Sequential Separations Chemistry

Presenter & PI:

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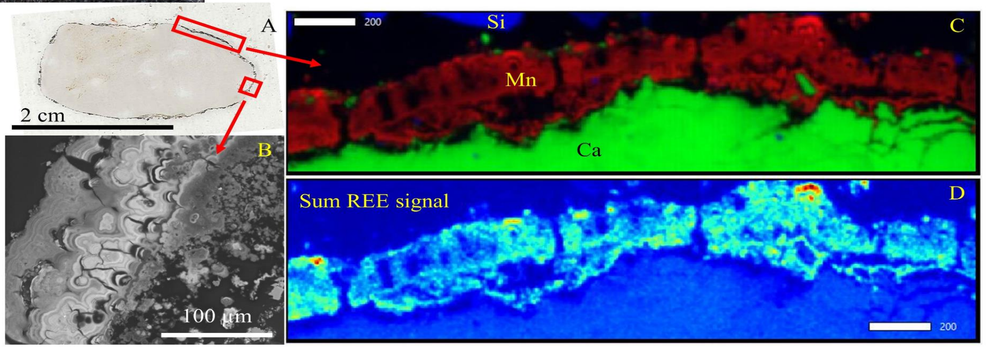

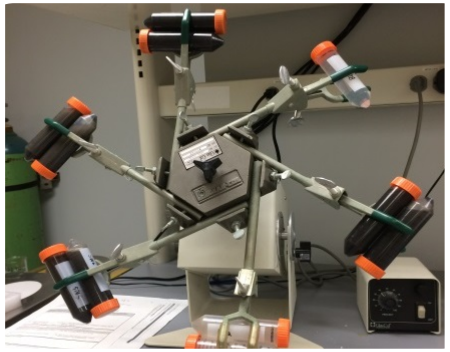

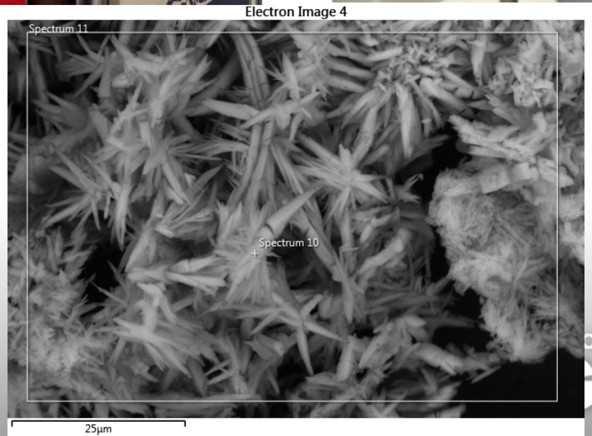

RIC Portfolio Strategy

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

Opportunity for Coal-Based Feedstocks

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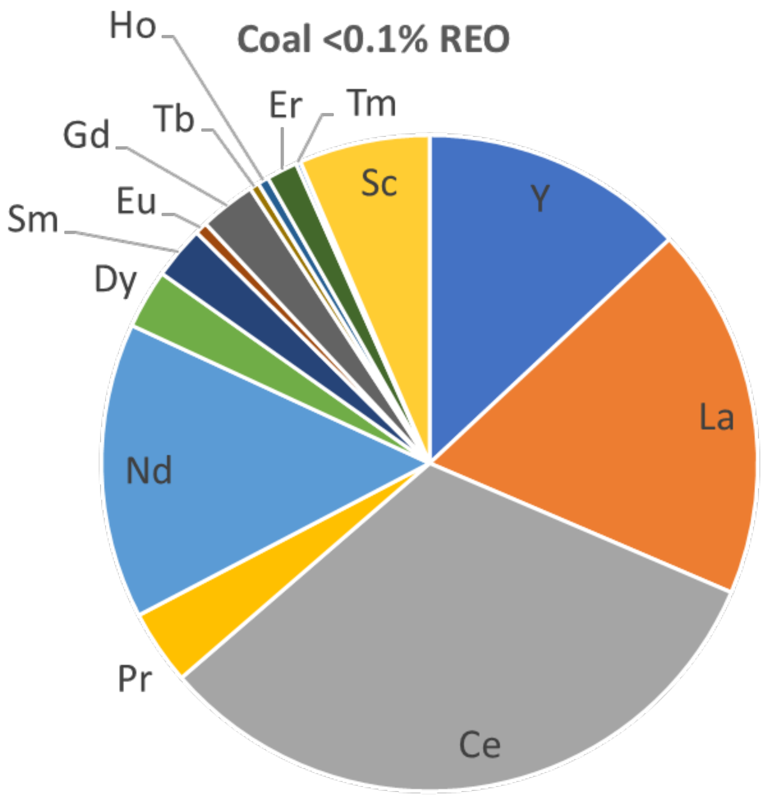
Filling the First Gap to a Domestic REE Supply Chain

- Coal-based feed sources include:
  - Coal (anthracite, bituminous, subbituminous, lignite)
  - Coal refuse
  - **Fly ash**
  - **Acid mine drainage (AMD)**
  - Mining underclay and shale
- These feed sources could be utilized with other domestic REE resources to produce the foundation for a domestic REE supply chain



Key: Little-to-no U, Th

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 3.2)

Results compared to benchmark:

- **80% reduction** in reagent consumption
- Reduction in process steps/complexity: e.g. **no pre-treatment (grinding, floatation) and reduction of solvent separations**
- Reduction in process intensity: **ambient temperature and pressure**
- **Patent pending for sequential separations from coal refuse and AMD solids***

How have project goals changed?:

- Pandemic hindered some upscaling laboratory work to a certain extent
- Increased focus on maturing technologies:
  - Rapid move to larger scale experiments
  - Validation on representative feedstocks provided from industrial partners

Industry input/validation:

- Partnered with key collaborators on the ground in Wyoming for PRB powerplant refuse
- TCF is facilitating pilot-scale projects are underway/development with industry partners

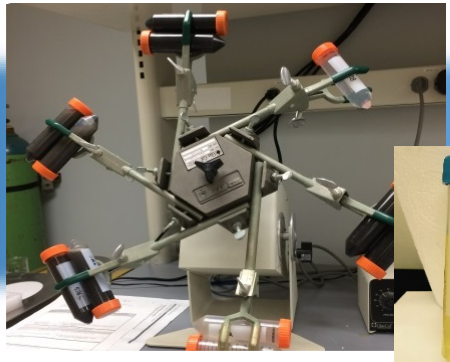
*Stuckman, M.Y., Lopano, C.L. and Tarka, T. (2020) U.S. Provisional Application Serial No.: 63/053,925

