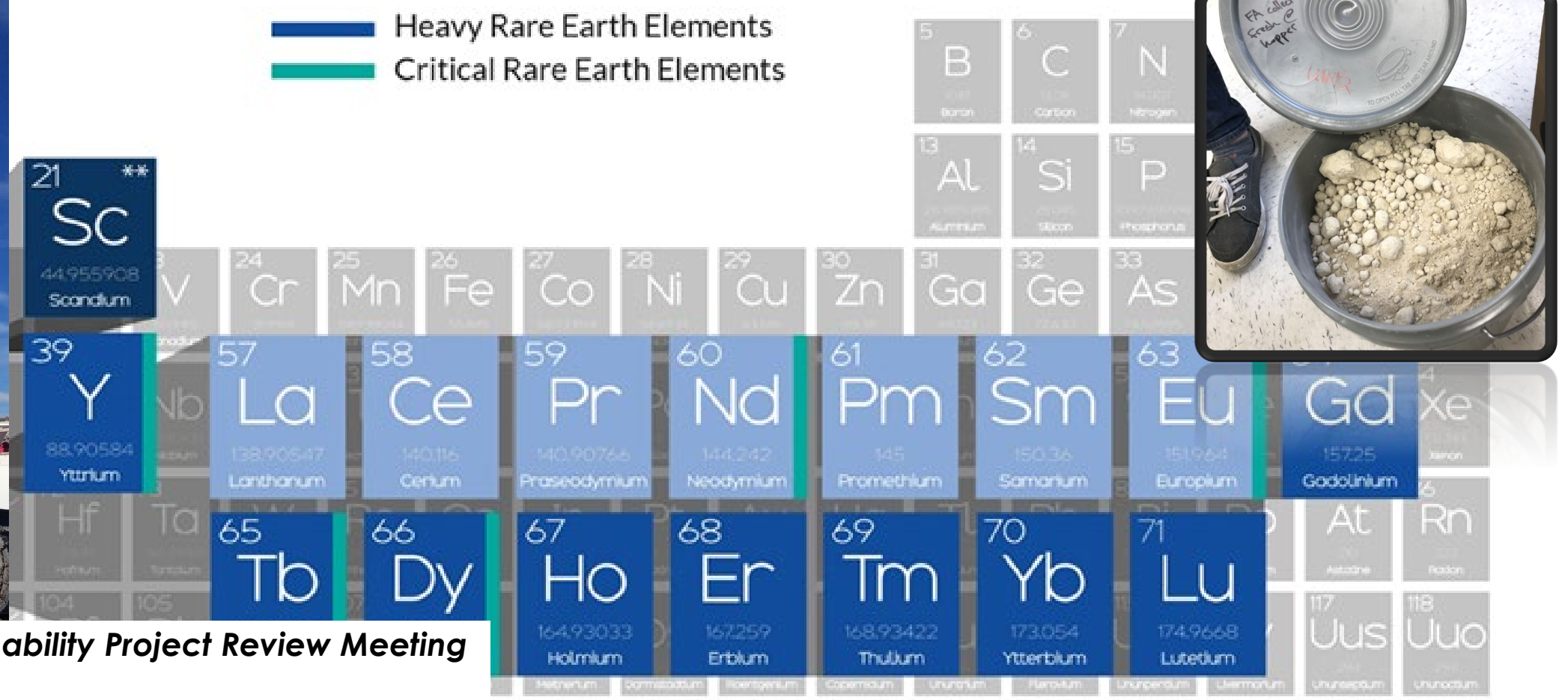
REE Extraction from Powder River Basin Coal Byproducts

TCF 20-21358 & FWP-1022420

Christina Lopano
Research Geochemist, NETL-RIC



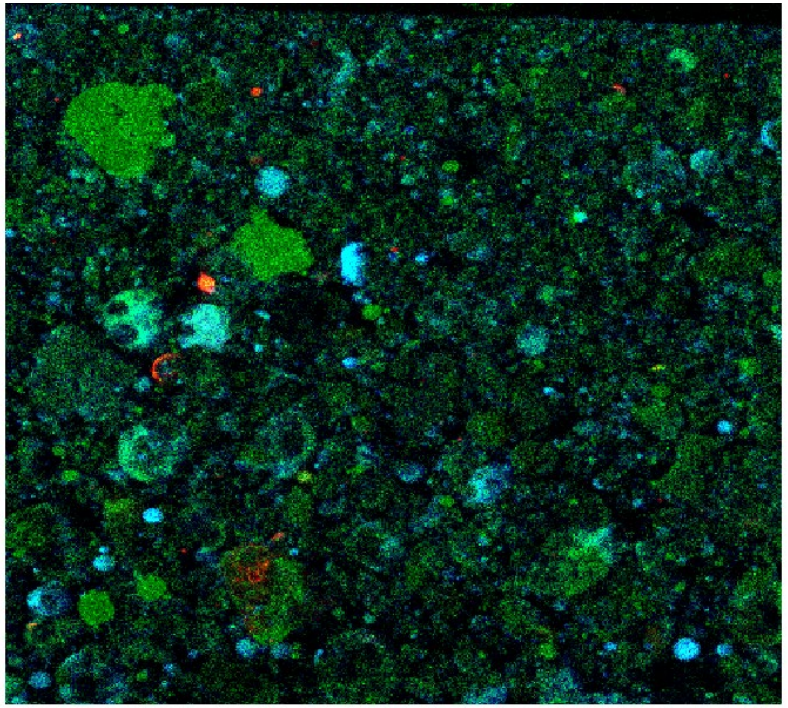
2024 Resource Sustainability Project Review Meeting
April 2, 2024

Outline

Moving towards using the 'whole buffalo'

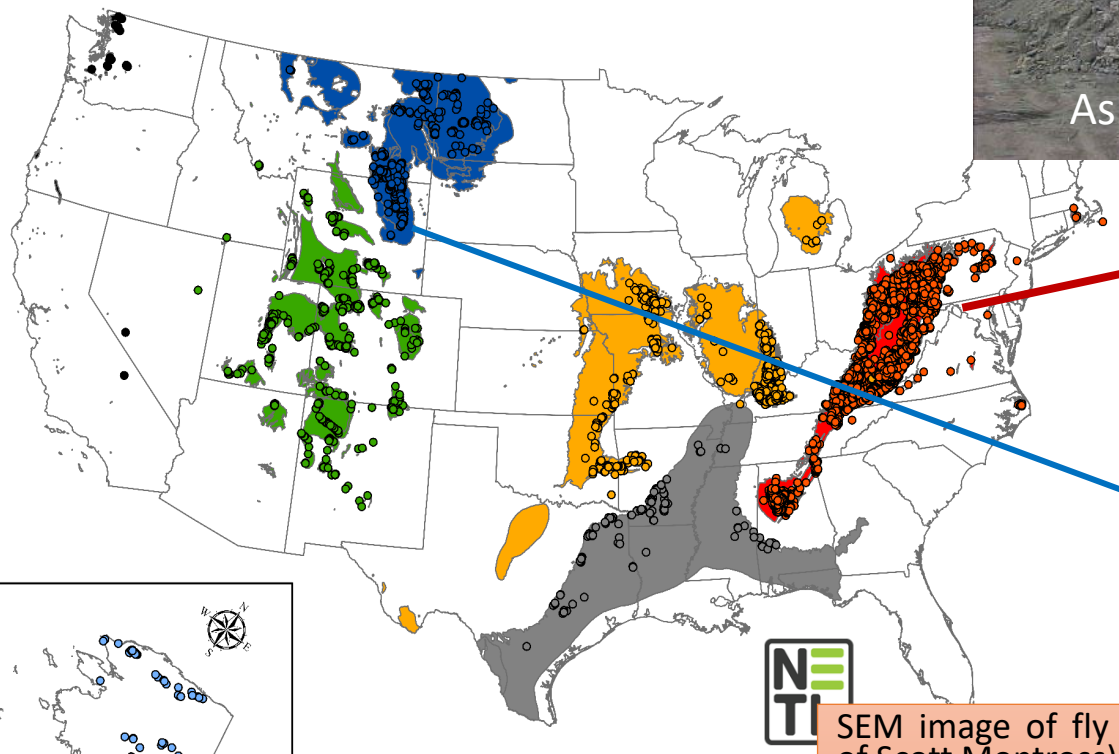
- Background
  - (Brief)Coal Ash background
  - Characterization Informed recovery
- FWP 1022420 (Task 18)
  - Evaluating Beneficial Reuse
- TCF 20-21358
  - No-cost extension for project through Sept 2024
  - Piloting and trouble-shooting barrel scale extractions
  - Process evaluation and scale-up
  - Incorporating other novel technologies
  - Finalizing scale up

