NETL Critical Minerals Research

Transformative Technology Focused on American Advantages

Burt Thomas, NETL
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Unrealized Environmental Benefits

AMD,
Coal Ash,
Mine and Drilling Waste

Resources That Will Grow into the Future

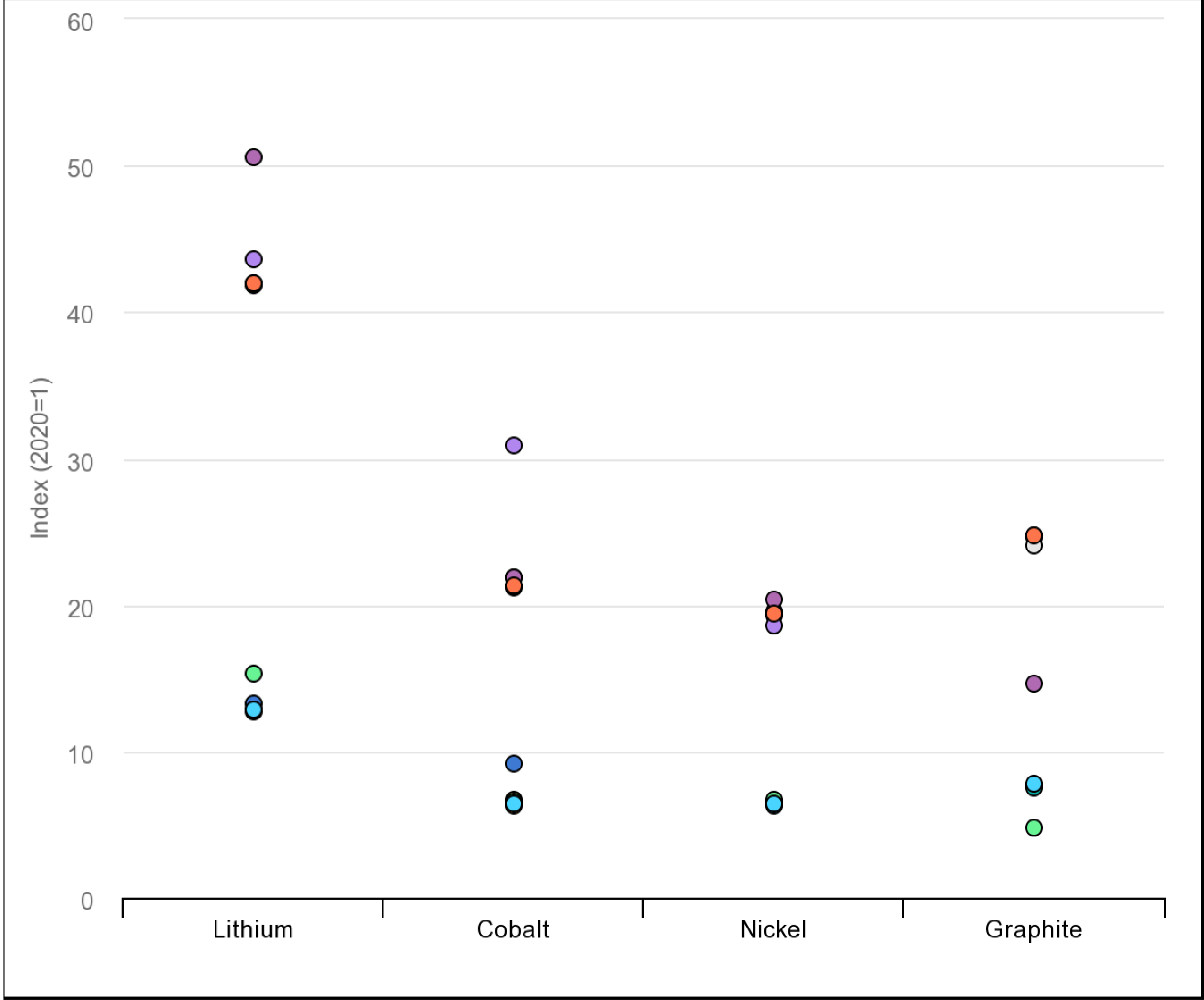
Produced Water
Mineral Carbonation
Wastes

Legacy of Fossil Energy Leadership

Repurpose FE Infrastructure
World's Largest Coal Mines
World Leader in Drilling

NATIONAL ENERGY TECHNOLOGY LABORATORY

IEA 2040 Demand Scenarios



NETL EY2022 Critical Minerals FWP

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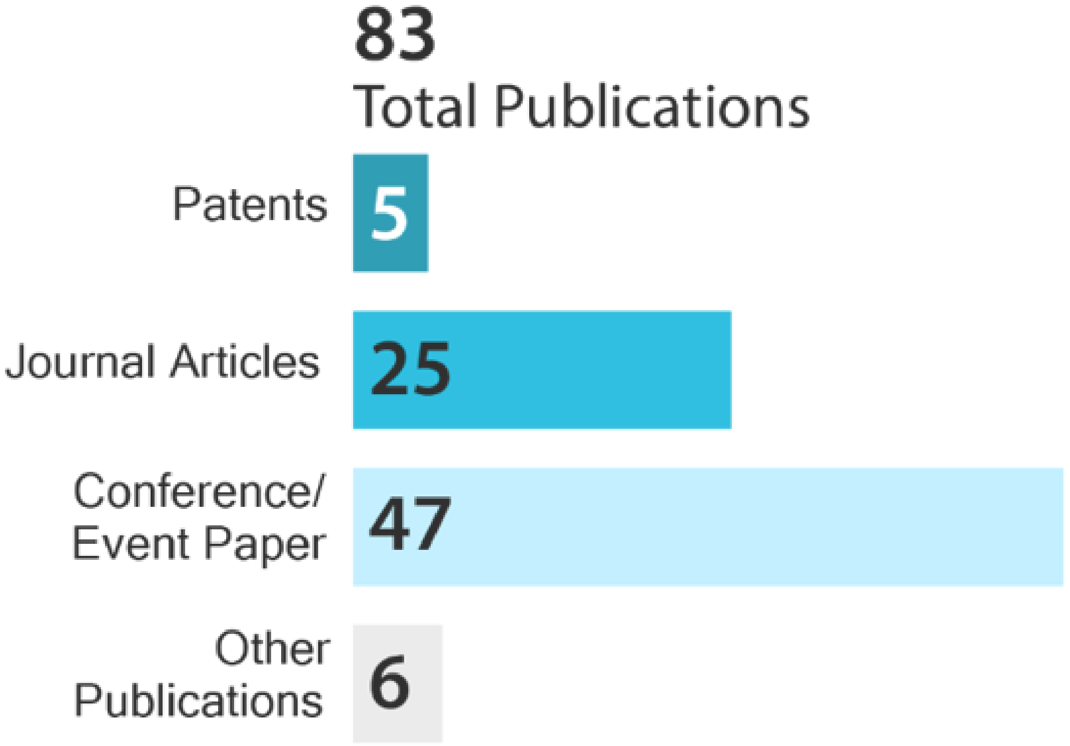
Following the Science to Deliver Unconventional Resources

