	Lime	Kittanning	UG	Flooded
AMD_7	PA	Greene	6.58	Lime	Pittsburgh	UG	Flooded
AMD_8	WV	Preston	2.69	Ammonia	Freeport	UG	Above drainage
AMD_9	WV	Preston	2.70	Lime	Freeport	UG	Above drainage

UG, underground mine; SM, surface mine

Center for Coal and Energy Analytical Laboratory (NRCCE) used an ICP-OES to analyze the other major ions. AMDp was digested using a sodium peroxide (Na_2O_2) fusion and re-dissolved in hydrochloric acid. This method appears to be comparable with the United States Environmental Protection Agency's total digestion method 3052 for REEs. Method detection limits (MDL) for the aqueous rare earths were typically in the 0.02 ppb range, while the solid REE analysis had MDL ranging from 5 to 0.5 ppm. Major metal ions were measured in aqueous samples with MDL similar to those of the aqueous REEs.

Aqueous samples were collected in a clean 1000-mL HDPE sample bottle. Next, this sample was then split into two separate containers (one preserved and one raw) for further analysis. Dilute nitric acid (2%) was added to the preserved sample bottle to prevent precipitation or adsorption of the target analytes during shipping. Afterwards, the raw water samples were stored at 4 °C, until it was ultimately delivered to the NRCCE laboratory for major ion analysis. Finally, the aqueous REE samples were shipped to the TestAmerica laboratory in their preserved state.

Precipitates were collected by hand using a shovel or post-hole digger at or near the edge of the drying cell. These samples were placed in new 1-gallon HDPE sample buckets. Later, the AMDp samples were split into 50-mL representative aliquots for the ICP analysis in a laboratory setting. These sub-samples were then placed in 50-mL digestion tubes for transport to SGS Canada Inc. for analysis.

Representative samples of entire AMDp cells were often difficult to impossible to safely obtain due to the depth and semi-liquid consistency of the precipitate. Therefore, many of the collected samples were located near the edge of drying cell ponds. Due to this sampling procedure, bias may have been introduced into some of the results. For example, the AMDp may stratify within the settling pond with varying qualities dependent upon depth. Alternatively, where allowed, various AMDp samples were collected at differing depths across a drying cell for select sites. Figure 2 shows a typical AMDp drying cell where representative samples were difficult to obtain. Finally, at sites that pump an AMDp product to abandoned underground mine works, the samples were collected from the clarifier underflow.

Several authors, including Seredin and Dai [44], Moldoveanu [45], and Gupta [46], have used different classifications methods to assist in analyzing potential REE resources. These classifications can be based on supply-demand relationships (critical REE versus excessive REE) or simple atomic number (heavy REE vs. light REE). For this paper, the following classifications will be observed:

- Heavy REEs (HREE): Sc, Y, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu
- Light REEs (LREE): La, Ce, Pr, Nd, Sm, Eu



Fig. 2 Typical AMDp drying pond found in NAPP

- Total REEs (TREE): HREE + LREE
- Critical REEs (CREE): Y, Nd, Eu, Tb, Dy

3 Results and Discussion

The data from the field sampling campaign was used to assess the prospectivity of the REE resource in AMD. Key questions include the concentration of REEs in AMD and the factors that influence concentration, the overall size of the potential resource, the market value, conceptual framework for extraction and processing, and environmental and civil considerations. Each question is addressed in further detail below.

3.1 Concentration of REEs in AMD and AMDp

Tables 2 and 3 show the analytical results of the sampling campaign for AMD and AMDp respectively. TREE concentration averaged 258 $\mu\text{g/L}$ for the aqueous AMD influent. This low REE concentration may seem to preclude AMD as a viable REE feedstock; however, the high enrichment factor after treatment of AMD is significant. Of the samples tested, the average concentration of REEs in AMDp was 517 g/t: a concentration factor of 2000 times, with individual REE concentration factors varying from 1300 to 8400 times. These data show that the process of AMD migration through coal strata and the subsequent treatment of AMD produce a net enrichment, because the average TREE concentration in AMDp (517 ppm) is considerably higher than that of US coal (66 ppm) or the crustal abundance (206 ppm) [19, 47]. Also, REE concentrations in AMD treatment plant effluent was extremely low, often below detection limits, indicating the REEs exited the treatment plant as a precipitate.

Table 2 Average REE concentrations for aqueous AMD influent at nine treatment facilities in PA and WV

Site	(txt)	AMD_1	AMD_2	AMD_3	AMD_4	AMD_5	AMD_6	AMD_7	AMD_8	AMD_9	Mean	% TREE
Mine type	(txt)	UG	UG	SM	UG	UG	UG	UG	UG	UG	–	–
Horizon	(txt)	AD	BD	AD	AD	AD	BD	BD	AD	AD	–	–
Seam(s)	(txt)	UFP	PITT	KITT	KITT	UFP	KITT	PITT	UFP	UFP	–	–
AMD samples	(#)	4	12	17	4	17	4	13	6	4	9	–
Sc	(ug/L)	2.63	0.83	6.11	38.70	46.50	3.16	3.82	8.05	11.38	13.46	5.2%
Y	(ug/L)	18.38	2.15	41.51	355.03	72.84	16.70	13.27	42.42	66.78	69.90	27.1%
La	(ug/L)	10.48	0.42	11.55	34.65	12.75	2.53	0.32	10.08	20.08	11.43	4.4%
Ce	(ug/L)	31.23	1.41	35.69	137.60	48.81	7.73	1.49	37.33	72.88	41.57	16.1%
Pr	(ug/L)	4.83	0.22	4.34	27.18	7.86	1.07	0.35	6.08	11.40	7.04	2.7%
Nd	(ug/L)	23.00	1.14	20.06	172.15	40.39	5.70	2.55	31.10	56.35	39.16	15.2%
Sm	(ug/L)	6.35	0.27	5.34	72.05	12.27	1.73	0.92	9.25	16.98	13.90	5.4%
Eu	(ug/L)	1.40	0.06	1.40	19.78	3.22	2.83	0.29	2.27	4.15	3.93	1.5%
Gd	(ug/L)	6.98	0.43	7.72	103.08	17.80	3.13	1.83	11.60	20.90	19.27	7.5%
Tb	(ug/L)	0.96	0.05	1.31	15.80	3.35	0.51	0.28	1.80	3.25	3.03	1.2%
Dy	(ug/L)	5.05	0.36	7.95	82.30	20.82	3.15	1.78	10.32	17.40	16.57	6.4%
Ho	(ug/L)	0.86	0.05	1.51	14.40	4.04	0.61	0.42	1.82	3.08	2.98	1.2%
Er	(ug/L)	2.18	0.20	4.26	34.95	11.79	1.60	1.21	4.95	8.15	7.70	3.0%
Tm	(ug/L)	0.28	0.01	0.53	4.33	1.49	2.64	0.15	0.62	1.03	1.23	0.5%
Yb	(ug/L)	1.58	0.13	3.12	23.53	9.14	1.05	0.81	3.88	6.50	5.52	2.1%
Lu	(ug/L)	0.23	0.01	0.45	3.43	1.30	2.62	0.13	0.55	0.88	1.06	0.4%
pH	(pH)	2.73	6.91	3.46	3.17	2.88	5.38	6.71	3.92	2.70	4.20	–
TREE	(ug/L)	116	8	153	1139	314	57	30	182	321	258	100.0%
HREE	(ug/L)	39	4	74	676	189	35	24	86	139	141	54.6%
LREE	(ug/L)	77	4	78	463	125	22	6	96	182	117	45.4%
CREE	(ug/L)	49	4	72	645	141	29	18	88	148	133	51.4%

SM, surface mine; UG, underground mine; AD, above drainage; BD, below drainage; UFP, Upper Freeport; KITT, Kittanning; PITT, Pittsburgh

3.1.1 TREE in Pre and Post Water Treatment

Further evaluation of the influent and effluent streams at each site confirmed that the bulk of the REEs were recovered into the AMDp. Figure 3 compared these influent and effluent streams from the nine sites. From these data, it was shown that the AMD treatment process reduced the REEs in the effluent by an average of 78%. Likewise, the major polluting metals (Al, Fe, Mn, Mg) were also reduced by an average of 57%. As a result, an economic method for recovering REEs from AMDp could further incentivize operators to meet or even exceed the governing effluent limits.

Results from this characterization of REEs in AMD by-products indicated that on average, AMDp contained 517 ppm of REEs on a dry weight basis, as seen in Table 3. In addition, Table 4 shows the 95% upper and lower confidence intervals for repeat samples taken from the same site. In many cases, samples from a given site showed very little variability with respect to REE concentration and distribution. This finding is likely due to the large time scales and spatial scales that govern AMD production and migration. Thus, the

concentration of REEs in AMD represents the integration over several decades and large volumes of rock.

3.1.2 Factors Controlling REE in AMD and AMDp

Each coal mine has unique geochemical features even among those that are in relatively close geographic proximity and coal seam. Furthermore, the elevation of the mine works, whether above or below drainage, also has a clear effect on the quantity of REEs in the aqueous AMD discharging from the mine. Treatment chemistry further influences the REE concentration in AMDp based on the type of treatment required at the mine. As shown in Tables 2 and 3, the sites AMD_2, AMD_6, and AMD_7 have significantly lower TREE concentrations, in both the AMD and AMDp, than the other mines. These three mines are all below-drainage flooded mine complexes. The water chemistry of these flooded AMD mines differs significantly from above-drainage mines. Typically, the pH of AMD discharged from these mines are of higher value (as seen in Table 2) since the oxidizing conditions that produce AMD are not present.

Table 3 Average REE concentrations for AMDp at nine treatment facilities in PA and WV

Site	(txt)	AMD_1	AMD_2	AMD_3	AMD_4	AMD_5	AMD_6	AMD_7	AMD_8	AMD_9	Mean	% TREE
Mine type	(txt)	UG	UG	UG	UG	SM	UG	UG	UG	UG	–	–
Horizon	(txt)	AD	AD	AD	AD	AD	AD	BD	BD	BD	–	–
Seam(s)	(txt)	KITT	UFP	UFP	UFP	KITT	UFP	KITT	PITT	PITT	–	–
AMDp samples	(#)	14	12	52	12	52	12	13	40	36	27	–
Sc	(g/t)	13.25	14.54	54.87	14.54	15.56	13.71	9.85	3.88	1.32	15.72	3.0%
Y	(g/t)	198.21	141.42	98.33	129.01	396.74	96.37	52.40	8.31	6.67	125.27	24.2%
La	(g/t)	44.94	94.03	20.39	126.75	110.31	149.96	8.85	2.98	3.11	62.37	12.1%
Ce	(g/t)	138.14	127.42	72.07	130.31	296.27	169.00	24.60	8.13	7.22	108.13	20.9%
Pr	(g/t)	21.72	20.05	11.43	19.89	37.21	23.28	3.71	1.16	0.90	15.48	3.0%
Nd	(g/t)	114.07	96.42	55.58	95.92	163.92	111.92	17.38	5.48	4.36	73.89	14.3%
Sm	(g/t)	37.48	29.29	16.74	28.38	41.36	30.18	4.73	1.93	0.82	21.21	4.1%
Eu	(g/t)	9.40	7.35	4.28	7.08	10.84	7.21	1.25	0.64	0.30	5.37	1.0%
Gd	(g/t)	49.36	35.69	24.17	34.98	61.18	35.33	8.52	2.25	1.18	28.07	5.4%
Tb	(g/t)	6.92	5.80	4.43	5.62	10.22	5.53	1.43	0.55	0.30	4.53	0.9%
Dy	(g/t)	37.10	31.15	26.11	32.47	61.72	31.13	8.05	1.94	0.78	25.61	5.0%
Ho	(g/t)	6.86	5.96	5.18	6.25	12.64	6.04	1.84	0.46	0.20	5.05	1.0%
Er	(g/t)	17.38	15.48	14.01	16.45	34.18	16.05	4.72	1.07	0.46	13.31	2.6%
Tm	(g/t)	2.12	2.16	1.95	2.21	4.48	2.06	0.68	0.47	0.40	1.83	0.4%
Yb	(g/t)	11.72	12.12	11.15	12.54	25.38	11.61	3.19	0.70	0.37	9.87	1.9%
Lu	(g/t)	1.76	1.80	1.68	1.86	3.70	1.72	0.57	0.35	0.30	1.53	0.3%
U	(g/t)	7.41	6.83	5.38	8.19	5.22	4.83	0.58	0.75	0.94	4.46	0.9%
Th	(g/t)	4.91	14.37	9.64	7.39	3.96	8.98	0.38	0.82	0.64	5.67	1.1%
TREE	(g/t)	710	641	422	664	1286	711	152	40	29	517	100.0%
HREE	(g/t)	345	266	242	256	626	220	91	20	12	231	44.6%
LREE	(g/t)	366	375	180	408	660	492	61	20	17	286	55.4%
CREE	(g/t)	366	282	189	270	643	252	81	17	12	235	45.4%
TREE Enrichment	(–)	624	1995	1344	3647	8412	6111	2675	1360	3712	2007	–

SM, surface mine; UG, underground mine; AD, above drainage; BD, below drainage; UFP, Upper Freeport; KITT, Kittanning; PITT, Pittsburgh

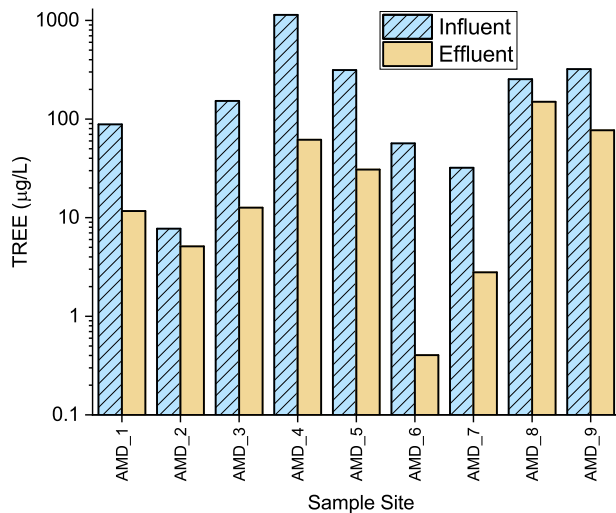
The current data generally shows that increased pH in raw AMD corresponds to a lower TREE concentration. The quantity of free hydrogen ions available for leaching is a major factor in liberating REEs from the surrounding strata. A correlation of influent water pH and TREE concentration in AMD was derived from the dataset. Figure 4 shows this relationship. Of interest is the lack of data between the pH values 4 and 5 labeled as an “un-buffered zone,” where Fe and Al buffering in AMD results in areas of pH stability in the regions above and below the pH range of 4 to 5, respectively. This bimodal behavior is likely due to the carbonate buffering in the upper pH range and pyrite oxidation at the lower pH range as described by Cravotta et al. [48]. Indeed, this bimodal distribution is a result of the differences in geochemistry between the flooded underground and above-drainage mines. This differentiation may indicate that different processing paths will be required for the different influent geochemistry profiles.

When compared with the average crustal abundance and the average content of REEs in coal, the AMDp contained a

significantly higher abundance of REEs as shown in Fig. 5. Except for Sc, all the REEs in AMDp were found in higher concentrations than in those of either the crustal abundance or native coal material. On average, the REEs in AMDp were 3.5 times more concentrated than the crustal abundance and more than 10 times more concentrated than typical REEs found in coal [19, 47]. More important is the interaction between AMD and the mineralogy of the coal seam. AMD typically seeps through not just the coal seam but the surrounding strata as well. As indicated by Zhang et al. [49], the REEs typically are associated with the gangue materials within the coal seam and not the coal itself.

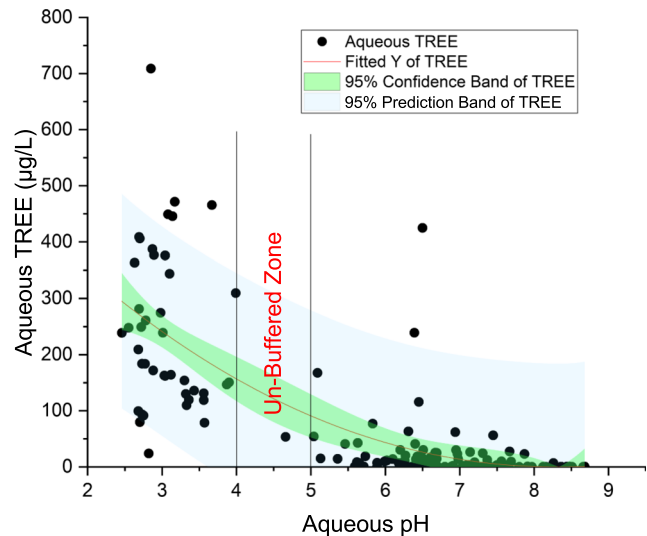
3.2 Basin Production Estimate

The results from the sampling campaign are analogous to an initial prospecting survey and may be used to approximate the overall regional production at a high level. Unfortunately, comprehensive AMD flowrate datasets are practically

Comparison of TREES in Influent and Effluent of AMD Sites**Fig. 3** Difference in the influent and effluent TREE values for nine NAPP AMD sites

nonexistent due to the complexity of flow interactions, large seasonal variations, and the temporal nature of the effluent constituents. As a result, multiple AMD outfall datasets were compiled to estimate the regional AMD flow rate estimate by the authors. These data are composed of projects completed by the West Virginia Water Research Institute, Pennsylvania Abandoned Mine Land Department, West Virginia Department of Environmental Protection, and various studies from others [50–52].

In all, this regional estimate encompasses over 1100 unique AMD outlets, predominately in the NAPP region and indicated that the regional AMD flow rate is approximately 94,700 L/s. Consequently, this estimate may be considered conservative in relation to the actual flow rate. Previously, Stewart et al. provided a regional flow estimate of 417,448 L/s [53]. By comparison, the methods used by Stewart could lead to overestimation of the true quantity of AMD due to the incorrect assumption that all coal mining leads to the generation of AMD and neglecting the spatial reduction of multi-seam extraction, which is common in Central Appalachia (CAPP). Given these complexities, an accurate and precise determination of AMD flowrate for the Appalachian basin would require a more extensive study well beyond the scope of this research. Nevertheless, for the

**Fig. 4** Relationship between pH and aqueous TREE concentrations

purpose of the current study, both Stewart's methodology and the authors' methodology were used to estimate the high and low AMD flow rate values, respectively. In addition, the REE content of this AMD was assumed to be the average for the NAPP values shown in Table 5. Given these inputs, the estimated REE production from AMD was determined to be between 771 to 3400 t of REEs per year. The high variance in the two estimated production rates indicates that further exploration of the resource is required to identify an economically feasible process to extract REEs from AMD.