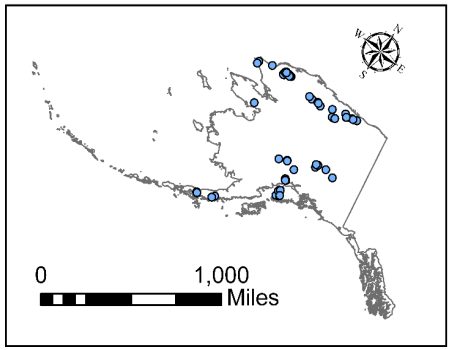
CeSiCa 1mm*1mm map



Initial Coal Combustion Ash Characterization: APP vs. PRB

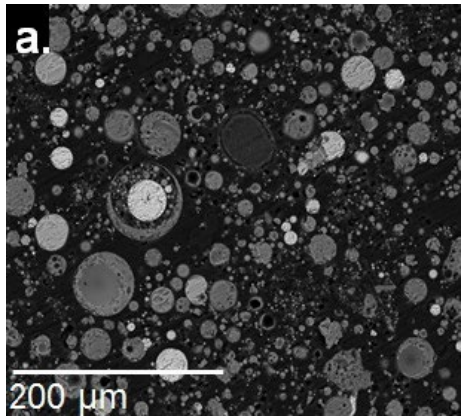
~ 60% Ash is Disposed as Waste (millions of tons/yr)

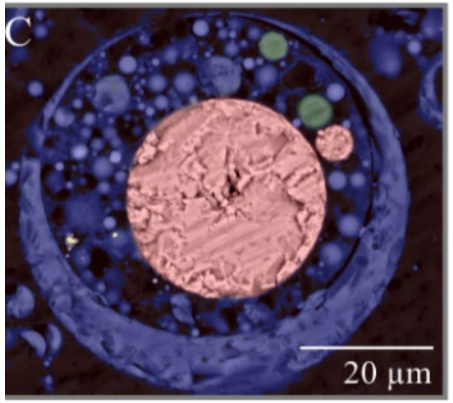




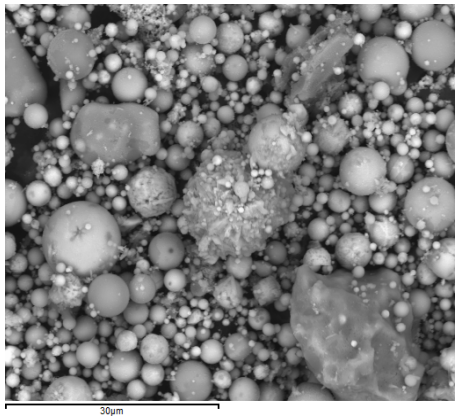
SEM image of fly ash (courtesy of Scott Montross)
Phases identified:
amorphous Si-Al -purple
Fe-oxide - red
Ca-oxide - green
REE mineral - yellow

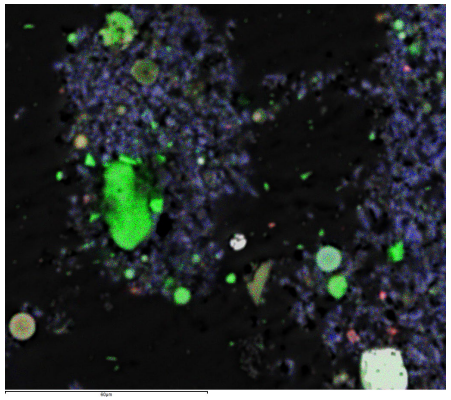
Appalachian basin (APP) coal ash: 5.5 M tons/yr, Al-rich
REE encapsulated in AlSi-rich spherical glass





Powder Riven basin (PRB) coal ash: 8.9 M tons/yr, Ca-rich
Amorphous particles with Ca-oxide crust





The Opportunity: Coal Ash

Powder River Basin

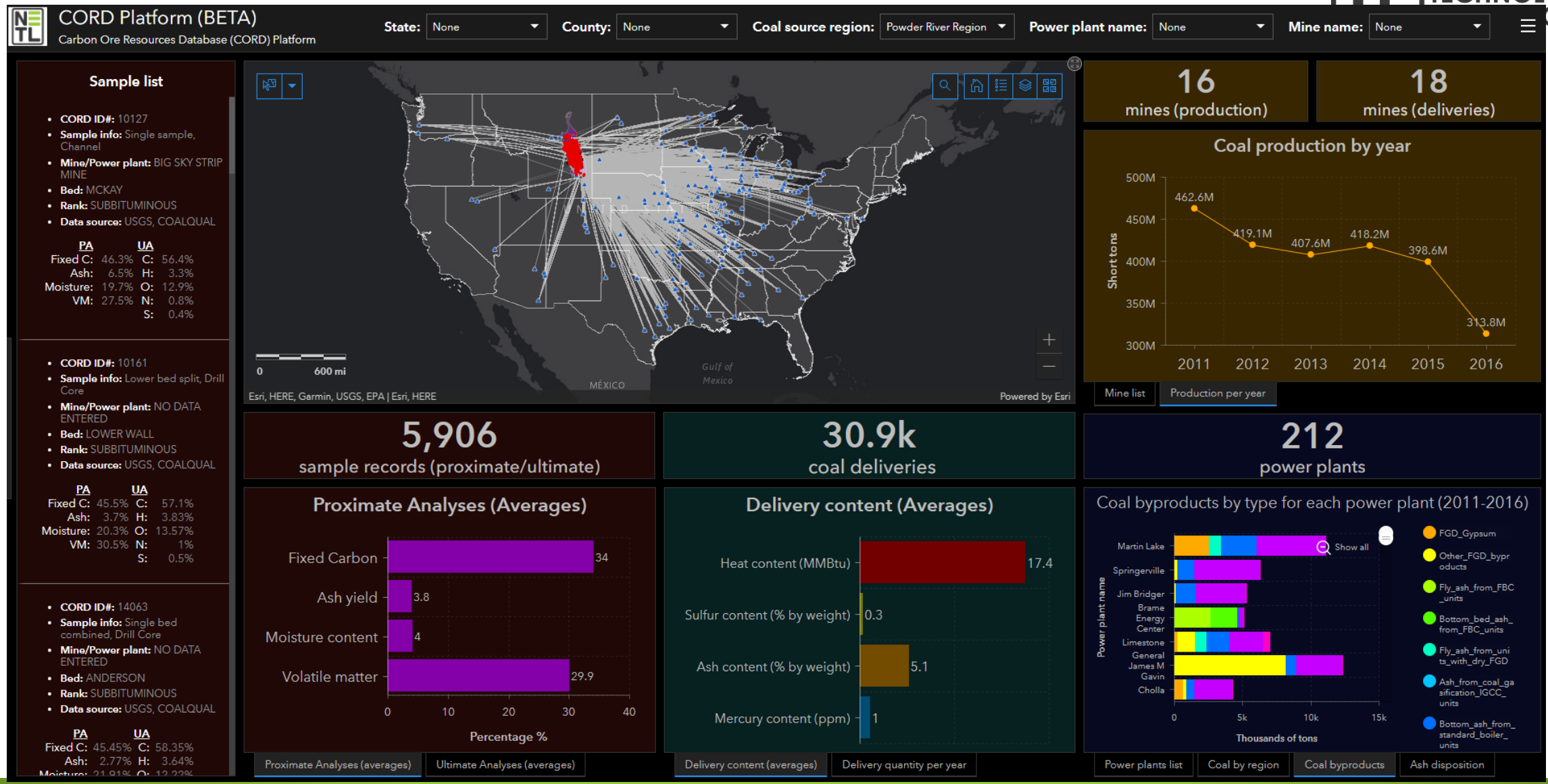
- ***Combustion Process Increases REE & CM Concentrations***

- ***Abundant waste material across the U.S.***
  - *Landfills around the U.S. contain **1.5 billion tons of impounded ash***
  - *Geographically distributed, including by coal type*
  - *Review, closure, and/or re-impoundment in progress by statute*

- ***Opportunities exist for regional facility (TCF-20-21358)***
  - *100 million tons are impounded in the Upper Mountain Region (WY, MT, CO, & ND) Approximately 1.25 million tons of ash are generated annually in the region*
  - *Could support a 5 ton per day REE facility for over 20 years*
  - *TCF-20-21358 (Stated Dec 2020, no-cost extension – goal **end Sept. 30, 2024**)*

- ***Challenge:** What to do with residual wastes? (EY2023 **FWP1022420**, Task 18)*

NETL Data Analytics: Understanding the Resources



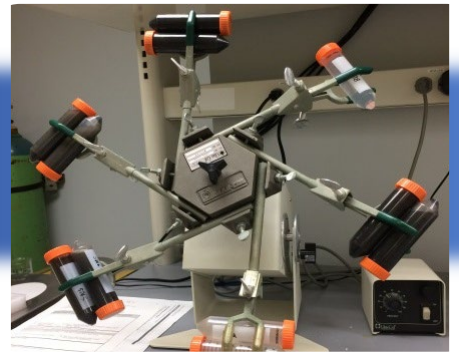
Justman et al (2022) https://doi.org/10.1016/j.dib.2021.107761

