Rare Earth Elements from Coal and By-Products: Separation Technologies

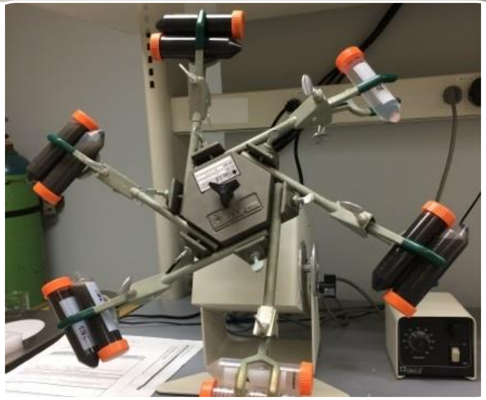
NETL RIC – REE FWP
Task 3 (3.1 & 3.2)

Presenters:
Christina Lopano (NETL, RIC)
Circe Verba (NETL, RIC)

September 16, 2020

NATIONAL ENERGY TECHNOLOGY LABORATORY



U.S. DEPARTMENT OF ENERGY

RIC Portfolio Strategy

How We are Approaching the Problem

Understanding & Finding the Best Resources

- Understanding REE occurrences in coal and related measures
- Finding the high-quality resources: high concentration, easily extractable, abundant quantity

Making the Numbers Work

- Discovering & Maturing New Production Pathways
- Understanding Markets, Projections, and the Barriers Holding Industry Back

Enabling Domestic Innovation

- Identifying process bottlenecks, research targets, and market opportunities through systems analysis
- Developing the enabling technologies & cutting-edge computational tools (e.g. CFD models) to help drive commercialization and scale up

Project Goals

RIC Separation Chemistry (RIC FWP Task 3)

Purpose: Utilize advanced characterization to develop innovative extraction and enrichment technologies to unlock the potential of coal to create a domestic REE/CM industry.

Strategic Alignment: 1. Economic and Energy Security through the production of minerals critical to domestic industries and which underpin the energy technologies of the future. 2. Creating new market and valuable products from coal

Technology Benchmarking: RIC Separations technologies have exhibited the potential to dramatically reduce reagent consumption, process complexity/intensity, and therefore **cost** compared to existing REE production pathways.

- RIC processes developed have exhibited a potential for a reduction in acid consumption compared to benchmark.
- Use of benign, organic acids and processes to reduce environmental impact
- Techno-economic analyses are being in progress for all RIC separations technologies to further explore process performance.

Project Current Status

NETL - RIC Separation Chemistry (Task 3)

Results compared to benchmark:

- **80% reduction** in reagent consumption
- Reduction in process steps/complexity: e.g. **no pre-treatment (grinding, floatation) or reduction of solvent separations**
- Reduction in process intensity: **ambient temperature and pressure**

How have project goals changed?:

- Increased focus on maturing technologies:
  - Rapid move to larger scale experiments
  - Validation on representative feedstocks provided from industrial partners
  - Extended engagement with industry for partnership

Industry input/validation:

- Regular communication with extensive list of industry partners
- Field tests and pilot-scale projects are underway/development with industry partners, and more are planned
- Active discussions on technology licensing and industry needs

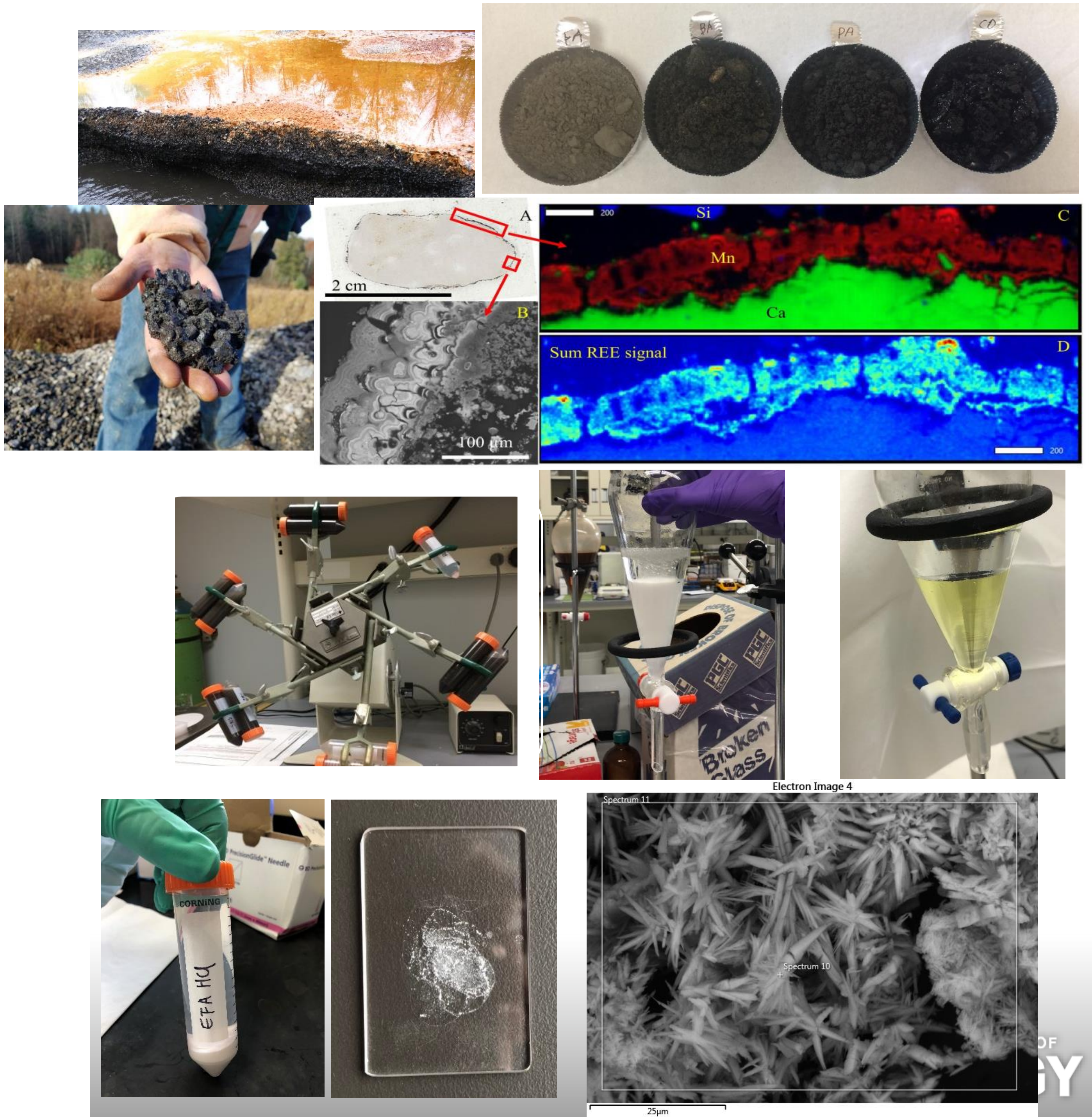
Sequential Separations Chemistry

Presenter & PI:

Christina Lopano (NETL, RIC)

Researchers: Mengling Stuckman (LRST), Ward Burgess (LRST), Ben Hedin (ORISE), Josh Miller (ORISE), Gordon Chiu (ORISE), Alison Fritz (ORISE), Murphy Keller (RIC), Evan Granite (RIC), Bret Howard (RIC), Tom Tarka (RIC)

NATIONAL ENERGY TECHNOLOGY LABORATORY

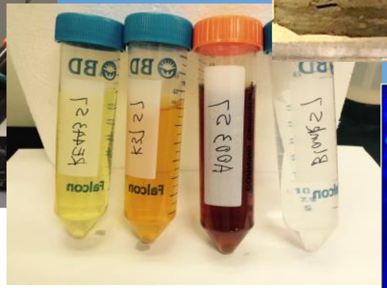


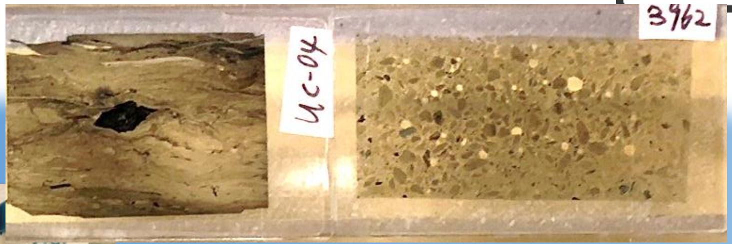
Understanding the resource

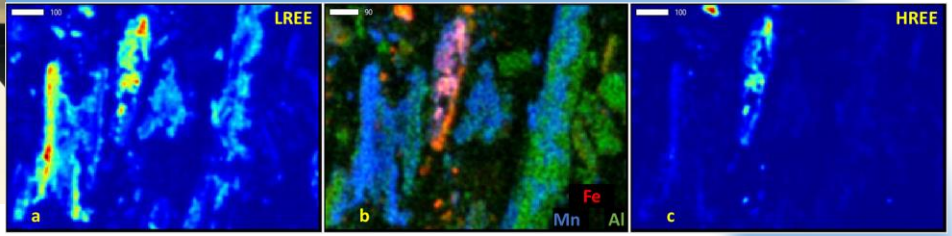
Task 3.2: Ash & AMD Characterization to Recovery