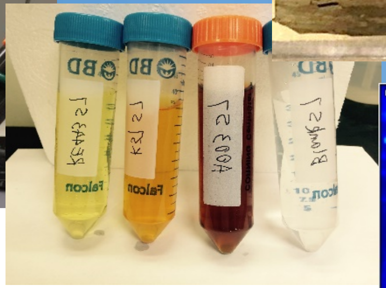
Understanding the resource

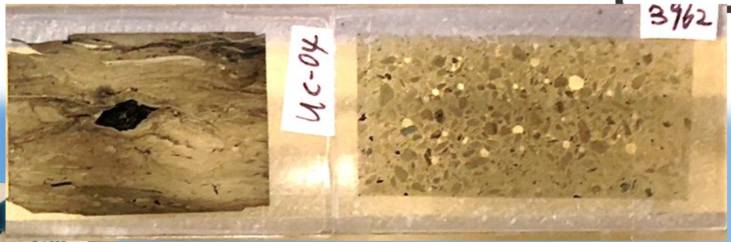
Ash & AMD Characterization to Recovery

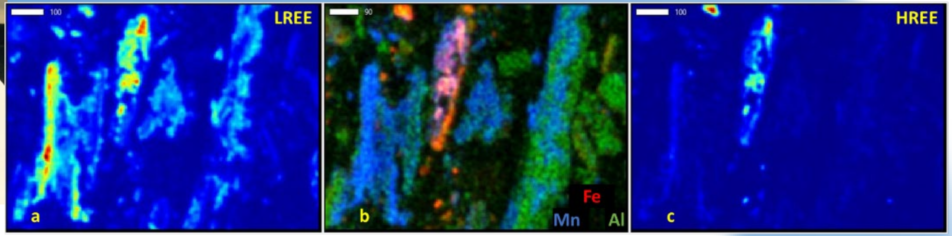
AMD solids

Fly ash



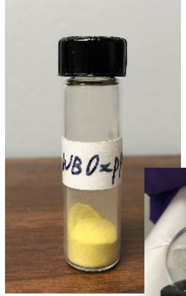


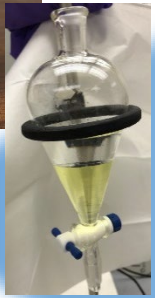


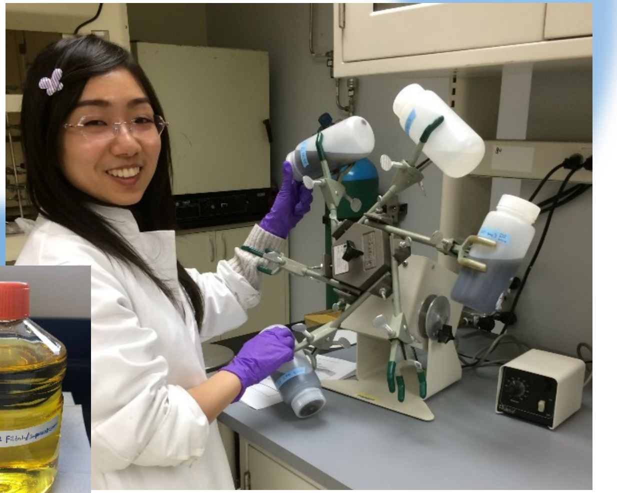


Utilize sequential extraction techniques to **characterize** major REE-hosting solid fractions in different CCBs and to **innovate targeted extractions** for efficient and economical REE recovery.