Past 3-Year Totals



New Project Areas

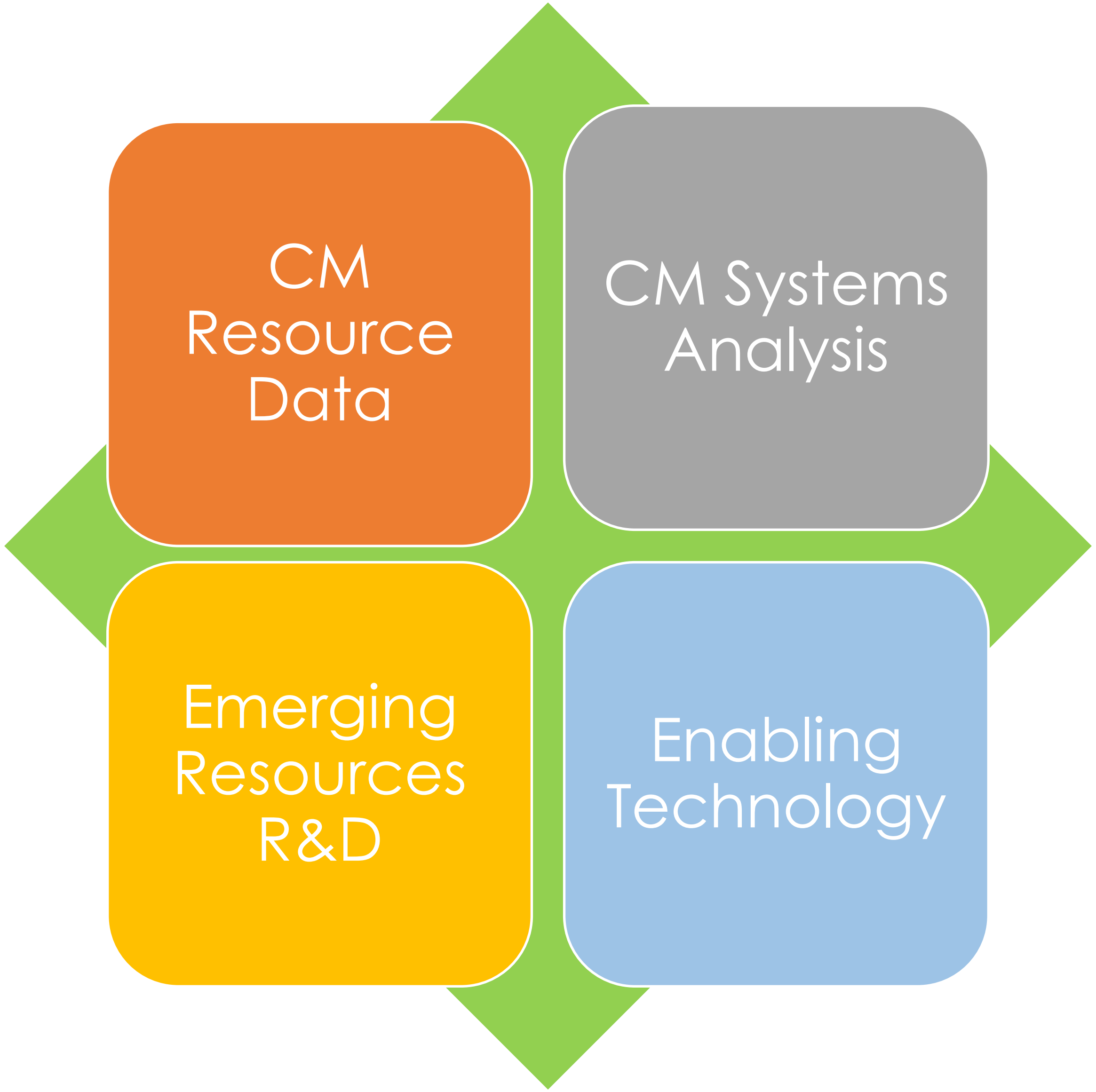
In Situ Recovery (ISR)

- minimize impacts, energy use

Produced Water (PW)

- Li, Co, REE co-produced with PW recovery and reuse

AMD treatment solids (AMD)


CM Resource Data
CM Systems Analysis
Emerging Resources R&D
Enabling Technology

NETL PI	Task #	CM Resource Data	EY18	EY19	EY20	EY21	EY22	EY23	EY24	EY25	Resource Target
					FWP Tot.		4422	3762	1304		
Rose	9.1	URC – CM Resource Prediction Methodology									
Rose	9.2	Improve Prediction of REEs in Sedimentary/Coal Lithofacies									
Rose	9.4	Developing a CM Data Framework for CORE-CM Data, Waste and By-Products									
Kutchko	10	Lithium Brine Resource Characterization in US Shale Plays									PW
						Tot.	0	0	0		