AMD solids

Fly ash

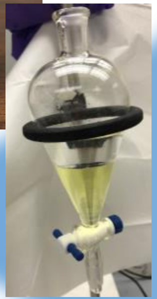


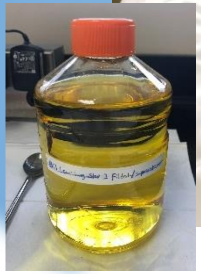


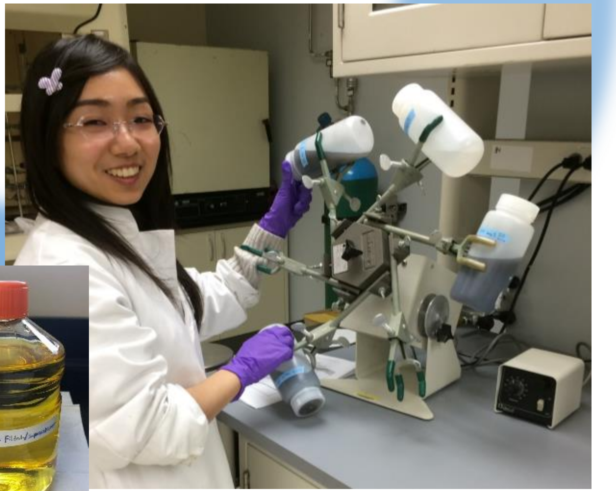


Goal: Utilize sequential extraction techniques to characterize major REE-hosting solid fractions in different CCBs and to **innovate targeted extractions** for efficient and economical REE recovery.

- A workflow to identify REE & CM host phases & binding environment
- Bulk Chemistry, Titrations, Sequential Extractions
- Advanced Characterization & Identify targets and Lixiviant
- Selective Extraction Processes Optimize Extraction Efficiency



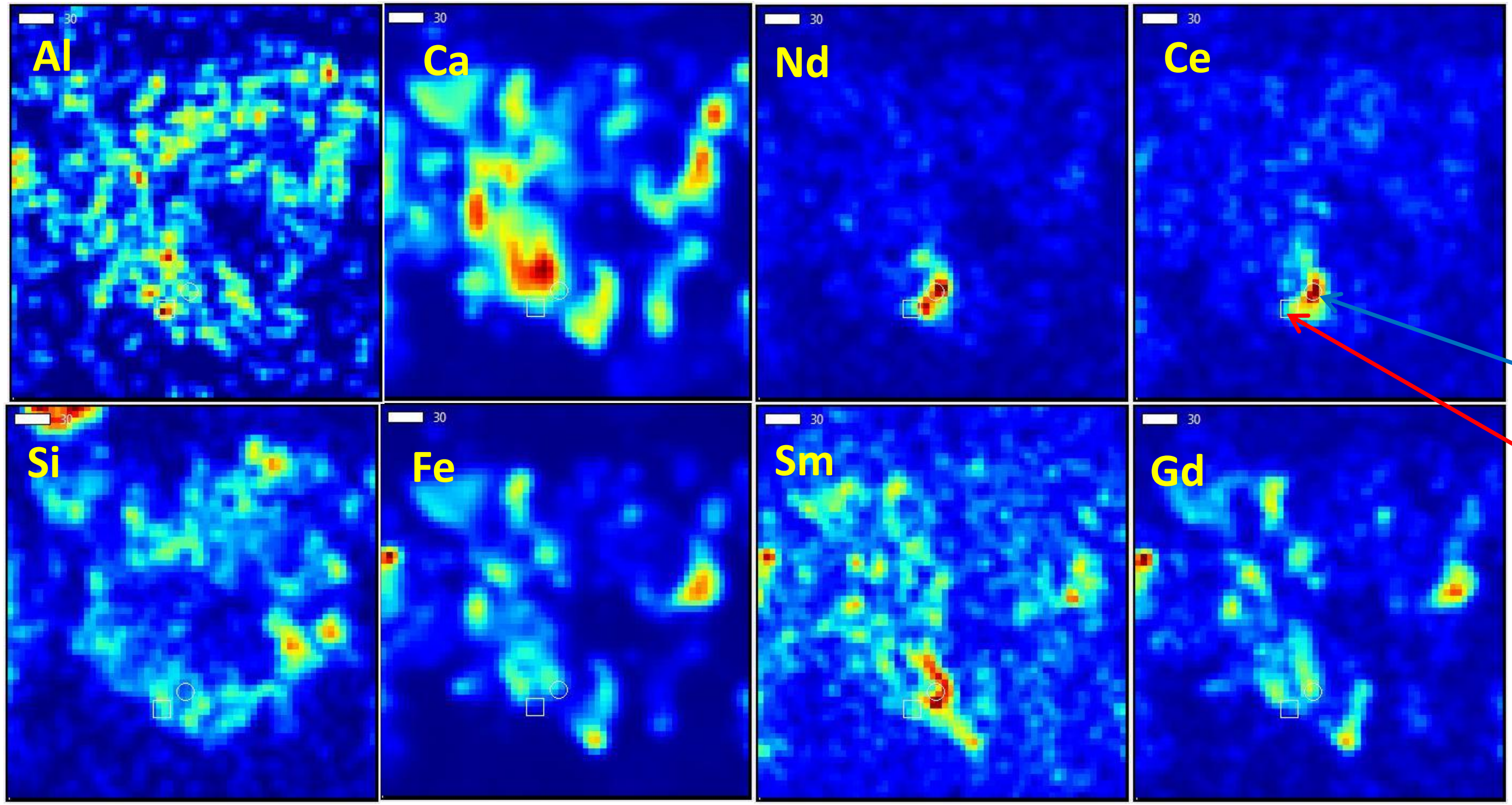




Example: Characterization to Recovery

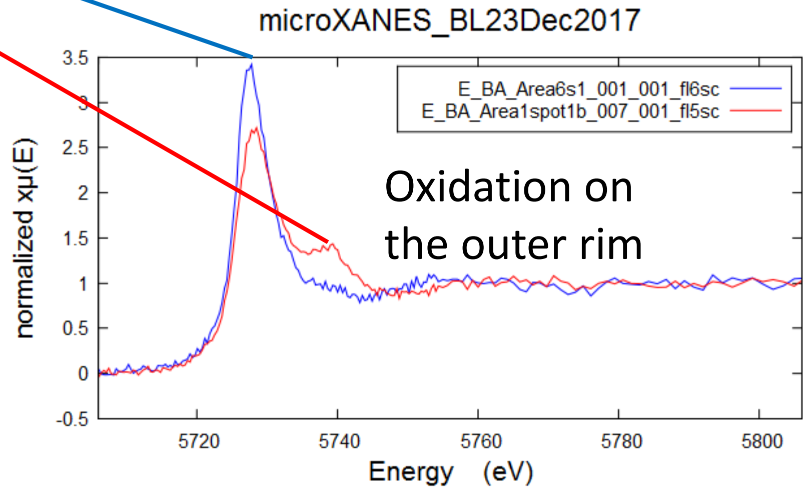
Synchrotron analysis identifies REE-hosting phases in Ca-rich ash samples

Light REEs (e.g. Ce, Nd) w/ Ca-rich AlSi, and heavy REEs (e.g., Sm, Gd) w/ Fe-rich AlSi



During coal combustion, Ce diffused into Ca phases and is susceptible to Ce oxidation during coal combustion

$$Ce(III) + O_2 = Ce(IV)O_2$$



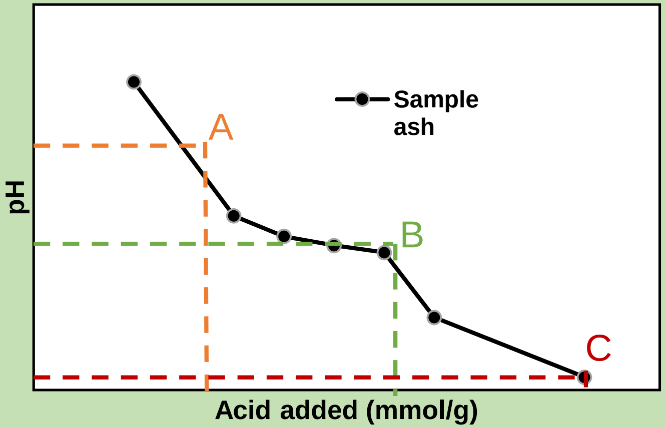
The chemical distribution and evidence of oxidation illustrates that Ce (and REEs) are easily accessible, not armored by glass (e.g. like Appalachian basin ashes)

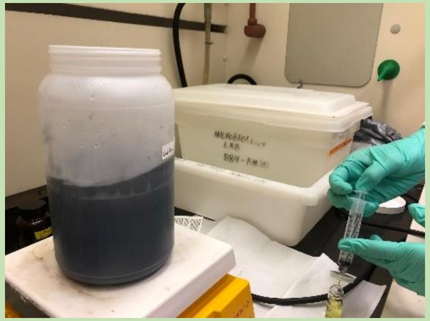
Proof of Concept & Validation: PRB Ash

REY PLS generated from PRB fly ash, REE processing with recyclable solvent extraction for REY purification