3.3 Valuation

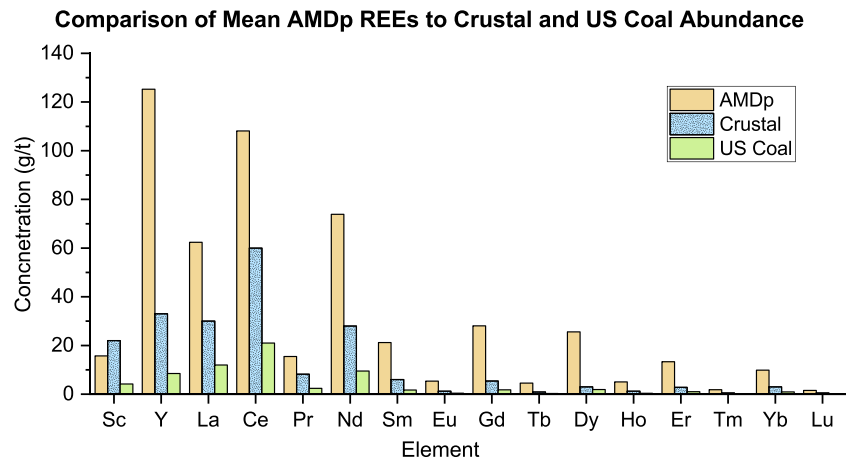
To estimate the contained value of REEs in AMD, an average price deck for the REEs was compiled for the lanthanide series plus yttrium from 2008 through 2015 using the USGS Mineral Yearbooks [54–61]. These 8 years contain the global REE peak prices observed during 2011 as well as the preceding and post market minimums. A similar process for economic valuation has been used in similar coal-based REE deposits [62, 63]. Scandium was not included in this analysis, as the unit high price tends to grossly distort the final values. Additionally, the current global production of scandium is very small, and a large influx of Sc to the market could drastically change the supply and demand relationship [64].

Table 4 AMDp 95% upper and lower confidence intervals for mean TREE values

Site	(txt)	AMD_1	AMD_2	AMD_3	AMD_4	AMD_5	AMD_6	AMD_7	AMD_8	AMD_9
Mean TREE	(g/t)	711	29	1286	710	422	152	40	664	641
95% UCL	(g/t)	507	24	1202	585	406	131	17	504	575
95% LCL	(g/t)	916	33	1369	836	439	173	64	825	707

UCL, upper confidence level; LCL, lower confidence level

Fig. 5 Comparison of mean AMDp REE concentrations to that of crustal and US coal abundance values [19, 47]



The referenced prices were provided on an oxide basis and were averaged across the 8-year span for the present data. Next, the oxide prices were converted to metal equivalents using standard metal to oxide ratios. Table 6 shows the price deck used for this preliminary valuation.

From these prices, two different economic indicators were evaluated for the mean AMDp REE concentration (minus Sc). First, the basket price was determined by weighting the elemental price by the elemental distribution within the AMDp. This indicator was representative of a what 1 kg of final REE metal product would command on the open market, assuming a representative distribution of REEs were produced from the mean AMDp values. This could also be viewed as the gross average selling price for the AMDp product before fixed and variable mining costs are deducted. Additional assumptions in the generation of this metric assume that all elements have demand in the market and all were equally recoverable in the refining process. Overall, the basket price would be a poor indicator when choosing between two projects; however, it does provide a good comparison of an ore's potential value when identical elemental prices were used between projects.

The second indicator evaluated was the in situ price. This value represents the unitized value of 1 t of the resource in the ground. In relation to AMDp, this metric would correspond to

1 t of AMDp, on a dry weight basis, located in a storage pond. This price was also exclusive of mining, processing, and milling costs; therefore, it was not an indicator of economic viability. Furthermore, this price assumed all elements were fully recovered and salable. Nevertheless, this benchmark may be used to compare the gross unitized value of reserves and resources between multiple projects. When the in situ price of \$89.08/kg TREE was applied to the REE production models

Table 6 Price deck used for economic evaluation consisting of average pricing from USGS Mineral Yearbooks (2008–2015)

Element (txt)	Mean Concentration (g/t)	% TREE (%)	Elemental Value (\$/kg)	Basket Price (\$/kg)	In situ Price (\$/ton)
Sc*	15.72	—	\$5628.83	—	—
Y	125.27	25.0%	\$85.53	\$21.36	\$10.72
La	62.37	12.4%	\$32.73	\$4.07	\$2.04
Ce	108.13	21.6%	\$35.23	\$7.60	\$3.81
Pr	15.48	3.1%	\$123.96	\$3.83	\$1.92
Nd	73.89	14.7%	\$109.10	\$16.07	\$8.06
Sm	21.21	4.2%	\$158.86	\$6.72	\$3.37
Eu	5.37	1.1%	\$1817.44	\$19.47	\$9.77
Gd	28.07	5.6%	\$183.49	\$10.27	\$5.15
Tb	4.53	0.9%	\$1438.75	\$13.00	\$6.52
Dy	25.61	5.1%	\$681.84	\$34.81	\$17.46
Ho	5.05	1.0%	\$859.11	\$8.65	\$4.34
Er	13.31	2.7%	\$195.83	\$5.20	\$2.61
Tm	1.83	0.4%	\$2093.80	\$7.66	\$3.84
Yb	9.87	2.0%	\$455.48	\$8.96	\$4.49
Lu	1.53	0.3%	\$3269.27	\$9.95	\$4.99
TREE	502	100.0%	—	\$177.62	\$89.08
HREE	215	44.6%	—	\$119.87	\$60.12
LREE	286	55.4%	—	\$57.76	\$28.97
CREE	235	45.4%	—	\$104.73	\$52.52

Table 5 Low and high regional flow rate estimates

Regional AMD flow estimate	Units	Low ¹	High ²
PA	(L/s)	51,401	—
WV	(L/s)	24,095	—
OH	(L/s)	18,900	—
MD	(L/s)	317	—
Total	(L/s)	94,712	417,448
TREE concentration (mg/L)	(mg/L)	0.258	0.258
TREE load	(t/year)	771	3400

¹ Regional flow estimates based on proprietary AMD studies

² Regional flow estimate by Stewart et.al. [53]

*Sc Excluded from evaluation due to the inherent volatility

in Table 5 at the mean aqueous inflow concentration, a value of approximately \$69M/year to \$303M/year was observed.

To compare the viability of AMDp as a reasonable REE feedstock, the two aforementioned price indexes were applied to 58 different REE resources. The assays for these projects were compiled from NI 43–101, JORC, or SAMREC statements [65]. As a means of comparison, the in situ price for each resource was plotted against that resource's basket price, as shown in Fig. 6.

The AMDp ranks reasonably well among the other resources, indicating that it has a moderate potential as a feasible resource. While AMDp does have a lower in situ price than many other reserves, it also has several unique qualities that are more amenable to processing than traditional hard-rock ores. For example, AMDp does not rely on traditional extraction, comminution, or physical separation as part of the processing flowsheet. AMDp processing to recover REEs would likely occur on brownfield sites that are already permitted for waste disposal. Furthermore, AMDp possesses a significant basket price when compared to other resources.

While this research shows that the production potential of REEs through AMD is below that of the current US demand, AMD is still significant as a steady and reliable domestic source. AMD typically loses acidity over time; however, new mining works are constantly being added that could create the oxidizing environment necessary for future AMD production. Additionally, the generation of REEs through AMD flows is stable over long periods of time; as a result, this resource could be used to supplement other US-based REE sources.

Lastly, AMDp is viewed by the industry as an impediment and the treatment, storage, and removal are conducted in a manner that minimizes cost. As a result, many of the AMDp resources are currently pumped underground or disposed of in impoundments. These practices do not allow for the recovery of REEs from the AMD treatment waste streams. Furthermore, there are many potential positive environmental impacts that could be achieved with the beneficiation of AMDp.

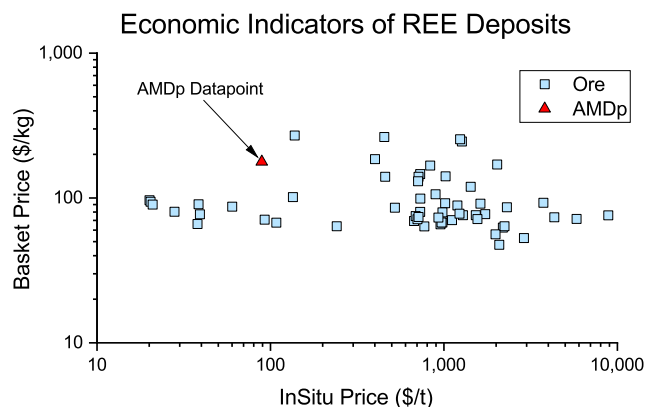


Fig. 6 Comparison of the basket and in situ price index for NAPP AMDp and 58 other REE resources. Ore-based project data after Lifton [65]

3.4 Conceptual Framework for Extraction and Processing

Currently, REEs are processed from a large variety of feedstocks that utilize a multitude of mineral processing and hydrometallurgical technologies [66]. By emulating these proven mining and hydrometallurgical processes in the REE industry, a high-level conceptual framework can be applied to AMDp. Figure 7 shows this theoretical flowsheet that could be used in the production of REEs from AMDp.

Initially, the AMDp would need to be extracted from the current in situ location. This material handling process could involve several mining practices from loading and hauling to pumping to transporting the feedstock to a processing facility. Once at the facility, several costly steps that are used in hard-rock ore processing could be bypassed due to the amorphous consistency of the precipitate. For example, extensive sizing processes like crushing and grinding as well as physical concentration such as flotation would not be necessary to classify and concentrate the feed material.

Next, the hydrometallurgical process used in the REE industry typically requires the REEs to be in an aqueous form. Likewise, the AMDp would need to be converted from the current oxide form into a soluble feedstock. Multiple leaching routes are available to accomplish this solubilization.

Separation of the REEs from other gangue metals in the AMDp could be accomplished using a variety of techniques. Currently, ion exchange, solvent extraction, or selective precipitation are used to recover REEs in an oxide form. Once separated, the REE oxides could be packaged and transported

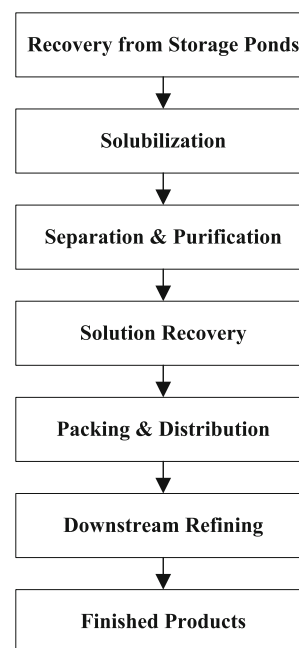


Fig. 7 Conceptual framework for extraction and recovery of REEs from AMDp

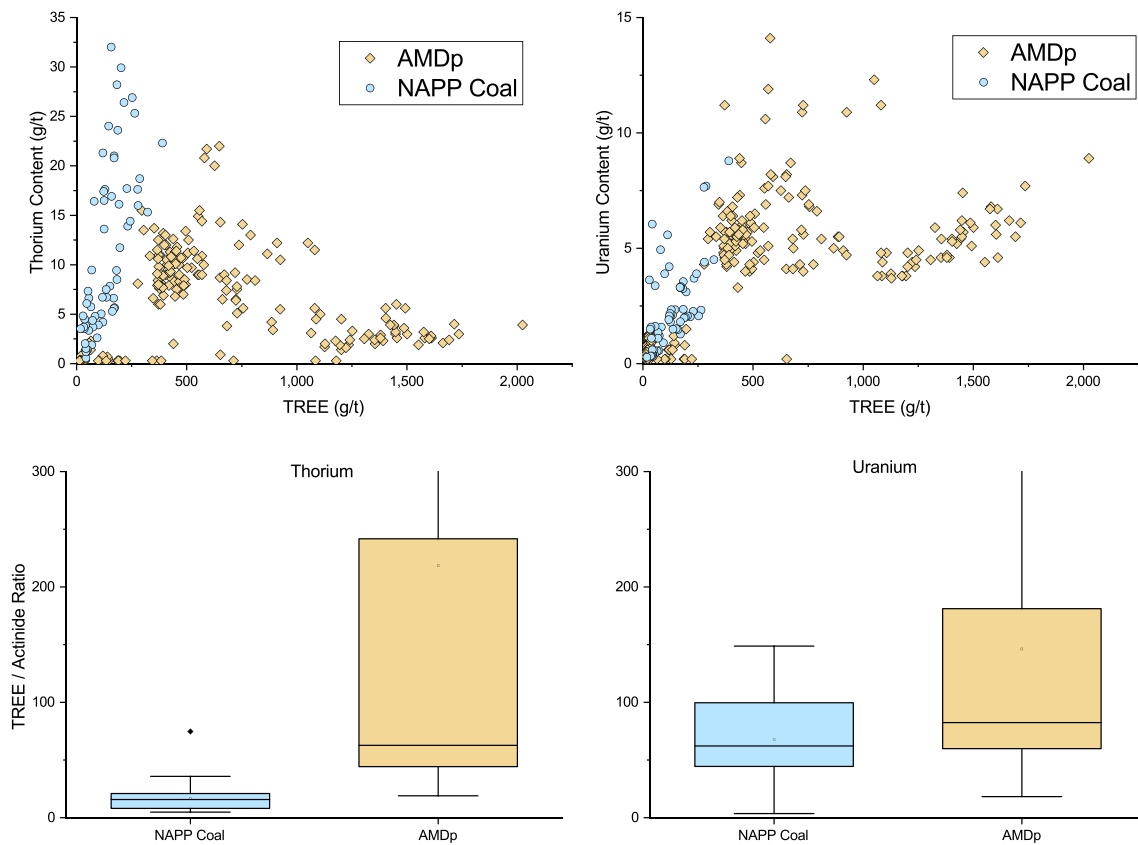


Fig. 8 Comparison of U and Th between NAPP coal and AMDp

to a toll refiner with advanced capabilities to turn the oxides into metal. Typically, these processes utilize a type of smelting or electrolysis to isolate REE metals. Finally, these metals would constitute a finished product that can be sold on the open market.

3.5 Environmental and Civil Considerations

AMD treatment within the coal industry currently focuses on simply meeting effluent limits. In meeting these limits, the AMD treatment process does not maximize the removal of metals and REEs. This compliance-based practice thus creates opportunities to increase treatment of the influent to further remove metals before the effluent is discharged into the environment. Should REEs become a revenue stream for AMD plant operators, the overall process could incentivize private or governmental organizations to purchase and treat additional AMD streams that are currently polluting waterways.

Incidentally, the REE revenue could even change mining practices within the Appalachian region. Currently, AMD-producing material is separated using specific material handling plans that result in this material being stored in non-oxidizing conditions or acid-producing overburden is mitigated with alkaline amendments. Alternatively, lined, spoil containment areas could be created in the form of heap-leaching

structures. These leach beds would intentionally channel AMD to treatment plants where processing would subsequently follow. As a result, the pyritic AMD-producing spoil would not have an opportunity to adversely affect external waterways.

For most hard-rock REE deposits, uranium and thorium are common contaminants that require specialized handling and disposal during the treatment process. Notably, AMDp has very low concentrations of these elements relative to similar grade REE deposits. This decreased occurrence of the actinides is common among coal and coal byproduct REEs feedstocks; however, AMDp is also significantly lower in these actinides than NAPP coal sources, as shown in Fig. 8 [67].

Thermodynamic considerations (e.g., pH–EH diagrams) show that uranium and thorium typically do not mobilize in solution at pH values greater than 1 [68]. Since typical AMD does not reach these low pH values, AMDp samples often contain very low concentrations. The AMDp samples in this study exhibited an average uranium and thorium concentration of 4.46 and 5.67 g/t, respectively. Conversely, monazite (a typical REE-bearing mineral) ores routinely contain 4 to 12% thorium along with uranium [69]. REE deposits with high concentrations of these actinides need to be evaluated with particular attention to these elements as demonstrated by the 2002 closure of the Mountain Pass mine [5].

4 Conclusions

In all, nine AMD sites were evaluated for REE content in both raw water and AMDp. This research has verified that REEs concentrate in the by-products of AMD treatment. These concentrated REEs in AMDp may also possess the qualities needed to justify their use as a viable feedstock resulting in a US-based REE supply. Additionally, a conceptual framework was presented to show different unit operations that could be implemented for the beneficiation of REEs from AMD. Finally, by utilizing these precipitates to refine the REEs, certain environmental incentives may mitigate additional AMD pollution.

The following key findings were developed during this research:

- Data from 81 samples showed that the REE concentration in AMD inflows was a strong function of pH.
- For AMD influent samples with a pH < 4, the average TREE concentration was 371 µg/L.
- For AMD influent samples with a pH > 4, the average TREE concentration was 88 µg/L.
- Typically, the data showed that net-alkaline flooded underground mines had significantly lower TREE flux than net-acidic aboveground and surface mines.
- Traditional AMD treatment captured approximately 78% of the TREES, leaving a precipitate with an average concentration of 517 g/t.
- A regional flow rate estimate showed that the total amount of REEs produced from AMD can vary between 771 and 3400 t per annum.
- The AMDp data indicated that the precipitate contains concentrations of thorium and uranium that are less than 6 g/t.

Acknowledgments This material is based upon work supported by the U.S. Department of Energy under Award Number DE-FE0026927.

Compliance with Ethical Standards

Disclaimer This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the US Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the US Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the US Government or any agency thereof.

Conflict of Interest The authors declare that they have no conflict of interest.