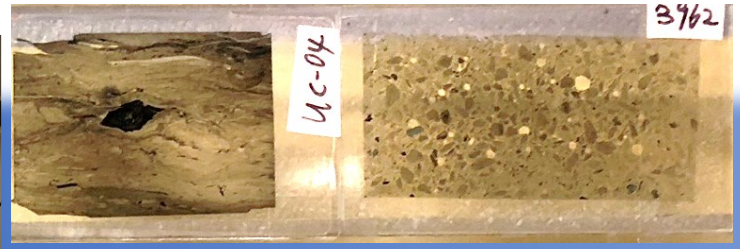
Technical Approach

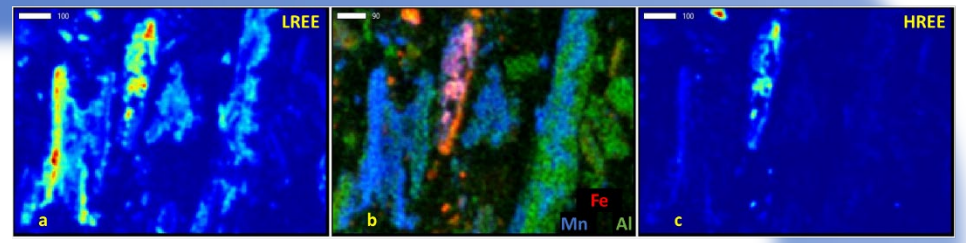
Fundamentally Understanding the Resource

AMD solids

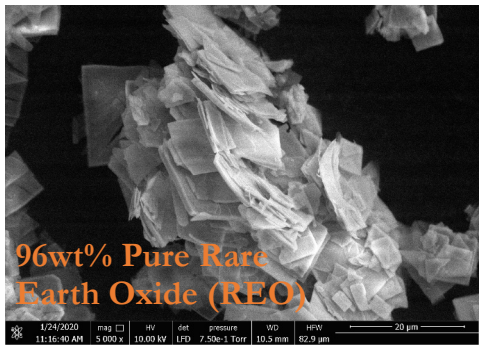
Fly ash

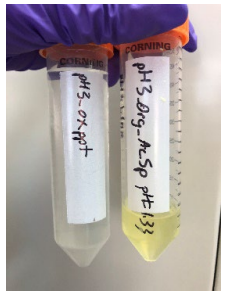


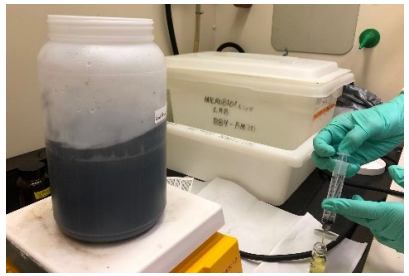




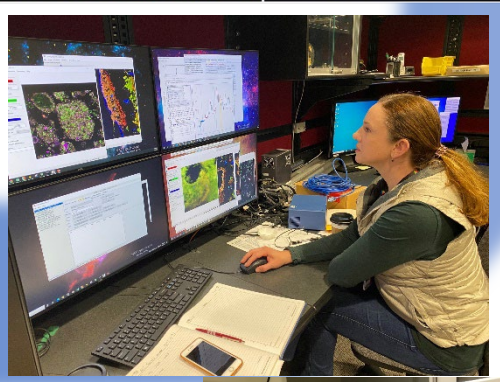
Utilize **characterization** of major REE-hosting solid fractions in different CCBs to **innovate targeted extractions** for efficient and economical REE recovery.







Stuckman, M.Y., Lopano, C.L. and Tarka, T. (2021)
U.S. Patent Pending, Serial No.: 63/053,925
https://netl.doe.gov/node/10318



Targeted Rare Earth Extraction (TREE)*

Targeting Calcium-Rich Ashes & AMD solids

TREE Advantages over REE mining:

1. Domestic/ local waste feedstocks
2. No-pretreatment
3. Up to 90% acid reduction
4. No heating/ no pressure
5. Reduced solvent use
6. Less waste management cost
7. Additional value streams such as cobalt, nickel or scandium

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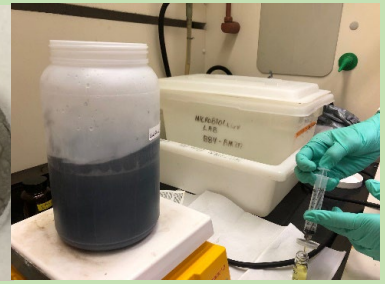
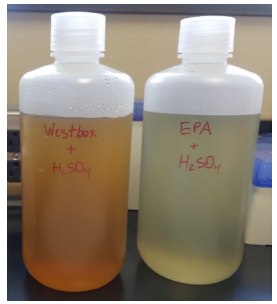
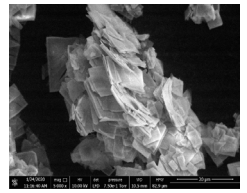


AMD solids Fly ash TREE process



REE leachate



*Stuckman, M.Y., Lopano, C.L. and Tarka, T. (2021) U.S. Patent Pending, Serial No.: 63/053,925
https://netl.doe.gov/node/10318

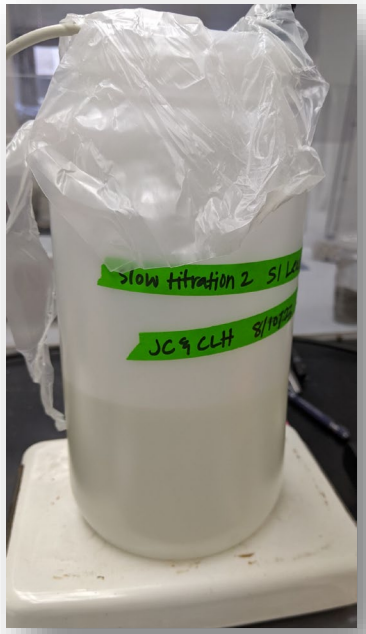
REE & CM Extraction Process for Calcium-Rich Coal Ash

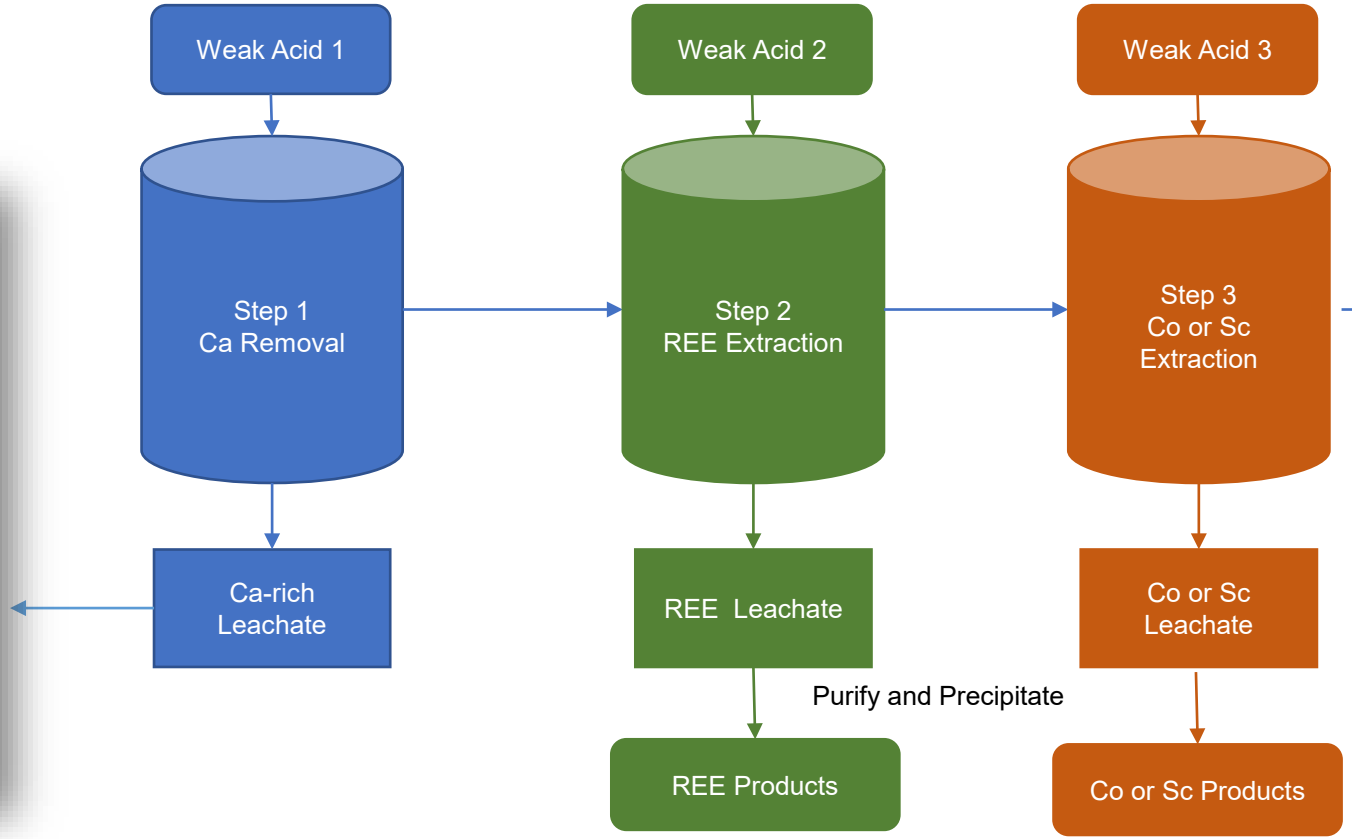
Technical Challenges: Determine value added opportunities for entire feedstock.

FWP 1022420 (Task 18) Principal Investigator: Christina Lopano

Other Key Personnel: Mengling Stuckman, Barbara Kutchko, Brian Strazisar, Meghan Brandi, Colleen Hoffman, Jason Cheng, Ward Burgess, Maximilian Barczok (LRST)

End Product: Evaluation of Waste Stream Optimization potential of the patent-pending targeted rare earth extraction (TREE) process.