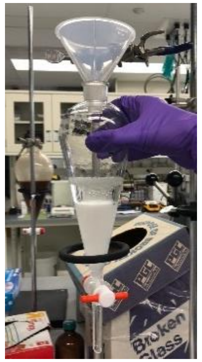
Fly ash

pH titration curve for step leaching





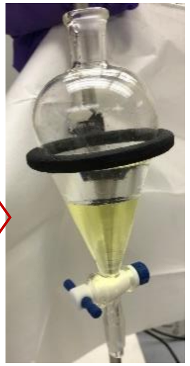
Leaching for REY PLS



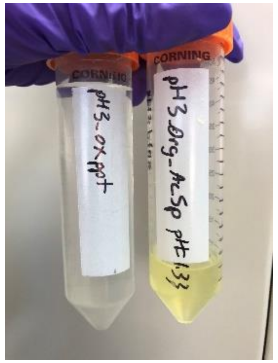
Solvent

PLS

Reduced solvent use

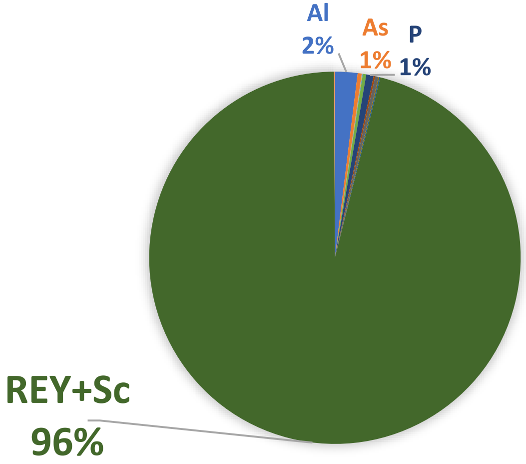


Stripping

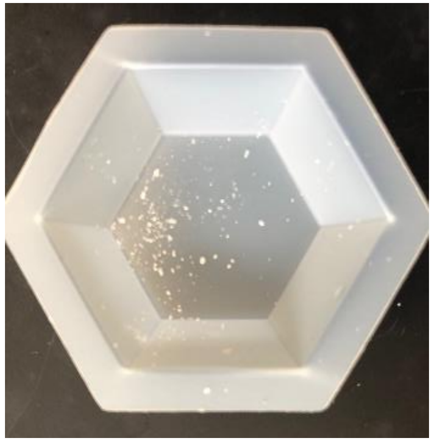


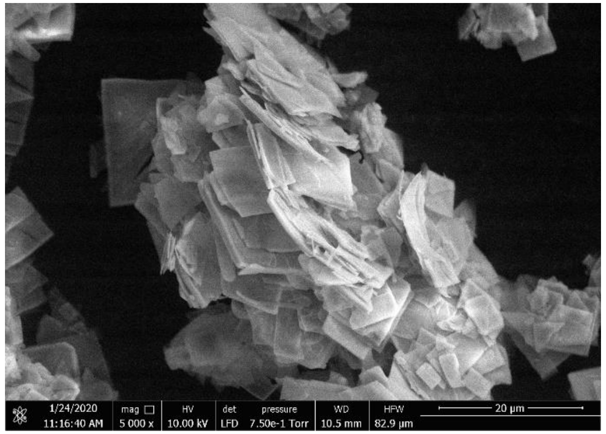
Oxalic acid precipitation

MAJOR ELEMENTS OF PRODUCTS

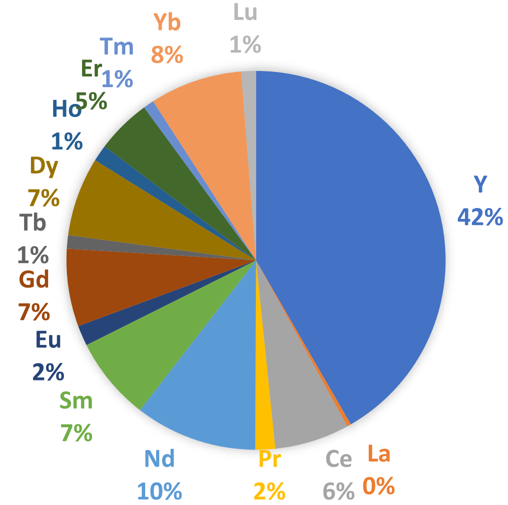


Products with up to 96%wt REOs





PRODUCTS WITH 57% CRITICAL REES



Scale up and Optimization – Underway 2020

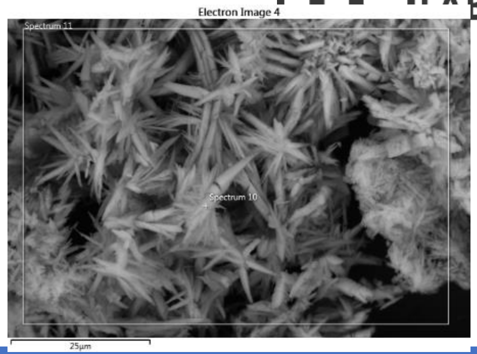
Research Success Metric: Fly ash

Yearly progression demonstrated

Powder River Basin Ash

Est. 3630 metric tons REO/yr

38% of US annual demand



EY	Wt% REOs	TRL Level	%Recovery	Notes
2018	27%	1 - 2	8%	Ca, Fe and Na impurities, solid harvesting challenges
2019	30%	2 - 3	40% (80%HREEs)	K impurity, ox ppt need optimization
2019 - 2020	96%	2 - 3	> 80%	**Sequential Leaching Patent**, further upscaling and process optimization in progress
2020	>90% and other by-products	3 - 4	> 80%	Received 70lb PRB fly ash from EPRI (Oct. 2019) Additional ashes (variable Ca-content) – in progress Further optimization
Future	>90% and other by-products	4+	> 80%	Collaboration with Univ WY (TCF proposal)

C. Lopano, M. Stuckman, and T. Tarka, "**Step-Leaching Process of REE from Select Coal Combustion Fly Ashes Using Mild Inorganic Acids at Ambient Conditions,**" U.S. Provisional Application Serial No. 63053,925, July 2020.

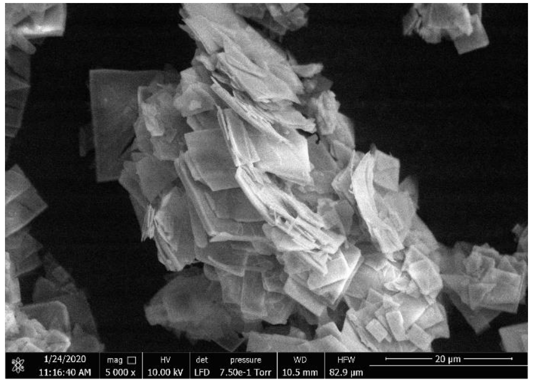
Recovery from Calcium-rich Ash

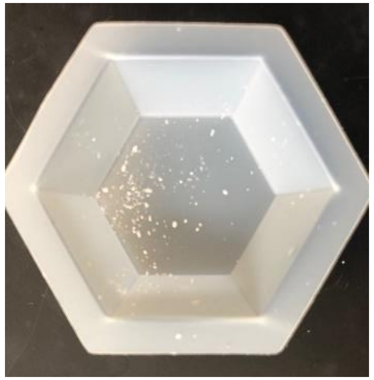
Targeting Powder River Basin (PRB) Ashes to Reduce Extraction Steps & Conditions

NATIONAL ENERGY TECHNOLOGY LABORATORY

PRB Fly Ash

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

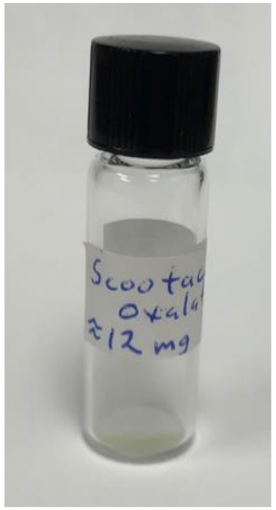
NEWS DIRECTOR | Article Updated: June 23, 2020 | COMMENTS OFF

Share on Facebook Tweet this!