References

1. Fernandez V (2017) Rare-earth elements market: a historical and financial perspective. *Resour Policy* 53:26–45. <https://doi.org/10.1016/j.resourpol.2017.05.010>
2. Schulz KJ, DeYoung JH, Seal RR, Bradley DC (2017) Critical mineral resources of the United States - economic and environmental geology and prospects for future supply Professional Paper 1802
3. Jordens A, Cheng YP, Waters KE (2013) A review of the beneficiation of rare earth element bearing minerals. *Miner Eng* 41:97–114. <https://doi.org/10.1016/j.mineng.2012.10.017>
4. Cox C, Kynicky J (2018) The rapid evolution of speculative investment in the REE market before, during, and after the rare earth crisis of 2010–2012. *Extr Ind Soc* 5:8–17. <https://doi.org/10.1016/j.exis.2017.09.002>
5. Hellman PL, Duncan RK (2014) Evaluation of rare earth element deposits. *Appl Earth Sci* 123:107–117. <https://doi.org/10.1179/1743275814Y.00000000054>
6. Smyth J (2018) Lynas eyes legal action after Malaysia rare-earths blow. *Financ Times* London 18
7. Imholte DD, Nguyen RT, Vedantam A, Brown M, Iyer A, Smith BJ, Collins JW, Anderson CG, O'Kelley B (2018) An assessment of U.S. rare earth availability for supporting U.S. wind energy growth targets. *Energy Policy* 113:294–305. <https://doi.org/10.1016/j.enpol.2017.11.001>
8. U.S. Geological Survey (2018) Mineral Commodity Summaries 2018: US Geological Survey
9. Humphries M (2012) Rare earth elements: the global supply chain
10. Campbell GA (2014) Rare earth metals: a strategic concern. *Miner Econ* 27:21–31. <https://doi.org/10.1007/s13563-014-0043-y>
11. Goodenough KM, Wall F, Merriman D (2017) The rare earth elements: demand, global resources, and challenges for resourcing future generations. *Nat Resour Res* 27:1–16. <https://doi.org/10.1007/s11053-017-9336-5>
12. Van Gosen B, Verplanck PL, Emsbo P (2019) Rare earth element mineral deposits in the United States
13. Preston JS, Cole PM, Craig WM, Feather AM (1996) The recovery of rare earth oxides from a phosphoric acid by-product. Part 1: leaching of rare earth values and recovery of a mixed rare earth oxide by solvent extraction. *Hydrometallurgy* 41:1–19. [https://doi.org/10.1016/0304-386X\(95\)00051-H](https://doi.org/10.1016/0304-386X(95)00051-H)
14. Preston JS, Cole PM, Du Preez AC, Fox MH, Fleming AM (1996) The recovery of rare earth oxides from a phosphoric acid by-product. Part 2: the preparation of high-purity cerium dioxide and recovery of a heavy rare earth oxide concentrate. *Hydrometallurgy* 41:21–44. [https://doi.org/10.1016/0304-386X\(95\)00067-Q](https://doi.org/10.1016/0304-386X(95)00067-Q)
15. Preston JS, Du Preez AC, Cole PM, Fox MH (1996) The recovery of rare earth oxides from a phosphoric acid by-product. Part 3. The separation of the middle and light rare earth fractions and the preparation of pure europium oxide. *Hydrometallurgy* 42:131–149. [https://doi.org/10.1016/0304-386X\(95\)00079-V](https://doi.org/10.1016/0304-386X(95)00079-V)
16. Preston JS (1996) The recovery of rare earth oxides from a phosphoric acid byproduct. Part 4. The preparation of magnet-grade neodymium oxide from the light rare earth fraction. *Hydrometallurgy* 42:151–167. [https://doi.org/10.1016/0304-386X\(95\)00082-R](https://doi.org/10.1016/0304-386X(95)00082-R)
17. Binnemans K, Jones PT, Blanpain B, Van Gerven T, Yang Y, Walton A et al (2013) Recycling of rare earths: a critical review. *J Clean Prod* 51:1–22. <https://doi.org/10.1016/j.jclepro.2012.12.037>
18. Rademaker JH, Kleijn R, Yang Y (2013) Recycling as a strategy against rare earth element criticality: a systemic evaluation of the potential yield of NdFeB magnet recycling. *Environ Sci Technol* 47:10129–10136. <https://doi.org/10.1021/es305007w>
19. Finkleman RB (1993) Trace and minor elements in coal. In: Engel MH, Macko SA (eds) *Org. Geochem.* Springer, Boston, p 594

20. Schofield A, Haskin L (1964) Rare-earth distribution patterns in eight terrestrial materials. *Geochim Cosmochim Acta* 28:437–446. [https://doi.org/10.1016/0016-7037\(64\)90117-6](https://doi.org/10.1016/0016-7037(64)90117-6)
21. Zubovic P, Stadnichenko T, Sheffey NB Distribution of minor elements in coals of the Appalachian region, Washington, D.C, p 1966
22. Cravotta CA (2008) Dissolved metals and associated constituents in abandoned coal-mine discharges, Pennsylvania, USA. Part 1: Constituent quantities and correlations 23:166–202. <https://doi.org/10.1016/j.apgeochem.2007.10.011>.
23. United States Department of Energy (2017) Rare earth elements from coal and coal byproducts
24. Hower J, Granite E, Mayfield D, Lewis A, Finkelman R (2016) Notes on contributions to the science of rare earth element enrichment in coal and coal combustion byproducts. *Minerals* 6:32. <https://doi.org/10.3390/min6020032>
25. Ziemkiewicz PF, He T, Noble A, Liu X (2016) Recovery of rare earth elements (REEs) from coal mine drainage. West Virginia Mine Drain. Task Force Symp., Morgantown, WV
26. Skousen JG, Sexstone A, Ziemkiewicz PF (2000) Acid mine drainage control and treatment. *Reclam Drastically Disturb Lands*, pp 1–42
27. Hoehn RC, Sizemore DR (1977) Acid mine drainage (AMD) and its impact on a Virginia stream. *Water Resour Bull* 13:153–160. <https://doi.org/10.1111/j.1752-1688.1977.tb02000.x>
28. Acid Mine Drainage Prediction (1994) Washington, D.C. EPA 530-R-94-036
29. Akcil A, Koldas S (2006) Acid mine drainage (AMD): causes, treatment and case studies. *J Clean Prod* 14:1139–1145. <https://doi.org/10.1016/j.jclepro.2004.09.006>
30. Kalin M, Fyson A, Wheeler WN (2006) The chemistry of conventional and alternative treatment systems for the neutralization of acid mine drainage. *Sci Total Environ* 366:395–408. <https://doi.org/10.1016/j.scitotenv.2005.11.015>
31. Kleinmann RLP (2001) Prediction of water quality at surface coal mines. *Natl Mine L Reclam Cent Located West Virginia Univ Morgantown, West Virginia* 239:247
32. Hill DW (1969) Neutralization of acid mine drainage. *Ater Pollut Control Fed* 41:1702–15.
33. Ziemkiewicz PF (1998) Steel slag : applications for AMD control. *Proc 1998 Conference Hazard Waste Res*, p 44–62.
34. Gazea B, Adam K, Kontopoulos A (1996) A review of passive systems for the treatment of acid mine drainage. *Miner Eng* 9:23–42. [https://doi.org/10.1016/0892-6875\(95\)00129-8](https://doi.org/10.1016/0892-6875(95)00129-8).
35. USEPA (1983) Design manual: neutralization of acid mine drainage. Cincinnati, OH
36. Ackman TE (1982) Sludge disposal from acid mine drainage treatment. Avondale, MD
37. Payette C, Lam W, Angle C, Mikula R (1991) Evaluation of improved lime neutralization processes. *Proc. Second Int. Confrence Abat. Acidic Drain.*, Monreal, Can
38. Johnson DB, Hallberg KB (2005) Acid mine drainage remediation options: a review. *Sci Total Environ* 338:3–14. <https://doi.org/10.1016/j.scitotenv.2004.09.002>
39. Demchak J, Skousen J, McDonald LM (2013) Longevity of acid discharges from underground mines located above the regional water table. *J Environ Qual* 33:656. <https://doi.org/10.2134/jeq2004.6560>
40. Light DDM, Donovan JJ (2015) Mine-water flow between contiguous flooded underground coal mines with hydraulically compromised barriers. *Environ Eng Geosci* 21:147–164. <https://doi.org/10.2113/gsegeosci.21.2.147>
41. Capo RC, Winters WR, Weaver TJ, Stafford SL, Hedin RS, Stewart BW (2001) Hydrogeologic and geochemical evolution of deep mine discharges, Irwin Syncline, Pennsylvania. *Proc. - West Virginia Surf. Mine Drain. Task Force Symp.*, vol 22, p 144–53
42. Skousen J, Simmons J, McDonald LM, Ziemkiewicz P (2002) Acid-base accounting to predict post-mining drainage quality on surface mines. *J Environ Qual* 31:2034. <https://doi.org/10.2134/jeq2002.2034>
43. Mack B, McDonald LM, Skousen J (2010) Acidity decay of above-drainage underground mines in West Virginia. *J Environ Qual* 39:1043. <https://doi.org/10.2134/jeq2009.0229>
44. Seredin VV, Dai S (2012) Coal deposits as potential alternative sources for lanthanides and yttrium. *Int J Coal Geol* 94:67–93. <https://doi.org/10.1016/j.coal.2011.11.001>
45. Papangelakis VG, Moldoveanu G. Recovery of rare earth elements from clay minerals. 1st Eur Rare Earth Resour Conf 2014:191–202
46. Gupta T, Ghosh T, Akdogan G, Srivastava VK (2017) Characterizing rare earth elements in Alaskan coal and ash. *Miner Metall Process* 34:138–145. <https://doi.org/10.19150/mmp.7614>
47. Taylor SR (1964) Abundance of elements in the crust: a new table. *Geochim Cosmochim Acta* 28:1273–1285. [https://doi.org/10.1016/0016-7037\(64\)90129-2](https://doi.org/10.1016/0016-7037(64)90129-2)
48. Cravotta CA, Brady KB., Rose AW, Douds JB (1999) Frequency distribution of the pH of coal-mine drainage in pennsylvania. *US Geol Surv Water-Resources Investig Report* 99-4018A, pp 313–24
49. Zhang W, Rezaee M, Bhagavatula A, Li Y, Groppo J, Honaker R (2015) A review of the occurrence and promising recovery methods of rare earth elements from coal and coal by-products. *Int J Coal Prep Util* 35:295–330. <https://doi.org/10.1080/19392699.2015.1033097>
50. Cravotta CA (2008) Dissolved metals and associated constituents in abandoned coal-mine discharges, Pennsylvania, USA. Part 2: geochemical controls on constituent concentrations. *Appl Geochem* 23:203–226. <https://doi.org/10.1016/j.apgeochem.2007.10.003>
51. Goode DJ, Cravotta CA, Homberger RJ, Hewitt MA, Hughes RE, Koury DJ, et al (2013) Water budgets and groundwater volumes for abandoned underground mines in the Western Middle Anthracite Coalfield, Schuylkill, Columbia, and Northumberland Counties, Pennsylvania—preliminary estimates with identification of data needs. Reston, VA
52. Denicola TA, Donovan JJ, Leavitt BR, Sharma S (2013) Geochemistry of mine pool discharges in the Pittsburgh Coal Basin Thesis Submitted to: The Eberly College of Arts and Sciences at West Virginia University in partial fulfillment of the requirements for the degree of Masters of Science In Geology Departme
53. Stewart BW, Capo RC, Hedin BC, Hedin RS (2016) Rare earth element resources in coal mine drainage and treatment precipitates in the Appalachian Basin, USA. *Int J Coal Geol* 169:28–39. <https://doi.org/10.1016/j.coal.2016.11.002>
54. Cordier DJ, Hedrick JB (2010) 2008 Minerals yearbook - rare earths
55. Cordier DJ (2011) 2009 Minerals yearbook
56. Gambogi BJ, Cordier DJ (2012) 2010 Minerals yearbook
57. Gambogi J (2013) 2011 Minerals yearbook
58. Gambogi J (2013) 2012 Minerals yearbook - rare earths
59. Gambogi J (2016) 2013 Minerals yearbook - rare earths
60. Gambogi J (2014) 2014 Minerals yearbook - rare earths
61. Gambogi J (2018) 2015 Minerals yearbook
62. Honaker RQ, Groppo J, Yoon R-H, Luttrell GH, Noble A, Herbst JA (2017) Process evaluation and flowsheet development for the recovery of rare earth elements from coal and associated byproducts. *Miner Metall Process* 34:107–115. <https://doi.org/10.19150/mmp.7610>
63. Noble A, Luttrell GH (2016) Micro-pricing: the value of trace rare earth elements in coal and coal byproducts. 2016 SME Annu Conference Expo; Preprint N:1–6
64. Binnemans K, Jones PT, Müller T, Yurramendi L (2018) Rare earths and the balance problem: how to deal with changing markets? *J Sustain Metall* 8:126–146. <https://doi.org/10.1007/s40831-018-0162-8>
65. Lifton J, Hatch G (2016) Technology Metals Research. <http://www.techmetalsresearch.com/metrics-indices/tmr-advanced-rare-earth-projects-index/>. Accessed 10/09/2017

66. Verbaan N, Bradley K, Brown J, Mackie S (2015) A review of hydrometallurgical flowsheets considered in current REE projects
67. National Energy Technology Laboratory UD of E (2018) Rare earth element database. https://edx.netl.doe.gov/ree/?page_id=1587. Accessed 12/14/2018
68. Kim E, Osseo-Asare K (2012) Aqueous stability of thorium and rare earth metals in monazite hydrometallurgy: Eh-pH diagrams for the systems Th-, Ce-, La-, Nd- (PO₄)-(SO₄)-H₂O at 25 °C. *Hydrometallurgy* 113–114:67–78. <https://doi.org/10.1016/j.hydromet.2011.12.007>
69. Gupta CKK, Krishnamurthy N (1992) Extractive metallurgy of rare earths. vol 37. <https://doi.org/10.1179/imr.1992.37.1.197>.

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.



The Occurrence and Concentration of Rare Earth Elements in Acid Mine Drainage and Treatment Byproducts. Part 2: Regional Survey of Northern and Central Appalachian Coal Basins

Christopher R. Vass¹ · Aaron Noble² · Paul F. Ziemkiewicz¹

Received: 6 May 2019 / Accepted: 15 July 2019
© Society for Mining, Metallurgy & Exploration Inc. 2019

Abstract

Many modern industries rely on rare earth elements (REEs) to produce products that are essential to both civil and defense applications. In a prior study (Vass et al., 2019), the authors showed that REE grades in acid mine drainage (AMD) and associated byproduct precipitates from AMD treatment (AMDp) warrant evaluation as a feedstock for REE production. The current work extends that effort through a broad survey of 141 AMD treatment sites in Northern and Central Appalachia. In this study, 185 raw AMD and 623 AMDp field samples were obtained and analyzed to assess the REE and major metal concentrations. Results show that an average of 282 µg/L and 724 g/tonne of REEs occur in AMD and AMDp respectively. Additionally, both basins contained similar distributions of REEs, and these distributions tended to favor heavy and critical REEs when compared with traditional REE ore deposits. Geospatial analysis identified a total resource of 340 tonnes stored at the 141 sites sampled in this study. While this analysis did not quantify the basin-wide REE inventory, it does indicate the impact that processing cut-off grades will have on the overall AMDp resource base.

Keywords Acid mine drainage · Rare earth elements · Coal byproducts

1 Introduction

Rare earth elements (REEs) are essential for many industrial processes and high-tech end use applications, including catalysts, metallurgy, petroleum refining, catalytic converters, ceramics, glass additives, phosphors, magnets, and electronics [1]. From 2015 to 2018, the USA consumed between 9500 and 10,500 metric tons of REEs per year and was heavily reliant on imports from China over that period [2]. Given the variety of end use applications for REEs, future demand projections for specific REEs are difficult to predict; however, the exponential growth in electronic devices as well as the lack of suitable REE substitutes in these products suggests that REEs will continue to be a significant and strategic mineral resource for the foreseeable future [3, 4]. In particular, several researchers have noted a strong

future demand for yttrium, neodymium, europium, terbium, and dysprosium, all of which are often denoted critical REEs by the US Department of Energy [5, 6].

Given the risks associated with REE supply shortages, a multitude of stakeholders including researchers, national governments, and private companies have attempted to identify alternative and unconventional REE resources. For example, in the mid-1990s, research in South Africa investigated the feasibility of recovering rare earth oxides from byproducts of the phosphoric acid production process [7–10]. These studies showed that process is technically feasible, and the researchers were ultimately able to produce high-grade Nd-Pr oxide products. In addition, other researchers recently reviewed recycling of REEs from electronic scrap [11]. Unfortunately, this study showed that up to 2011, most of the efforts in this area were restricted to laboratory-scale research and the end-of-life recycling rate of REEs was less than 1%. According to the U.S. Geological Survey, recycling and alternative sources of REE still only account for limited quantities, and no large-scale commercial efforts have been initiated [2, 12]. Even if successful, these efforts will not fully compensate for the projected increase in demand over the next several years [13].

Another potential source of REEs that has received recent attention is geologic material associated with coal and coal

✉ Christopher R. Vass
chris.vass@gmail.com

¹ West Virginia Water Research Institute, PO Box 6064,
Morgantown, WV 26506, USA

² Virginia Tech Mining and Minerals Engineering, Holden Hall 100,
Virginia Tech, 445 Old Turner Street, Blacksburg, VA 24061, USA

byproducts. While the presence of REEs in coal has long been established by many researchers, dating back to at least the 1960s and 1970s [14–16], efforts to extract and concentrate these elements are fairly recent. In 2015, the U.S. Department of Energy—National Energy Technology Laboratory initiated 10 projects representing \$10.6 million in funds to investigate the technical and economic feasibility of recovering REEs from coal and coal byproducts [12, 17]. Many of these initial studies focused on solid-phase feedstocks, including coal tailings (refuse) and coal fly ash [18–35]; however, another potential resource is the aqueous-phase acid mine drainage (AMD) generated through coal mining. Successfully developing this resource has the potential to remediate past environmental disturbances, while addressing the issue of resource scarcity.

The first paper in this series identified the presence of REEs in AMD and assessed the general prospectivity of this potential resource [36]. This preliminary work surveyed nine Northern Appalachian (NAPP) AMD sites and identified higher occurrences of REEs in the more acidic AMD flows. Additionally, the initial prospecting study indicated that over 75% of the REE flux is captured and enriched in the AMD treatment byproducts, often called AMD sludge or AMD precipitate (AMDp). This traditional treatment was shown to concentrate REEs by a factor of 2000 when comparing the initial aqueous inflows with the solid byproducts. Overall, this study not only confirmed the prospectivity of the resource but also identified additional questions that must be addressed to better understand the quantity and quality of the resource. Most notably, the limited number (nine) and geographic region (NAPP) of sample sites precluded generic conclusions applicable to the larger coal mining district.

The current technical literature lacks data from systemic studies that describe the content and distribution of REEs in AMD and AMDp. As a result, few researchers have critically analyzed the value chain that can be derived from this current waste stream. Given the promising findings in the initial survey, the authors pursued a comprehensive sampling program to characterize the AMD-based REE resource in two important Eastern US coal fields. The program included 141 AMD treatment sites in the Northern and Central Appalachian coal basins. The sites were extensively sampled to determine regional production, storage, elemental distributions of REEs, and critical minerals within the AMD-based resource. Lastly, the study investigated the effects that different cut-off grades would have on the overall size of the sampled resource.