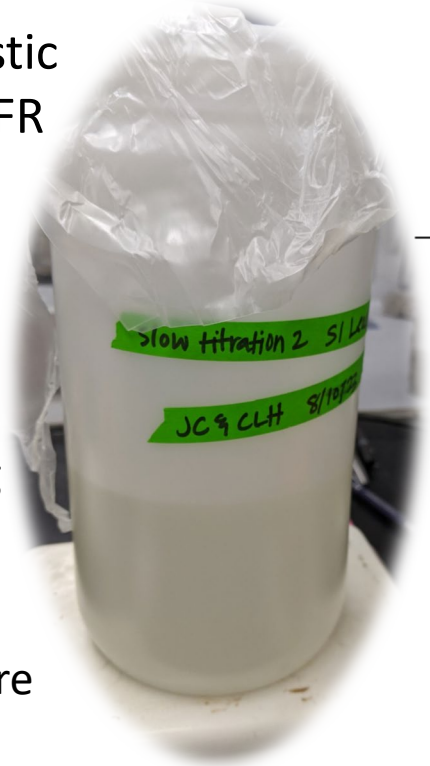




CM Extraction Process for Calcium-Rich Coal Ash

TREE step leaching – Value added (S1 Residual Leachate)

- S1 extract is not considered hazardous waste based on EPA's toxicity characteristic and other hazardous criteria under 40 CFR part 261.
- ICP-OES/MS analysis of leachate shows promising chemistry



Four proposed potential uses for the leachate:

1. Salt Brine for Winter De-Icing and Anti-icing
2. Additive in CO_2 geologic storage or CO_2-enhanced Oil Recovery
3. CO_2 carrier in liquid-solvent direct air capture process
4. Heat Reservoir in Enhanced Geothermal System

Further study is needed to evaluate efficacy

Table 2. Known De-icer/anti-icer Parameters for Product Approval Compared to TREE S1 Leachate

	Organizations[1]			Dry Fork[3]			Laramie River Station[3]	
Parameter	PNS (PNS, 2010)	CO DOT (CDOT, 2017)	MN DOT (Mn/DOT, 2022)	1	2	3	4	5
As (ppm)	5	5	0.05	0.006	<0.005	<0.0005	<0.005	<0.005
Ba (ppm)	100	10	10	2.331	5.284	2.252	0.89	1.010
Cd (ppm)	0.2	0.2	0.2					
Cr (ppm)	1	1	1					
Cu (ppm)	1	1	0.2	0.199	0.033	0.022	0.014	0.017
Pb (ppm)	1	1	0.01	0.001	0.005	0.001	<0.00067	<0.00067
Hg (ppm)	0.05	0.5	0.0005					
Se (ppm)	5	0.3	5	0.040	0.016	0.126	0.055	0.036
Zn (ppm)	10	10	10	0.414	1.454	0.208	0.101	0.099
Mo (ppm)		15						
PO_4^{-3} (ppm)	2500	25	10					
CN^- (ppm)	0.2	0.125	0.2					
NH_3 (ppm)		5						
Corrosion Rate (%)	30	30	30					
Brine solution (%)[2]	variable	variable	variable	0.48%	0.5%	0.58%	0.62%	0.65%
pH	6.0-9.0	6.0-9.0	6.0-9.0	7.84	7.10	6.5-7.2	6.29	6.26

[1] All three organization basic parameters are highlighted in grey. Both the Minnesota and Colorado Department of Transport require prior approval from the Pacific Northwest Snow fighters for new product list before submission to their organizations. Additional biological, chemical, and toxicity tests are included in the Table 3.
[2] Minimum requirements are between 25-34% brine solution
[3] TREE S1 leachate: 1: DFFA_HCl_S1; 2: DFFA_S1; 3: DFFA_HCl S1; 4: LRSFA1_HCl_S1; 5: LRSFA1_S1

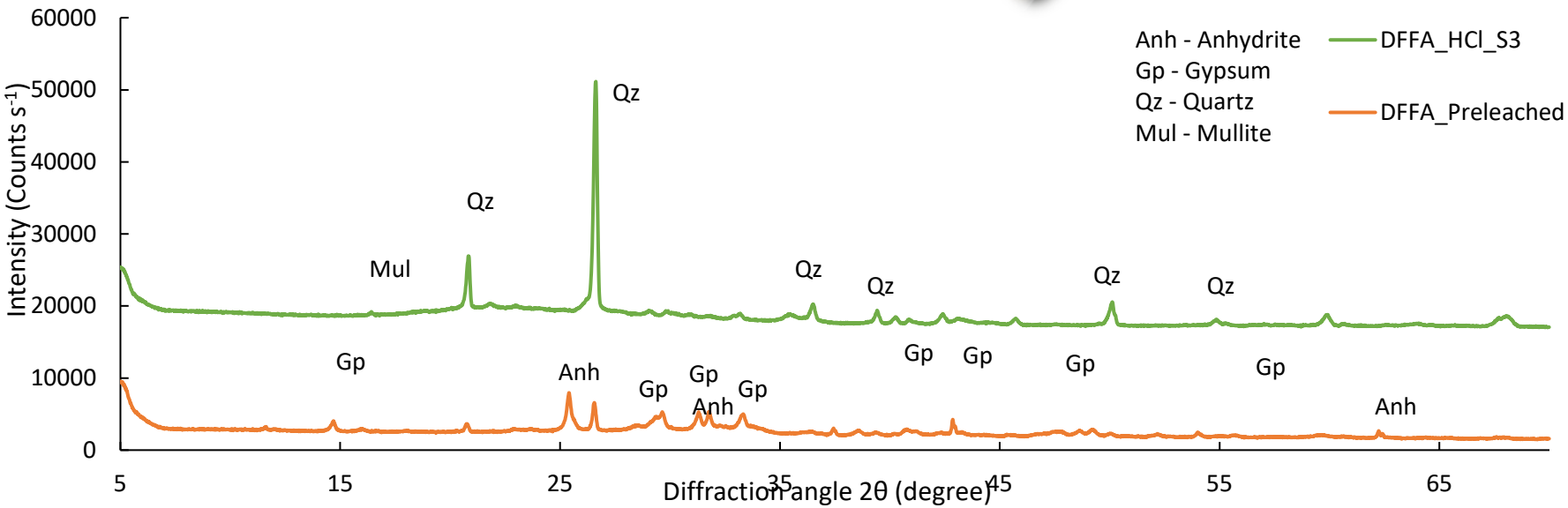
REE/CM Extraction Process for Calcium-Rich Coal Ash

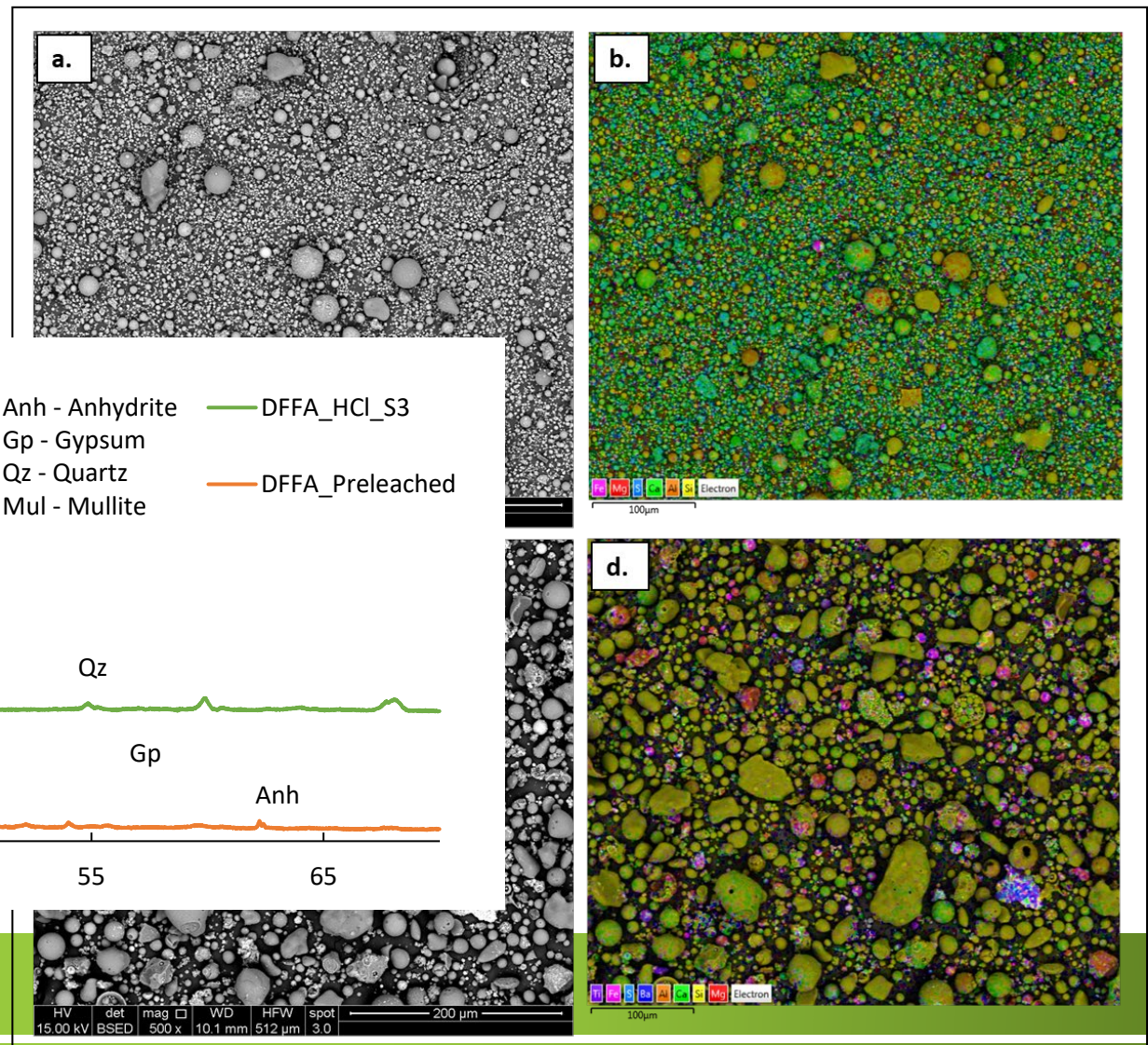
DFFA

Evaluation of TREE Step 2 or 3 residual solids

Promising results in terms of mineralogy and chemical morphology for TREE residuals (step 3)