Recovery from AMD Treatment Wastes

Passive Remediation Systems Produce a Stable, REE-Rich Material

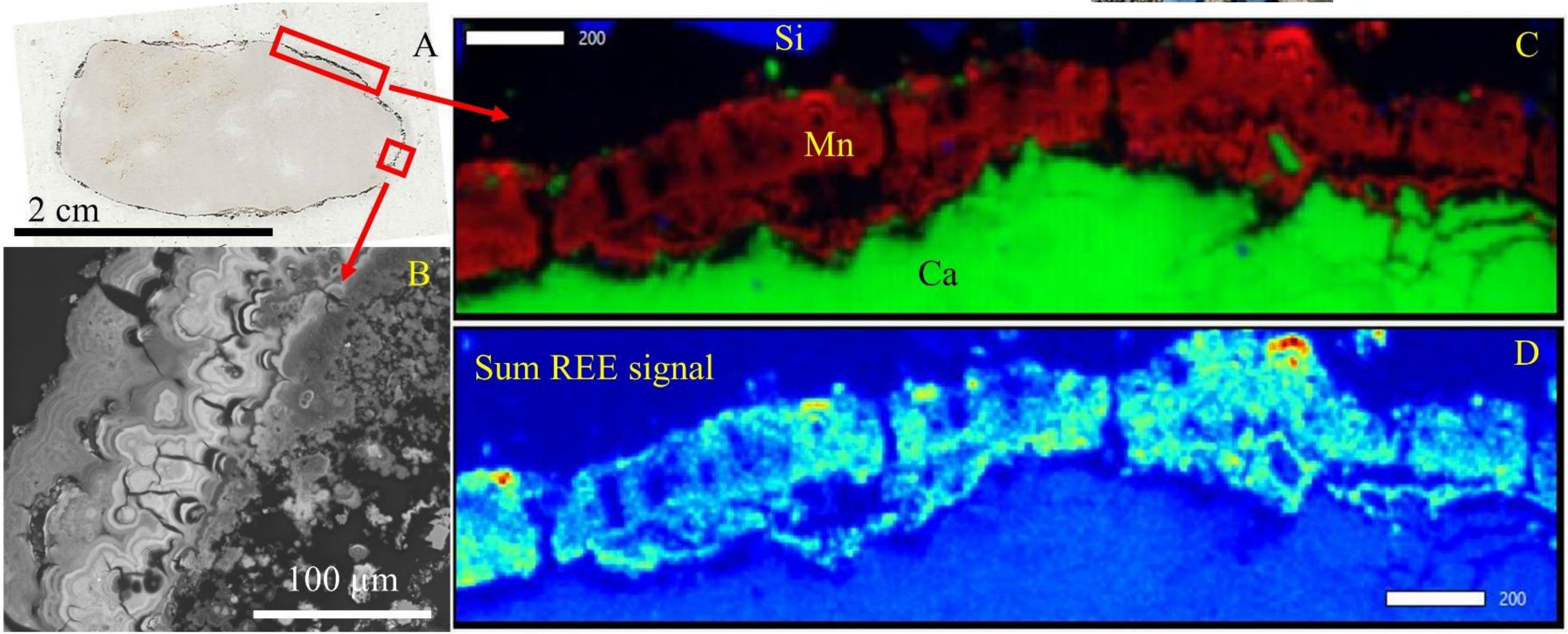
- **<u>REE and other precious metals</u> precipitate from AMD**
- **Higher concentration (>1,500 ppm) resource**
- **REE value could result in widespread deployment of low-cost AMD cleanup systems**



Final products: <u>16%Co</u>, 11% Mn, 6.2%Ni, 4.4%Zn, <u>2.7% REY</u>

Example: Characterization to Recovery

Synchrotron analysis identifies REE-hosting phases in AMD remediation solids



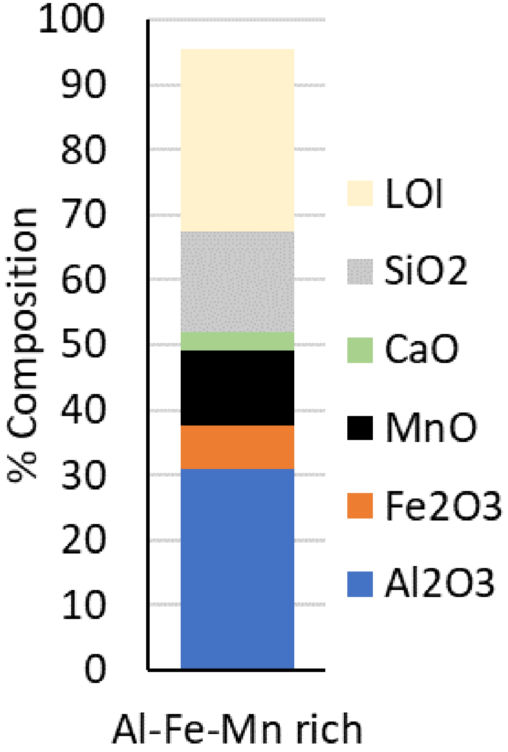
Strong correlation with Mn-oxides

Proof of Concept: AMD Solids

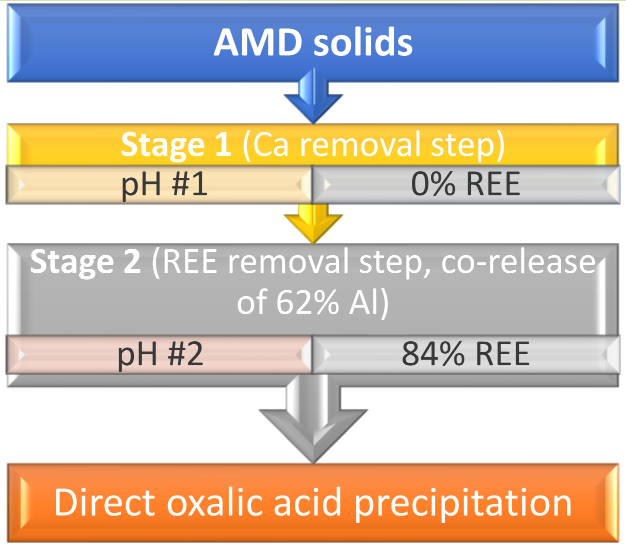
Example: Step-leaching for AMD solids via pH titration characterization

Westbox (Al-, Mn-, Fe-rich)

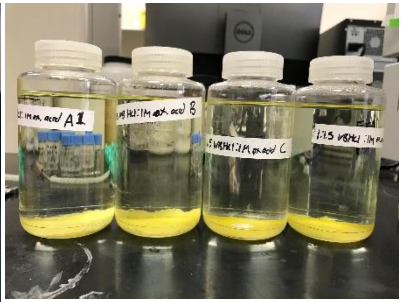
1,800 ppm REE



Hedin et al (2019) International Journal of Coal Geology

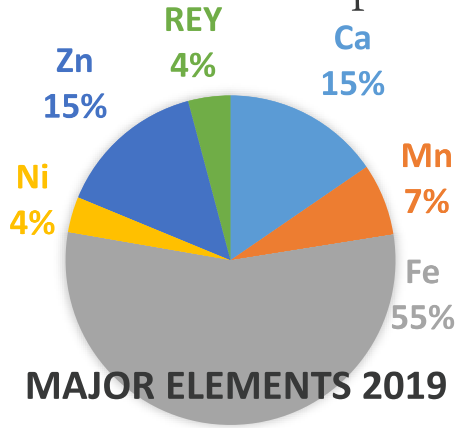


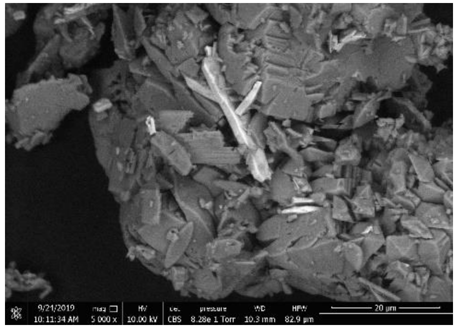
Large scale leachate



Ox precipitation

2019: 2 g products with 4%wt REOs from 40g AMD solids, with Fe and Ca impurities; Adjustments pending 2020





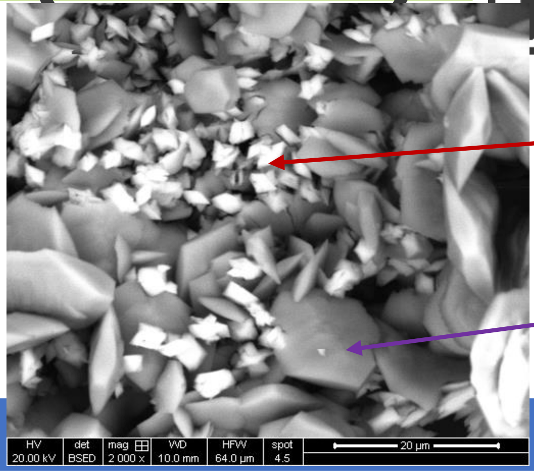
Research Success Metric: AMD solids (Task 3.2)

Yearly progression demonstrated

AMD waste solids

Est. 1102 metric tons REO/yr

12% of US annual demand



EY	Wt% REOs	TRL Level	%Recovery	Notes
2018	9%	1 - 2	60%	Mn and Fe impurities, with 10%Co, 26%Ni and 21%Zn
2019	4%	2	80%	Fe and Ca impurities were further addressed, leachate underwent L:L separation for comparison
2019	13%	2 - 3	> 80%	Reduced impurities with 48% Zn, 11%Ni, 2%Co Additional AMD solid field sampling (early 2020)
2020	95% (mg scale)	2 – 3	>80%	**ROIs in prep**; By-product recovery in development Upscaling and optimization of lab scale processes
Future	>90% and other by-products	3 - 4	>80%	Collaboration with Hedin Environmental, Inc. Explore biotechnologies to sequester, recover and purify REEs and critical elements in planning