2 Materials and Methods

2.1 Overall Experimental Objectives and Approach

The current study employed a large-scale regional sampling campaign to evaluate the concentration and quantity of REEs

in AMD and AMDp across the Northern Appalachian and Central Appalachian (CAPP) coal basins. The NAPP and CAPP coal basins vary significantly in regard to coal seam quality and geologic lithology [16]. The NAPP basin coal is associated with younger deposits and the coals typically contain a higher sulfur concentration that is more suitable for use in steam generation. Alternatively, the CAPP basin contains both metallurgical and steam coal with a generally lower overall sulfur content [17, 18]. Because of these differences, the two basins were recognized as separate sample populations.

Following the sampling campaign, the individual solid-phase (AMDp) and aqueous (AMD) sample splits were characterized for REE and major metal content. The data was then analyzed to determine the following: (1) the typical aqueous and AMDp REE concentrations and the factors that influence those concentrations; (2) any differences between the two basins with respect to concentration or distribution of REEs; (3) the potential size of the REE resource that can be realized from AMD; and (4) the effect that process cut-off grade may have on the overall AMD-based REE resource in the Appalachian basin.

2.2 Site Selection and Sampling Locations

Throughout the study, 141 coal-based AMD treatment site outflows were sampled in the NAPP and CAPP coal basins. Each of these sites employs active chemical treatment of AMD to meet regulatory effluent discharge limits. As a result, both AMD and AMDp were available for sampling. Figure 1 shows the location and number of sampling sites within each county and coal basin. Table 1 shows the general sampling characteristics of sites within each basin.

2.3 Site Sampling Protocols

Sampling was conducted in two campaigns. The initial sampling consisted of a regional survey of 141 AMD discharges and formed the basis for estimating the REE resource available in surface AMDp storage cells and the annual REE production rate (flux) based on AMD generation regardless the disposition of AMDp. For example, AMDp might be stored in surface cells, buried in surface mining operations, or injected into deep mine voids. Only the former was available for sampling. A subsequent, intensive sampling campaign focused on potentially attractive sites based on either surface sludge resource or REE flux. A maximum of ten AMDp samples were taken on each site. Thus, between one and ten samples were collected and analyzed for each of the 141 sites shown in Fig. 1. Statistical analysis was conducted on those sites with multiple samples to assess variation within a single site.

The detailed sampling and analytical procedures have been described in our prior study [36], and the pertinent details are repeated here for convenience. Aqueous samples were

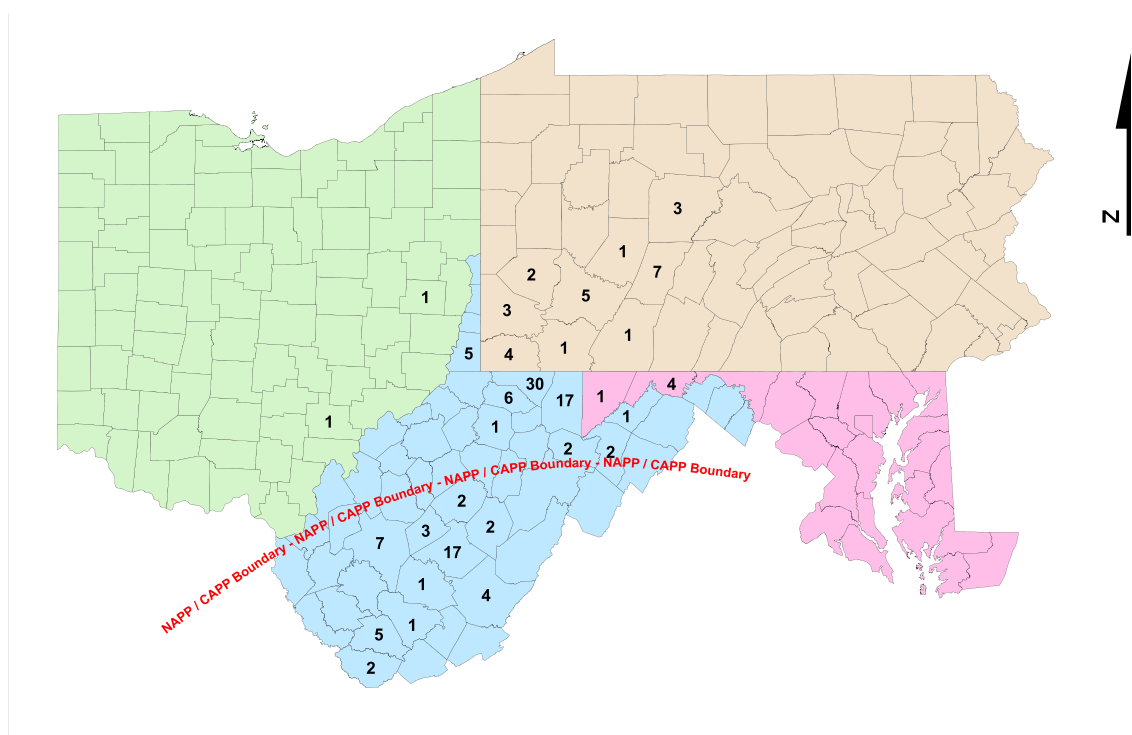


Fig. 1 County-level map showing the number of AMD sites sampled per county and Northern vs. Central Appalachian boundary

collected in a clean 1000-ml HDPE sample bottle. Next, this sample was split into two separate containers (one preserved and one raw) for further analysis. Nitric acid (2%) was added to the preserved sample bottle for REE analysis, whereas the raw sample was evaluated for major ions. Afterwards, the raw water sample was stored at 4 °C, until it was ultimately delivered to the National Research Center for Coal and Energy (NRCCE) analytical laboratory at West Virginia University, for analysis. Finally, the aqueous-phase REE concentrations were determined by TestAmerica, Inc. While on site, raw (untreated) AMD was characterized with respect to flow rate, temperature, electrical conductivity, and pH.

AMDp samples were collected by hand using a shovel or post-hole digger at or near the edge of the drying cell. For intensive sampling, up to nine samples were taken across each drying cell or from multiple cells if present. Samples were placed in new 1-gallon HDPE sample buckets. Later, the AMDp samples were

split into 50-ml representative aliquots for ICP analysis in a controlled environment. These sub-samples were then placed in 50-ml digestion tubes for transport to SGS Canada Inc. for determination of REE and major ions.

While efforts were made to ensure the integrity of the sampling process, representative samples of entire AMDp cells were often difficult to obtain in a safe manner due to the depth and semi-liquid consistency of the precipitate. Typical AMDp drying/storage cells are up to 3 m in depth. As a result, the degree to which the samples are representative of the entire cell is unknown. For example, AMDp often stratifies vertically as operating conditions at the AMD treatment plant vary. We attempted to minimize this effect by sampling from the surface to maximum practical depth. Where practical, multiple AMDp samples were collected at differing depths across a drying cell. Also, some locations used clarifiers for solid/liquid separation and pump the underflow directly to abandoned underground mine works; these samples were collected directly from the clarifier underflow. In either case, the sampling methods used in this study were deemed appropriate for the study objectives and scope of work, which seek to address large-scale variation across the entire basin. Detailed geospatial resolution on single AMDp storage sites is beyond the scope of this current work but is recommended for future studies.

Table 1 AMD sites and sampling quantities by basin. Note some sites contained multiple AMDp storage cells serving a given AMD discharge point. (CAPP, NAPP = Central and Northern Appalachian Coal Basins respectively)

Basin	Treatment Sites		Number of Samples	
	AMD	AMDp	AMD	AMDp
CAPP	44	56	51	141
NAPP	97	96	134	482
TOTAL	141	152	185	623

2.4 Sample Analysis and Characterization

The collected aqueous and precipitate samples were analyzed using ICP-MS for the REEs by TestAmerica Laboratories,

Inc., and SGS Canada Inc., respectively. Additionally, West Virginia University's NRCCE Analytical Laboratory used an ICP-OES to analyze the other major ions. All of these laboratories are certified by their respective state/provincial agencies to assay the respective analytes. AMDp was digested using a sodium peroxide (Na_2O_2) fusion and re-dissolved in hydrochloric acid. This method is comparable with the United States Environmental Protection Agency's total digestion method 3052 for TREEs as well as U.S. Geologic Survey's Method 20 for ICP-OES-MS analysis. Minimum detection limits for the aqueous rare earths were typically in the 0.02-ppb range, while the solid REE analysis had MDL's ranging from 5 to 0.5 ppm. Major metal ions were measured in aqueous samples with MDL's similar to those of the aqueous REEs. Finally, all solid samples are reported on a dry basis.

2.5 Data Analysis and Modeling

The mass of REEs in a given storage cell was calculated using the cell volume, the measured REE concentration on a dry-weight basis, the measured moisture content sample, and the measured AMDp density according to

$$\text{REE Mass} = \text{Area} \times \text{Depth} \times (1 - \text{Moisture Content}) \times \text{REE Content}_{\text{DWB}} \times \text{Density} \quad (1)$$

For the volumetric calculations, additional geographic data was collected on the location, size, and depth of each AMDp storage cell during the on-site sampling campaign. Afterwards, where applicable, these dimensions were confirmed using geospatial software and satellite imagery. In cases where depth data was not available, it was estimated based on the observable height of the drying cell above grade, not to exceed 10 ft. The moisture content of each AMDp sample was determined by full desiccation and reported with the REE analysis by SGS Canada Inc. Lastly, an average sludge density was determined to be 2.20 g/cc (95% confidence interval = 2.16 to 2.23) based on gravimetric analysis of 9 random samples from the population. This value was used in calculations for all sites.

With the large quantity of data gathered through both field sampling and analytical analyses, modeling methods were employed to determine the most influential factors controlling REE content in AMD and AMDp. A partial least squares analysis was conducted to determine the most significant variables in predicting the AMD REE content based on the field and analytical variables. Next, multiple linear regression was used to model the REE concentration based on the significant variables.

A similar analysis was attempted for AMDp; however, results were unsuccessful. While AMD REE concentrations can be predicted using the identified independent variables, additional and unmeasured process variables interfered with the

prediction models. Model correlation coefficients never exceeded 0.55 indicating poor precision. It is likely that the wide array of treatment methods and operating conditions inhibited the successful completion of the modeling of AMDp concentrations based on AMD qualities.

To assess the resource, AMDp was analyzed using a grade-tonnage model. To apply this method to the AMDp resource, each site was considered to be an individual block. This methodology was used to then calculate the cumulative tonnage of REEs and the average grade of all the sites (blocks) inclusive of the cut-off grade. Grade-tonnage models are used to graphically show how different processing cut-off grades will impact the overall size of a resource.

Different classifications have been used by several authors including Seredin and Dai [37], Cox and Kynicky [38], and Binnemans et al. [39] to analyze the occurrence of REEs. These designations may be defined by an organization based on simple atomic numbers (light REE vs. heavy REE) or can be based on other relationships, such as supply and demand (critical REE vs. excessive REE). For this paper, the following classifications will be observed:

- Heavy REEs (HREE)—Sc, Y, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu
- Light REEs (LREE)—La, Ce, Pr, Nd, Sm, Eu
- Total REEs (TREE)—HREE + LREE
- Critical REEs (CREE)—Y, Nd, Eu, Tb, Dy

3 Results and Discussion

3.1 Concentration of REEs in AMD

Table 2 shows the average concentrations of REEs and major metals in the raw AMD for both CAPP and NAPP samples. The average TREE concentrations in raw AMD varied by 75 $\mu\text{g/L}$ between the two basins; however, a two-tailed t test failed to reject the null hypothesis ($p = 0.32$), indicating that the observed difference in REE content between the two basins is not significant. The element-by-element comparisons show that Sc was the only REE that produced a p value (0.01) less than the critical level ($\alpha = 0.05$), indicating that the NAPP AMD samples are significantly enriched in Sc when compared with the CAPP AMD samples. Alternatively, the major metal data does show a significant difference for many of the metals evaluated in this study. The t tests indicate that the NAPP samples were significantly enriched in Al, Fe, Mg, Na, Si, and SO_4 . In addition, the average Cl content was very high in the NAPP samples; however, the t test failed to reject the null hypothesis due to the high variance in Cl values measured in the NAPP AMD samples (range 0.02 to 14,501 mg/L). The high Na and Cl values in NAPP AMD can be

Table 2 REE concentrations for raw aqueous AMD influent in the Appalachian basin study

	CAPP AMD (<i>n</i> = 52)			NAPP AMD (<i>n</i> = 133)				
		Confidence	CI:mean		Confidence	CI:mean	Capp vs. Napp ¹	
Element	Mean	Interval	Ratio	Mean	Interval	Ratio	<i>p</i> value	< α ?
REE (µg/L)								
Sc	3.09	1.11	0.36	6.38	1.56	0.25	0.01	Yes
Y	49.69	20.38	0.41	81.08	24.17	0.30	0.13	
La	26.82	15.08	0.56	21.21	6.76	0.32	0.44	
Ce	53.66	27.43	0.51	63.57	19.29	0.30	0.58	
Pr	8.03	3.92	0.49	9.85	2.84	0.29	0.49	
Nd	37.22	17.06	0.46	46.14	13.29	0.29	0.46	
Sm	9.73	4.01	0.41	13.33	3.61	0.27	0.26	
Eu	2.64	0.98	0.37	3.80	1.03	0.27	0.19	
Gd	12.39	4.92	0.40	18.66	5.22	0.28	0.16	
Tb	1.95	0.71	0.36	3.15	0.84	0.27	0.09	
Dy	10.57	4.28	0.40	17.06	4.83	0.28	0.12	
Ho	1.95	0.73	0.37	3.31	0.90	0.27	0.08	
Er	4.99	2.08	0.42	8.34	2.42	0.29	0.11	
Tm	0.81	0.24	0.30	1.29	0.30	0.23	0.06	
Yb	3.89	1.57	0.40	6.40	1.81	0.28	0.11	
Lu	0.71	0.21	0.29	1.08	0.25	0.23	0.08	
TREE	228.14			304.67			0.32	
HREE/TREE	39.5%			48.2%				
CREE/TREE	44.7%			49.6%				
Major ions (mg/L)								
Al	12.99	5.18	0.40	23.14	4.86	0.21	0.02	Yes
Ca	167.95	27.18	0.16	177.47	22.77	0.13	0.64	
Fe	22.37	14.57	0.65	60.07	22.32	0.37	0.04	Yes
Mg	123.84	26.96	0.22	75.82	10.79	0.14	0.00	Yes
Mn	10.74	3.36	0.31	9.49	2.44	0.26	0.58	
Na	36.72	18.74	0.51	523.52	187.96	0.36	0.00	Yes
Si	10.98	2.25	0.21	14.28	1.66	0.12	0.03	Yes
Cl	5.30	2.92	0.55	306.42	242.47	0.79	0.12	
SO ₄	1090.94	196.48	0.18	1717.29	340.54	0.20	0.03	Yes

¹ *p* value as determined by two-tailed, equal variance *t* test, α value of 0.05 used for significance

explained by the depositional setting, as the NAPP coal formed in this basin is associated with a marine environment [16]. Likewise, Fe was also more prevalent in the NAPP basin which is consistent with higher pyritic sulfur.

The full distribution of TREE data for the NAPP and CAPP raw AMD samples is shown in Fig. 2. The significant overlap in the datasets provides graphical confirmation of the *t* test results and suggests that the same geochemical processes dictate the REE concentration in AMD in both basins. This outcome is expected as AMD chemistry represents the large-scale integration of reactions that occur at small scales, such as the pore water surrounding pyritic vs. non-pyritic rock grains, and localized oxidizing vs. reducing environments. Integration

occurs over the scale of mines ranging from hundreds of acres to 20 square miles or more in the case of large, underground mines. The more interesting component of this plot is the large range of TREE concentrations for both basins. The NAPP basin in particular has TREE concentrations that span five orders of magnitude, with a low 0.25 $\mu\text{g/L}$ and a high of 3100 $\mu\text{g/L}$. Altogether, this result indicates that the processes that control AMD formation also control REE leaching and occurrence in the AMD discharge [40].

To assess the distribution of individual REEs, the data was normalized to the REE content of a standard chondrite sample [41]. Figure 3 shows the average results of this chondrite normalization along with bands for the 95%

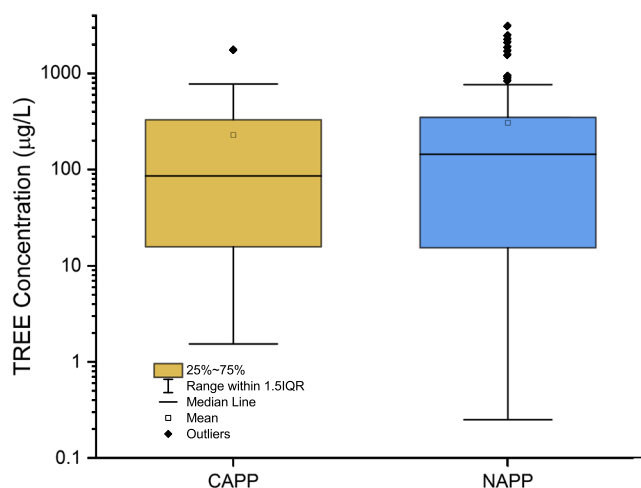


Fig. 2 Distribution of total REEs in NAPP and CAPP raw AMD samples

confidence interval. Similar to the TREE data, the NAPP and CAPP distributions have significant overlap, further confirming the quantitative results of the *t* test. With regard to the general shape of the curve, chondrite normalized REE plots for coal-based materials typically follow a serially decreasing order from La to Lu, with the lone exception being the Eu anomaly [29]. The chondrite-normalized AMD plots follow this trend but show some deviation for La and Ce (particularly, the NAPP curve, where La and Ce are both less than Pr). This result may indicate that AMD has a slight tendency to extract middle and heavy REEs from coal strata while extracting La and Ce at a lower rate. This result can be explained geochemically, as the La and Ce in the coal measures are often associated with phosphate mineralization, such as monazite [31]. These rare earth phosphates are extremely resistant to acid attack and are not normally soluble in the pH ranges present in AMD [42].