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

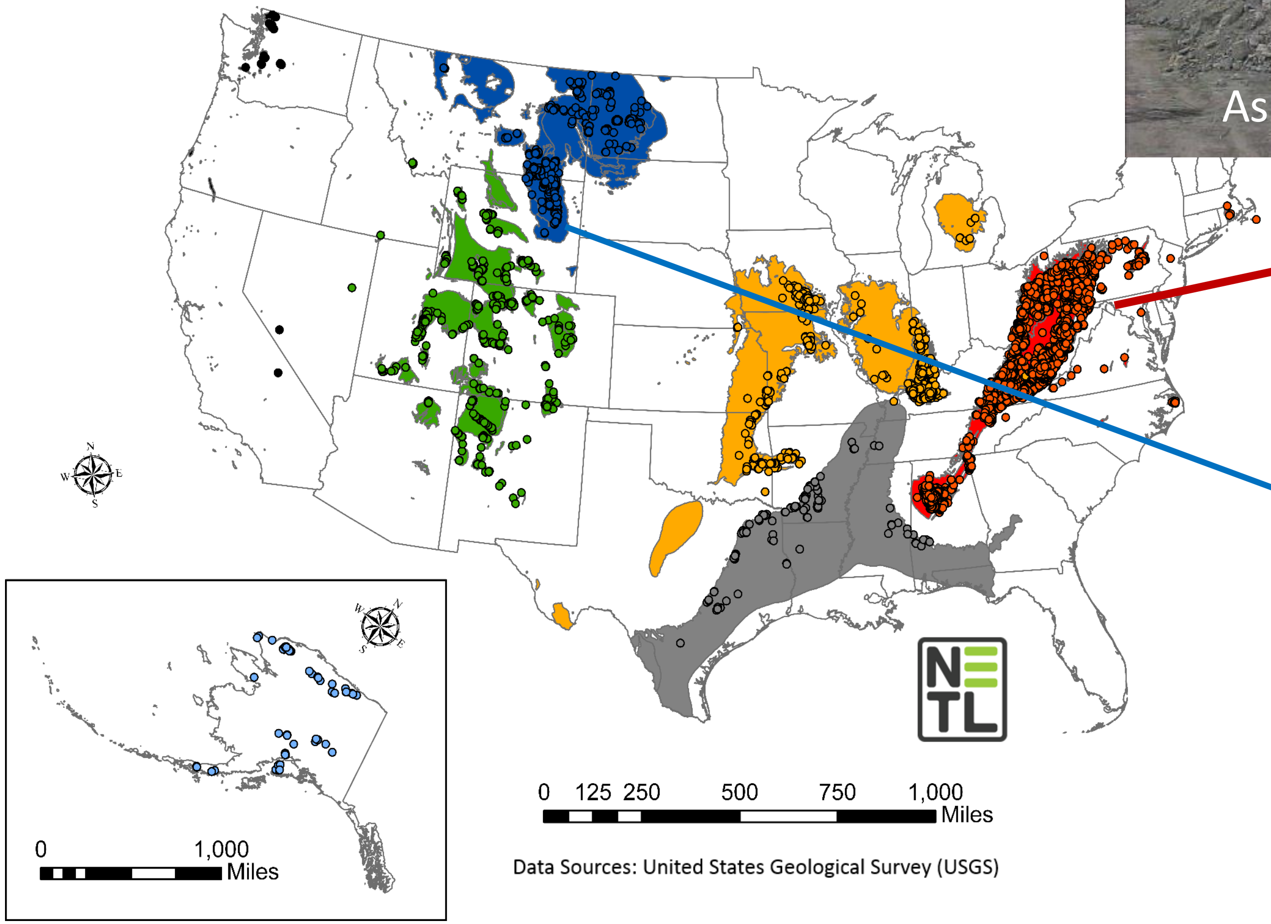


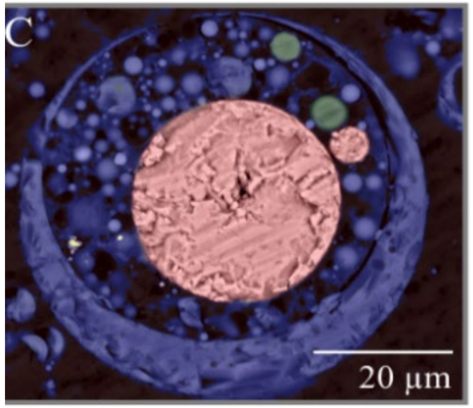




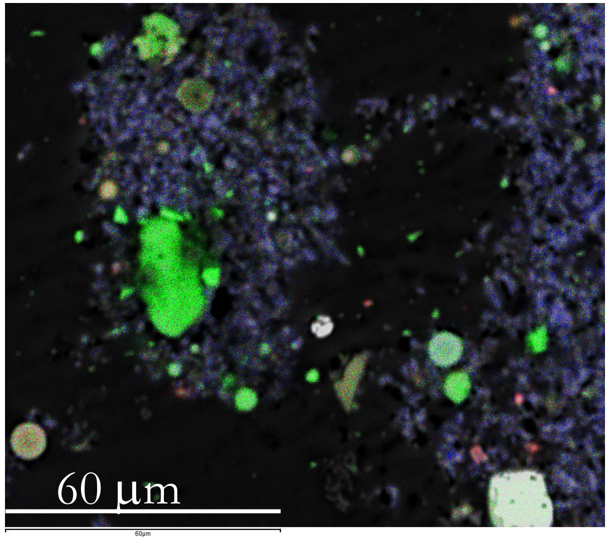
Coal Combustion Ash wastes

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



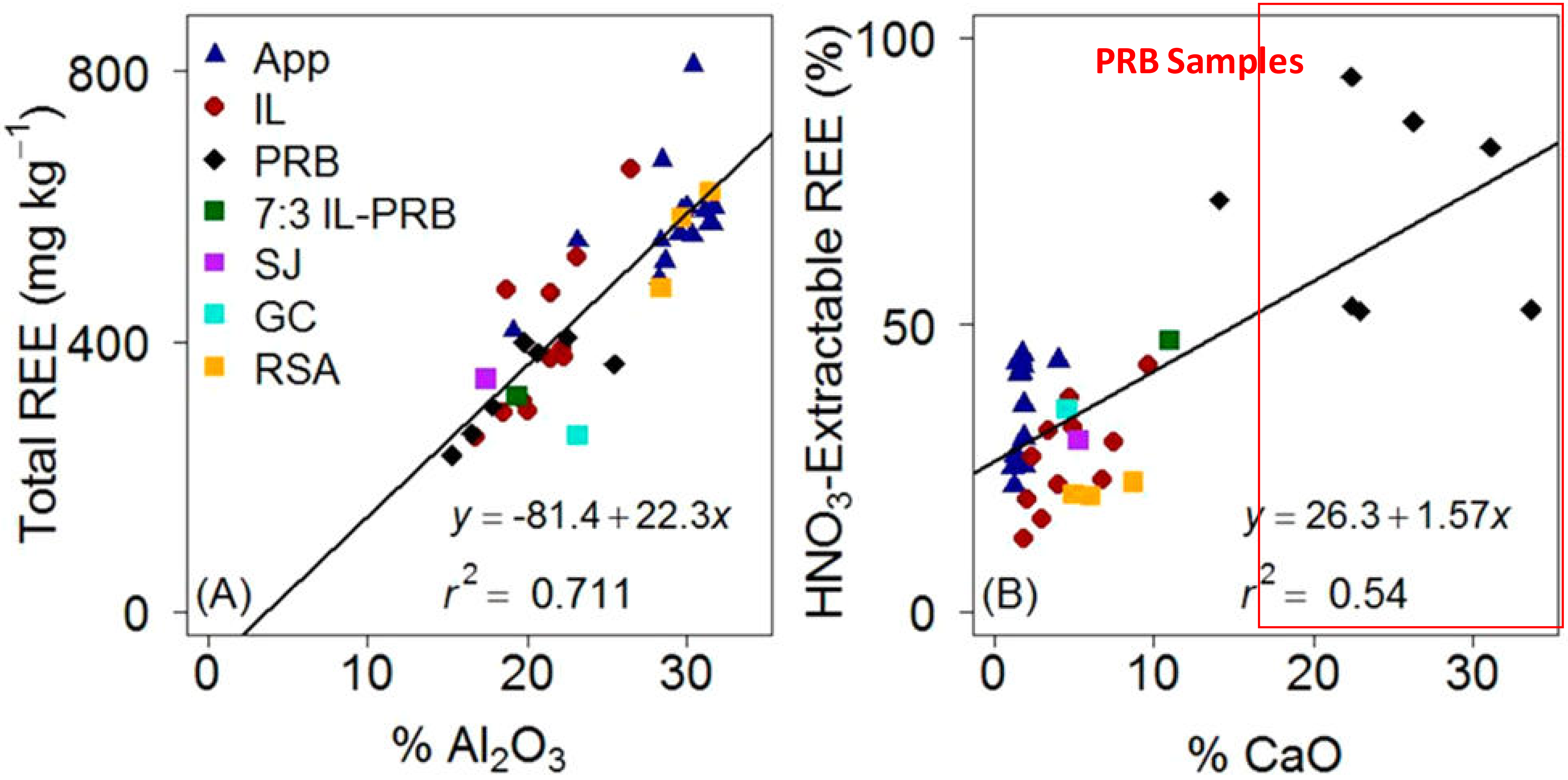


SEM BSE image of fly ash particle
Phases identified:
amorphous Si-Al -purple
Fe-oxide - red
Ca-oxide - green
REE mineral - yellow



REE recovery potential from PRB Coal byproducts

Ca-rich Ash samples from Powder River Basin (PRB) have more mobile REEs compared to Al-rich Appalachian ash, due to different REE binding nvironments (Ca/Mg oxides as opposed to glass phase) during coal combustion.



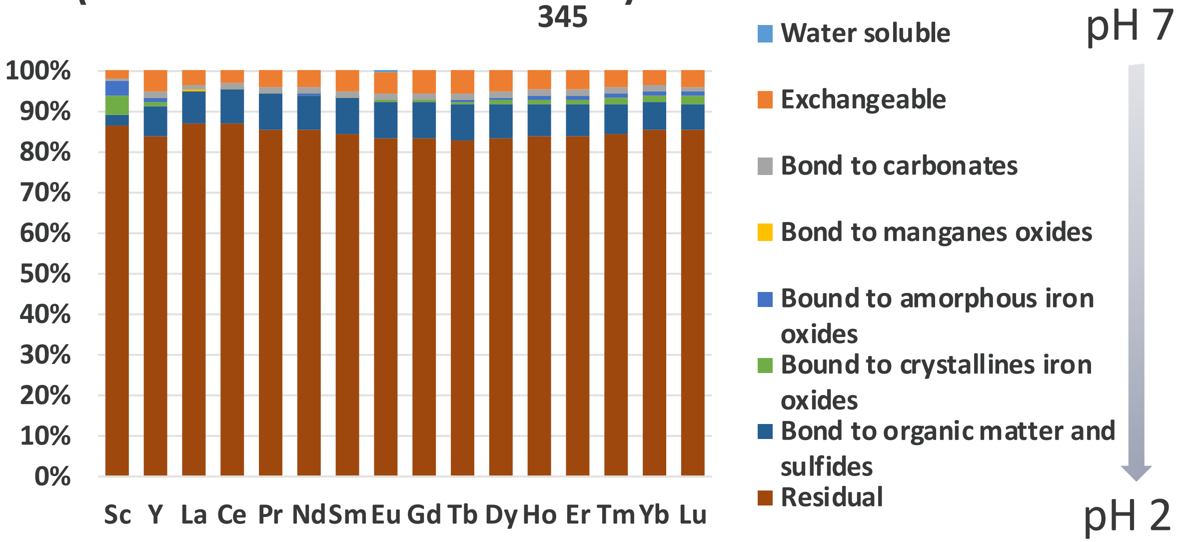
Taggart, R.K., Hower, J.C., Dwyer, G.S., Hsu-Kim, H., 2016. Trends in the Rare Earth Element Content of U.S.-Based Coal Combustion Fly Ashes. Environmental Science & Technology 50, 5919-5926.

Sequential Extraction for Characterization

Appalachian Ash versus PRB Ash

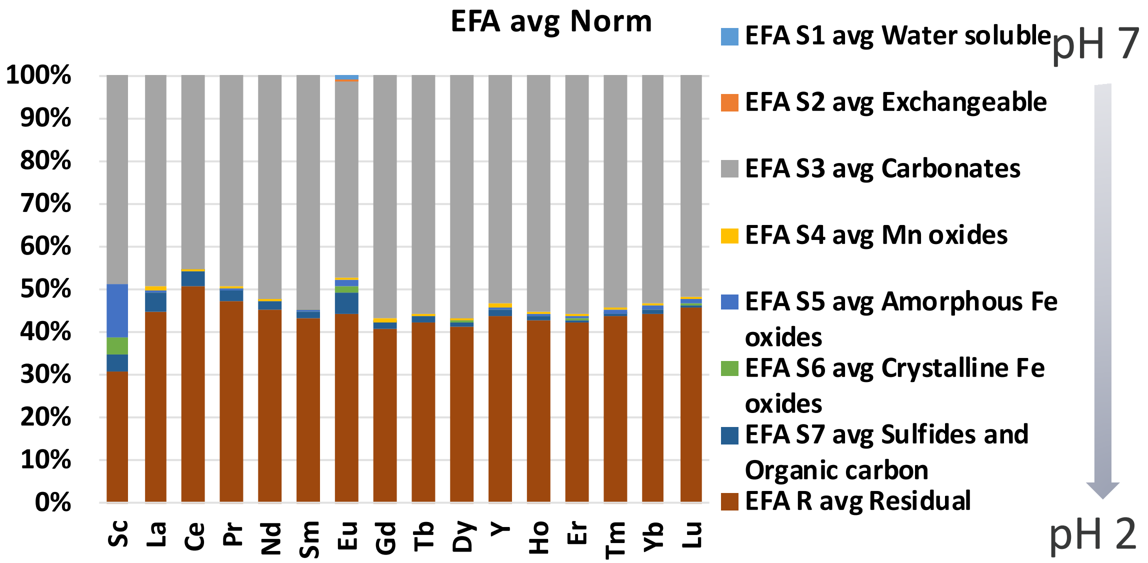
<u>Fly Ash 345 (313ppm REE+Y)</u>

- derived from Appalachian Basin coal (4%wt Ca)
- REE associated mainly with Residual phase (aluminosilicates)



<u>EPRI-FA (264ppm REE+Y)</u>

- derived from Powder River Basin coal (20%wt Ca)
- >60% REE released in "carbonate" phase extraction