Partners & Collaboration

Outside Organizations Engaged in Research

- Hedin Environmental
- University of Pittsburgh
- EPRI (Electric Power Research Institute)
- University of Wyoming (PRB ash) – opportunity to collaborate and facilitate contact with industry partners in the Powder River Basin
- University of Chicago & Argonne National Lab – approached NETL researchers (Lopano & Stuckman) to partner on a DOE-BES proposal for the development of an advanced detector for measurement of REE in complex geologic matrices to be built at Sector 13 at APS. (Awarded)

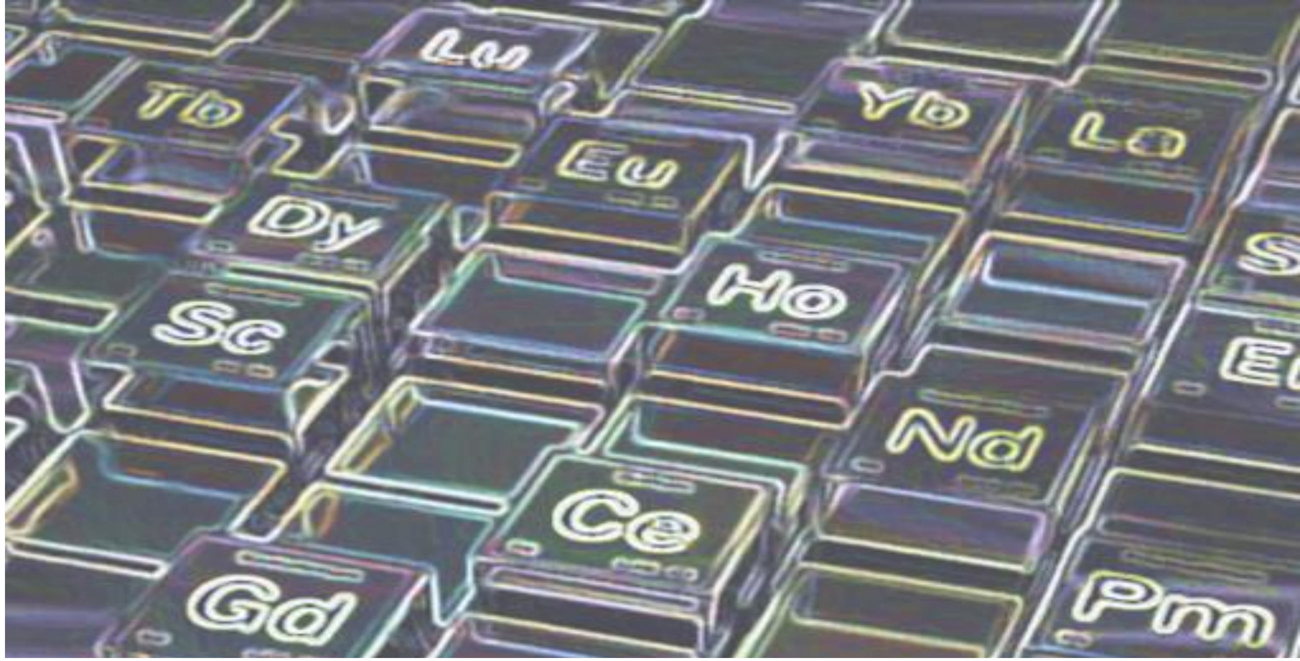
3.1 Waste Stream: Ion Exchangeable REE Extraction

Presenter:

Circe Verba (NETL, RIC)

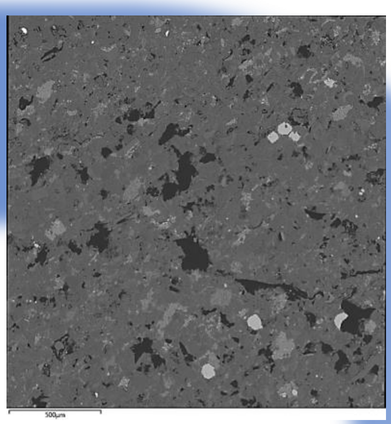
Researchers: Jon Yang (ORISE), Burt Thomas (LRST), Scott Montross (LRST), Brian Kail (LRST), Walter Wilfong (LRST), Mark McKoy (RIC), Tom Tarka (RIC)

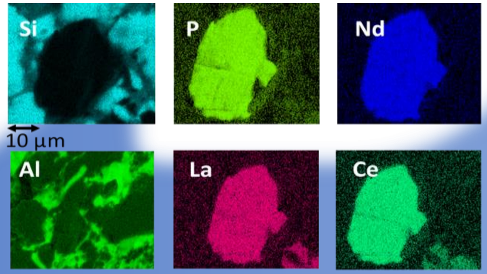
NATIONAL ENERGY TECHNOLOGY LABORATORY

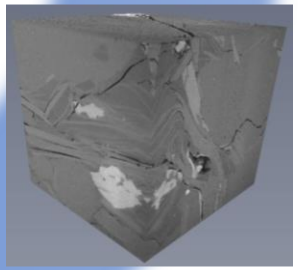


Understanding the resource

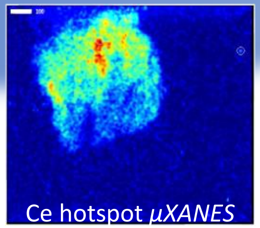
Important to see both the Forest and the Trees

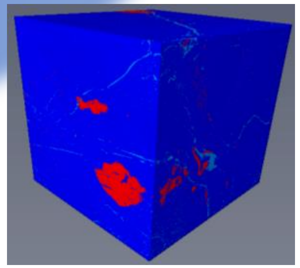






2D to 3D





Quantification to inform future REE extraction techniques & optimal candidate feedstocks with salable REE concentrations

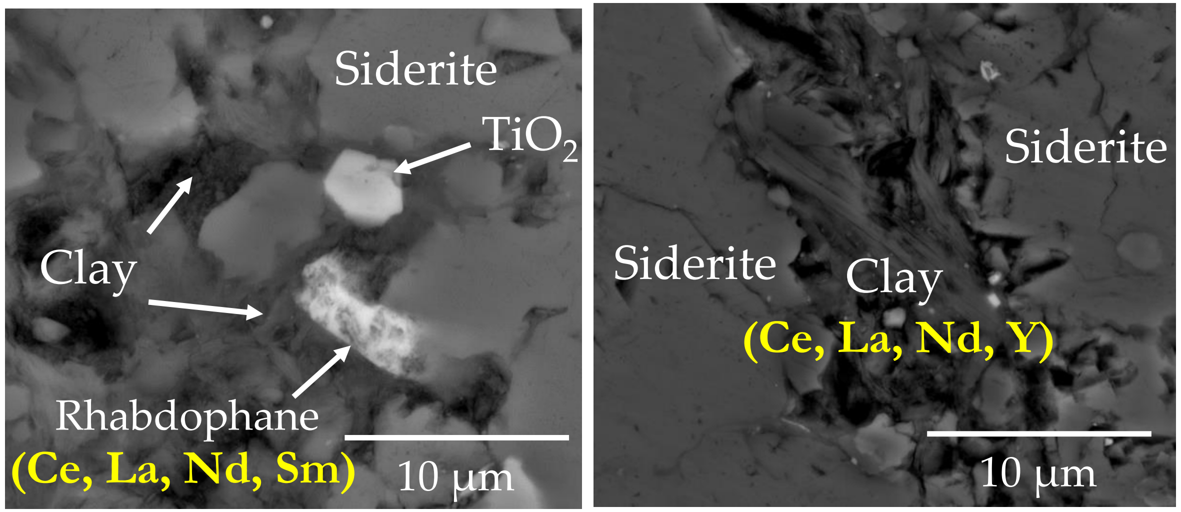
- A workflow to identify petrophysical properties
- Elemental spectroscopy & bulk phase identification
- Isolate distribution on primary REE phases
- Individual minerals