NETL PI	Task #	Emerging CM Resources R&D	EY18	EY19	EY20	EY21	EY22	EY23	EY24	EY25	Resource Target
Lopano	18	Ca-Ash Extraction Technology									Ash
Lopano	3	CM Recovery from AMD Solids using Adv. Characterization									AMD
Gulliver	4	Biologically Enhanced Redox for CM in AMD solids									AMD
Verba	5	Heap Leaching of underclay resources						0			Underclay
Thomas	6	In situ extraction from unconventional systems									ISR
Verba	7	CM Recovery from Mineral Carbonation (CDR) waste streams									CDR waste
						Tot.	0	0	0		

NETL PI	Task #	Enabling Technologies	EY18	EY19	EY20	EY21	EY22	EY23	EY24	EY25	Resource Target
Gray	12	MUST Sorbent Development for Produced Water									PW
Gray	13	CHEFS Functionalized hollow fiber sorbents for critical mineral recovery									AMD
Dogan	11	Novel Alloy Materials From Domestically Abundant - REE									
Baltrus	14	Novel Fiberoptic Sensors for Critical Minerals									
McIntyre	15	LIBS downhole and in AMD streams									ISR
Lopano	16	Sorbent for Li recovery derived from AMD treatment solids									PW
Thomas	17	Li Carbonation of Produced Water									PW
						Tot.	0	0	0		

NETL PI	Task #	Critical Minerals Systems Analysis	EY18	EY19	EY20	EY21	EY22	EY23	EY24	EY25	Resource Target
Summers	8.1	LCA Baseline for Conventional REE and Framework for Evaluating Others									
Summers	8.2	CM Embedded Demand Database									
Summers	8.3	Cost and Env. Perf. Optimization of CM Extraction using TEA and CORE CM									
Summers	8.4	Process Flowsheet Modeling									
						Tot.	0	0	0		

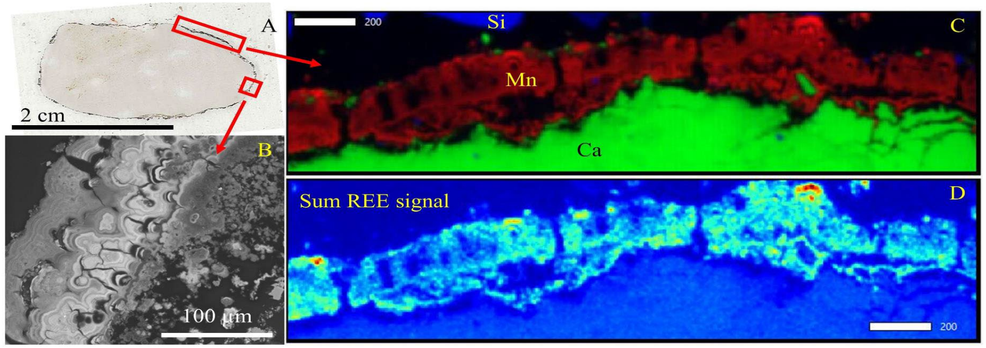
Task 3.0: Characterization Informed Recovery of Critical Minerals in Acid Mine Drainage Treatment Systems

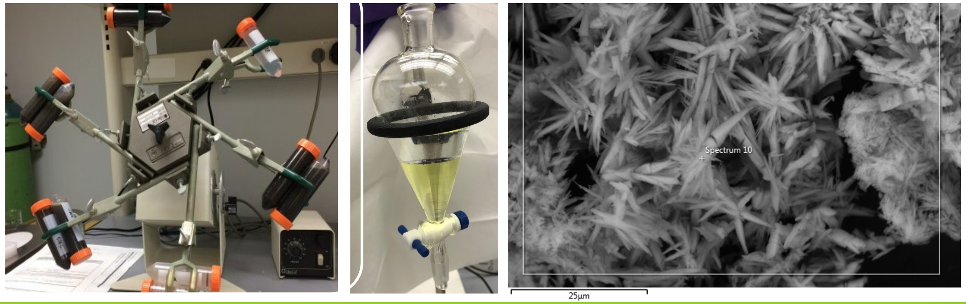
2022	2023	2024	Total Task Value (2022 – 2024)
$	$	$	$

Task Team Members

Principal Investigators: Christina Lopano, Mengling Stuckman

Other Key Personnel: Ward Burgess, Alison Fritz, Camille Sickler (Pitt), Ben Hedin (Hedin Environmental),





End Product:

- Utilize advanced characterization to determine binding conditions of CM in AMD treatment systems.
- Develop innovative & informed extractions targeting the major REE and CM-hosting solid fractions for efficient and economical REE/CM recovery.

Task 4.0: Biological Recovery of Critical Minerals from Acid Mine Drainage Treatment Solids