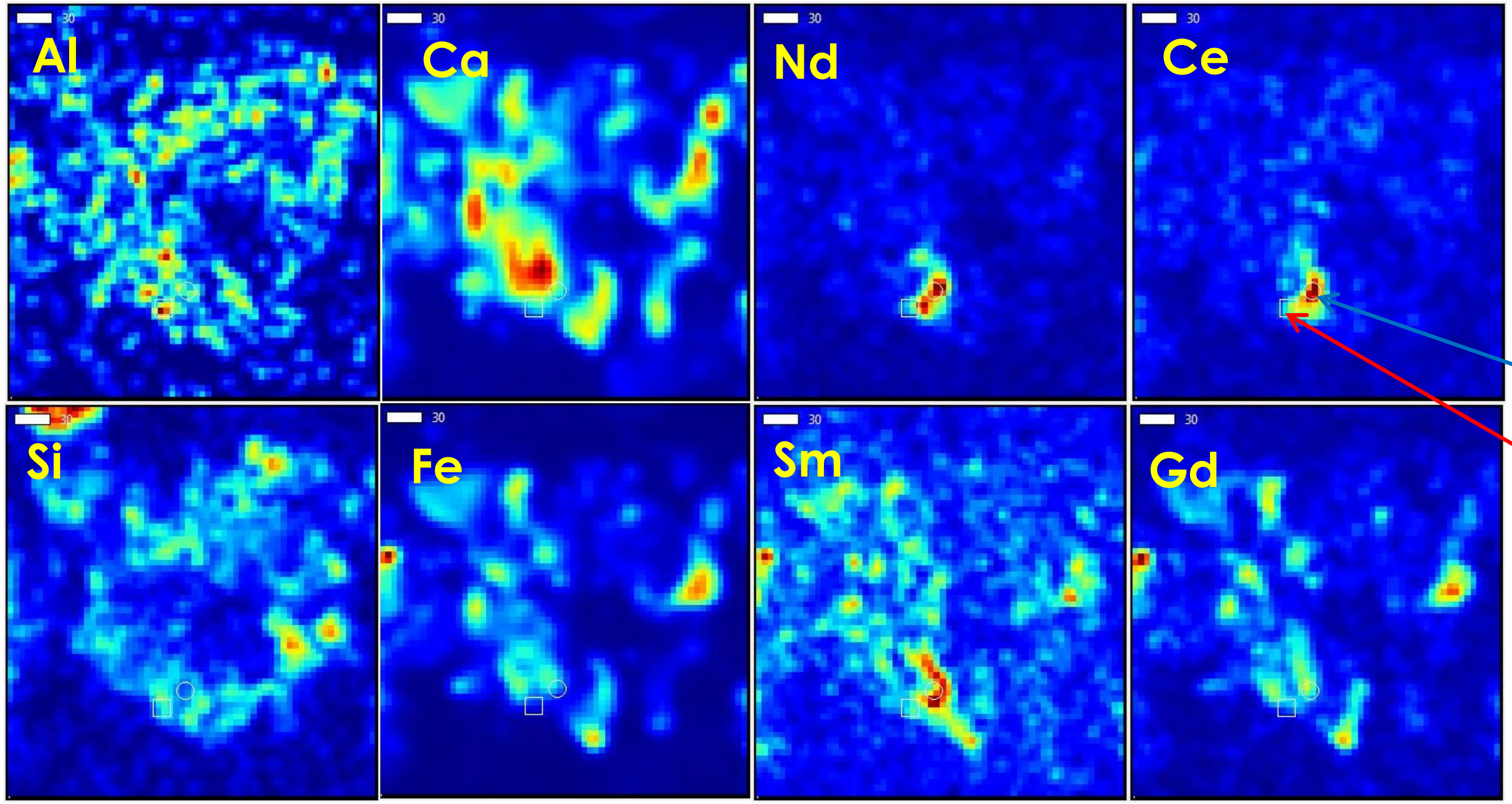


Lin, R., Stuckman, M., Howard, B.H., Bank, T.L., Roth, E.A., Macala, M.K., Lopano, C., Soong, Y., Granite, E.J., 2018. Application of sequential extraction and hydrothermal treatment for characterization and enrichment of rare earth elements from coal fly ash. Fuel 232, 124-133.