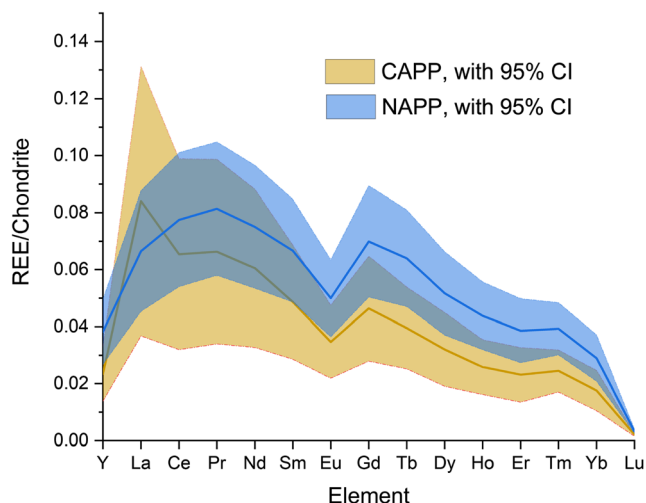


Fig. 3 Chondrite-normalized REE distribution in raw AMD, with chondrite normalization after Korotev [41]

3.2 AMD Modeling and Analysis

As shown in Fig. 2, the REE content of raw AMD can vary by several orders of magnitude. REE determination by analytical methods requires specialized equipment and is expensive. As a result, we attempted to develop predictive models to estimate REE content in AMD discharges based on readily available site characteristics and field analytical parameters. Initially, graphical analyses were conducted to compare the REE content to (1) the AMD discharge rate and (2) the outflow pH. Figure 4 shows REE concentration as a function of discharge rate for the NAPP and CAPP datasets. While the plot does show a slight negative correlation (i.e., higher discharges tend to yield lower REE concentrations), the R^2 value indicates low precision and poor predictive ability.

With regard to the two basins, the NAPP data tended to have a higher population of high-flow/low REE outflows, as well as low-flow/high-REE outflows. This reflects the very large, consolidated AMD treatment plants serving flooded underground coal mine complexes. Largely, mines in the Pittsburgh coal seam tend to be net alkaline. The CAPP data was more centrally distributed in both regards.

Similarly, Fig. 5 shows TREE concentration as a function of pH. This data also shows a strong negative correlation (i.e., lower pH correlates with higher REE concentrations), but pH alone is not sufficient to explain all the variance in the data. Moreover, this data confirms the bimodal pH distribution that was originally proposed in the early prospectivity study [36]. Due to the nature of Al and Fe buffering in AMD solutions, the region between pH 4.5 and 5.5 is sparsely populated since small changes in acidity result in stability in the 2.5–4.5 region where Fe^{3+} and Al^{3+} precipitate. Likewise, at pH 6.0, Fe^{2+} oxidizes and precipitates resulting in stability in the upper pH region. These interactions were discussed extensively by Cravotta et al. [43].

Due to the bimodal distribution, a boundary between these two populations at pH five was chosen to delineate the two

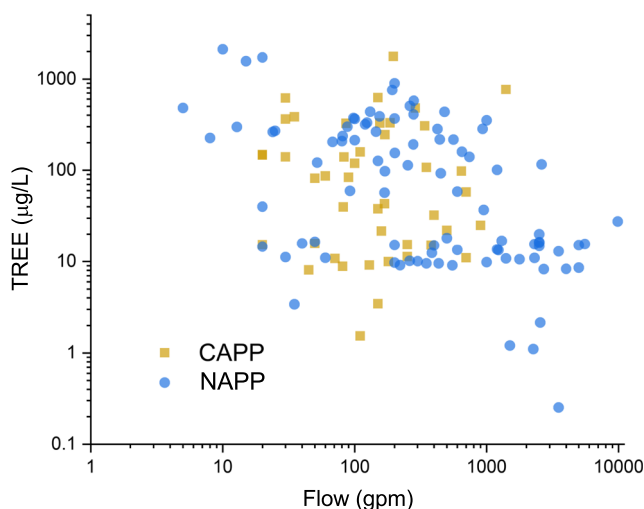


Fig. 4 Total REE concentration in AMD as a function of outflow rate

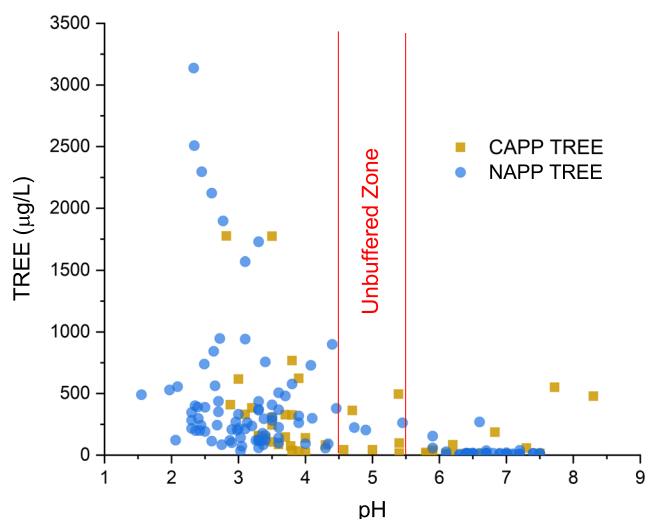


Fig. 5 Relationship between pH of raw AMD and the concentration of TREE in the aqueous phase

populations since below five AMD is, by definition, acidic, while above five, it becomes increasingly net alkaline. This behavior is indicative of the difference in geochemistry from flooded underground mines and those that are above drainage and produce an acidic discharge [44]. Likewise, this extended exploration study also confirms that the net alkaline discharges typically have lower REE content than acidic AMD discharges.

As neither total flow nor raw water pH was sufficient to predict the REE content of AMD, a partial least squares analysis was conducted to also include major metal concentrations in the prediction. Generally, pH and major metals are monitored as part of the National Pollution Discharge Elimination System (NPDES) permit and would be readily available for all AMD outflows. Results from this analysis indicated that five factors can explain over 75% of the variance in concentration of TREES in the AMD dataset. These factors, in order of importance, include the Mn concentration, Al concentration, raw water pH, Si concentration, and Mg concentration. Figure 6 shows the results from a multiple linear regression with an R^2 value of 0.63 using these factors. The moderate correlation between Mn and Al in AMD may suggest that the mode of REE occurrence in the host strata is associated with these elements, with specific examples being manganese oxides and aluminosilicates. This result coincides with prior findings from Bryan et al. [45], which show a strong correlation between Al concentration and REE concentration for samples in the USGS COALQUAL database.

3.3 Concentration of REEs in AMDp

Table 3 shows the average concentrations of REEs and major metals in the AMDp for both CAPP and NAPP samples. TREE concentrations in CAPP averaged 669 g/t while those

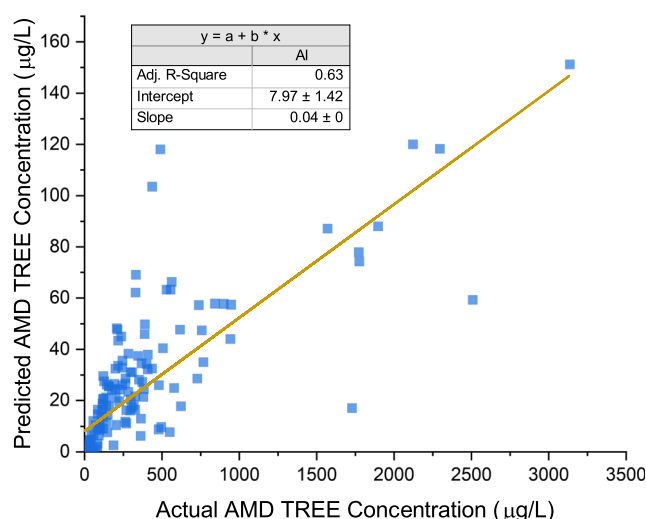


Fig. 6 Results of a multiple linear regression predicting TREE concentrations raw AMD using pH and major metal concentrations

in NAPP averaged 750 g/t. This result is consistent with the mean raw water TREE concentrations observed for each basin; however, the two-tailed t test indicates that the differences, in both TREE and individual REEs, are normally significant (at $\alpha = 0.05$) with the primary exceptions being Ce, Pr, and Nd. In general, the precision of the AMDp samples is much higher than that of the AMD samples, which may be attributed to larger sample sizes. In addition to the REEs, the t tests also confirm that the major metal ions were more prevalent in the AMDp samples from the NAPP vs. the CAPP basin. The moisture content between the AMDp was also slightly higher in the NAPP basin likely due to the more prevalent use of clarifiers in AMD treatment where samples were taken at the underflow before the AMDp was disposed of via underground injection. Additionally, it is important to note the low concentration of both Th and U in the AMDp samples as many conventional REE deposits generate significant environmental liabilities during processing. This confirms the observations seen in the preliminary study that indicated Th and U were not mobilized from the parent material at typical pH values associated with AMD.

The full distribution of TREE data for the NAPP and CAPP AMDp samples is shown in Fig. 7. Like the AMD samples (Fig. 2), this plot shows a large overlap between the distributions from the two basins; however, the NAPP data does have some considerable outliers exceeding 2000 g/t. The lower values on this plot (< 50 g/t) are predominantly from net alkaline AMD outflows with low REE concentrations.

Like the AMD samples, a chondrite-normalized plot was created to assess the distribution of individual REEs in AMDp, as shown in Figure 8. The pattern is similar to that of the raw AMD samples with the exception being the scale of the y-axis and the narrower confidence intervals. As mentioned above, these smaller confidence

Table 3 REE concentrations for AMDp at 141 sites across the CAPP and NAPP basins

Element	CAPP AMDp (<i>n</i> = 141)			NAPP AMDp (<i>n</i> = 482)			CAPP vs. NAPP ¹	
	Confidence		CI:mean	Confidence		CI:mean		
	Mean	Interval	Ratio	Mean	Interval	Ratio	<i>p</i> value	< α ?
REEs (g/t)								
Sc	12.64	1.47	0.12	20.83	1.42	0.07	0.00	Yes
Y	151.92	18.46	0.12	192.84	15.77	0.08	0.01	Yes
La	79.88	10.73	0.13	58.21	3.91	0.07	0.00	Yes
Ce	161.71	17.32	0.11	162.65	10.83	0.07	0.93	
Pr	23.87	2.68	0.11	24.26	1.68	0.07	0.82	
Nd	104.77	11.48	0.11	113.62	8.21	0.07	0.29	
Sm	26.45	2.99	0.11	31.93	2.40	0.08	0.02	Yes
Eu	6.46	0.76	0.12	8.38	0.64	0.08	0.00	Yes
Gd	34.52	4.27	0.12	44.10	3.47	0.08	0.01	Yes
Tb	5.09	0.63	0.12	6.96	0.54	0.08	0.00	Yes
Dy	28.25	3.47	0.12	38.91	3.04	0.08	0.00	Yes
Ho	5.41	0.66	0.12	7.43	0.58	0.08	0.00	Yes
Er	14.18	1.71	0.12	19.88	1.54	0.08	0.00	Yes
Tm	1.86	0.23	0.13	2.82	0.21	0.08	0.00	Yes
Yb	10.45	1.20	0.12	15.09	1.17	0.08	0.00	Yes
Lu	1.56	0.19	0.12	2.33	0.18	0.08	0.00	Yes
TREE	669.01			750.26			0.00	Yes
HREE/TREE	39.7%			46.8%				
CREE/TREE	44.3%			48.1%				
Major ions and other parameters								
Al (%)	7.57	0.47	0.06	9.25	0.47	0.05	0.00	Yes
Ca (%)	2.76	0.75	0.27	6.94	0.67	0.10	0.00	Yes
Fe (%)	6.66	1.28	0.19	11.31	1.25	0.11	0.00	Yes
Mg (%)	4.51	0.82	0.18	2.73	0.26	0.10	0.00	Yes
Mn (%)	2.69	0.53	0.20	1.55	0.15	0.10	0.00	Yes
Na (%)	0.18	0.02	0.10	0.14	0.01	0.09	0.01	Yes
Si (%)	15.83	1.85	0.12	9.65	0.62	0.06	0.00	Yes
Cl (g/t)	68.33	10.08	0.15	130.47	24.63	0.19	0.07	
SO ₄ (%)	2.85	0.49	0.17	4.50	0.34	0.08	0.00	Yes
Co (g/t)	381.20	81.76	0.21	579.98	55.52	0.10	0.00	Yes
U (g/t)	4.83	0.60	0.12	7.03	0.51	0.07	0.00	Yes
Th (g/t)	6.60	0.82	0.12	7.49	0.48	0.06	0.09	
Moisture (%)	72.32	3.61	0.05	78.73	1.40	0.02	0.00	Yes

¹ *p* value as determined by two-tailed, equal variance *t* test, α value of 0.05 used for significance

intervals may be dictated by the high number of samples in each distribution. In addition, this chondrite-normalized plot largely confirms the *t* test results indicating that NAPP AMDp has a higher concentration of many of the REEs, except Ce, Pr, and Nd.

In addition to the chondrite-normalized distribution, the average raw element-by-element distribution of REEs in AMDp is shown in Fig. 9. The distribution

between the two basins is relatively similar with minor variations in the elements Y, La, and Ce. Both distributions follow the Oddo-Harkins rule whereby elements with even atomic numbers are more common than their neighboring odd-numbered elements [46, 47]. Furthermore, two of the three most abundant elements (Y and Nd) are CREEs that carry significant supply chain risk [5].

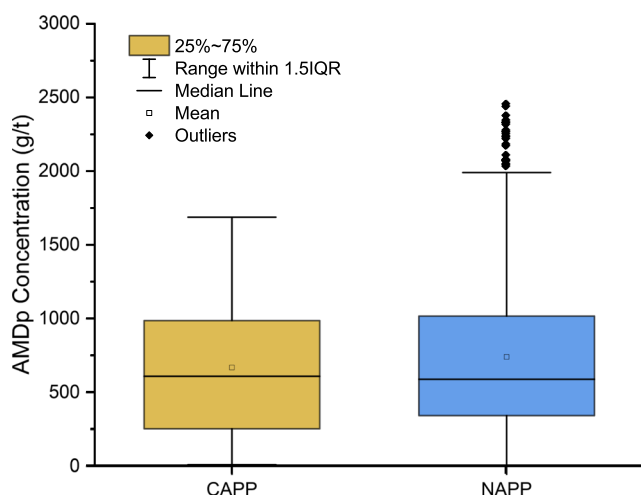


Fig. 7 Distribution of total REEs in NAPP and CAPP AMDp samples

3.4 Resource Assessment

For each site that contained AMDp, the quantity of on-site sludge as well as the steady-state flow of AMD was estimated to assess the resource potential of both in-place resource and annual production. For the in-place resource, a total of 1.8 MM tonnes of AMDp were accounted for on a dry basis with a tonne-weighted average grade of 187 g/t. It is important to note that the majority of AMDp generated at treatment sites is disposed of through underground injection or placed in surface cells and subsequently buried. As a result, this estimate only reflects the tonnage that is currently accessible at the 141 sampled AMD sites. Despite this limitation, the sampled resource was shown to contain approximately 340 tonnes of rare earth elements. Table 4 shows the AMDp tonnage data by basin.

While there was a significantly larger number of samples and mass of AMDp located in the NAPP region, the weighted

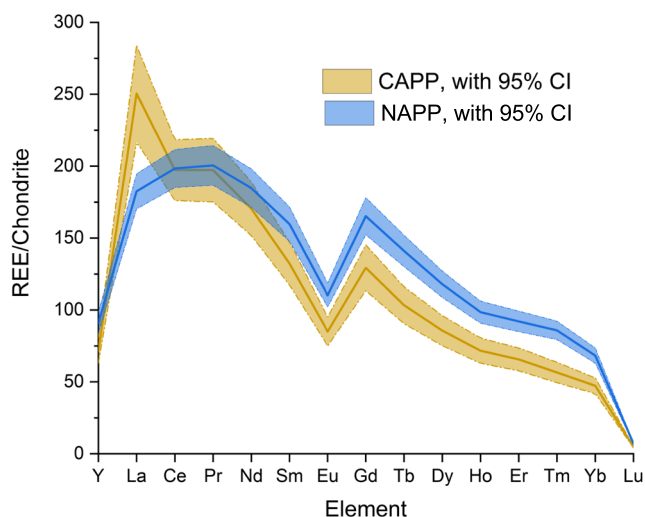


Fig. 8 Chondrite-normalized REE distribution in AMDp; with chondrite normalization after Korotev [41]

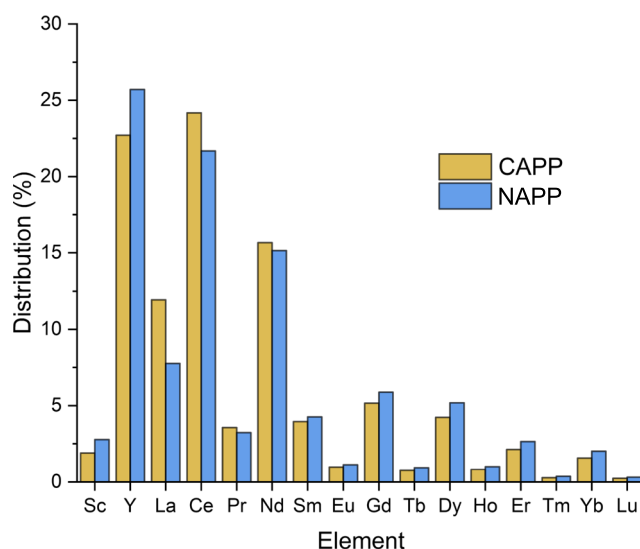


Fig. 9 Distribution of REEs between the NAPP and CAPP basins

average grade of this area was significantly lower than that of the AMDp located in the CAPP region. The difference in grade between the two basins can be contributed to the higher number of flooded underground mines with high pH and low TREE values. This result is significant, as low-grade feedstocks may be too costly to transport to a refining process. Furthermore, the overall total tonnage may seem low; however, AMD is often treated in perpetuity resulting in a steady supply of REEs that can supplement other feedstocks. For the 141 sites surveyed in this study, the total REE flux passing through AMD treatment systems totaled 13,000 kg/year.

In addition to the raw resource data, a supplemental study was conducted to investigate the influence of cut-off grade on the resource availability. Table 5 shows the percentage of TREE tonnes available given a nominal cut-off grade for all AMDp samples included in this study. This table shows that 67% of the AMDp mass in the dataset has a TREE concentration well below the grade of 100 g/t, while the remaining 33% contains 91% of the overall TREE mass. Furthermore, by increasing the cut-off grade to 300 g/t would result in the exclusion of 80% of the AMDp mass, while retaining 76% of the TREE mass.

A compilation of both the assay and tonnage data for AMDp allows for the generation of grade-tonnage curves for each element and the aggregated TREE. As an example, Fig. 10 shows the grade-tonnage relationship for REEs. The purpose of this exercise it to show how a minimal cut-off grade could impact the AMDp resource base. For example, if a cut-off grade of 1000 g/t is applied to this data, this would leave approximately 86 tonnes of REEs with an overall average grade of approximately 1400 g/t.