2022	2023	2024	Total Task Value (2022 – 2024)
$	$	$	$

Task Team Members

Principal Investigator: Djuna Gulliver

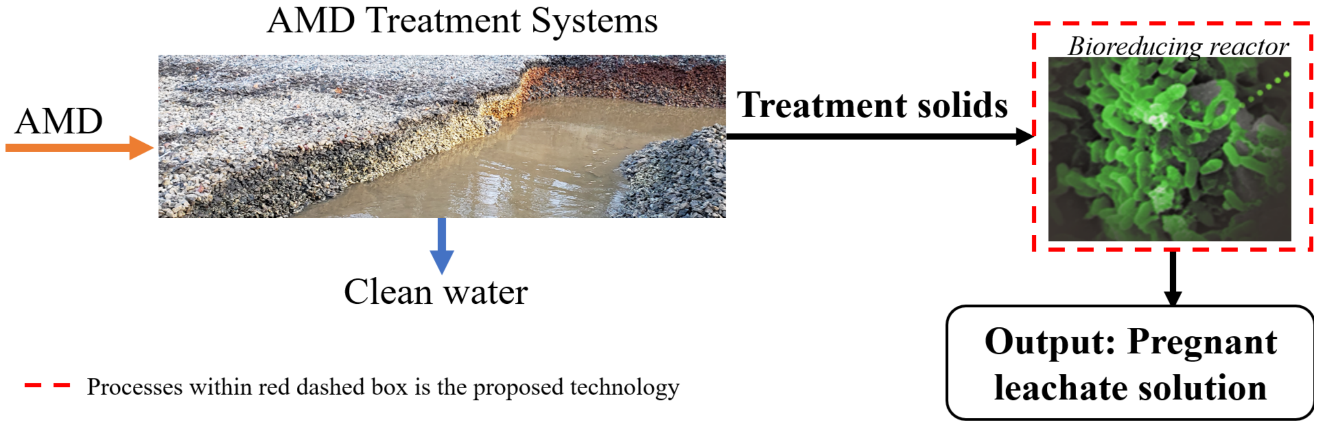
Other Key Personnel: Nancy Trun, Rowan Terra, Christina Lopano, Mengling Stuckman, Meghan Brandi

- Research Question: Is there a way to release critical minerals (CMs) from acid mine drainage (AMD) treatment solids without chemical reducing agents?
- Objective: Develop a biological process to facilitate release of CMs from AMD treatment solids.

End Product:
A biological method to produce CM pregnant leachate solution from AMD waste.

Benefits:

1. Capitalize a waste product.
2. Reduce the cost and environmental impact from conventional CM recovery methods.
3. Explore novel domestic resources and extraction technologies.



Task 5.0: Heap Leaching of Underclay Resources

2022 $	2023 $	2024 $	Total Task Value (2022 – 2024) $

Task Team Members

Principal Investigator: Circe Verba

Other Key Personnel: Jon Yang, Sophia Bauer, Tom Paronish, Dustin Crandall, Alison Fritz, Priscilla Prem

Characterize geologic source of REE amenable to recovery and commercial production → Waste coal & ion absorbed clays → Upscaling & validation → Disseminate

End Product:

- Mature and optimize the heap leach process for REE extraction from clays and legacy coal wastes to facilitate transfer of technology to U.S. industry.
- Disseminate data from REE extraction (organic and conventional methods) from legacy coal mining and related waste streams.

Technical Challenges: Extraction of CM are dependent on the feedstock composition and extraction technology. Laboratory testing showed heap leaching hydrodynamic challenges (e.g., porosity) and restricted CM recovery at larger scales.

Task 6.0: In Situ Extraction from Unconventional Systems

2022 $	2023 $	2024 $	Total Task Value (2022 – 2024) $

Task Team Members

Principal Investigator: Jon Yang

Other Key Personnel: Burt Thomas, Scott Montross, Sophia Bauer, Andrew Gordon, Thomas Paronish, Circe Verba, Dustin Crandall

End Product:
Mineralogy, leach chemistry, and accessibility evaluations of non-mineable coal and metalliferous shale leading to potential in situ recovery pilot test.

EY22

Identify and Characterize Target CM Mineralization

1. Catalogue samples.
2. Characterize CM mineralization/enrichments.

EY23

Leach Chemistry

1. Test reactivity.
   - Reagent consumption.
   - Gangue reactivity.
   - Operational windows.
2. In situ conditions (T/P/Eh).

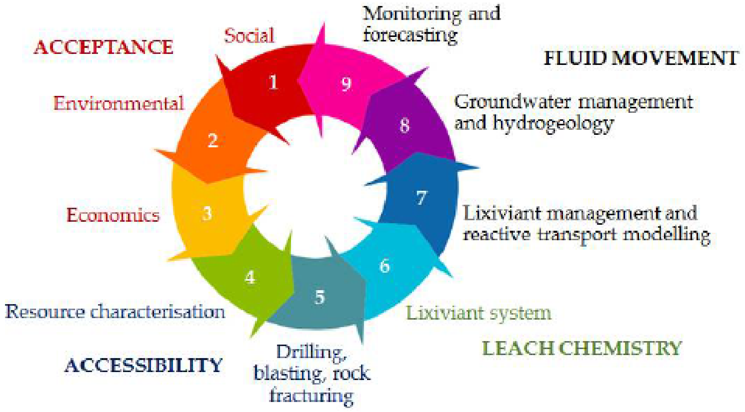
EY24

Accessibility

1. Ore/lixiviant contact strategies.
   - External partnerships are possible.*

Pilot Test Assessment

1. Develop external partners for potential pilot test evaluations.**



(Robinson, et al., 2016)

Technical Challenges: Technical challenges to in situ recovery of critical minerals in hard rock environments.

Task 7.0: CM Recovery from Mineral Carbonation Waste Streams

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2022 $	2023 $	2024 $	Total Task Value (2022 – 2024) $

Task Team Members

Principal Investigator: Circe Verba

Other Key Personnel: Jon Yang, Sophia Bauer

Extracting the critical mineral content of these mafic and ultramafic rocks represents a value-added proposition for the mineral carbonation process that could potentially defray costs of carbon capture while simultaneously providing a modest stream of critical minerals.

- Mineral resources include mafic and ultramafic rocks which can contain appreciable levels of critical minerals.
- Evaluate new or legacy materials: sulfide ore, **olivine**, serpentine, wollastonite.

End Product:

- Identify research needs related to CM recovery from diverse mineralization feedstocks
- Recover CM while protecting mineralization potential

U.S. DEPARTMENT OF ENERGY

Technical Challenges: Must find a suitable mafic feedstock/waste material that contains both sufficient CM and geochemistry is conducive to carbon capture strategies. NETL legacy materials will serve as a first look to establish proof of concept extraction method (e.g., alkaline lixiviant).