PRB ash: Synchrotron Micro-analysis

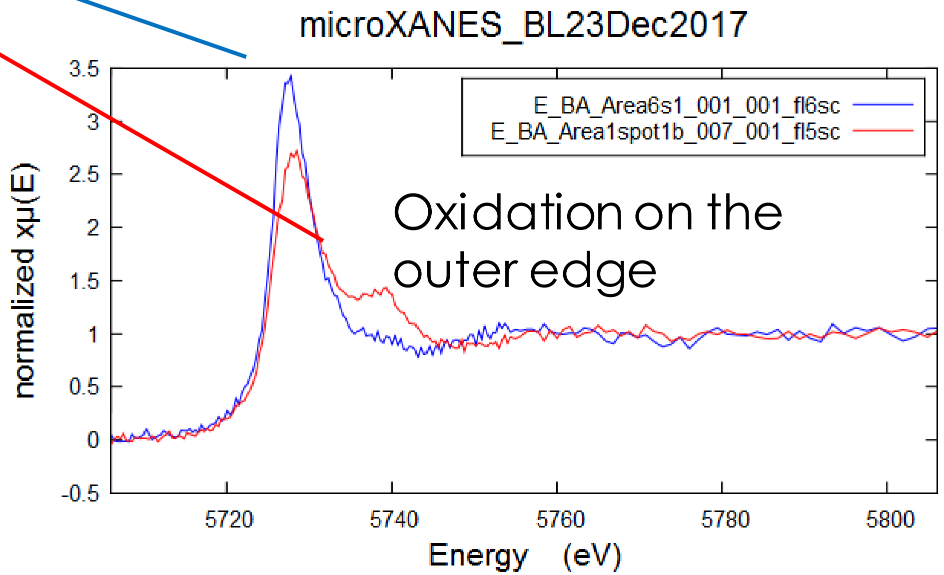
Example:Ca-, Mg-rich Bottom Ash

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



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

Ce(III) + O2 = Ce(IV)O2



Stuckman et al. (2019), PCC

Characterization Informing Extraction

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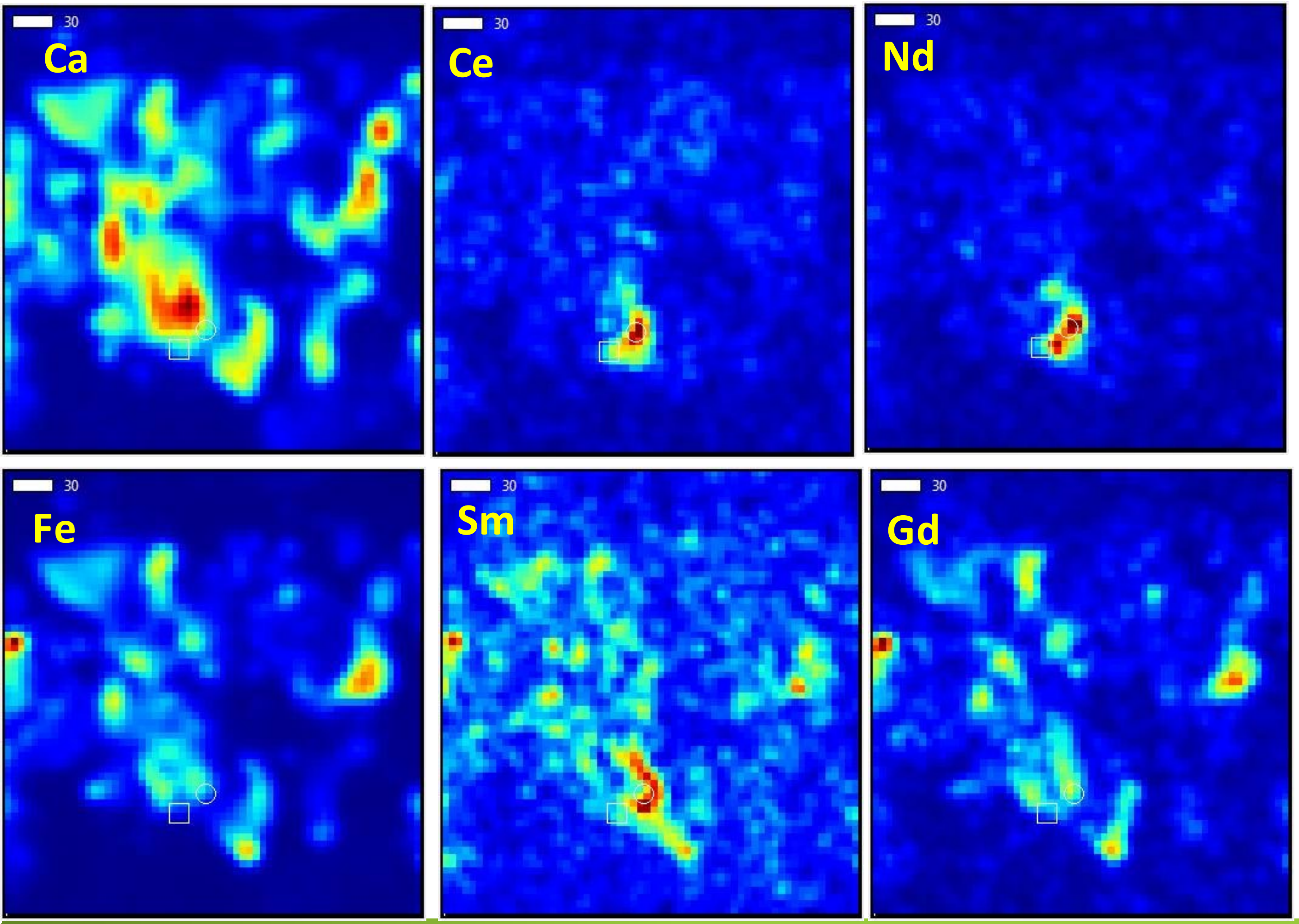
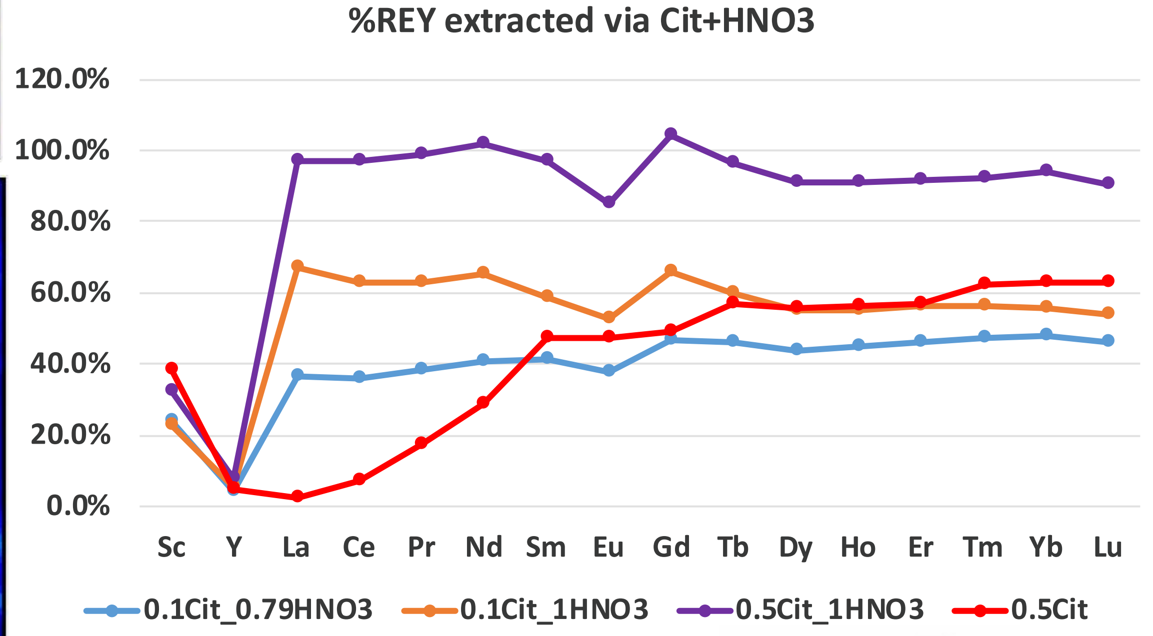
Example: Ca-, Mg-rich CCBs

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

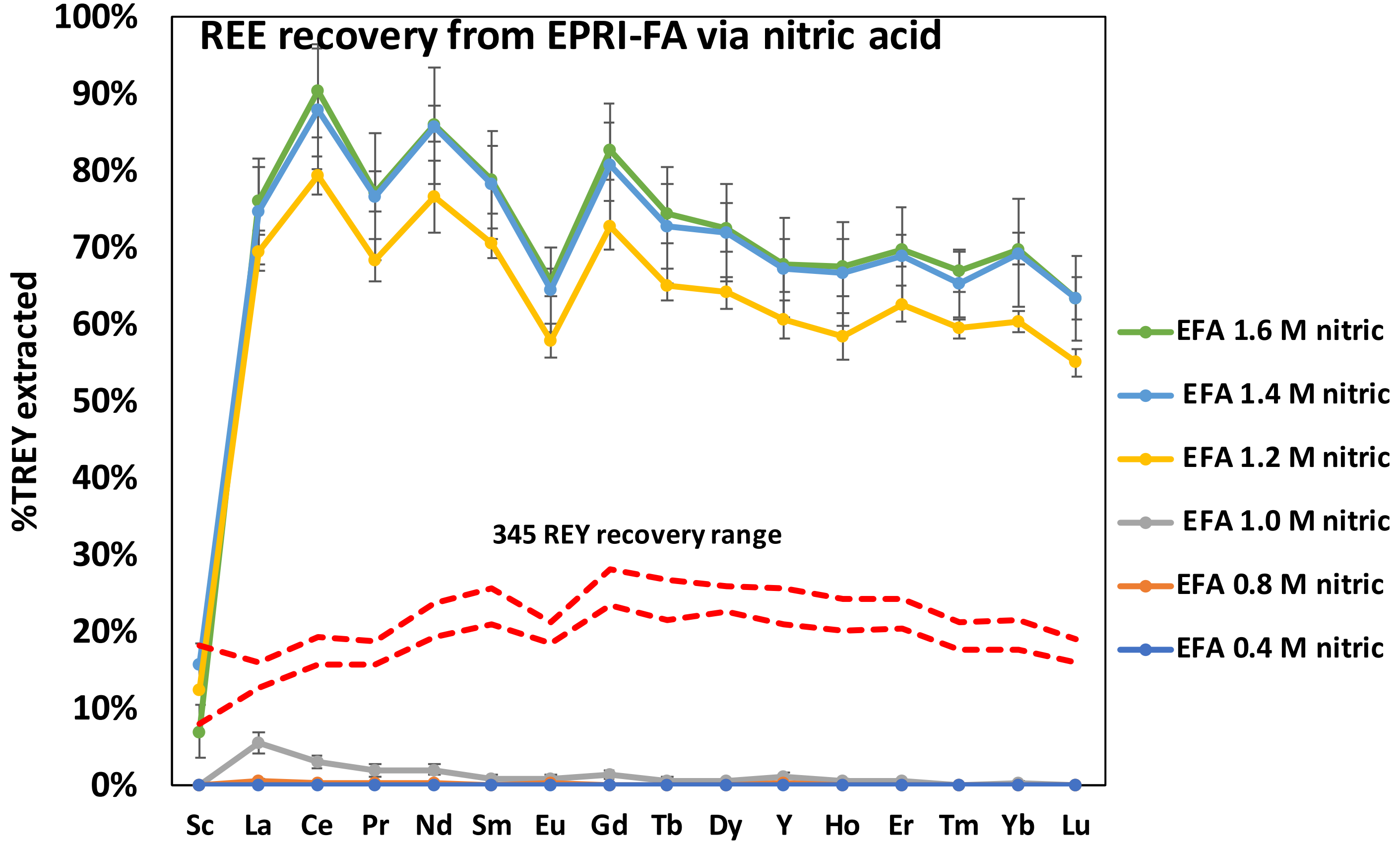


- HNO_3 targets acid soluble Ca phases (e.g., CaO, $CaCO_3$), end pH<4
- Citric acid targets Fe mineral phases
- Notice 0.5M Cit can selectively extract 60% HREEs (Sm-Lu) and 40% Sc, targeting dissolution of REE in Fe phases



Take-Away: Characterization and Recovery

Inorganic Acid Extraction Test: PRB vs AP Fly ash



- Compared to AFA, REY from PRB ash samples can be mobilized under relatively simple conditions
- Diffused in Ca-rich glass rather than trapped w/in Al-Si glassy phases
- Ce is readily oxidized & accessible
- Acid will first dissolve Ca phases and then REYs together with Al and Fe

diluted acid and room temperature, L:S ratio = 10:1, 24 hr on rotator

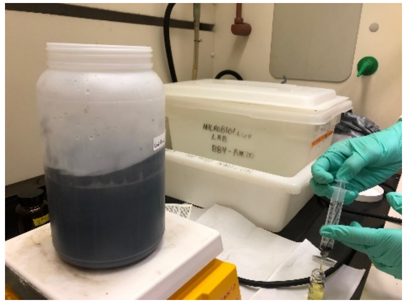
Stuckman et al. (2019), The International Pittsburgh Coal Conference