The grade-tonnage model graphically represents the available resource should a cut-off grade be applied for economic reasons. Figure 10 indicates that a low cut-off grade will be

Table 4 AMDp and TREE resources by coal basin

Parameter	Units	CAPP	NAPP	Total
Count	(#)	58	95	153
Mass weighted average grade	(g/t)	338	152	187
Mass weighted average moisture	(%)	55.8	43.8	46.1
Dry volume	(m ³)	5,495,964	23,681,794	29,177,758
Dry mass	(tonne)	342,382	1,475,304	1,817,686
TREE mass	(tonne)	116	224	340

required for AMDp to provide a meaningful mass of REEs. However, the mass of AMDp does not fluctuate linearly with the TREE mass. This analysis indicates that a processing cut-off grade may exclude a significant portion of AMDp currently stockpiled, but at the same time, it will not exclude the majority of REEs contained in the AMDp resource. As a result, not all AMD sites are equal candidates for consideration as a REE feedstock. While this is indicative of the AMDp sampled in the current dataset, the AMD treatment process itself may be changed to produce a more amenable AMDp product for REE beneficiation.

A similar exercise was conducted for the AMD samples and the results are shown in Fig. 11. This plot shows both cumulative REE flux (kg/year) and cumulative AMD flow (gpm) as a function of the individual REE concentration. When organized in this manner, this data indicates the total REE resource available for production and the volume of AMD that must be handled if a suitable recovery technology can produce a nominal REE concentration. For example, if a technology can successfully recover REEs from a raw AMD stream containing 500 µg/L, approximately 4100 kg/year of REEs could be produced, and the total system would need to handle just under 3000 gpm across the best sites included in this study. If the technology can only upgrade REEs from sources containing 1000 µg/L, the total REE production drops to under 900 kg/year, and the water handling requirement drops to 200 gpm. While the prior assessment estimated a

regional production capacity, this data only applies to the limited number of samples evaluated in this study, but the assessment methodology can be easily updated as more sites are evaluated.

3.5 Resource Outlook and Criticality

Since the REEs typically occur together within a deposit, they are generally lumped into a single category as TREE. Furthermore, they will also be classified as LREE, HREE, or CREE to identify sub-groups of the REEs that occur within the deposit. For economic consideration, these metrics can be misleading as it assumes all of the REEs can be equally separated from a given feedstock. Additionally, not all REEs have the same economic value due to varying prices and future demand. For example, La and Ce are relatively abundant and are currently in a state of oversupply within the REE markets [39].

As a result, other criteria are better suited for evaluating REE feedstocks based on current market trends. One such method is the outlook coefficient (C_{Outlook}) as defined by Seredin and Dai below [6]:

$$C_{\text{Outlook}} = \frac{\left(\frac{\text{Nd} + \text{Eu} + \text{Tb} + \text{Dy} + \text{Er} + \text{Y}}{\sum \text{REE}} \right)}{\left(\frac{\text{Ce} + \text{Ho} + \text{Tm} + \text{Yb} + \text{Lu}}{\sum \text{REE}} \right)} \quad (2)$$

Table 5 Implication of cut-off grade on processable AMDp and TREES

Cut-off grade (g/t)	AMDp mass (tonnes)	TREE mass (tonnes)	Average grade above cut-off (g/t)	% AMDp mass (%)	% Tree mass (%)
0	1,817,686	340	128	100	100
100	599,762	309	330	33	91
150	577,048	306	387	32	90
200	480,522	291	446	26	86
250	466,489	288	475	26	85
300	364,463	258	543	20	76
400	286,463	231	659	16	68
500	203,259	194	734	11	57
750	116,508	141	1,019	6	42
1000	48,099	86	1,400	3	25

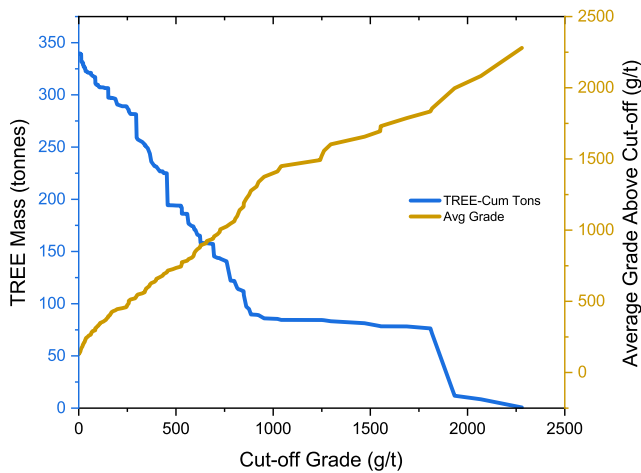


Fig. 10 Grade-tonnage curves indicating resource mass and average grade given a processing cut-off level

In other words, the more valuable critical REEs drive the metric value higher, while the REEs that are oversupplied reduce the value of the metric. This criterion was then applied to the AMDp sites and 58 conventional REE deposits [48]. As shown in Fig. 12, the AMDp is generally found to be more favorable from a critical REE content perspective than many of the conventional deposits. This can be attributed to the relative abundance of Y and Nd in the AMDp. As a result, while the overall resource base may be limited, the REEs in AMD do represent a unique and highly valued deposit that may support future growth areas.

4 Conclusions

As part of a regional survey, 141 AMD sites were evaluated for REE content in both raw water and AMDp in two separate campaigns across the CAPP and NAPP basins. This research has shown that REEs concentrate in the byproducts of AMD

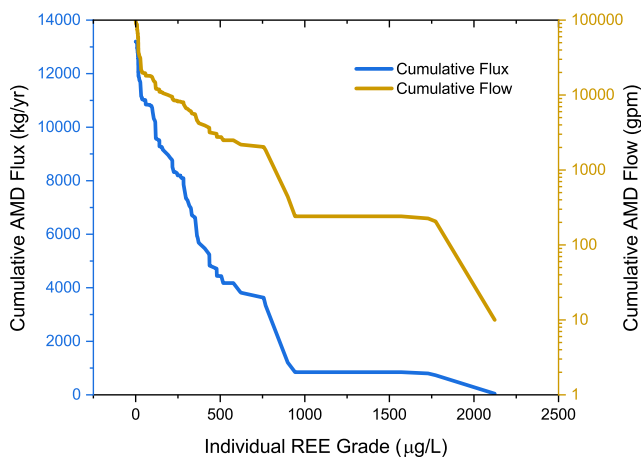


Fig. 11 Indication of total REE resource available based on an aqueous REE grade

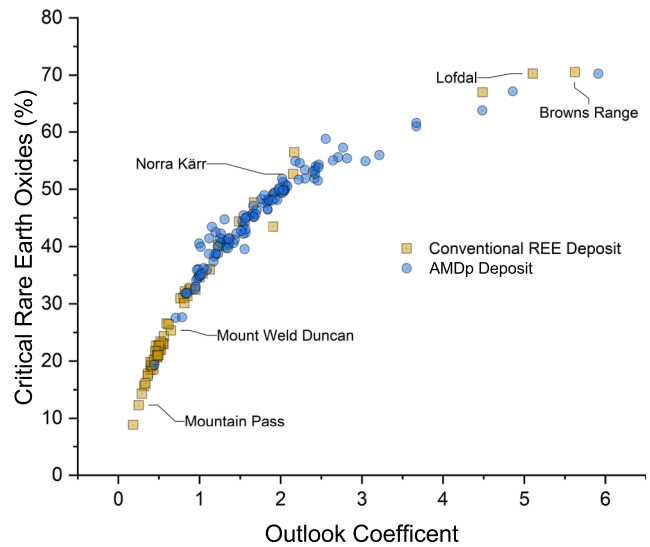


Fig. 12 Arrangement of AMDp in relation to conventional REE deposits based on the outlook coefficient after Seredin and Dai [6]

treatment across both basins with limited variation. The distribution of the REEs in the AMD byproduct was also similar among the two regions. Additionally, the overall inventory of available AMDp and TREEs was calculated for the sites in the dataset. Finally, a grade-tonnage curve was created for the AMDp showing that a significant portion of AMDp contains a low grade of TREEs indicating alternative AMD treatment process may be required to create high-quality AMDp.

In summary, the following key findings were developed during this research:

- The concentration of REEs in AMD varied from 0.25 to 3140 µg/L with an overall number average of 282 µg/L. Little variation was observed between the NAPP and CAPP basins.
- Least squares regression analysis showed that the most important factors dictating the REE content in AMD include the raw water pH as well as the concentrations of Mn, Al, Si, and Mg.
- The concentration of REEs in AMDp varied from < 5 to 2458 g/t with an overall number average of 724 g/t. A significant difference ($\alpha = 0.05$) was observed between the NAPP and CAPP basins with the NAPP number average being 750 g/t and the CAPP average being 669 g/t.
- The average distribution of REEs in both AMD and AMDp strongly favored Y (25%), Ce (22%), and Nd (15%). Little deviation was observed between the NAPP and CAPP basins.
- The 141 sites surveyed in this study contain approximately 340 tonnes of REEs in AMDp storage cells and will generate approximately 13,000 kg/year in AMD. Grade-tonnage curves show how these resource bases are influenced by potential process cut-off grades.

- The C_Outlook criterion shows that the distribution of REEs in AMD and AMDp is more favorable than most conventional REE deposits. One site sampled in this study had a C_Outlook value greater than 6.0, representing one of the most promising resources ever identified in the literature.

Acknowledgements This material is based upon the work supported by the U.S. Department of Energy under award number DE-FE0026444.

Compliance with Ethical Standards

Conflict of Interest The authors declare that they have no conflict of interest.

Disclaimer This report was prepared as an account of work sponsored by an agency of the US Government. Neither the US Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the US Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the US Government or any agency thereof.

References

1. Haque N, Hughes A, Lim S, Vernon C (2014) Rare earth elements: overview of mining, mineralogy, uses, sustainability and environmental impact. *Resources* 3:614–635. <https://doi.org/10.3390/resources3040614>
2. U.S. Geological Survey (2018) Mineral Commodity Summaries 2018: US Geological Survey 2018.
3. Campbell GA (2014) Rare earth metals: a strategic concern. *Miner Econ* 27:21–31. <https://doi.org/10.1007/s13563-014-0043-y>
4. Goodenough KM, Wall F, Merriman D (2017) The rare earth elements: demand, global resources, and challenges for resourcing future generations. *Nat Resour Res* 27:1–16. <https://doi.org/10.1007/s11053-017-9336-5>
5. Bauer D, Diamond D, Li J, McKittrick M, Sandalow D, Telleen P (2011) Critical Materials Strategy
6. Seredin VV, Dai S (2012) Coal deposits as potential alternative sources for lanthanides and yttrium. *Int J Coal Geol* 94:67–93. <https://doi.org/10.1016/j.coal.2011.11.001>
7. Preston JS, Cole PM, Craig WM, Feather AM (1996) The recovery of rare earth oxides from a phosphoric acid by-product. Part 1: leaching of rare earth values and recovery of a mixed rare earth oxide by solvent extraction. *Hydrometallurgy* 41:1–19. [https://doi.org/10.1016/0304-386X\(95\)00051-H](https://doi.org/10.1016/0304-386X(95)00051-H)
8. Preston JS, Cole PM, Du Preez AC, Fox MH, Fleming AM (1996) The recovery of rare earth oxides from a phosphoric acid by-product. Part 2: the preparation of high-purity cerium dioxide and recovery of a heavy rare earth oxide concentrate. *Hydrometallurgy* 41:21–44. [https://doi.org/10.1016/0304-386X\(95\)00067-Q](https://doi.org/10.1016/0304-386X(95)00067-Q)
9. Preston JS, Du Preez AC, Cole PM, Fox MH (1996) The recovery of rare earth oxides from a phosphoric acid by-product. Part 3. The separation of the middle and light rare earth fractions and the preparation of pure europium oxide. *Hydrometallurgy* 42:131–149. [https://doi.org/10.1016/0304-386X\(95\)00079-V](https://doi.org/10.1016/0304-386X(95)00079-V)
10. Preston JS (1996) The recovery of rare earth oxides from a phosphoric acid byproduct. Part 4. The preparation of magnet-grade neodymium oxide from the light rare earth fraction. *Hydrometallurgy* 42:151–167. [https://doi.org/10.1016/0304-386X\(95\)00082-R](https://doi.org/10.1016/0304-386X(95)00082-R)
11. Binnemans K, Tom P, Blanpain B, Van GT, Yang Y, Walton A et al (2013) Recycling of rare earths : a critical review. *J Clean Prod* 51: 1–22. <https://doi.org/10.1016/j.jclepro.2012.12.037>
12. Gambogi J (2015) Minerals Yearbook:2018
13. Rademaker JH, Kleijn R, Yang Y (2013) Recycling as a strategy against rare earth element criticality: a systemic evaluation of the potential yield of NdFeB magnet recycling 2013.
14. Finkelman RB, Stanton RW (1978) Identification and significance of accessory minerals from a bituminous coal. *Fuel* 57:763–768. [https://doi.org/10.1016/0016-2361\(78\)90135-7](https://doi.org/10.1016/0016-2361(78)90135-7)
15. Schofield A, Haskin L (1964) Rare-earth distribution patterns in eight terrestrial materials. *Geochim Cosmochim Acta* 28:437–446. [https://doi.org/10.1016/0016-7037\(64\)90117-6](https://doi.org/10.1016/0016-7037(64)90117-6)
16. Zubovic P, Stadnichenko T, Sheffey NB (1966) Distribution of minor elements in coals of the Appalachian region. Washington, D.C.
17. United States Department of Energy (2017) Rare earth elements from coal and coal byproducts.
18. Hower JC, Granite EJ, Mayfield DB, Lewis AS, Finkelman RB (1900) Notes on contributions to the science of rare earth element enrichment in coal and coal combustion byproducts. <https://doi.org/10.3390/min6020032>
19. Stuckman MY, Lopano CL, Granite EJ (2018) Distribution and speciation of rare earth elements in coal combustion by-products via synchrotron microscopy and spectroscopy. *Int J Coal Geol* 195: 125–138. <https://doi.org/10.1016/j.coal.2018.06.001>
20. Honaker RQ, Zhang W, Yang X, Rezaee M (2018) Conception of an integrated flowsheet for rare earth elements recovery from coal coarse refuse. *Miner Eng* 122:233–240. <https://doi.org/10.1016/j.mineng.2018.04.005>
21. Honaker RQ, Groppo J, Yoon R-H, Luttrell GH, Noble A, Herbst JA (2017) Process evaluation and flowsheet development for the recovery of rare earth elements from coal and associated byproducts. *Miner Metall Process* 34:107–115. <https://doi.org/10.19150/mmmp.7610>
22. Zhang W, Yang X, Honaker RQ (2018) Association characteristic study and preliminary recovery investigation of rare earth elements from fire clay seam coal middlings. *Fuel* 215:551–560. <https://doi.org/10.1016/j.fuel.2017.11.075>
23. Laudal DA, Benson SA, Palo D, Addleman RS (2018) Rare earth elements in North Dakota lignite coal and lignite-related materials. *J Energy Resour Technol* 140:062205. <https://doi.org/10.1115/1.4039738>
24. Laudal DA (2017) Evaluation of rare earth element extraction from North Dakota coal-related feed stocks. University of North Dakota, Grand Forks
25. Lin R, Stuckman M, Howard BH, Bank TL, Roth EA, Macala MK et al (2018) Application of sequential extraction and hydrothermal treatment for characterization and enrichment of rare earth elements from coal fly ash. *Fuel* 232:124–133. <https://doi.org/10.1016/j.fuel.2018.05.141>
26. Lin R, Howard BH, Roth EA, Bank TL, Granite EJ, Soong Y (2017) Enrichment of rare earth elements from coal and coal by-products by physical separations. *Fuel* 200:506–520. <https://doi.org/10.1016/j.fuel.2017.03.096>
27. Lin R, Bank TL, Roth EA, Granite EJ, Soong Y (2017) Organic and inorganic associations of rare earth elements in central Appalachian coal. *Int J Coal Geol* 179:295–301. <https://doi.org/10.1016/j.coal.2017.07.002>

28. Hower JC, Groppo JG, Joshi P, Dai S, Moecher DP, Johnston MN (2013) Location of cerium in coal-combustion fly ashes: implications for recovery of lanthanides. *Coal Combust Gasif Prod* 5:73–78. <https://doi.org/10.4177/CCGP-D-13-00007.1>
29. Kolker A, Scott C, Hower JC, Vazquez JA, Lopano CL, Dai S (2017) Distribution of rare earth elements in coal combustion fly ash, determined by SHRIMP-RG ion microprobe. *Int J Coal Geol* 184:1–10. <https://doi.org/10.1016/j.coal.2017.10.002>
30. Taggart RK, Hower JC, Hsu-Kim H (2018) Effects of roasting additives and leaching parameters on the extraction of rare earth elements from coal fly ash. *Int J Coal Geol* 196:106–114. <https://doi.org/10.1016/j.coal.2018.06.021>
31. Hower JC, Berti D, Hochella MF, Mardon SM (2018) Rare earth minerals in a “no tonstein” section of the Dean (Fire Clay) coal, Knox County, Kentucky. *Int J Coal Geol* 193:73–86. <https://doi.org/10.1016/j.coal.2018.05.001>
32. Joshi P, Preda D, Skyler DA, Tsinberg A, Green BD, Marinelli WJ, (2015) Recovery of rare earth elements and compounds from coal ash. 8969688 B2
33. Huang Q, Noble A, Herbst J, Honaker R (2018) Liberation and release of rare earth minerals from Middle Kittanning, Fire Clay, and West Kentucky no. 13 coal sources. *Powder Technol* 332:242–252. <https://doi.org/10.1016/j.powtec.2018.03.063>
34. Honaker R (2017) Pilot-scale testing of an integrated circuit for the extraction of rare earth minerals and elements from coal and coal byproducts using advanced separation technologies 2017.
35. Zhang W, Rezaee M, Bhagavatula A, Li Y, Groppo J, Honaker R (2015) A review of the occurrence and promising recovery methods of rare earth elements from coal and coal by-products. *Int J Coal Prep Util* 35:295–330. <https://doi.org/10.1080/19392699.2015.1033097>
36. Vass C, Noble A, Ziemkiewicz P (2019;In Press) The occurrence and concentration of rare earth elements in acid mine drainage and treatment byproducts. Part 1: initial survey of the Northern Appalachian coal basin. *Mining Metall Explor*. <https://doi.org/10.1007/s42461-019-0097-z>
37. Seredin VV, Dai S (2012) International journal of coal geology coal deposits as potential alternative sources for lanthanides and yttrium. *Int J Coal Geol* 94:67–93. <https://doi.org/10.1016/j.coal.2011.11.001>
38. Cox C, Kynicky J (2018) The rapid evolution of speculative investment in the REE market before, during, and after the rare earth crisis of 2010–2012. *Extr Ind Soc* 5:8–17. <https://doi.org/10.1016/j.exis.2017.09.002>
39. Binnemans K, Jones PT, Muller T, Yurramendi L. Rare earths and the balance problem: how to deal with changing markets? *J Sustain Metall* 2018;8:126–46. doi:<https://doi.org/10.1007/s40831-018-0162-8>, 146.
40. Skousen JG, Ziemkiewicz PF (1995) Acid mine drainage control and treatment. West Virginia University, Morgantown
41. Korotev RL (2009) “Rare earth plots” and the concentrations of rare earth elements (REE) in chondritic meteorites 2009. <http://meteorites.wustl.edu/goodstuff/ree-chon.htm>.
42. Kim E, Osseo-Asare K (2012) Aqueous stability of thorium and rare earth metals in monazite hydrometallurgy: Eh-pH diagrams for the systems Th-, Ce-, La-, Nd- (PO₄)-(SO₄)-H₂O at 25 °C. *Hydrometallurgy* 113–114:67–78. <https://doi.org/10.1016/j.hydromet.2011.12.007>
43. Cravotta CA, Brady KB, Rose AW, Douds JB (1999) Frequency distribution of the pH of coal-mine drainage in Pennsylvania. In: *US Geol Surv Water-Resources Investig Report* 99-4018A, pp 313–324
44. Leavitt, B.R., Stiles, J.M., Donovan, J.D., Ziemkiewicz, P.F. 2005. Strategies for Cooling Electric Generating Facilities Utilizing Mine Water: Technical and Economic Feasibility. In: *Proceedings of the 22nd Annual Int'l Pittsburgh Coal Conference*. 12-15 Sep 2005. Pittsburgh PA, USA.
45. Bryan RC, Richers D, Anderson HT, Gray T. Assessment of rare earth elemental contents in select United States coal basins. 2015.
46. Oddo G (1914) Die Molekularstruktur der radioaktiven Atome. *Zeitschrift Für Anorg Chemie* 87:253–268. <https://doi.org/10.1002/zaac.19140870118>
47. Harkins WD (1917) The evolution of the elements and the stability of complex atoms. I. A new periodic system which shows a relation between the abundance of the elements and the structure of the nuclei of atoms. *J Am Chem Soc* 39:856–879. <https://doi.org/10.1021/ja02250a002>
48. Lifton J, Hatch G (2016) Technology Metals Research. <http://www.techmetalsresearch.com/metrics-indices/tmr-advanced-rare-earth-projects-index/>. Accessed 10/09/2017