- Mineralogy and chemistry more consistent with class F ash (quartz/mullite),
- Calcium and sulfate phases removed





REE/CM Extraction Process for Ca-Rich Coal Ash

Evaluation of TREE Step 2 or 3 residual solids:

- ICP-OES/MS analysis of residual solids show that chemistry of post-TREE reacted solids show promising chemistry for use as concrete additives.
- Compare pre- and post-reaction solids to ASTM C616 23 class requirements for fly ash used in concrete.

Potential uses for the Ca-leached solids being explored:

1. Cement additive (convert PRB ash from Class C to Class F).
2. Use as feedstock for the development of zeolitic materials.*

*Future Studies - LDRD proposal has been **accepted** for 2024*

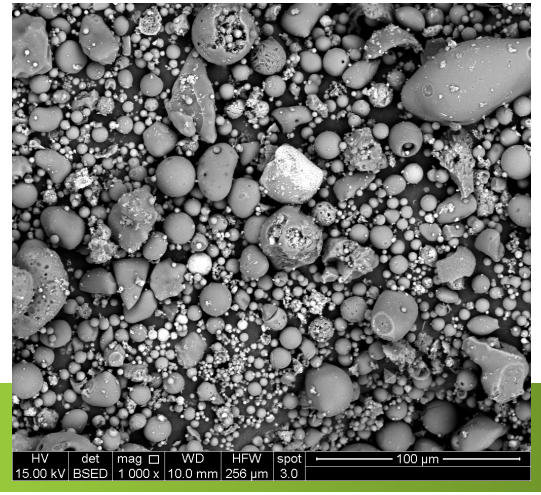
ASTM Class Chemical Requirements for Fly Ash for use in Concrete Compared to Rinsed TREE Residual Solids

	ASTM Concrete Class Standards (ASTM C616 23 e1)			Dry Folk Fly Ash Batch leaching				Laramie River St. 1 Fly Ash Batch leaching			
				Step 2[1]		Step 3[2]		Step 2[3]		Step 3[4]	
	N	F	C	ns	s	ns	s	ns	s	ns	s
Silicon dioxide (SiO_2) plus aluminum oxide (Al_2O_3) plus iron oxide (Fe_2O_3) min, %	70	50	50	73.4	75.4	77	76.8	73.7	74.6	73.2	76.1
Calcium oxide (CaO), %	report only	18.0 max	>18.0	7.7	8.7	6.9	7.1	9.7	9.9	6.3	6.7
Sulfur trioxide (SO_3), max, %	4	5	5	2.33	0.8	1.14	0.54	0.64	0.22	0.5	0.21
Moisture content, max, %	3	3	3	5.83	5.05	1.72	2.09	2.66	2.67	3.33	4.85

All samples were rinsed with double deionized water before drying and being further processed (see methods section 2.3). Loss of ignition was unable to be collected due to limited sample and is not included in this table. The blue column highlights the potential viable options for residual solids that can be used in cementitious materials, and the grey highlights ASTM requirements.

ns = non-sieved
s = sieved to ≤ 300 µm (sieve #50)

Below are the original samples names for the above samples.
1. DFFA_S2_R3
2. DFFA_S3_R2
3. LRSFA1_S2_R3
4. LRSFA_S3_R2

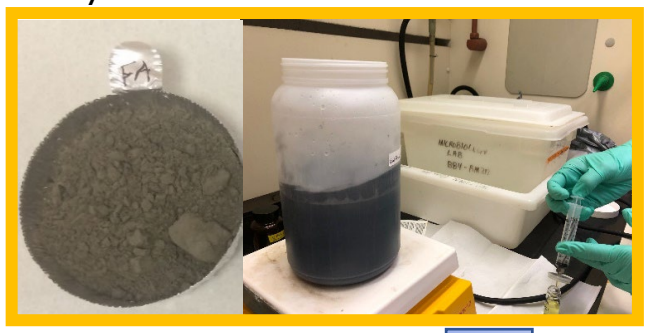


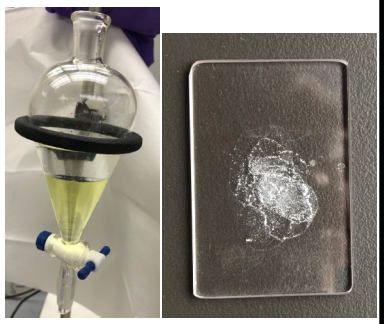
Bridging the "Valley of Death"

Targeting PRB Ashes for cost-saving and eco-friendly REE/CM extractions

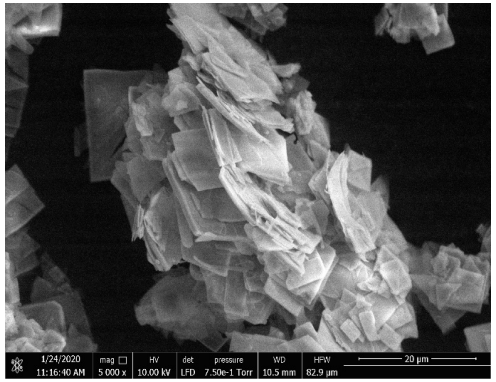
NATIONAL ENERGY TECHNOLOGY LABORATORY

Fly Ash Extraction





Step-leaching at ambient conditions
Targeted Rare Earth Extraction (TREE)
U.S. Patent Pending Serial No.: 63/053,925



e.g. 96wt% Pure Rare Earth Oxide (REO)

From Bench to Pilot: $1.6 million TCF Project

Wyoming partners committed to technology maturation:

- **University of Wyoming School of Energy Resources**
- **Campbell County**
- **City of Gillette**

State, Campbell County pursue rare earth opportunities

By Greg Johnson, Gillette News Record | Via Wyoming News Exchange Jul 5, 2020 Comments OPEN ACCESS

Rare Earth Elements Project Receives Federal Funding

NEWS DIRECTOR | Article Updated: June 23, 2020 | COMMENTS OFF

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U.S. DEPARTMENT OF ENERGY

Projected Started December 2020

TCF-20-21358 Team

CRADA Agreement 1037 (NETL, UWy, ECED)

NETL (Pgh, Alb)

- PIs: Christina Lopano, Thomas Tarka
- RIC PM: Christy Pecyna
- Research Team: Mengling Stuckman, Ward Burgess, Alison Fritz, Colleen Hoffman, Jason Cheng, Jon Yang, Patricia Saint-Vincent, Circe Verba, Brian Kail

University of Wyoming – School of Energy Resources

- PM – Scott Quillinan
- Research Team: Davin Bagdonas, Erin Phillips, Charles Nye, J. Fred McLaughlin

Energy Capital Economic Development (ECED)

- PM – Jim Ford
- City of Gillette, & Campbell County, Wy

Industry Support:

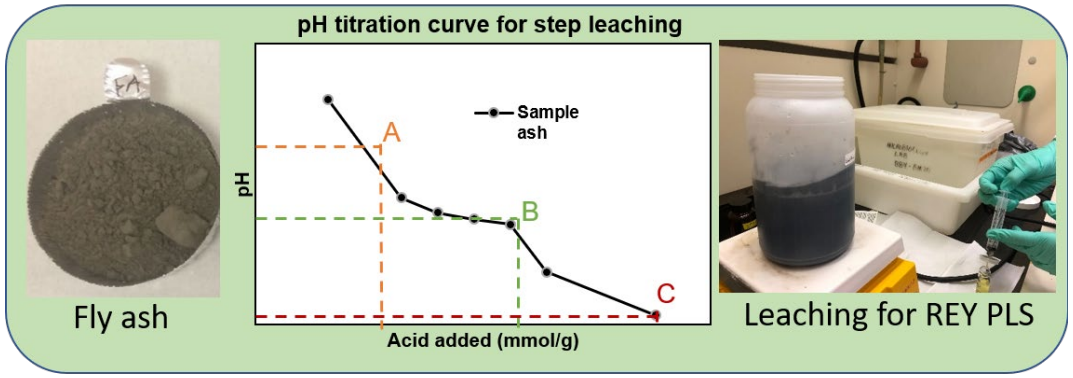
- Western Fuels, Wyoming, Inc. (Dry Fork Mine)
- Basin Electric Power Cooperative (Laramie River Station, Dry Fork Station)

Project Goals and Objectives

TCF-20-21358 Project Narrative

The project will create a small **pilot-scale production facility** that demonstrates the environmentally benign and economically viable production of REE from coal-related feedstocks. This will be achieved by working with **academic and industrial partners** to:

1. Identify the most promising feedstock(s) in the Powder River Basin (PRB) for the extraction of rare earth elements (REE) and critical metals (CM),
2. Perform extraction experiments to demonstrate the efficacy of extracting REE and CM in an economic manner, and
3. Up-scale NETL extraction technologies to a pilot scale in the PRB.