Recovery from Calcium-rich Ash

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

- **<u>80% extractability</u> achieved at <u>room temperature</u> using simple sequential leaching.**
- **<u>Reduced acid consumption</u> by targeting ash portion**
- **Addresses existing and legacy waste product**
  - Previous investigations into REE extraction from fly ash required additional processing steps to achieve >10% recovery

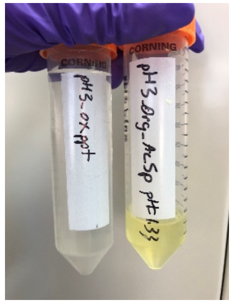
Fly Ash



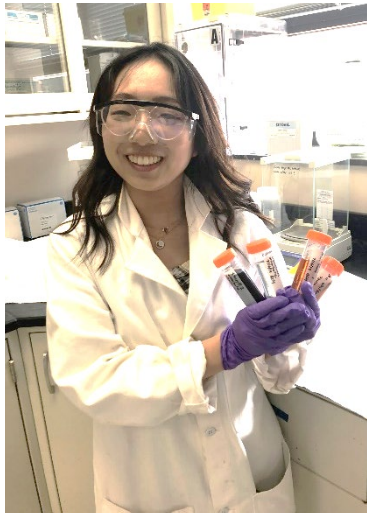
Step - Leaching

Extraction

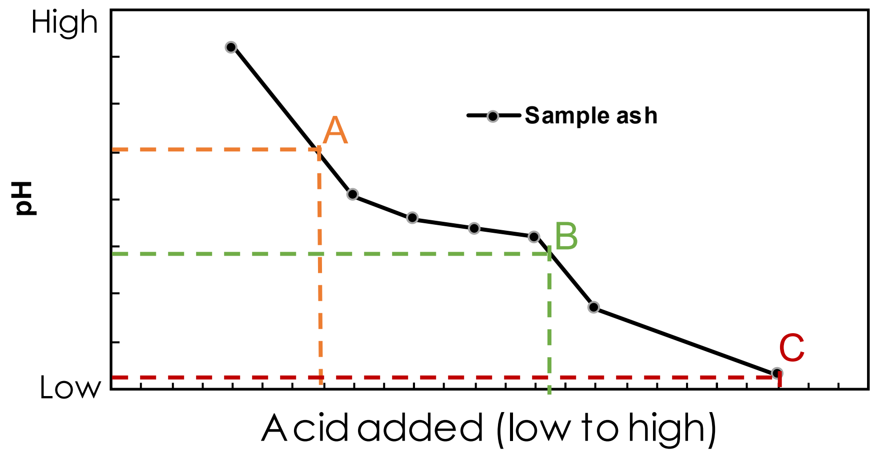
Stripping



Precipitation



pH titration curve for step leaching

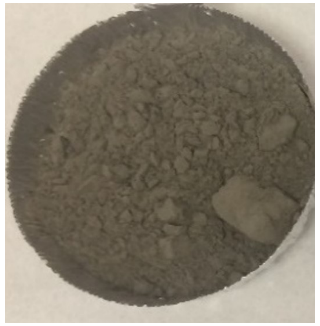


Stuckman, M.Y., Lopano, C.L. and Tarka, T. (2020) U.S. Provisional Application Serial No.: 63/053,925

Recovery from Calcium-rich Ash (TCF)

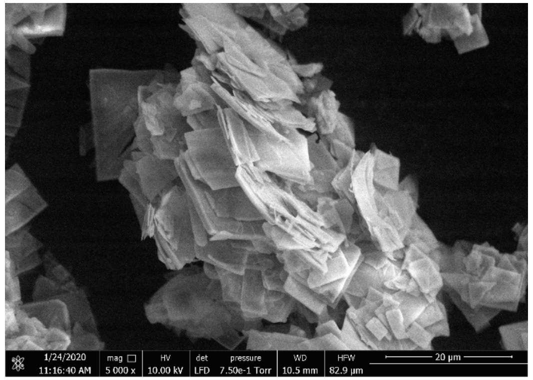
Targeting Powder River Basin (PRB) Ashes to Reduce Extraction Steps & Conditions

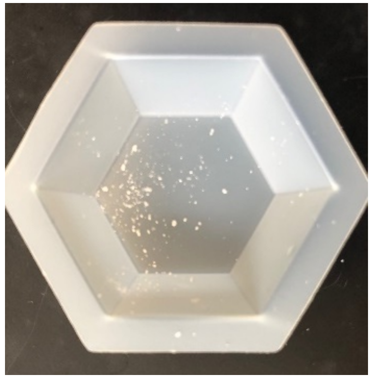
PRB Fly Ash



U.S. Provisional Application Serial No.: 63/053,925

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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Recovery from AMD Treatment Wastes

Passive Remediation Systems Produce a Stable, REE-Rich Material

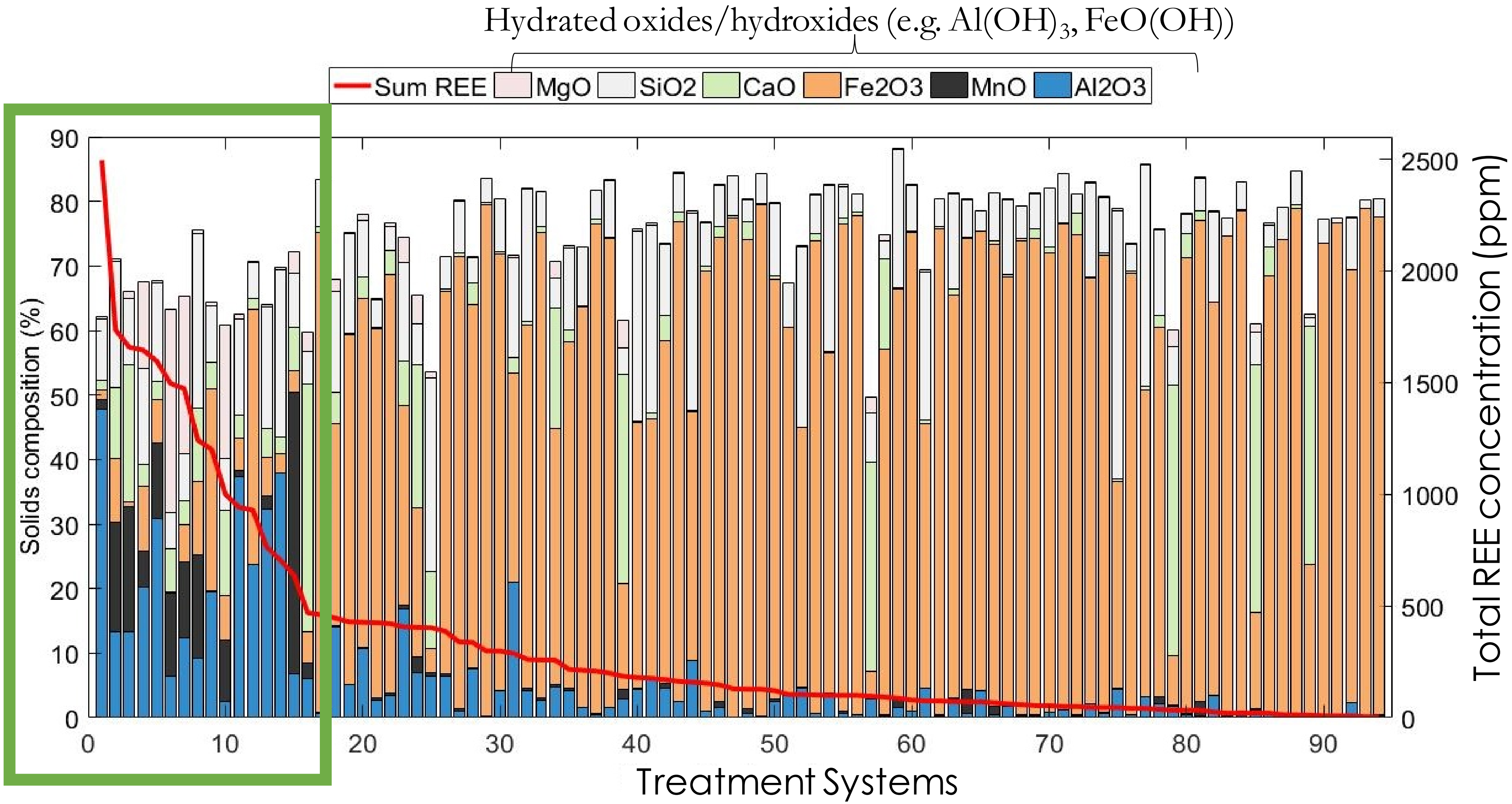
- <u>REE and other critical metals</u> (e.g. Co, Ni, Zn) precipitate from AMD
- Higher concentration (>1,500 ppm) resource
- REE value could result in widespread deployment of low-cost AMD cleanup systems
- Passive remediation beds serve as Natural Analogs

> - How are the REE & CM bound?
> - Can this information be used to inform novel sorbent and recovery technologies?