Photo from https://www.flickr.com/photos/piedmont_fossil/5710636433

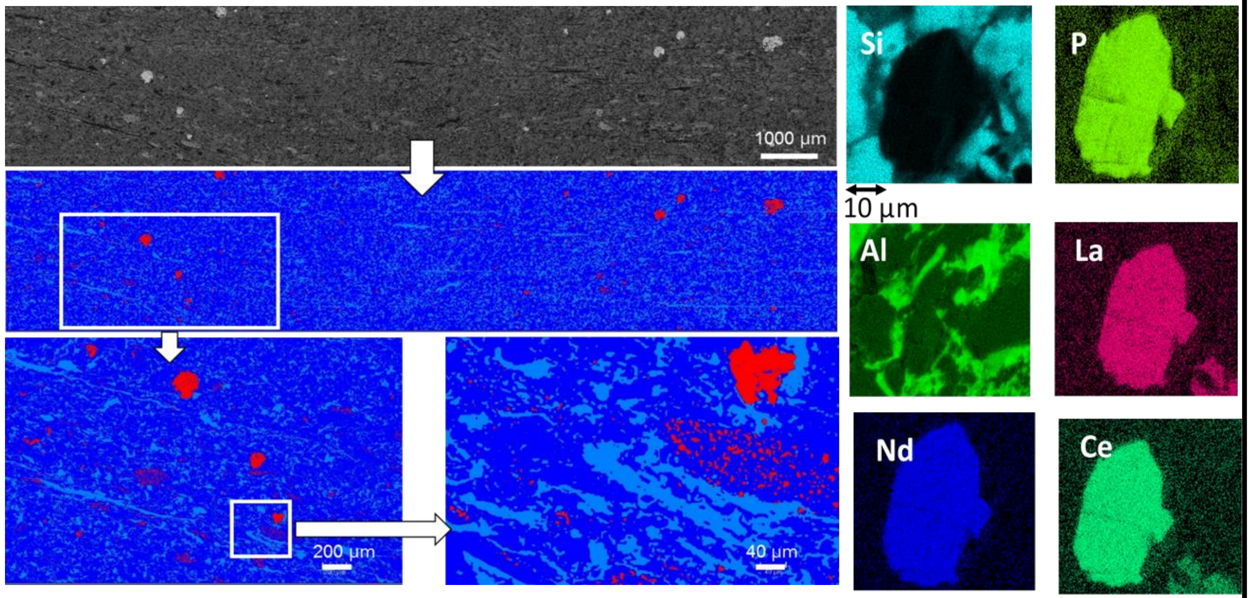
Understanding the Resource

Underclay & refuse

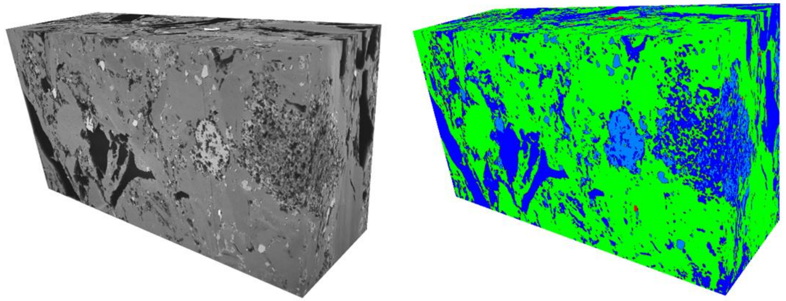
Individual Minerals



Bulk Material & Phases



3-D Pore Volume & Density Mapping



Multi-scale characterization enables an understanding of REE occurrences in the resource

Characterization to separations

Characterization data coupled with advanced image processing:

1) Determine the bulk mineralogy and clay composition via XRD.
2) Discover REE mineral phases (e.g. monazite (Ce, La, Nd-PO_4) and xenotime (Y-PO_4)) vs. clay bound minerals in the samples.

Our characterization work demonstrates:

- Lower Freeport, Middle Kittanning, 5 Block Coal, Pittsburgh, and Brookville underclay T
  - REE = 250-457 ppm.
- REE phosphates occur as mineral crystals in the **interparticle pore space** of the underclay or as crystals **embedded** within the matrix clay
- REE identified in carbonate and aluminum phosphate **diagenetic minerals**.
- A portion of the REE are likely in exchangeable form within clay as seen from sequential digest and synchrotron analysis.

Bulk of REE in exchangeable form and will be targeted using novel separation technologies

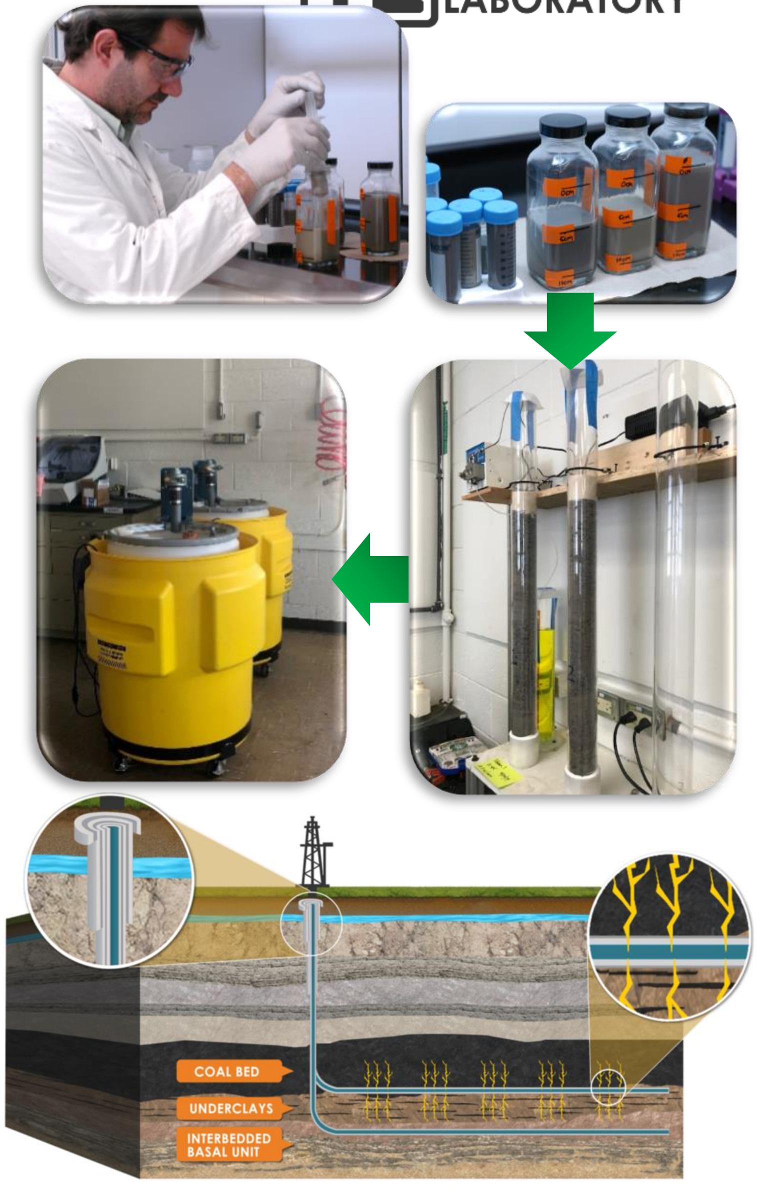
Yang, J, Verba, CA, Montross, Scott, Moore, Jessica, McDowell, Ronald, and Mark McKoy, 2019. *Microanalytical Characterization of REE Phases in a Glauconitic Sandstone*. Microsc. Microanal. 25 (2). doi: 10.1017/S1431927619013084.

Coal waste & underclay as a feedstock

- **Mild organic acid**: less hazardous chemicals than conventional approaches
- Targets accessible ion-exchangeable REE species & mineral surfaces at ambient pressure/temperature
- **Up to 33% of REE** without extracting other gangue materials, reducing chemical costs and downstream processing requirements

- <u>Multiple Potential Applications</u>:
  - ***Ex situ* heap leach recovery & plant processing** from coal mining waste and co-mined materials
  - ***In situ* recovery** from undisturbed sedimentary rock layers, open pits, or underground mines

C. Verba, M. McKoy, T. Tarka, S. Montross, J. Yang, "Process for Extraction of Recoverable Rare Earth Elements (REE) Using Organic Acids and Chelating Compounds," Patent Pending (non-Provisional Application filed, S-150,861), September 2020.

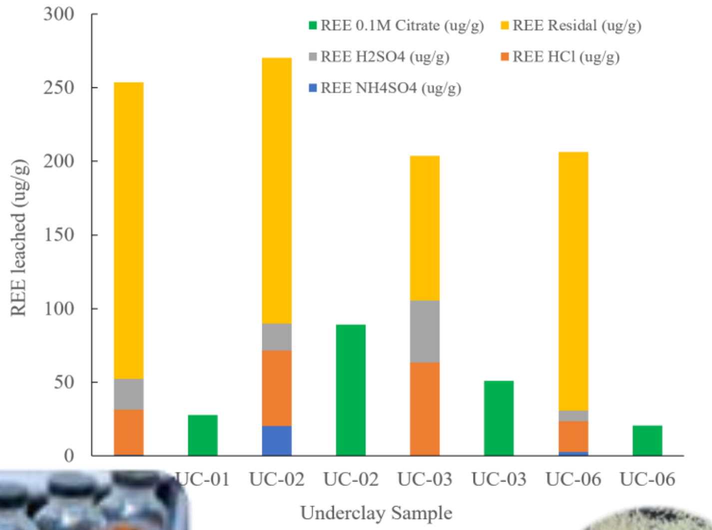


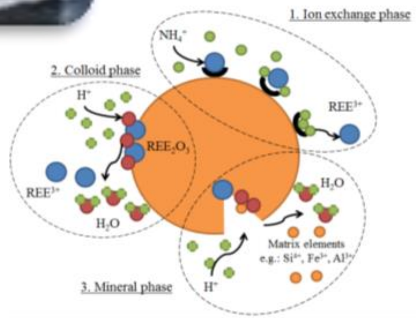
Waste Coal heap leaching applications

NATIONAL ENERGY TECHNOLOGY LABORATORY

Bench top experiments

- REE recovery is <u>4-10x greater</u> via chelation and ion-exchange using citrate-based solution than with ion exchange using ammonium sulfate.
- Optimizing the chemistry: 0.1 - 0.05 - 0.01 M Na-citrate
- Scale from 100 mL to 1 L to 55 gal – ongoing
- Synergistic effort BIAS Sorbent to Enable Solution Recycling: 181D Sorbent technology provides a means to strip and recover REEs into concentrates up to 3.6 wt%