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Appendix B: Legal Ownership and Control Report

DINSMORE & SHOHL LLP

Date: June 14, 2019

Report on Resource (REEs) Ownership and Control

RARE EARTH ELEMENTS

I. Conclusions and Recommendations

Various arguments can be made regarding who owns rare earth elements (“REEs”). Due to the lack of any prior litigation or legislation addressing ownership, who owns REEs and what regulations the extraction of REEs is subject are currently questions with no definitive answers. With regard to ownership, while many may perceive that the desire to develop REEs domestically will result in perhaps a “lawyer’s relief act,” one lesson from coalbed methane development is that business parties covering the range of potential “ownership interests” can, and often do, work out solutions where each party participates in the arrangement and profits, expenses, and liabilities are agreed upon based on discussions, negotiations, and factual matters. Thus, while some surface owners, coal owners, and reclamation site owners, including government entities, may seek court involvement in litigating the issues, others likely will be willing to enter into agreements to allow the development of REEs. Said development, however, will still be subject to governmental regulations, the exact identity of which is currently unknown, especially as “waste products” from extraction methods may well, independently, be the subject of state and federal regulations. What is known, however, is that the federal government has become increasingly interested in the extraction of REEs over the past two years. Based upon such interest, we may soon have guidance regarding ownership of REEs and what regulations will govern their extraction¹. Continuous monitoring in this realm is necessary to stay current with the state of REE ownership and the applicable regulations governing extraction. For now, what is left for analysis is what the courts have—and have not—said about what constitutes “minerals,” whether mine tailings are real or personal property, ownership according to that classification, and responsibility for byproducts of REE extraction.

II. Legal Definition of Minerals

Though the Pennsylvania Supreme Court and the Supreme Court of Appeals of West Virginia have both addressed what the term “mineral” entails, REEs have not explicitly been included in either description. For example, in Pennsylvania, the court has clarified that a “mineral should be viewed in the commercial sense and include inorganic substances that are mined or quarried which have sufficient value separated from the land to induce the expense and labor of severance for their own stakes.” *Hendler v. Lehigh V. R. Co.*, 58 A. 486, 487 (Pa. 1904). Pennsylvania also follows the rule of interpretation that the court will look to the popular and common use of the word and to the intent of the parties at the time of the reservation or grant in construing the meaning of the deed. *Vosburg v. NBC Seventh Realty Corp.*, 122 A.3d 393, 399 (Pa. Super. Ct. 2015).

¹ Of course, any legislative or executive guidance may still become the subject of litigation if the stakes warrant it. To date the legislative and executive guidance has taken the form of seeking to promote the development of REEs including allocation of funds, as discussed in Section VI of this Report.

The Supreme Court of Appeals of West Virginia has yet to create a bright line definition of “mineral” or “mineral rights”, but rather has held that what minerals are being conveyed can depend on the intent of the parties and language of the deed. Specifically, in the case of *Rock House Fork Land v. Raleigh Brick & Tile Co.*, the court has stated that:

[T]he terms mine and mineral are not definite terms. They are susceptible of limitation according to the intention with which the parties use them, and in their construction regard must be had, not only to the deed in which they occur, but also to the relative position of the parties interested, and to the substance of the transaction or arrangement which the grant embodies. Consequently, in themselves these terms are incapable of a definition which would be universally applicable.

Syl. Pt. 1, *Rock House Fork Land Co. v. Raleigh Brick & Tile Co.*, 97 S.E. 684, 685-86 (W. Va. 1918) (internal citations omitted). This case involved the conveyance of “all the coal and other minerals of every kind and description, except gas and oil in and underlying” the tract of land. *Id.* at 684. The defendant-surface owner sought to use the clay on the land and the plaintiff-mineral owner claimed that such use was improper because “the grant to it of the coal and other minerals except oil and gas passed [the] seam of clay.” *Id.* at 684-685. The court ruled that the conveyance of the clay was not intended because it was not a mineral or stone that was removed when the coal was mined and thus, the clay belonged to the surface owner. *Id.* 686. The court looked to the intent of the parties and determined that the surface owner did not intend to give the coal owner the right to the clay. *Id.*

The Supreme Court of Appeals of West Virginia has also addressed whether the reservation of the “oil, gas and other minerals” in a deed reserved the sand or gravel. See *West Virginia Dept’t of Highways v. Farmer*, 226 S.E.2d 717, 719 (W. Va. 1976). In that case, the owners of the mineral interests argued that they were entitled to compensation for the sand and gravel in an eminent domain proceeding. *Id.* at 719. The court ruled that the term “other minerals” created an ambiguity due to the lack of express language and the fact that, from the date that the deed was executed until the start of the eminent domain proceeding, no sand or gravel were sold from the land. *Id.* at 719-720. Thus, the court looked at extrinsic evidence to determine the intent of the parties. According to the court, because no prior owner of the minerals had ever attempted to exercise control over the sand and gravel, the parties to the 1911 deed could not have intended that the reservation of the oil, gas, and other minerals would include sand and gravel. *Id.* at 720. Moreover, the court held that, pursuant to the doctrine of *ejusdem generis*, “the enumeration of oil and gas [made] meaningless the term “other minerals,” except for minerals which are of the same kind, class or nature, that is, petroleum products.” *Id.* The court did state, however, that “[t]he word “mineral” in its ordinary and common meaning is a comprehensive term including every description of stone and rock deposit whether containing metallic or non-metallic substances.” *Id.* at 719 (citing *Robinson v. Wheeling Steel & Iron Co.*, 129 S.E. 311 (W. Va. 1925); *Ramage v. South Penn Oil Co.*, 118 S.E. 162 (W. Va. 1923); *Horse Creek Land & Mining Co. v. Midkiff*, 95 S.E. 26 (W. Va. 1918)).

The aforementioned case law demonstrates that courts in Pennsylvania and West Virginia may be reluctant to rule that the phrase “other minerals” includes REEs. Absent express language in the conveying instrument, the focus is on the intent of the parties (which is typically viewed by courts as a factual inquiry for a jury and not a legal determination for the court, likely leading to additional litigation and uncertainty) to the document and the circumstances surrounding the

document at the time that it was executed. Another distinction which heavily considers intent is the classification of minerals as real or personal property.

III. Real vs. Personal Property

This distinction is most prevalent in the classification of mine tailings. The term “mine tailings” is often used to refer to deposits of waste product resulting from mining operations. Many mine tailings were often deposited decades ago when their value was non-existent or unknown. Upon learning of the potential value of mine tailings, both land owners and mineral owners have initiated litigation asserting ownership of said mine tailings. Courts have made it clear that ownership is dependent upon whether the mine tailings are classified as real or personal property; however, courts are not in agreement as to when mine tailings are considered real property versus personal property. For example, courts have held the following:

- (1) The intention with which mine tailings are extracted and deposited determines their status as real or personal property;²
- (2) Abandoned mine tailings are real property (Pennsylvania follows this rule);³
- (3) Mine tailings that are mingled or embedded in earth are real property;⁴
- (4) Mine tailings deposited for purposes of disposal are real property;⁵ and
- (5) Mine tailings adapted, used, or treated as real property are real property.⁶

75 A.L.R. 4th 962.

As this list demonstrates, Pennsylvania is a jurisdiction where abandoned mine tailings are deemed real property. For example, in the *Lehigh Valley Coal* case, Lehigh Valley Coal acquired

² See *Hayes v. Alaska Juneau Forest Indus., Inc.*, 748 P.2d 332 (Alaska 1988); *Steinfeld v. Omega Copper Co.*, 141 P. 847 (Ariz. 1914); *State ex rel. Dept. of Water Res. v. Superior Court of Butte Cnty.*, 208 Cal. App. 2d 659 (Cal. St. App. 1962); *Conway v. Fabian*, 89 P.2d 1022 (Mont. 1962).

³ See *Ritter v. Lynch*, 123 F 930 (Nev. 1903); *Hayes*, 748 P.2d 332; *Jones v. Jackson*, 9 Cal 237 (Cal. 1858); *Baker v. White*, 322 P.2d 512 (Cal. Ct. App. 1958); *Superior Court of Butte Cnty.*, 208 Cal. App. 2d 659; *Elk Horn Coal Corp. v. Allen*, 324 S.W.2d 829 (Ky. 1959); *Conway*, 89 P.2d 1022; *Goldfield Consol. Milling & Transp. Co., v. Old Sandstrom Annex Gold Mining Co.*, 150 P. 313 (Nev. 1915); *Esmeralda Water Co. v. Mackley*, 208 P.2d 821 (Nev. 1949); *Gilberton Contracting Co. v. Hook*, 255 F. Supp. 687 (ED Pa 1966); *Commonwealth v. Steimling*, 27 A. 297 (Pa. 1893); *Fidelity-Philadelphia Trust Co. v. Lehigh Valley Coal Co.*, 143 A. 474 (Pa. 1928); *Stephens Hays Estate, Inc. v. Togliatti*, 38 P.2d 1066 (Utah 1934).

⁴ See *Conway*, 89 P.2d 1022; *Foreman v. Beaverhead Cnty.*, 161 P.2d 524 (Mont. 1945); *Rogers v. Cooney*, 7 Nev. 213 (Nev. 1872); *Re Appropriation of Easements for Highways Purposes*, 190 N.E.2d 446 (Ohio 1963).

⁵ See *Manson v. Dayton*, 153 F. 258 (Colo. 1907); *Hayes*, 748 P.2d 332; *Mathews Slate Co. v. Advance Indus. Supply Co.*, 172 NYS 830 (N.Y. App. Div. 1918).

⁶ See *Hayes*, 748 P.2d 332; *Superior Court of Butte Cnty.*, 208 Cal. App. 2d 659.

land containing a culm bank, the contents of which consisted of mine tailings from a neighboring mine. *Lehigh Valley Coal Co.*, 143 A. at 475. The estate of the owner of the neighboring mine sought to claim ownership of the culm bank on the basis that the contents of said culm bank consisted of coal byproduct from the decedent's mine. *Id.* The Supreme Court of Pennsylvania ruled that the mine tailings were real property belonging to the owner of the land on which the culm bank was located because the decedent had abandoned the mine tailings and ownership therein. *Id.* at 479. In analyzing whether the decedent had abandoned his interest in the culm bank, the Court recognized that the decedent had not deposited mine tailings on the culm bank since 1876, and at the time of the conveyance of the decedent's property in 1893, after the decedent's death, no mention was made of the culm bank and there was no attempt to include it in the conveyance. *Id.* at 476. According to the Court, the decedent appeared to merely be "getting rid of what was then generally regarded as a source of annoyance and expense." *Id.* at 477.

The theory of abandonment resulting in mine tailings that are categorized as the real property of the landowner on which the mine tailings are located has also been applied to mine tailings that are contained in water. See *Stephens Hays Estate, Inc. v. Togliatti*, 38 P.2d 1066 (Utah 1934). For example, in the *Togliatti* case, the plaintiffs brought an action to quiet title to copper contained within water which emanated from mine tailings from mines located upstream. *Id.* The Supreme Court of Utah held that the copper was real property that belonged to the owner of the land on which the water was located and not to the mine owners. *Id.* at 1069. Specifically, the court stated that to allow "tailings to flow where they may, without obstructions to confine them, is equivalent to abandonment." *Id.* at 1069 (citing Lindley on Mines § 426, 3d Ed.).

This case demonstrates that, once again, courts will look at the intent of the parties to determine whether mine tailings were abandoned. If abandoned, the tailings are part of the *real* property on which the tailings are located. If not abandoned, the tailings are the *personal* property of the mine owner. For example, if the mine owner fenced in the mine tailings and made attempts to protect them from theft or from leaching into the property of another (for instance water reserves), a court would likely deem such tailings as personal property belonging to the mine owner. Conversely, if the mine owner were simply dumping the mine tailings as though the tailings were unwanted refuse, a court would likely rule that the tailings were part of the real property where they ultimately rested. Moreover, given that sludge piles and water runoff can contain mine tailings from multiple mines owned by different persons or entities, a court might find that the commingling of said tailings, without any other evidence of intent to preserve the tailings, equates to abandonment, thus making the tailings real property belonging to the landowner on which the mine tailings are located. However, the ownership inquiry goes beyond this basic distinction between real and personal property.

IV. Ownership

Ownership rights in real property are often analogized to a bundle of sticks. One party may own the entire bundle, or multiple parties may each own one or more of the individual sticks. For example, where the mineral rights have been severed from the surface rights of a particular property, one party may own the surface of the property, while another party owns, or multiple parties own, certain specific minerals therein. To add an additional layer of nuance, the minerals themselves may be owned by certain parties while separate parties may hold the leasehold rights to said minerals.

These ownership scenarios are an example of why a party looking to purchase or lease an ownership interest in real property must carefully review the title to the subject property, particularly, the applicable deeds and leases, with specific emphasis on the original instruments which severed the ownership of the various types of minerals from the surface ownership. Because a purported owner may only transfer or reserve what it has legal title to, it is especially important to determine if and when any mineral rights were severed, and exactly what minerals were severed, from the fee interest.

In reviewing deeds, the general rule is that, if the deed is clear, any interpretation of ownership is limited to the words contained in the document. *See* 23 Am. Jur. 2d Deeds § 193 (2017). Only when the document is ambiguous may extrinsic evidence be considered in an attempt to determine the intent of the parties to the document. *See id.* (stating that “[w]hen the intent of the parties to a deed is not clear from its face, it must be construed in light of the terms used and the circumstances surrounding the deed.”). In other words, the general rule of deed construction followed in the United States is:

When interpreting a deed, the traditional rules of construction to determine the parties’ intention involve the following principles: (1) the nature and quantity of the interest conveyed must be ascertained from the deed itself and cannot be orally shown in the absence of fraud, accident, or mistake; (2) courts seek to ascertain not what the parties may have intended by the language but what is the meaning of the words they used; (3) effect must be given to all the language of the instrument, and no part shall be rejected if it can be given a meaning; (4) if a doubt arises concerning the interpretation of the instrument, it will be resolved against the party who prepared it; and (5) to ascertain the intention of the parties, the language of a deed should be interpreted in the light of the subject matter, the apparent object or purpose of the parties and the conditions existing when it was executed.

23 Am. Jur. 2d. Deed § 194 (2017). In addition to the foregoing, the Supreme Court of Appeals of West Virginia has generally held that “[p]arties are bound by general and ordinary meanings used in deeds,” while the Pennsylvania Supreme Court has stated that the following three rules apply when construing the terms of a deed:

(1) the nature and quantity of the interest conveyed must be ascertained from the instrument itself and cannot be orally shown in the absence of fraud, accident or mistake and we seek to ascertain not what the parties may have intended by the language but what is the meaning of the words; (2) effect must be given to all the language of the instrument and no part shall be rejected if it can be given a meaning; (3) the language of the deed shall be interpreted in the light of the subject matter, the apparent object or purposes of the parties and the conditions existed when it was executed.

See Syl. Pt. 1, *McDonough Co. v. E.I. DuPont DeNemours & Co., Inc.*, 280 S.E.2d 246 (W. Va. 1981); *Highland v. Commonwealth*, 161 A.2d 390, 398 (Pa. 1957).

Both the Pennsylvania Supreme Court and the West Virginia Supreme Court of Appeals have also addressed what language contained within a deed operates to convey the surface and minerals within real property. As the case law set forth below demonstrates, courts are hesitant to rule that the conveyance or reservation of certain minerals carries with it those minerals that are not expressly mentioned, especially when the existence or value of the mineral is unknown. Often,

courts look at the intent of the party at the time that the applicable deed or lease was executed. As discussed below, courts often rule that a party could not have intended to retain a mineral the value of which was unknown at the time of the conveyance or purported reservation. As the severance of most mineral estates took place long before the value of REEs was known, ownership of REEs will likely need to be determined on a case-by-case basis. It is possible that multiple owners may be deemed owners of the REEs depending on the circumstances, including the location of the REEs at the time of their extraction (as further complicated by the likelihood that such REE extraction was not the principal goal of the mining operation but was necessarily part and parcel of the removal of other minerals which were the target of the operation).