Photos courtesy of B. Hedin (Pitt)

Major Composition ~100 AMD solids

Solid compositional trends w/ REY



- ~50% critical REE
- 1.8 LREE:HREE
- <50 ppm U, Th
- Not classified as hazardous waste
- $3 to $400 REE value / tonne dry solid
- Similar or greater concentrations of CM (Co, Ni, Zn)

Characterization of AMD treatment solids

Hedin et al., IJCG, 2019: Appalachian AMD: 1,102 tons / year REO recovery potential (~12% US annual demand)

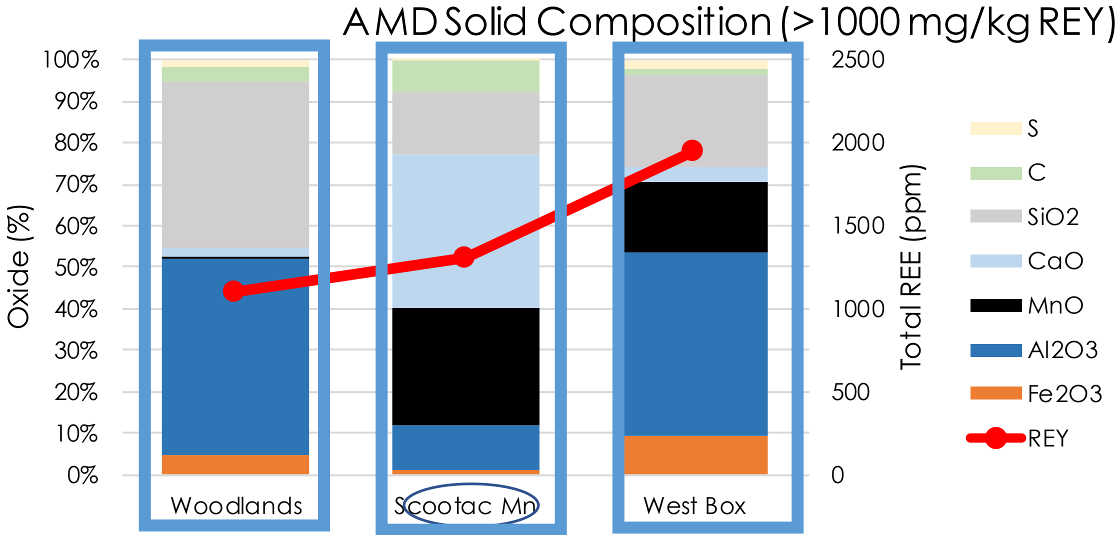
Characterization found **REYs in Al, Mn and Fe phases** in different solids

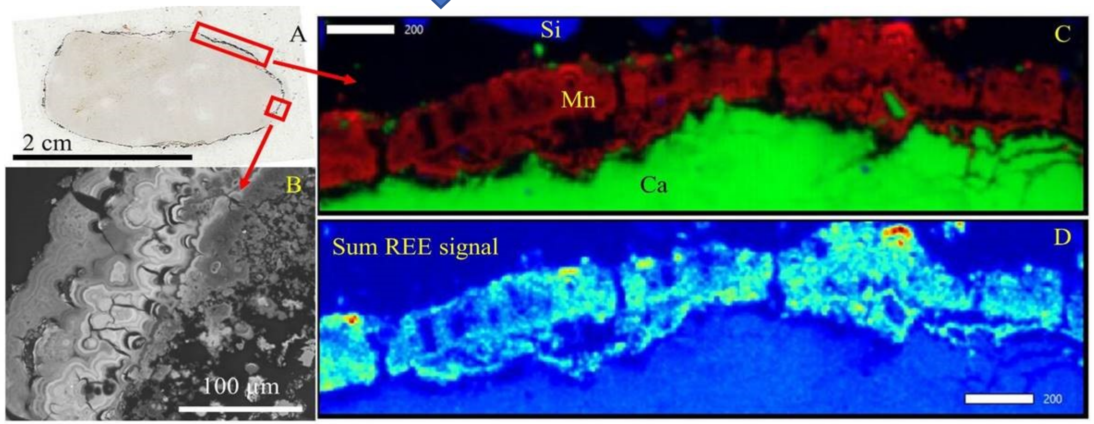
Remediation beds (limestone)

Woodlands (Al-rich)

Scootac Mn (Mn-, Ca-rich)

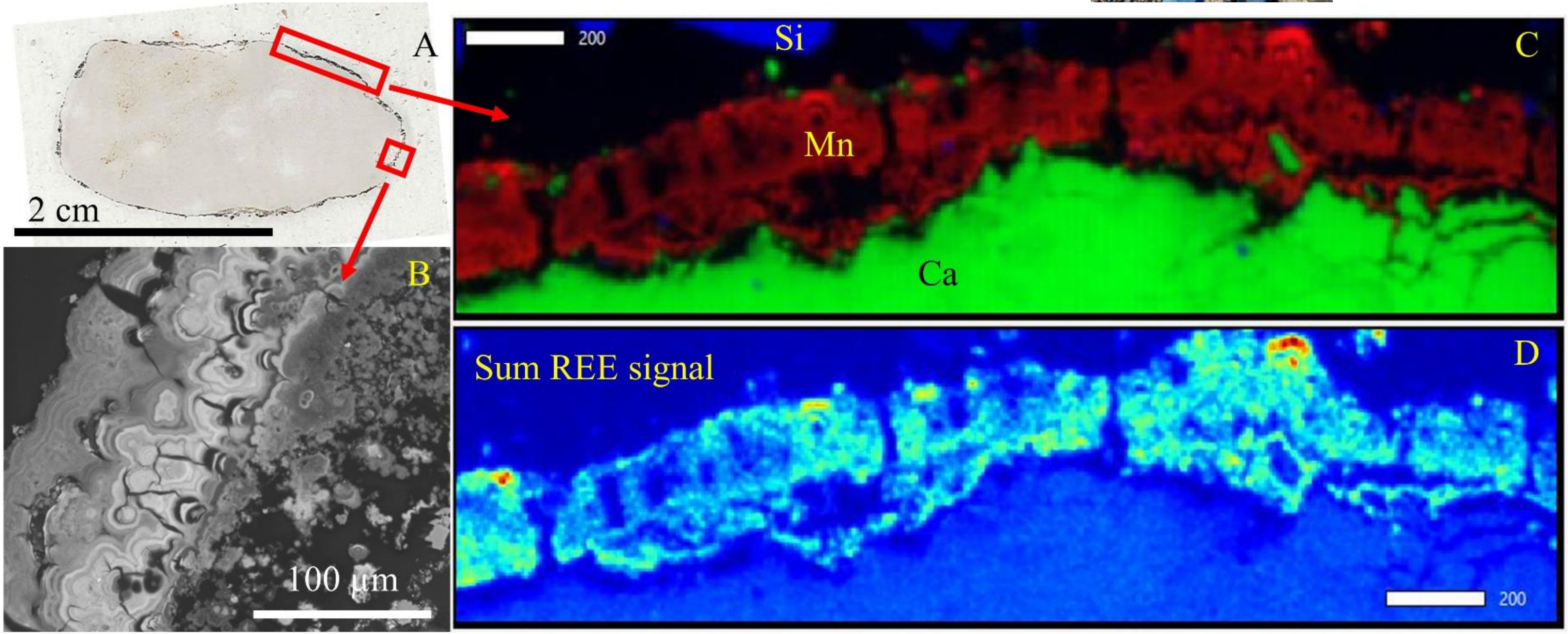
Westbox (Al-, Mn-, Fe-rich)