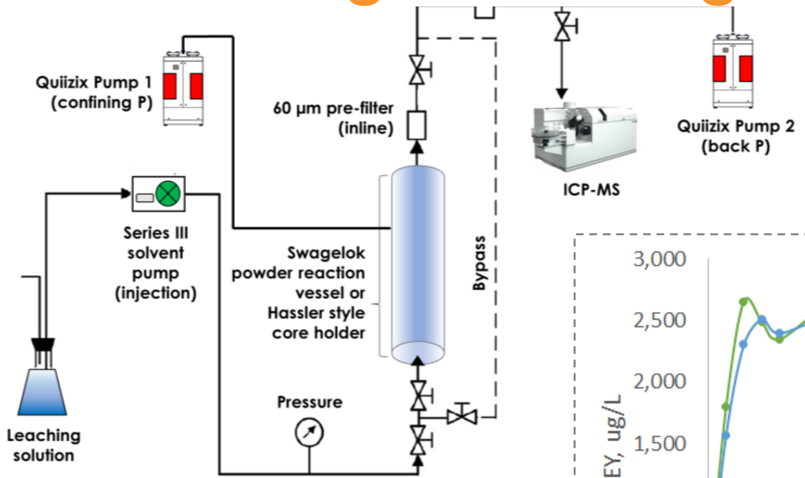


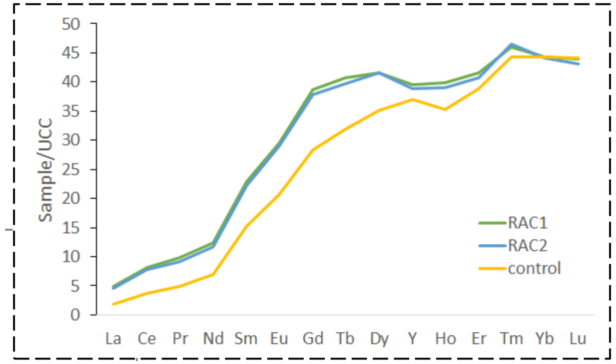
Reduces chemical cost and downstream processing

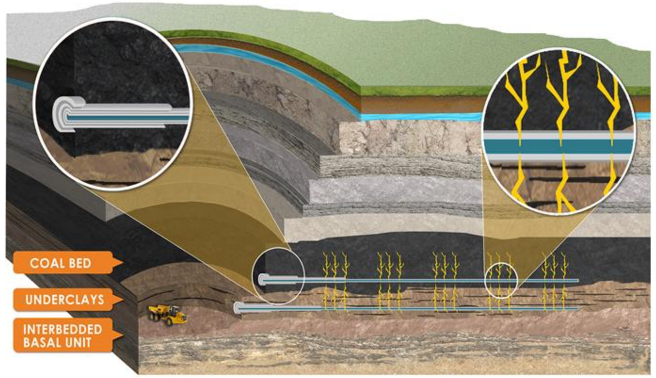
Publication: Montross et al. 2020, **Leaching of ionically bound rare earth elements from Central Appalachian coal seam underclays.** Minerals Special Issue: Leaching of Rare Earth Elements from Various sources. 10(6), 577.

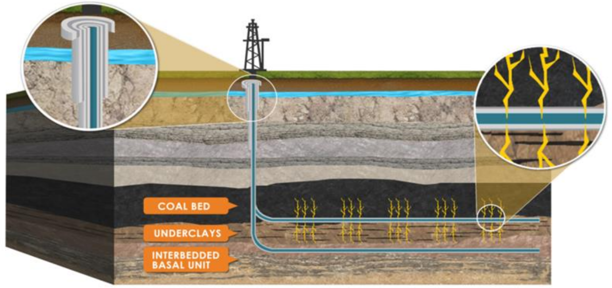
In-situ applications: underclay-coal partings

Flow-through & rocking autoclave experiments





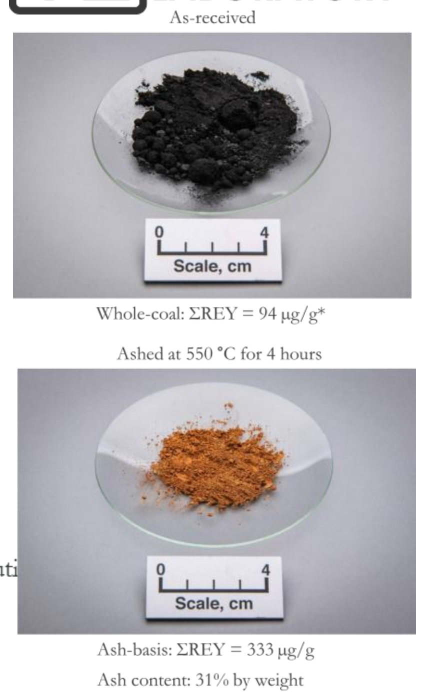


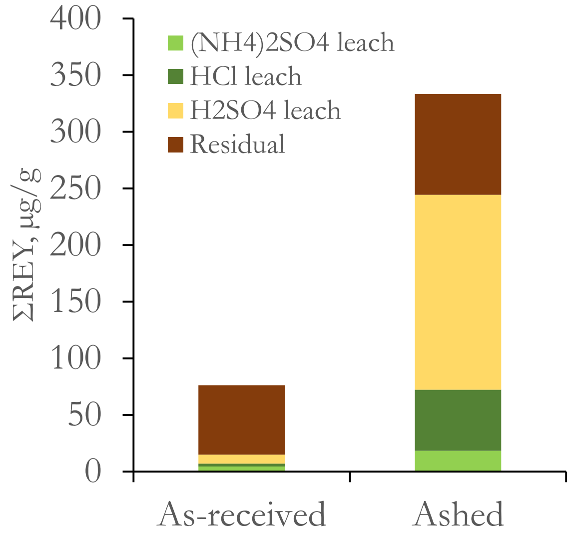


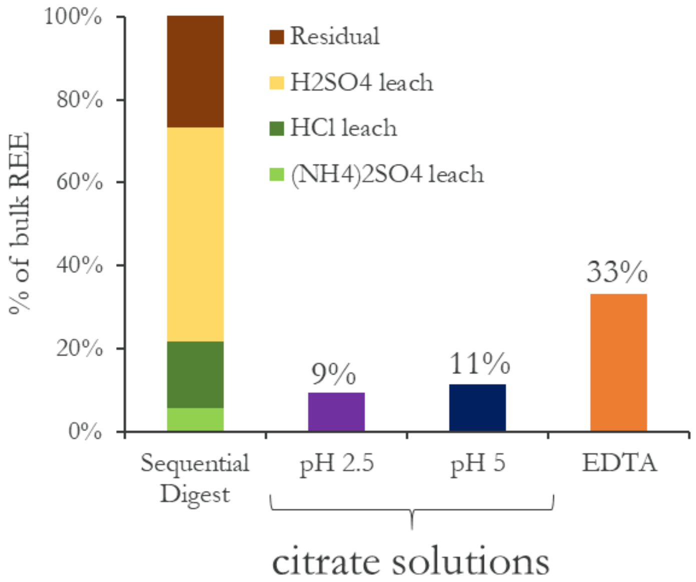
- Simulated downhole testing ranging from 20 min to 30 days; limited extraction <2.5%
  - 2-7 days for maximum REY extraction (lithology dependent)
- Citrate solutions show tendency towards **heavy REE recovery** relative to light REE
- Recycling solution will play a role to improve recovery

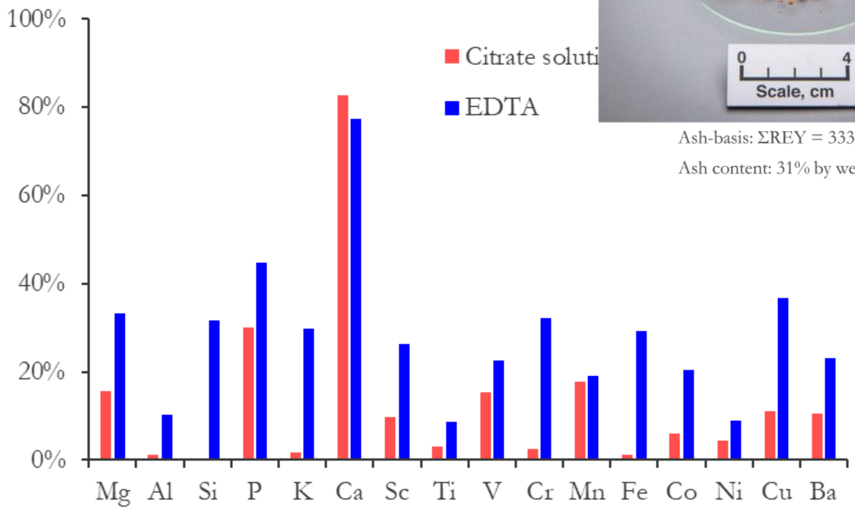
Waste Coal heap leaching applications

- National Mine Corp prep plant in Isabella, PA (Fayette Co.): coal plant fines requires heat treatment to condense REE with citrate(6% as received to 11% ashed)
- EDTA is a strong chelator extracting up to 33% REE, but releases 15-80% gangue elements and other metals; high MREE/HREE: LREE