As mentioned, those interested in recovering REEs may be faced with prior deeds and leases in the chain of title to property in which REEs are located that were executed at a time when any value or the potential profit from, and the possible existence of REEs, was not contemplated. REEs are not the first mineral to present such an issue. For example, before the value of coalbed methane was discovered, such gas was viewed as merely a safety concern rather than as a commercial product with a potential to generate profit. Once coalbed methane was discovered to be commercially valuable, litigation ensued in Pennsylvania and West Virginia among those holding ownership interests in the property wherein the gas was located. The conveyance of “surface only” in a deed or lease can also further complicate the ownership analysis, as shown by surface owners, coal owners, and oil and gas owners who engaged in litigation regarding who owned the rights to commercially develop coalbed methane.⁷

A. Coalbed Methane

Pennsylvania was the first state to decide ownership of coalbed methane in the case of *U.S. Steel v. Corp. v. Hoge*. See *U.S. Steel Corp. v. Hoge*, 468 A.2d 1380 (Pa. 1983). In *Hoge*, the deed at issue conveyed “all the coal of the Pittsburgh or River Vein underlying all that certain tract of land” to U.S. Steel; however, the grantor surface owners “reserve[d] the right to drill and operate through said coal for oil and gas . . .” *Id.* at 1382. In addressing who owned the gas imbedded in the coal, the court held that, so long as the gas was present in the coal, the ownership of the gas belonged to the coal owner, but as the gas migrates away from the coal owner’s dominion and control, it becomes the property of the surface owner. *Id.* at 1383. Importantly, in making its decision, the court discussed how it did not believe that the grantor intended to reserve the right to extract (what was then considered) a valueless and dangerous waste product at the time that the deed was executed. *Id.* at 1385.

West Virginia, unlike Pennsylvania, has refused to adopt a bright line rule regarding ownership of coalbed methane. Instead the Supreme Court of Appeals of West Virginia has held only that ownership of coalbed methane will be analyzed in a fact-based, case-by-case approach that considers factors such as the terms of the deed or lease, the date that the deed or lease was executed, and the intent of the parties to the deed or lease. *Energy Dev. Corp. v. Moss*, 591 S.E.2d 135, 138 (W. Va. 2003). For example, in the case of *Moss*, the court was asked to decide whether a standard oil and gas lease executed in 1986 conveyed to the lessee the right to drill into the lessor’s coal seams to extract coalbed methane. *Id.* The court, refusing to adopt a bright line rule, held that “in the absence of specific language to the contract or other indicia of the parties’ intent,

⁷ The right of coal owners to ventilate their operations for safety purposes has not typically been a point of disagreement unless that ventilation took the form of commercial enterprise capture techniques, or could amount to waste by going beyond appropriate safety precautions.

an oil and gas lease does not give the oil and gas lessee the right to drill into the lessor's coal seams to produce coalbed methane" *Id.* at 146.⁸ In making its decision, the court relied on the fact that, at the time and place of execution of the lease, extracting coalbed methane for profit was not common. *Id.* at 145. The Court also noted that West Virginia, unlike Pennsylvania, follows the rule of capture whereby "oil and gas belong to the owner of the land, and are part of it, so long as they are on it or in it subject to his control; but when they escape and go in to other land, or come under another's control, the title of the former owner is gone." *Id.*

Similar to coalbed methane, REEs are separate minerals found in or around coal seams, the value of which was unknown at the time of the execution of most applicable deeds and leases. Unlike coalbed methane, however, REEs never posed a safety concern in the context of mining operations, and REEs, when extracted along with the coal from below the surface, remain intact and located on the surface mixed with the residue of what was being intentionally mined, retaining their value rather than merely dissipating into the earth's atmosphere. Based on such facts, a direct comparison of coalbed methane to REEs is not particularly helpful; however, the aforementioned coalbed methane cases would indicate that courts in both Pennsylvania and West Virginia will likely consider factors such as whether the value of REEs was known at the time of execution of the applicable deeds and leases, as well as the identity of the ownership interest exercising dominion over the REEs. Specifically, a court may hold that a coal owner is the owner of the REEs located within the coal seam or within the "top" or "bottom" mined with the seam, while the surface owner may be deemed the owner of all REEs deposited in post-mining sludge piles on the surface of the land or present in water generated in the mining process that is treated and diverted to settlement treatment ponds before ultimately being routed to such sludge piles. The ultimate outcomes are difficult to predict. For example, West Virginia, in applying the rule of capture, could rule that the first to capture the REEs is the owner. As discussed below, however, many other aspects of ownership interests may complicate the analysis even further.

B. Surface Rights

In addition to the reservation of coalbed methane, the Supreme Court of Appeals of West Virginia has addressed whether a conveyance of the "surface only" of a tract of land acts as an effective reservation of the grantor's mineral rights. *See Faith United Methodist Church v. Morgan*, 745 S.E.2d 461 (W. Va. 2013). Specifically, in the case *Faith United Methodist Church v. Morgan*, the issue was whether a 1907 deed that conveyed the surface only of a tract of land also conveyed an interest in all oil and gas under the tract. *Id.* at 464. The court, in defining surface as the exposed area of land, improvements on the land, and any part of the underground actually used by a surface owner as an adjunct to surface use, held that surface rights do not include mineral rights and thus the oil and gas rights were not conveyed. *Id.* at 463, 483.

An argument could be advanced that once the REEs have been mined and deposited into sludge piles, or present in waste water being treated in settling ponds on the surface of the land, they may revert to the ownership of the surface owner. In this situation, based on *Hoge*, the surface owner may be able to claim ownership of the REEs because they are subject to the surface owner's dominion and control; however, as stated and discussed above, other factors come into play such as whether another mineral interest owner has taken actions to protect the sludge piles or whether

⁸ The Supreme Court of Appeals of West Virginia affirmed its holding in *Moss in Paulos v. LBR Holdings, LLC*, 792 S.E.2d 588 (W. Va. 2016).

an entity has been tasked with cleaning up old mine sites. To add more complexity, where such REEs wind up in the form of waste water, refuse, or sludge, the owner of that surface may be different than the owner of the surface overlying the underground area from which the REEs were mined. At values of potentially thousands of dollars per gram, it is anticipated that additional litigation and legislation will ensue as these ownership matters are clarified, and as the coalbed methane cases demonstrated, it is quite possible different states may reach different conclusions.

V. Liability Issues

Often times with ownership comes responsibility and the need to consider potential liabilities that may arise from the extraction of REEs. Although it is our understanding that the protocols for extraction being developed in the United States materially take into account environmental concerns, even best practices and techniques may result in unforeseen liabilities that do not come to light for many years. For example, over time, pollutants from coal refuse piles or mine tailings can seep into groundwater and contaminate local water supplies. In fact, REE mining operations in California were shut down many years ago in part due to pollution concerns. Marvin L. Astrada, *Revisiting the WTO Rare Earths Dispute – Law, Trade, Sovereignty, & Environmental Security in a Networked World*, 46 Syracuse J. Int'l L. & Com. 1, 18 (2018). REEs are “notoriously difficult to mine and process safely.” *Id.* at 19. This—along with China’s looser environmental regulations—explains why China produces ninety-seven percent of the world’s REEs. *Id.*⁹

Chinese companies use a technique called situ mining to extract REEs. Carley Doyle, *Lithium and Rare Earth Elements: The Dirty Business of Clean Energy*, 5 Chi.-Kent J. Env. Energy L. 1, 15 (2014-2015). This process requires injecting chemicals into mined ore to extract REEs. *Id.* This “leads to concerns of chemicals contaminating water supplies and farmland.” *Id.* The largest producing REE mine in the world, located in Baotou, China, failed to properly line its disposal site and now faces pollution challenges because its byproduct has been “seeping its toxins into the groundwater for the last twenty years.” *Id.* at 16. This is not an isolated instance. In Guyun Village, another Chinese community which survived on mining REEs, “[t]he acids used to extract the rare earths washed into nearby streams and rivers destroying rice paddies and fish farms and contaminating water supplies.” *Id.* Even as far back as the 1990s, “local farmers in this area saw livestock die, crops wither, and neighbors develop cancer.” *Id.*

Although the United States may have stricter environmental restrictions in place, the liability concern is still imminent. In the United States, other industries are experiencing liability many years down the road, even where their practices and protocols were in compliance at the time of the underlying activities and operations that subsequently developed problems. Abandoned mine sites which remained untreated have polluted local waterways, exposing mine owners to liability. Craig B. Griffin, *West Virginia’s Seemingly Eternal Struggle for a Fiscally and Environmentally Adequate Coal Mining Reclamation Bonding Program*, 107 W. Va. L. Rev. 105, 113-114 (2004). Often punishment included a hefty fine or revocation of future mining permits. *Id.* The United States Environmental Protection Agency (“EPA”) has even targeted the poultry industry for violations of the Clean Water Act. *See Alt v. EPA*, 758 F.3d 588 (4th Cir. 2014).

⁹ And China’s ability to control prices is often cited as a significant factor in the closing and eventual bankruptcy of Molycorp’s Mountain Pass Mine in 2015 which had been at one time a large producer of REEs.

Regardless of the current uncertainty surrounding the environmental effects of extracting REEs, the risk of future liability should be prevalent in the minds of those seeking ownership of these elements. The extraction of REEs is likely to become a focus of developing environmental regulations and legislation in the near future.

VI. Potential Pending Regulatory and Legal Changes

A. Regulation

To date, there are no specific federal regulations governing the mining or extraction of REEs. In the 2012 report issued by the EPA entitled “Rare Earth Elements: A Review of Production, Processing, Recycling, and Associated Environmental Issues” the EPA noted that the production of REEs would generally be governed by state environmental regulatory authorities and subject to the same requirements of other mining operations under federal guidelines, which include the National Environmental Policy Act, National Pollutant Discharge Elimination System, and Underground Injection Control.¹⁰ In addition, the EPA noted that because of the technologically enhanced naturally occurring radioactive materials (“TENORM’s”) generally associated with the extraction and development of REEs, additional restrictions and regulations applicable to TENORM’s would apply.

Neither Pennsylvania nor West Virginia has established state specific regulations governing the extraction of REEs. However, the state of Pennsylvania has established over seventy (70) specific permits and permitting requirements for the processing of residual waste, including a permit specific for the recycling of REEs from lamp phosphors.¹¹

Given the lack of specific regulations governing the extraction of REEs in both Pennsylvania and West Virginia, rules, regulations, and a permitting structure would need to be adopted. This process is typically slow and arduous as each state has specific requirements governing the proposal and adoption of agency rules. In cases where the REEs are being extracted from bond forfeiture sites, there is additional complexity because the private venture seeking access to the site would first have to come to an agreement with the reclamation agency in possession of the bond forfeiture site on issues such as indemnification, allowed uses, disposal, and additional reclamation. Moreover, the cliché that “possession is 9/10 of the law” could come into play here since a private venture entity would not likely be able to gain access to a forfeiture site controlled by a state reclamation agency without some agreement concerning assumption of liability by the entity for the “replacement” of the material from which REEs are extracted into some type of permitted disposal site, possibly the same site with some additional permitting restrictions. Such restrictions would have to be developed by the agency’s rulemaking procedures, and there would also likely be some required compensation to allow for the surface disturbance.

At the federal level, REEs are included in the definition of “critical minerals” as defined in EO 13817.¹² EO 13817 states:

It shall be the policy of the Federal Government to reduce the Nation’s vulnerability to disruptions in the supply of critical minerals, which constitute a strategic vulnerability for the security and prosperity of the United States. The United States

¹⁰ See *Rare Earth Elements: A Review of Production, Processing, Recycling, and Associated Environmental Issues* (2012) at pgs. 3-4 through 3-9.

¹¹ Pennsylvania Department of Environmental Protection General Permit Number WMGR133.

¹² See: *Final List of Critical Minerals 2018*, Department of The Interior, Office of the Secretary, 83 F.R. 23295

will further this policy for the benefit of the American people and in a safe and environmentally responsible manner, by:

- (a) identifying new sources of critical minerals;
- (b) increasing activity at all levels of the supply chain, including exploration, mining, concentration, separation, alloying, recycling, and reprocessing critical minerals;
- (c) ensuring that our miners and producers have electronic access to the most advanced topographic, geologic, and geophysical data within U.S. territory to the extent permitted by law and subject to appropriate limitations for purposes of privacy and security, including appropriate limitations to protect critical infrastructure data such as those related to national security areas; and
- (d) streamlining leasing and permitting processes to expedite exploration, production, processing, reprocessing, recycling, and domestic refining of critical minerals.

Under EO 13817, the United States Secretary of Commerce was tasked with issuing a report to include “recommendations to streamline permitting and review processes related to developing leases; enhancing access to critical mineral resources; and increasing discovery, production, and domestic refining of critical minerals.” The Commerce Department report, originally due in November, 2018 was finally issued on June 4, 2019 addressing six (6) “Calls to Action”: (1) Advance Transformational Research, Development, and Deployment Across Critical Mineral Supply Chains; (2) Strengthen America’s Critical Mineral Supply Chains and Defense , Improve Understanding of Domestic Critical Mineral Resources; (5) Improve Access to Domestic Critical Mineral Resources on Federal Lands and Reduce Federal Permitting Timeframes; and (6) Grow the American Critical Minerals Workforce . “Through the recommendations detailed in this report, the federal government will take unprecedented action to ensure that the United States will not be cut off from these vital materials”, commented Secretary of Commerce Wilbur Ross upon the release of the report.¹³

B. Legislation

Legislation pertaining to REEs has increased within the past two years. This increase has been at the federal level via proposed acts introduced by members of the United States House of Representatives and Senate. The proposed legislation has typically focused on providing funding for the development of technology to enable the extraction of REEs and limiting the amount of REEs imported from foreign jurisdictions.

Of the legislation introduced, two bills have been signed into law. Those two bills are H.R. 5515, known as the John S. McCain National Defense Authorization Act for Fiscal Year 2019 (“H.R. 5515”),¹⁴ and H.R. 5895, known as the Energy and Water, Legislative Branch, and Military Construction and Veterans Affairs Appropriations Act, 2019 (“H.R. 5895”).

¹³ See: *U.S. outlines critical mineral strategy*, North of 60 Mining News, June 5, 2019.

¹⁴ H.R. 5515 is set to be codified as 10 U.S.C. § 2533c.

The legal ramifications of H.R. 5515 and H.R. 5895 are simple. H.R. 5515 prohibits the United States Department of Defense from acquiring rare earth magnets from China, Russia, Iran, and North Korea, while H.R. 5895 was enacted to promote commercial-scale operations of the extraction of REEs in the United States through the separation of REEs from coal byproducts. H.R. 5895 provides that \$740,000,000.00 in funds shall be allocated toward such purpose. Said funds may be used for the acquisition of interests in real property; the acquisition of any facility or plant, or expansion thereof; and/or for conducting technological inquiries and research concerning the extraction, processing, use, and disposal of REEs.¹⁵ The United States Department of Energy is charged with carrying out the purposes of the portions of H.R. 5895 that are relative to the extractions of REEs.

Another bill that has been introduced, but not enacted as a law at this time, is H.R. 1407, known as the Materials Essential to American Leadership and Security Act (“H.R. 1407”). H.R. 1407 was introduced on March 7, 2017, and the purpose of said bill is to create the Strategic Materials Investment Fund to make loans to domestic producers of strategic and critical materials, such as REEs. H.R. 1407, Sec. 3(b). The funds may be used for acts consistent with the extraction and production of REEs, including the development of new technologies. For a recipient to be deemed eligible to receive a loan from the fund, the recipient must not have a history of financial insolvency or bankruptcy. *Id.* at 3(c)(2). The recipient also may not be controlled by the People’s Republic of China or the Russian government. *Id.* Repayment of the loan is due in full within five years of its distribution. *Id.* at 3(c)(3).

A second bill that has been introduced, but not enacted, is S. 1563, known as the Rare Earth Element Advance Coal Technologies Act (“S. 1563”). West Virginia Senator Joe Manchin introduced S. 1563 on July 13, 2017, and the bill, if enacted, would provide \$20,000,000.00 annually for the United States Department of Energy to carry out research to improve the economic viability of separating, extracting, and recovering REEs from coal byproducts. The funds would be available from 2019 until 2025.

A third bill, introduced but not enacted, is S. 1317, known as the American Mineral Security Act (“S. 1317”). This bill was introduced on May 2, 2019 by Alaska Senator Lisa Murkowski, co-sponsored, by Senator Manchin, which sets forth a comprehensive plan for fostering domestic production of minerals considered critical to the United States.¹⁶

The enacted and introduced legislation demonstrates the fact that the United States government is becoming increasingly aware of the importance of the domestic development of REEs to promote the national defense of the United States. Presumably, the legislation aimed at advancing the domestic production of REEs on a commercial-scale level will continue. For now, the funds have been pledged to the United States Department of Energy, but H.R. 1407 could be an indicator that the United States Congress would consider providing loans to private individuals and/or entities to advance the domestic productions of REEs.

From funding to extraction, REEs are a rising industry. Ownership of REEs is of major concern, and could potentially result in litigation. Whether REEs are included in the definition of “minerals” or not, the extracted REEs must be deemed personal or real property. If the REEs are real property, they belong to the landowner. Otherwise, the REEs likely belong to the mine owner. In making this determination the intent of the parties must be considered. Often, a determining

¹⁵ H.R. 5895 is carried out in accordance with 30 U.S.C. §§ 1602, 1603.

¹⁶ While beyond the scope of this report, *see Critical Minerals Alaska*, a magazine published by North of 60 Mining News on May 31, 2019 for detailed information on the uses and markets of most of the 35 minerals, metals and groups of elements considered critical to the economic wellbeing and security of the United States.

factor in this analysis is whether the possessor had an intent to abandon. If so, then the REEs will likely be deemed real property and will belong to the landowner. However, parties are free to make agreements and determine ownership of REEs without interference of the court. Of course, once ownership is determined, blame can also be assigned. It is important to consider the environmental impacts that REEs pose and what liability comes with ownership. Though very little action has been taken to regulate the extraction of REEs, there will likely be much to come, especially with the impetus provided by additional federal attention to REEs as discussed above.

The following Dinsmore & Shohl LLP attorneys participated in the preparation of this report:

F. Thomas Rubenstein
Paige Vagnetti
Lauren Cyphers (2019 Summer Law Clerk)
Dinsmore & Shohl LLP
215 Don Knotts Blvd., Suite 310
Morgantown, WV 26501
(304) 296-1100

John Rhorer
Kerry Irwin
Lance Sennett
Dinsmore & Shohl LLP
City Center
100 West Main St.
Suite 900
Lexington, KY 40507
(859) 425-1000

Bryon Collier
Dinsmore & Shohl LLP
611 Third Avenue
Huntington, WV 25701
(304) 529-6181

And we extend thanks and appreciation to:
WVU College of Law Student (and 2019 graduate) Lauren Payne
for her research assistance