Task 8. Critical Minerals Systems Analysis

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Understand Unconventional Costs, Performance, and Environmental Footprint

End Product:

- Identify cost and performance R&D needs
- Understand the CM supply chain and current markets for existing products,
- Evaluate the economic benefits of in-house transformational processes within the CM supply chain.

- Subtask 1 – LCA Baseline for Conventional REE and Framework for Evaluating Others
  This work builds on the literature review related to commercial REE LCAs and add an LCA analysis related to the use of unconventional waste feedstocks (i.e., fly ash and AMD) to determine the environmental footprint associated with the utilization of coal related wastes as a feedstock for the extraction of REEs.
- Subtask 2 – CM Embedded Demand Database
  This work is updating the current REE embedded demand database to highlight impacts of the pandemic and expand to include select CMs related to battery manufacturing (i.e., Li, graphite, Co)
- Subtask 3 – Process Flowsheet Modeling
  This work will continue to develop an independent baseline cost estimate for the extraction of REEs from a specific unconventional waste feedstock. This will include expanding the cost estimate for recovering REEs from coal refuse and develop a cost estimate for the extraction of REE from AMD with potential to begin developing an estimate for Li extraction from produced waters.

Task 9.0: Critical Minerals Resource Data

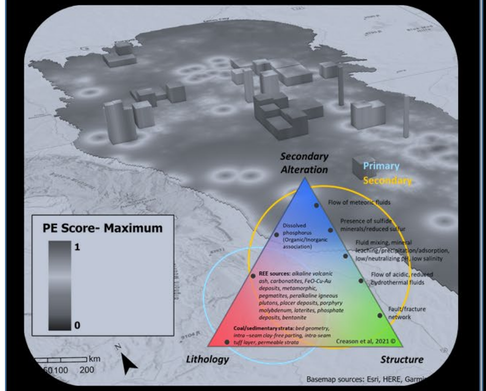
2022	2023	2024	Total Task Value (2022 – 2024)
$	$	$	$

Task Team Members

Principal Investigator: Kelly Rose
Co-Principal Investigators: Gabe Creason (9.1), Scott Montross, Devin Justman

Other Key Personnel: Patrick Wingo, Andrew Gordon, Rachel Yesenchak, ITSS EDX personnel

Unconventional REE/CM Resource Assessment



Creason, et al., (in review). *A Geo-Data Science Method for Assessing Unconventional Rare-Earth Occurrences in Sedimentary Systems.* Submitted to *Natural Resources Research.*

Systematic Methods & Data to Constrain REE/CM

Montross, et al., (2022). On a unified core characterization methodology to support the systematic assessment of rare earth element and critical mineral bearing unconventional carbon ores and sedimentary strata. *Minerals* Special Issue on REE/CM

Big data & digitalization to support REE-CM supply chain & waste beneficiation

Justman, et al. (2022). A database and framework for carbon ore resources and associated supply chain data. *Data in Brief.* https://doi.org/10.1016/j.dib.2021.107761

End Product:

- A systematic method for predicting and assessing unconventional CM resources.
- A systematic method for CM data collection and resource characterization.
- A virtual, online platform for visualizing and analyzing CM supply-chain and waste beneficiation.

Task 10.0: Critical Mineral Resource Characterization in U.S. Shale Plays

2022 $	2023 $	2024 $	Total Task Value (2022 – 2024) $

Task Team Members

Principal Investigators: Barbara Kutchko, Justin Mackey

Other Key Personnel: Mengling Stuckman, Ale Hakala, Christina Lopano

Objective: Fill lithium resource knowledge gaps through data collection and analysis of lithium brine resources to identify basin- specific/time-specific trends associated with U.S. domestic shale plays.

Year	Milestone
2022	Characterization lithium brine resource estimates within the Marcellus shale.
2022	Establish relationships with industry and regulatory stakeholders for data acquisition in other major shale plays.
2023	Characterize lithium brine resource potential in major U.S. domestic shale plays.

End Product: This work will culminate in a dataset and report detailing trends and quantity estimations of lithium brine resources from U.S. shale plays.

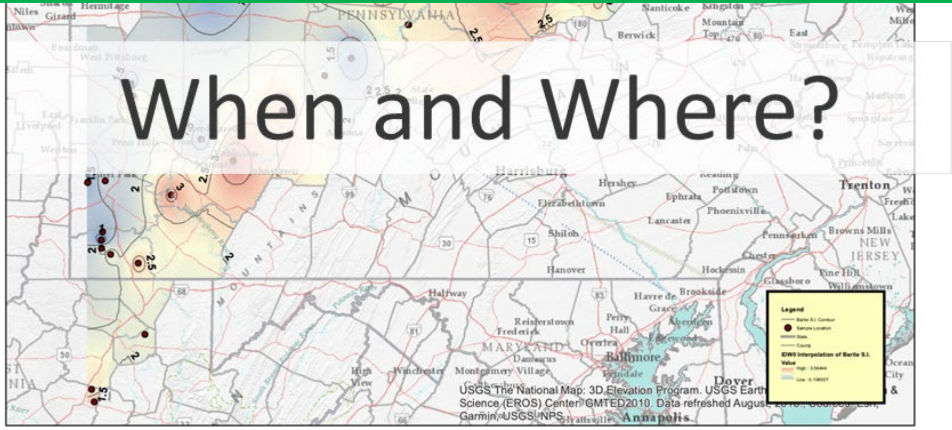


Figure 10-1: Barite mineral saturation indices modeled from published Marcellus production brine chemical analysis (Mackey, et al., 2021).

Mackey, J., Gardiner, J., Kutchko, B., Brandi, M., Fazio, J., and Hakala, A., "Characterizing mineralization on low carbon steel exposed to aerated and degassed synthetic hydraulic fracturing fluids," *Journal of Petroleum Science and Engineering*, (2021) 108514, https://doi.org/10.1016/j.petrol.2021.108514.

Technical Challenges: Identifying and filling knowledge gaps of shale related lithium resources.