Task Breakdown

TCF-20-21358 Project Narrative

Task 1: Feedstock Screening, Testing and Optimization (~ 12 months) (UWy, NETL), PI - Lopano

- Identify promising ash materials for extraction and upscaling. Down-select to 1 to 2 candidate ashes for larger scale extraction tests and process optimization.

Task 2: Chemistry & Reaction Optimization (~ 24 - 36 months) (NETL), PI - Lopano

- NETL has developed a patent-pending step leaching process (TREE) for extraction of REE from PRB ash that reduces acid consumption by 90% over other processes for PRB ash and effectively eliminates the presence of major cations (e.g., Ca and Fe) to increase the purity of REEs in the pregnant leach solution (PLS).

Task 3: Systems Analysis and Resource Assessment (~ 30 – 45 months) (NETL) PI – Tarka / Fritz

- NETL SEA will initiate a screening study to evaluate the economic performance of the sequential extraction process and subsequent product enrichment to higher purity concentrates. This work both builds the foundation for TEA work to be performed during the duration of the project and will inform research performed under Tasks 2 & 4.

Task 4: Pilot-Scale Process Operation (~ 36 - 45 months) (NETL, UWy, ECED), PI – Tarka / Fritz

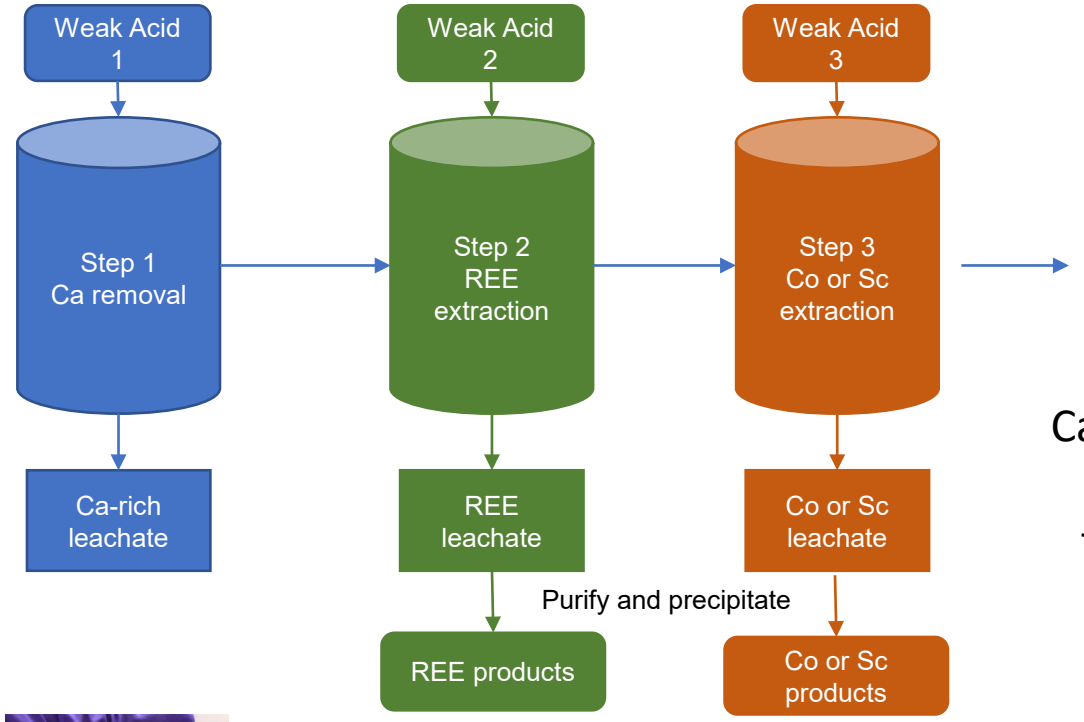
- Maturation of a pathway to extract and enrich REE from coal byproducts that technical risk is reduced, enabling the technology to be licensed and financed for deployment at a large scale. To achieve this, the project will culminate in the start-up and operation of a pilot-scale facility that demonstrates the performance and economic feasibility of the process. Produce 25 grams of 60% REO concentrate

Task 2 - Targeted Rare Earth Extraction (TREE)

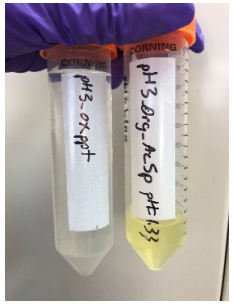
Ca-rich Powder River Basin (PRB) Ashes - Reduce Extraction Steps & Conditions

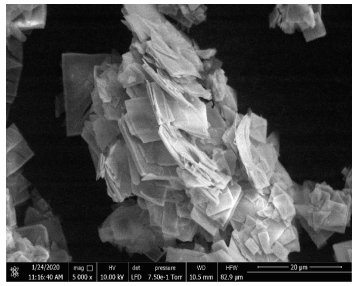
Bench Scale Summary

- *Up to a 3-step process:*
  (A) Ca, (B) then REY and (C) Sc
- *Up to **83% REY** achieved in Step 2; up to 61% Sc removal in step 3*
- *TEA Analyses aid optimization by fine-tuning reaction time, L:S, acid addition in each step.*
- Acid concentrations optimized for FA; *should* also work for LA, BA samples
- Other Co-products?: Ca-rich brine, Treated Ash



Ca & Sulfate removed from Ash





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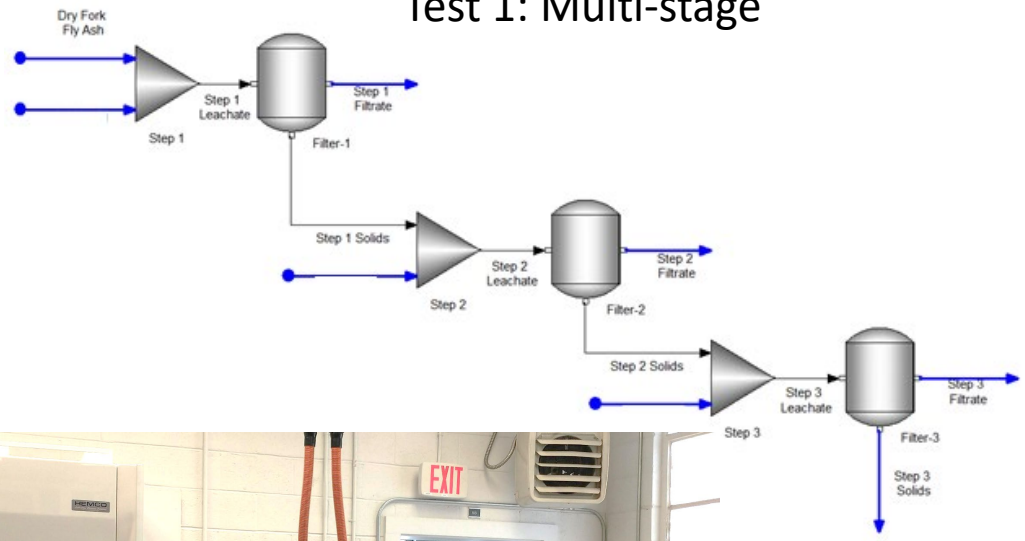
Scale-up of PRB Ash "TREE" leaching process

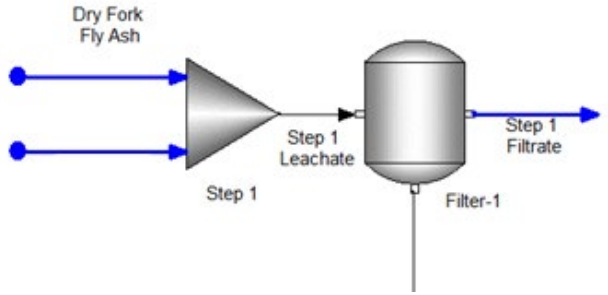
Testing reaction and process efficiencies on kilogram scale

- Reactor Design
  - 55-gallon HDPE barrel
  - 0.93 HP pneumatic drive mixer
  - 316 SS shaft
  - 4.5" A-310 axial flow impeller(316 SS) OR 7.5" marine propeller (316 SS)
  - Ventilation lines drawing >100 cfpm to handle off-gassing reactions (SO_2 production from fly ash)
  - Minimum 500 rpm needed for minimum degree of particle suspension
- Reaction Parameters
  - 4 kg fly ash
  - 80 L starting volume
  - 2 M HCl
  - Delivered at rates of 0.1 – 2 L/min