Publication: Yang, J., Montross., S., Sanville, H., **Verba, C.** *Evaluation of the Rare Earth Element Feedstock Potential of Coal Preparation Refuse*. In review

Collaboration & Planned Next Steps

NATIONAL ENERGY TECHNOLOGY LABORATORY

Coal waste & underclay

- Partnership with West Virginia Geological & Economic Survey → several closed and active mines supplied mine wall and refuse (200+ lbs rock)
  - S. West Virginia: Hernshaw mine
  - N. West Virginia: Leer mine
- Conversations with potential licensees: Contura Energy, Consol Energy, Arch Coal, National Steel Co (operated by National Mines Co), Amerex, Interest to apply technology to South American mines

- ➢ Validation & repeatability in laboratory REE recovery efforts (2020-2021)
  - ➢ Ex-situ: Crushed rock:
    - ➢ 55-gal barrel batch mixing – EY19 delay due to unfavorable feedstock
    - ➢ 5 → 15 kg gravity testing
  - ➢ In-situ: Powdered rock → rock core + recycled solution
- ➢ Planning field testing sites/ small scale demonstration contingent on partners

Coal waste & underclay as a feedstock: Preliminary Market Analysis

The United States consumes more than 900 million tons of coal per year.*

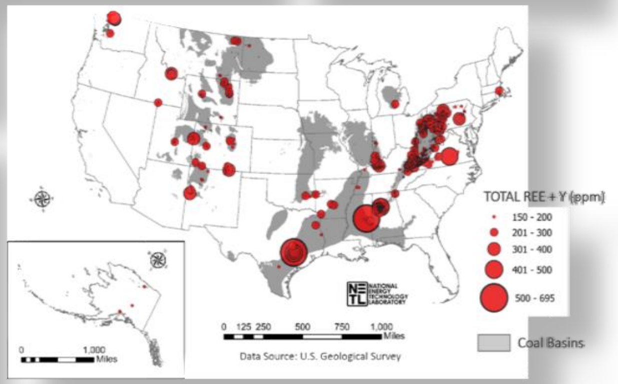
- 2 billion yards^3 coal refuse in Pennsylvania
- 10 million tons annually in Virginia
- 120 million tons of coal refuse from over 600 coal preparation plants in 21 coal-producing states.

Estimated REE value (total value / ionically extracted):
$6.2 - $250 billion / **$2 - $950 million**** in 23 coal-producing states

Market assessment:

- Citrate is ~4x lower than conventional mineral acids
- Citrate recycling would reduce operating costs further

Up to 50% of coal mined is left on the ground as waste.



** Waste material estimates from: ARIPPA 2019; RPM Solutions 2019
* Assuming 300 ppm, every ton of coal refuse may have $24 in raw REE value; 1 cubic yard is 1.3 tons of coal refuse with 30% extraction.

Conclusions To-Date

Status of REE Extraction Research

Material	Method	TRL	Recovery % (projected)	Impurities
AMD Solids	Seq. Extraction	3	4% - 72+% (>80%)	Co, Cu, Fe, Mn, Ni, Zn
Ca-Rich Ash	Seq. Extraction	3 - 4	40 (>80%)	Al, As, P
Underclay	Mild Acid	2 - 3	25 (33%)	<5% Al, Fe, K, Si
Waste Coal	Mild Acid	2 - 3	1.5% (20% solids)	Ca (60%), P (7%), Si, Al, K (0.2-5%)
Fines (ashed)	Mild Acid	2-3	11%	15-80% Al, Fe, Cu, etc

On-Going and Future Work:

- Optimization of Extraction Conditions
- Collaborate for further separations
- Collaborate for scale-up and field testing

Next-Steps: Enabling Domestic Innovation

Analysis to Understand Markets, Process Economics, and Potential "Gotchas"

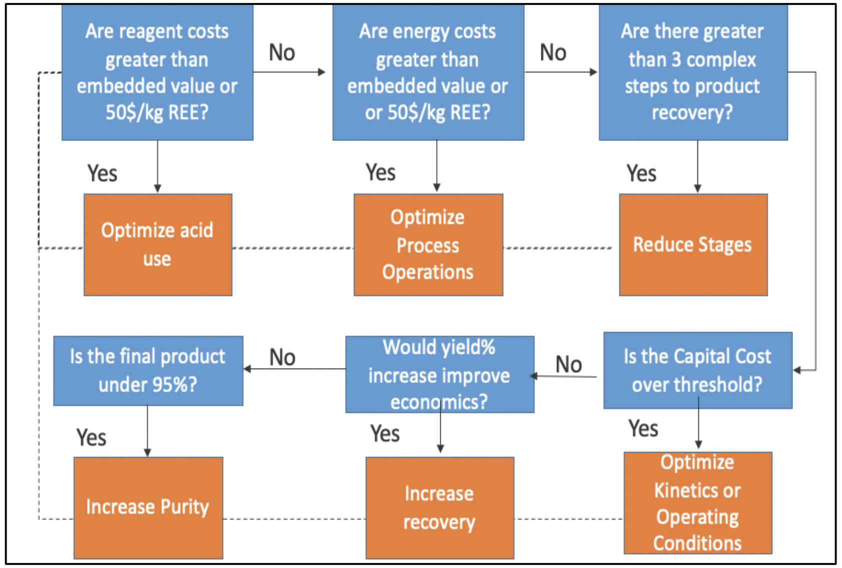
Understanding the Current State of the Art

- Techno-Economic Analysis for process economics & performance
- Life Cycle Analysis (LCA) for wholistic view

Reducing Development Time & Cost

- Process Screening to identify potential bottlenecks & guide research
- Sensitivity Analyses to Identify Major Cost & Performance Drivers
- Net Result: to inform best practices to aid in resource development

Process Development/ Optimization Decision Tree



REE Production Process Flow Sheet example

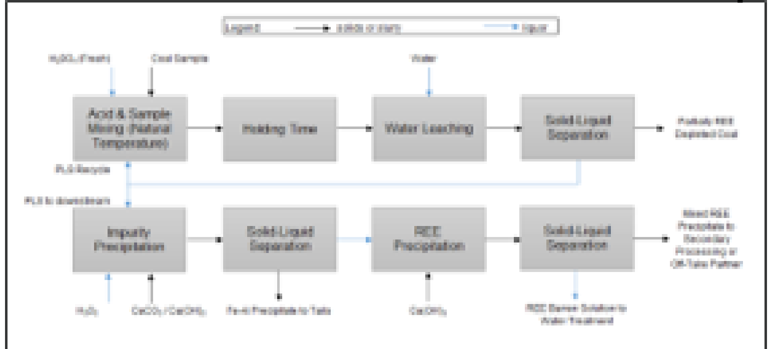


Figure I: Conceptual Flowsheet #1 – Sulphuric Acid Route

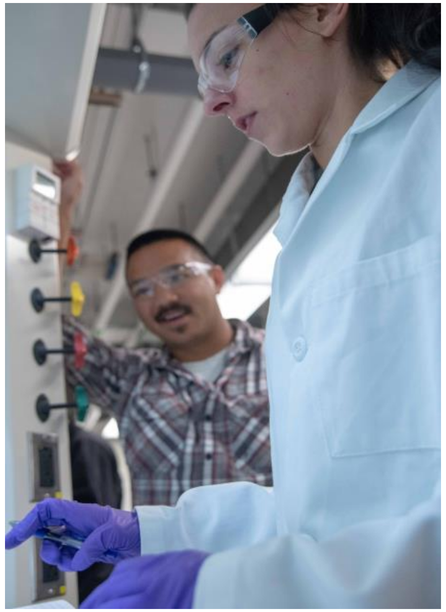
Sources: [1] USGS, [2] Adamas International and Argus Media, [3] "Pilot-Scale Testing of An Integrated Circuit for the Extraction of…", R. Honaker, University of Kentucky, Annual REE Review Meeting, Pittsburgh, PA, April 2018.

Acknowledgements

- NETL's REE Research Team and Management
- Brianna O'Neil-Hankle (MLEF; NETL)
- Sam Webb, Nick Edwards, and Sharon Bone (SSRL).
- Jim Britton, Ronald McDowell, Jessica Moore (West Virginia Geological Survey)
- Morgan Mosser (Leonardo Technologies)
- Stanley Sears (Greene Energy Resource Recovery)

This project was supported in part by an appointment to the Science Education Programs at NETL administered by ORAU through Oak Ridge Institute for Science and Education.

The synchrotron work was conducted on beamlines 2-3, 4-3 and 10-2 at the Stanford Synchrotron Radiation Lightsource (SSRL), a national user facility operated by Stanford University on behalf of the Department of Energy, Office of Basic Energy Sciences, through the Structural Molecular Biology Program, supported by DOE Office of Biological and Environmental Research and the National Institutes of Health.



SSRL