Task 11.0: Novel Materials from Domestically Abundant REEs

2022	2023	2024	Total Task Value (2022 – 2024)
$	$	$	$

Task Team Members

Principal Investigator: Richard Oleksak

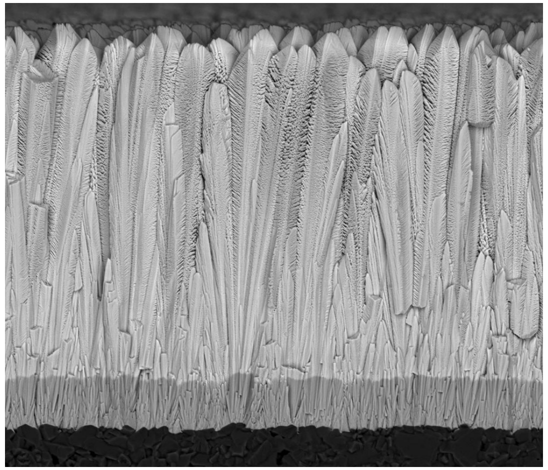
Other Key Personnel: Paul Jablonski, Martin Detrois, Michael Gao, Omer Dogan, Kyle Rozman, Shiqiang Hao

End Product:
New materials applications for domestically abundant REEs.

Two technologies are being pursued to increase the usage of domestically abundant REEs and/or enable the substitution of domestically scarce REEs:

(1) Hydrogen resistant pipeline steels

(2) Environmental barrier coatings



Technical Challenges: Reducing the cost-to-benefit ratio of domestic REE production.

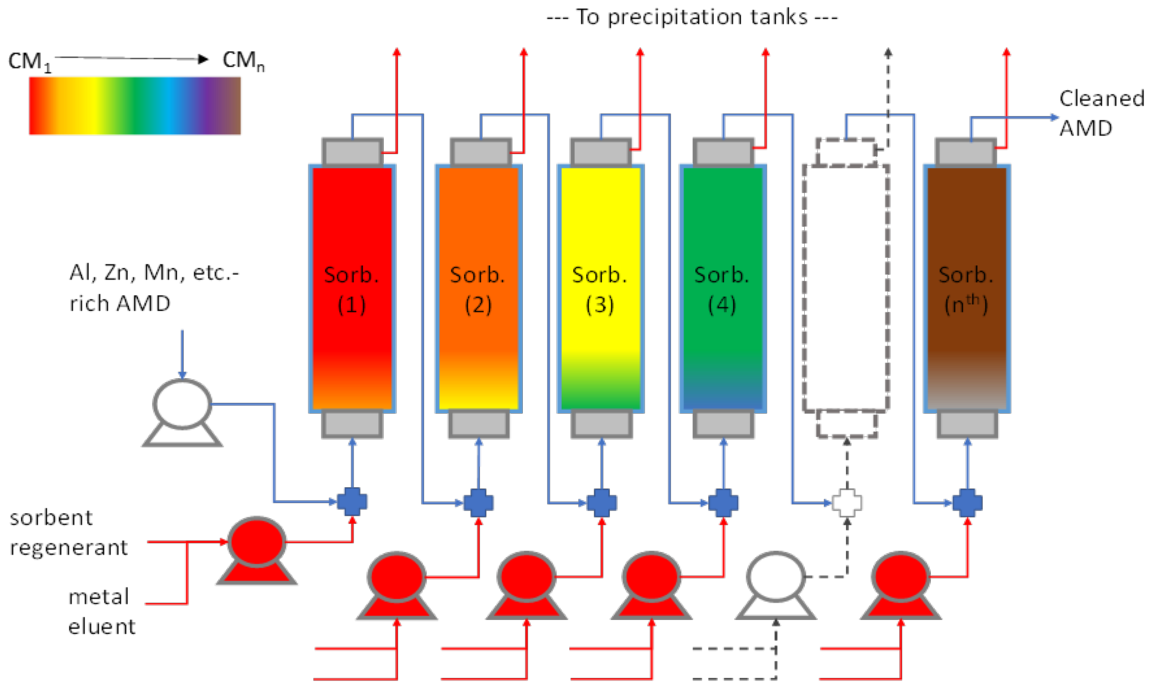
Task 12.0: MUST Sorbent Development for Produced Waters

2022 $	2023 $	2024 $	Total Task Value (2022 – 2024) $

Task Team Members

Principal Investigator: McMahan Gray

Other Key Personnel: Walter (Chris) Wilfong, Qiuming Wang



End Product: Precipitated solids enriched with one or a mixture of critical minerals.

Plan: Optimize the fractionation of adsorbed critical minerals across multiple sorbent beds during CM recovery, using a multi-bed adsorption system.

- Screen eluents to achieve maximal CM purities and minimal loss of the sorbent structure.
- Develop additional MUST formula with selectivity toward Li or other CM.

Technical Challenges: The presence of eluted trace Si reduces the purity of CM collected.

Task 13.0: CHEFS Functionalized Hollow Fiber Sorbents for Critical Mineral Recovery