Test 1: Multi-stage



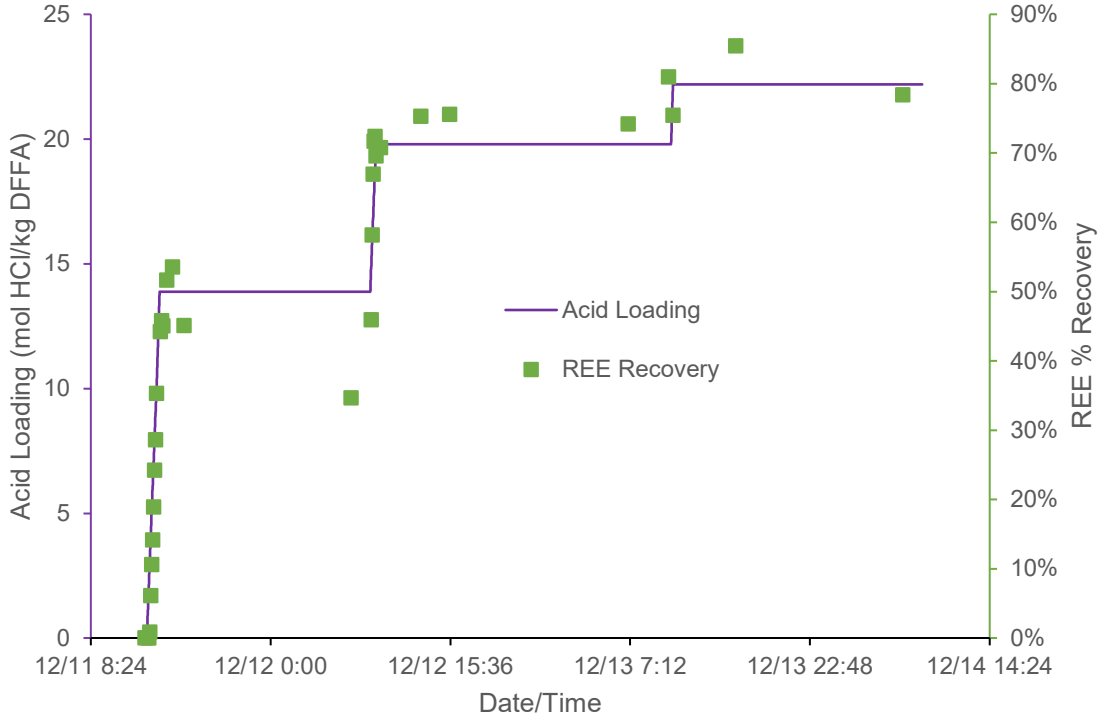
Test 2: Single-stage



Multi-disciplinary iteration for process scale-up

Testing Reaction and Process Efficiencies

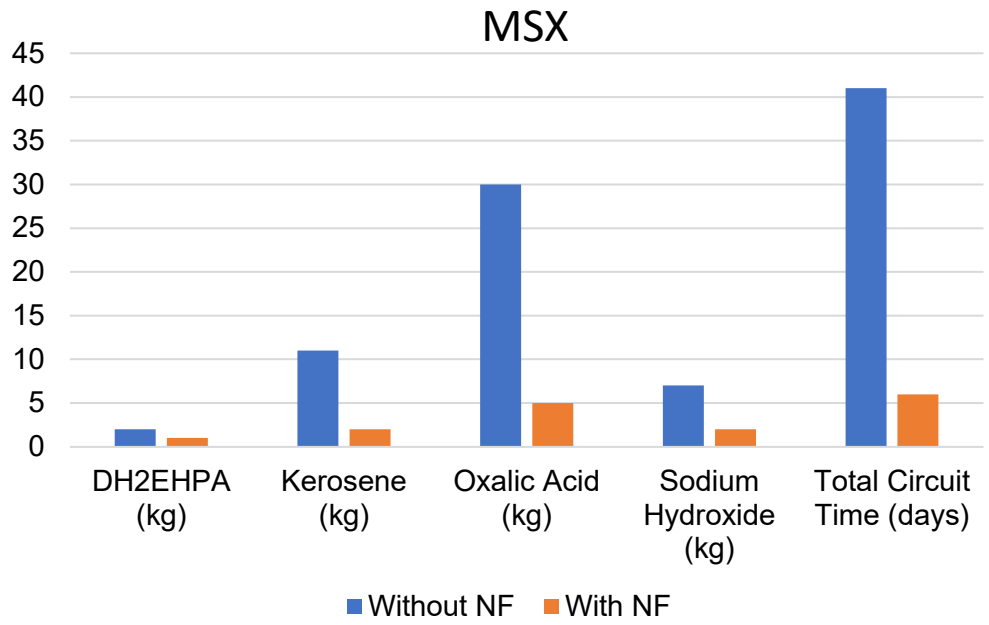
Leaching parameters including the **liquid to solid ratio**, **acid addition rate**, and **residence time** were updated based on 3 piloting tests by Jon Yang in Albany, OR.



Barrel Experiment Results:

- Highest REE extraction yields obtained in a single-stage leach **> 80% recovery**

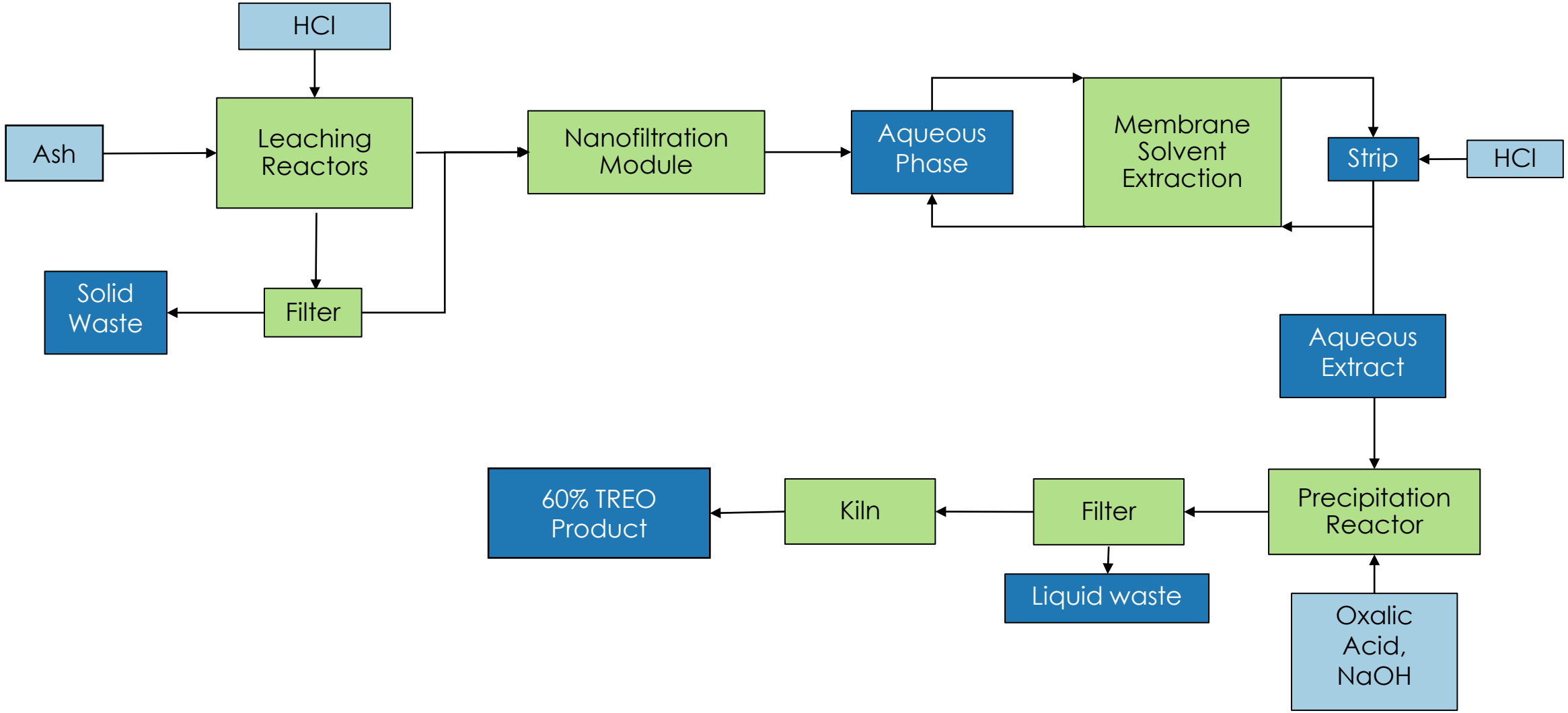
A **nanofiltration (NF)** module was suggested by collaborators Siefert and Burgess on the Reaction Engineering team (NETL-RIC)



NF is expected to **reduce** circuit **operation time**, organic reagent consumption, and precipitation **reagent consumption** by close to **7x**

Updated process flowsheet

Integrating more novel technologies (nanofiltration, MSX)



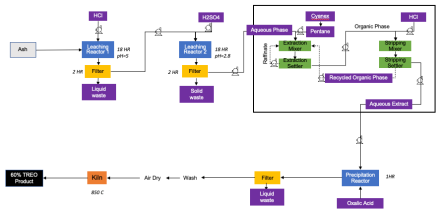
Task Timeline (Tasks 3 & 4) Fall 2021 – present