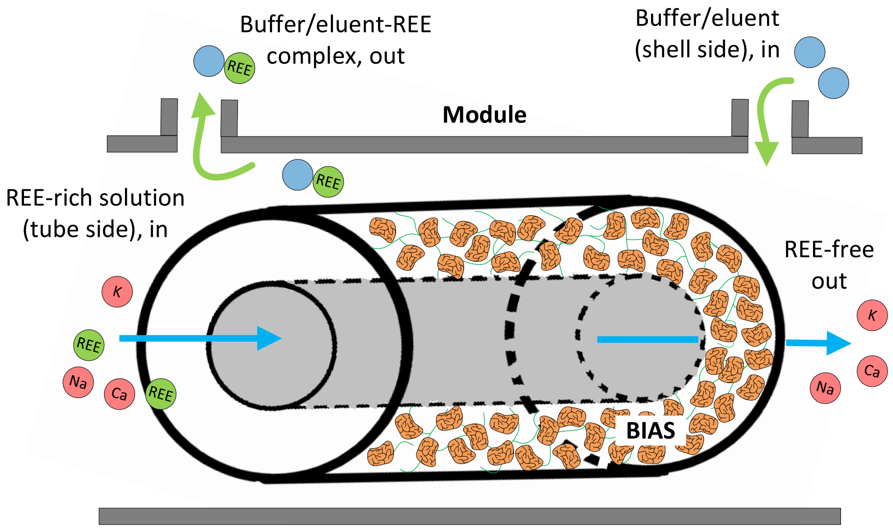
Task Team Members

Principal Investigator: McMahan Gray

Other Key Personnel: Qiuming Wang, Shouliang Yi, Walter Wilfong

- Determine concentration of target critical metals (CMs—Co, Cu, Al, REEs, etc.) and competing ions (fouling metals, heavy metals, and anions) from an authentic AMD solution.
- Characterize ideal single and mixed CM solutions for sorbent CMs selectivity and capacity studies.
- Refine sorbent formulations with different ratios of amine/crosslinker for their leach resistance to the solvent used in CHEFS preparation.
- Refine sorbent formulations to give at least 90% uptake of critical metals from ideal or authentic AMD solution.
- Determine a dope composition compatible with sorbent functional groups.
- Refine sorbent wt% in a dope to balance the metal uptake performance-CHEFS mechanical strength.
- Refine CHEFS solvent exchange process for an optimized CMs uptake.
- Optimize a CHEFS formula with > 90% recovery of critical metals from ideal or simulated AMD solutions in batch or flowing conditions.

End Product:
Optimize a CHEFS formula with minimal amine leaching and achieving > 90% recovery of CMs (Co, Cu, Al, REEs, etc.) from ideal or simulated AMD solutions.



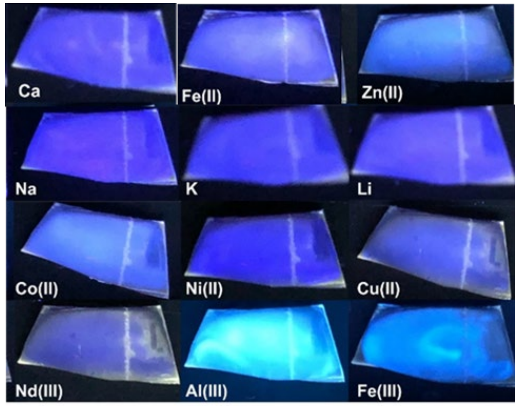
Task 14.0: Novel Fiber Optic Sensors for Critical Minerals

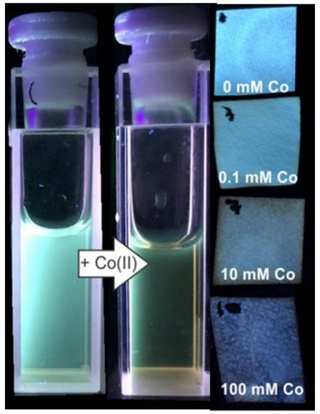
2022 $	2023 $	2024 $	Total Task Value (2022 – 2024) $k

Task Team Members

Principal Investigator: John Baltrus

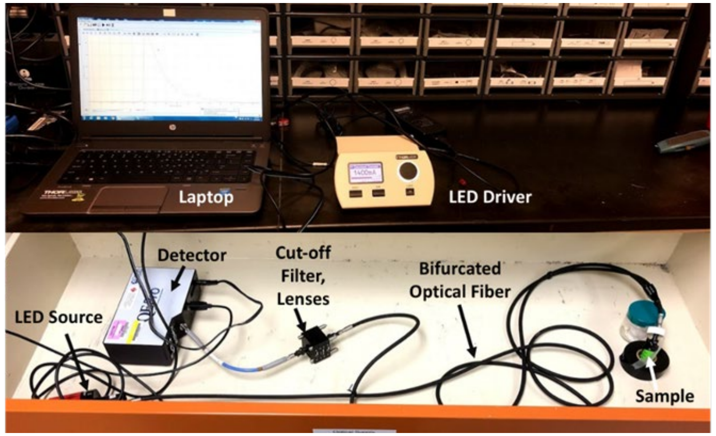
Other Key Personnel: Scott Crawford





End Product: Optically-based inexpensive, portable, and rapid detectors for REEs and other critical metals.

Plan Overview: Demonstrate a device for measurement of REEs and other critical elements in liquid streams at low ppm or ppb levels using an optical probe by identifying, synthesizing, and incorporating novel photoluminescent sensing materials targeting specific critical elements. This execution year will focus on Co and Al detection, testing of field samples, and development of other detection platforms, such as test strips and sensitizers specific to other critical elements, as time permits.



Technical Challenges: Low-cost optical-based detection of low ppm or ppb levels of critical elements in process streams.

Task 15.0: LIBS Downhole and in AMD Streams

2022	2023	2024	Total Task Value (2022 – 2024)
$	$	$	$

Task Team Members

Principal Investigator: Dustin McIntyre

Other Key Personnel: Scott Montross, Dan Hartzler, Jonathan Yang, Kelly Rose

End Product: Functional downhole REE measurement system.

- The objective of this project is to determine the feasibility of using the subsurface LIBS sensor as a downhole REE measurement device for coal seams in the Powder River Basin.
- Initial work will focus on the feasibility of measurements ~~with~~ of a coal core within a commercial LIBS unit, as well as with the miniaturized LIBS probe in the laboratory setting.
- Additional work will focus on how well the miniaturized LIBS probe can measure REEs in AMD fluids.
- Continued work will explore the adaptation of the current subsurface probe to an open wellbore for solids measurements along the sidewall.

Task 16.0: Sorbent for Li Recovery Derived from Acid Mine Drainage Treatment Solids

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2022	2023	2024	Total Task Value (2022 – 2024)
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Task Team Members

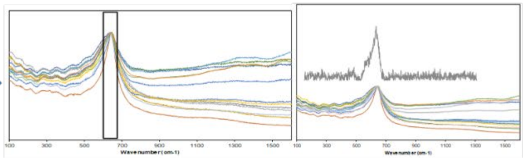
Principal Investigators: Christina Lopano, Mengling Stuckman

Other Key Personnel: Wei Xiong


AMD solids


Raman spectroscopy

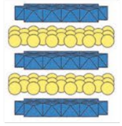
Data processing

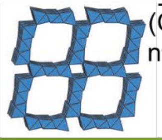


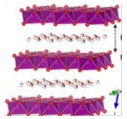
Peak identification and summary in table

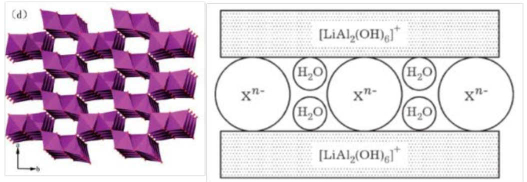
Sample	St 1 TS 3	St 1 TS 5	St 1 TS 6	St 1 TS 8	St 1 TS 9	St 2 TS 1	St 2 TS 2	St 2 TS 5	St 2 TS 6	St 2 TS 7	St 3 TS 1	St 3 TS 2	St 3 TS 6	St 3 TS 7	St F TS 1	St F TS 2	St F TS 3	St F TS 4	St F TS 7	Sc Mn TS 5	Sc Mn 1	Sc Mn 3	Wb TS 1	Wb TS 2	Wb HCl 1	Wb HCl 2	Wb HCl 3
Manganite					◊	◊		◊			◊	◊	◊	◊	◊			◊								◊	◊
Vernadite						◊					◊			◊	◊			◊			◊	◊		◊			
Todorokite	◊	◊	◊	◊	◊		◊	◊	◊	◊		◊	◊			◊	◊		◊	◊			◊		◊		
Hausmannite																										◊	◊


Manganite
$MnO(OH)$
(tunnel)


Vernadite
MnO_2*nH_2O
(layer)


Todorokite
$(Ca,Na,K)_x(Mn^{4+},Mn^{3+})_6O_{12}*3.5H_2O$
(tunnel)


Hausmannite
$Mn^{2+}Mn_2^{3+}O_4$
(spinel)



pyrolusite type structure γ-MnO_2 (left) or the schematic of γ-AlO_2 (right) for Li recovery

End Product:

A low-cost Li sorbent synthesized from AMD treatment wastes to generate robust Li concentrate from different oil and gas (O&G) produced waters with various total dissolved solids, Li, and Ca contents.

Approach:

EY22: AMD waste characterization and preliminary Li sorbent laboratory synthesis.

EY23: Li sorbent development, optimization, and characterization.

EY24: Li selectivity testing in complex brine water matrices and further optimization.

Task 17.0: Li Extraction via Carbonation of Produced Water

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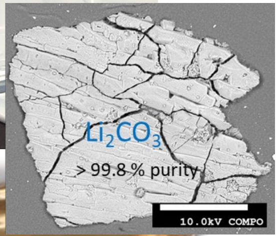
Task description

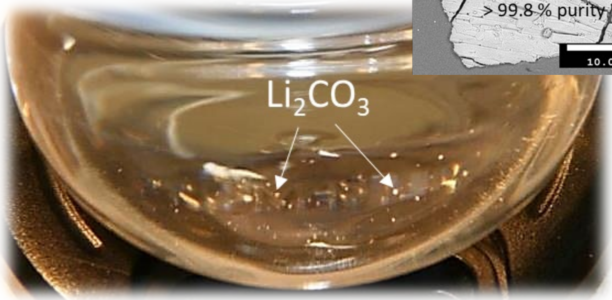
- **Technology:** Brine carbonation in ambient environment by controlled CO_2 injection that causes critical mineral precipitation (base: US10,315,926 and US16/537,985)
- **Questions to be addressed:**
  - Scalable
  - Corecovery of other valuable minerals

Expected outcomes:

- The successful implementation is expected to:
  - Enhance domestic critical mineral supply chains
  - Make use of industrial byproduct including O&G produced water and CO_2
  - Promote carbon sequestration

End Product:
A low capex, low opex, and environmentally benign process that can simultaneously extract Li and generate Li_2CO_3 directly in brines, O&G produced water, etc., without adsorbent (or ion exchange), absorbents, membranes, acid, freshwater, separate carbonation step.





Task 18.0: REE/CM Extraction Process for Calcium-Rich Coal Ash

2022	2023	2024	Total Task Value (2022 – 2024)
$	$	$	$

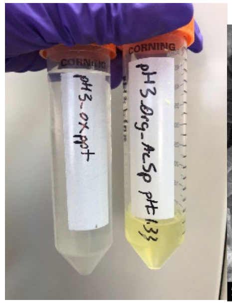
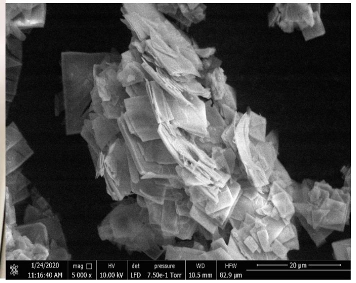
Task Team Members

Principal Investigators: Christina Lopano, Mengling Stuckman ~~(LRST)~~

Other Key Personnel: Ward Burgess, Dan Ross~~,~~ Alison Fritz, Djuna Gulliver, Bret Howard, Meghan Brandi, Barbara Kutchko





End Products:

- Understanding of REE distributions in Ca-rich ash.
- Optimization of extractions and separations for Ca-rich ash, recommendations for different types (BA, FA, LA).
- A preliminary assessment of the potential for using CO_2 derived biolixiviants for extraction.
- Evaluate the effectiveness of MSX process to selectively recover REY from dilute leachates produced by sequential leaching.