CRADA signed Dec 2020 (Start of project); no-cost Extension to 9/30/2024

Task 3

Initial systems design and high-level cost estimate (2021)

Pilot Plant Mass and Energy Balance (Fall 2022)



Final Systems Design and High-Level Cost Estimate (Spring 2024)

Techno-Economic Evaluation of Process Performance and Economics (Fall 2024)

Task 4

Identify environmental health and safety needs (2021)

Start equipment specification and procurement (Winter 2022)

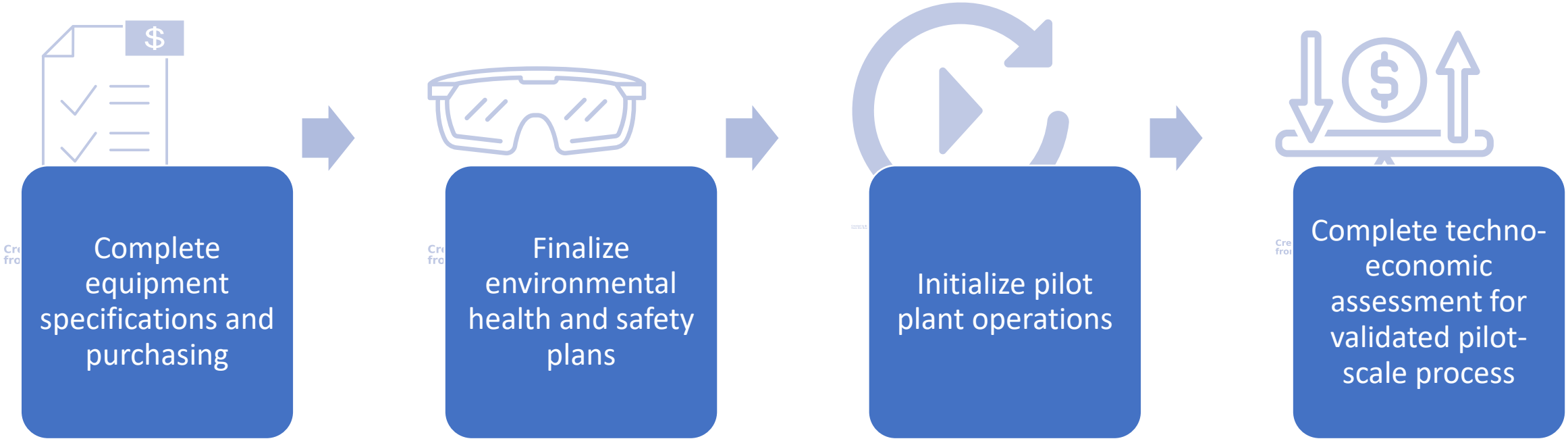
Complete equipment procurement (Spring 2024)

Equipment layout and environmental health and safety plan (Summer 2024)

Produce 25 grams of 60% REO concentrate (Fall 2024)

Next steps

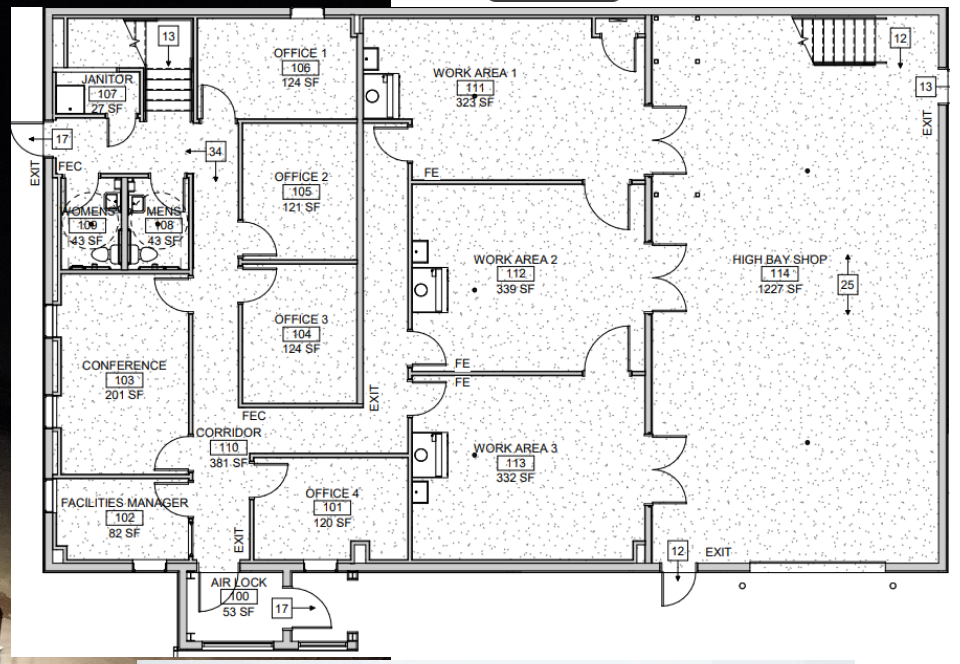
TCF-20-21358



Task 4: Wyoming Innovation Center

NATIONAL ENERGY TECHNOLOGY LABORATORY

NETL TCF Project – first tenant



REE Recovery from PRB Coal Wastes: Pilot at WIC

TCF-20-21358

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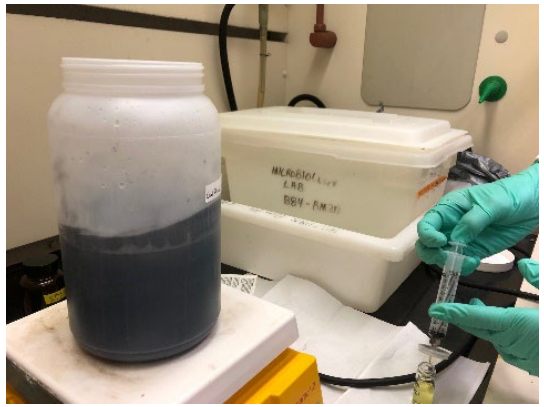

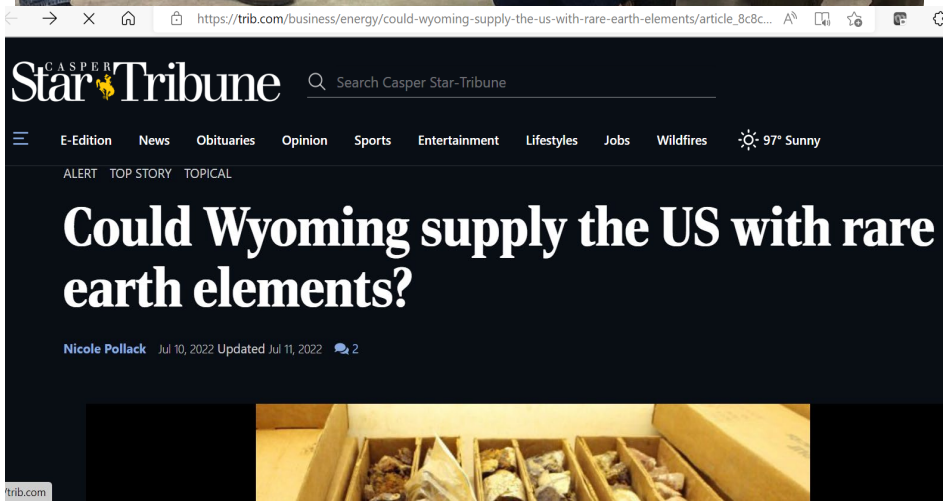

Acknowledgement

This work was performed in support of the U.S. Department of Energy's Fossil Energy and Carbon Management Critical Minerals & Rare Earth Element Research programs.

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

Task Milestones

Identifier	Type	Expected Completion Date	Description	Status
EY22.18.B	Major	06/2023	Assessment of viable coal byproduct feedstocks from PRB coal using sequential leaching methods.	Completed.
EY23.18.A	Project	06/2023	Evaluation of step 1, Ca-rich residual leachates for beneficial reuse	Completed.
EY23.18.B	Project	09/2023	Comparison of ash properties before and after undergoing TREE leaching	Completed. Some additional preparations underway for further comparisons.
EY23.18.C	Major	12/2023	Complete data analysis of Ce-XANES collected at synchrotron facilities over the duration of this project.	Completed. Manuscript in prep.

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

Outreach Products Released and In Preparation

- Stuckman, M., Hoffman, C., Lopano, C., and Hower, J., "Advancing Rare Earth Element Characterization to Inform Recovery from Coal Ash Materials," oral presentation, American Chemical Society Annual meeting and exposition, San Francisco, CA, August 2023.
- Lopano, C., Stuckman, M., Tarka, T., and Thomas, R.B., "Critical Mineral Resources from Wastes: Characterization Informed Separations from Fossil Energy Byproducts," Invited oral presentation, American Chemical Society Annual meeting and exposition, San Francisco, CA, August 2023.

- Hoffman, C.L., Brandi, M., Kutchko, B.G., Strazisar, B., Burgess, W., Cheng, C.M., Stuckman, M.Y., Lopano, C.L. Potential reuses of post leachate Powder River Basin fly ash solids from TREE critical mineral recovery process (NETL internal technical report, in preparation).