Example: Characterization to Recovery

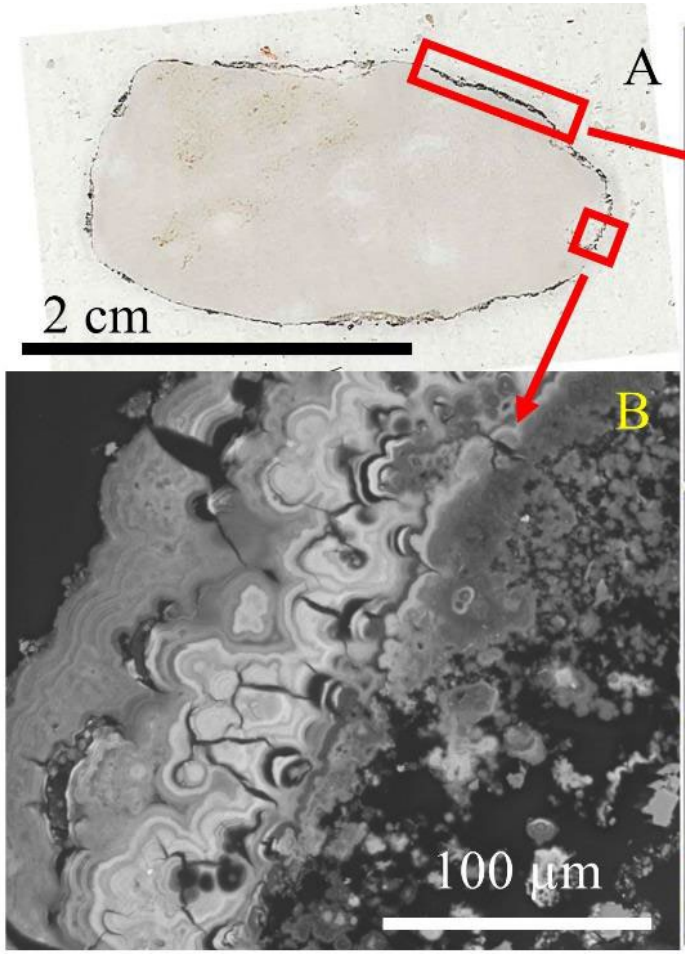
Synchrotron analysis identifies REE-hosting phases in AMD remediation solids

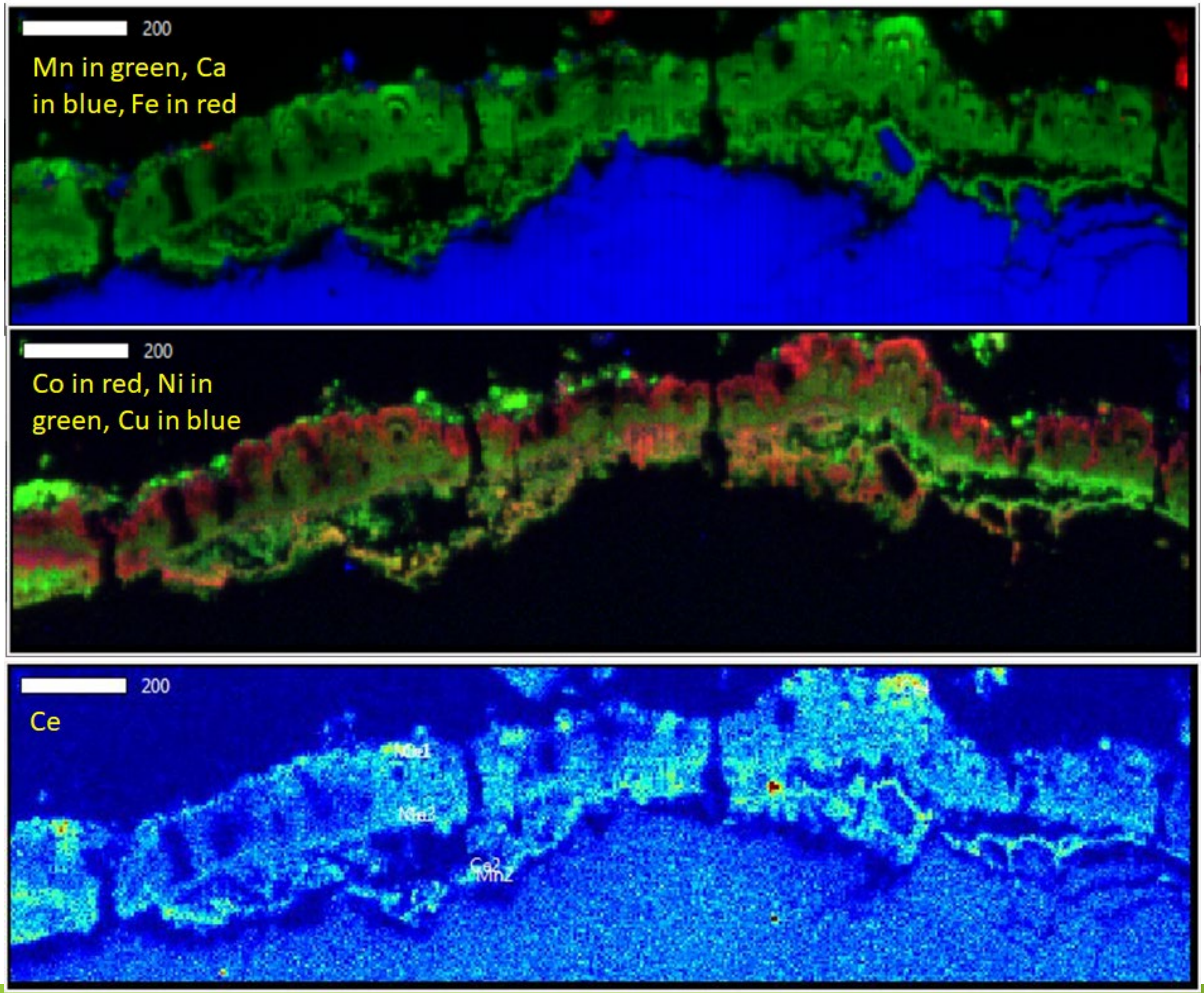


Strong correlation with Mn-oxides

Critical Metals: Scootac-Mn

Associations w/ Mn – but distributions vary





Co-localization vs. co-recovery

Leaching trends inform binding environment

REY (Ni,Li&Zn) release with Al, Mn and Fe

- surface complexation

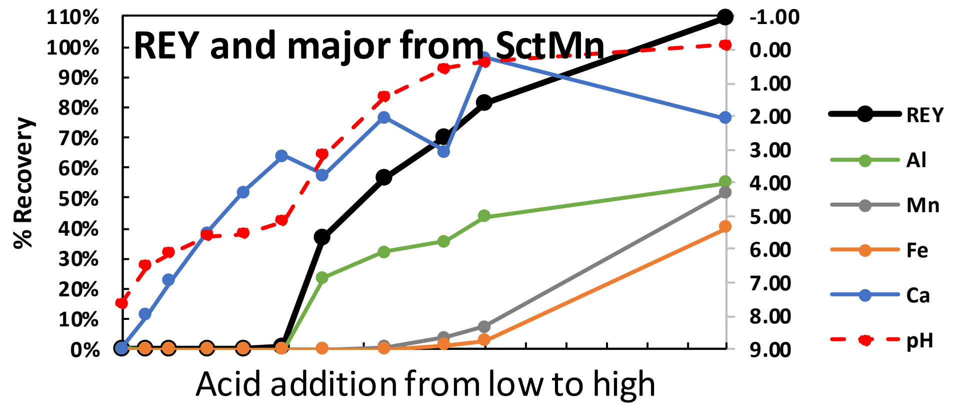
Ce & Sc release at lower pH

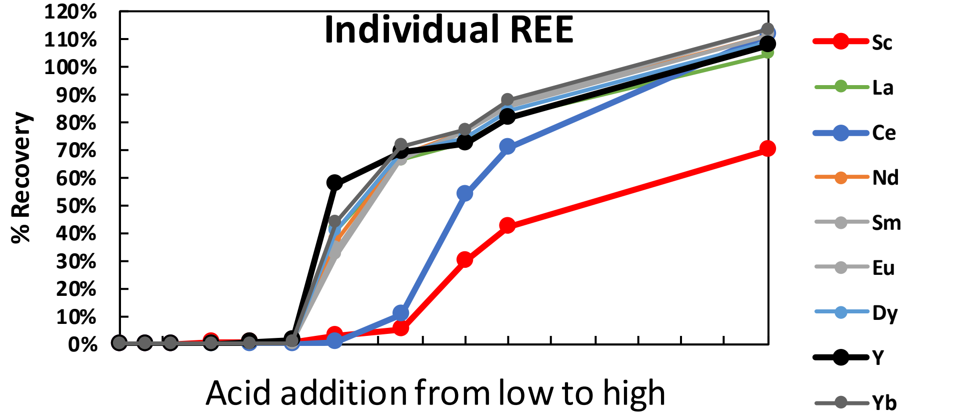
- Ce(IV) bound with Mn phase
- Sc bound with Fe phase

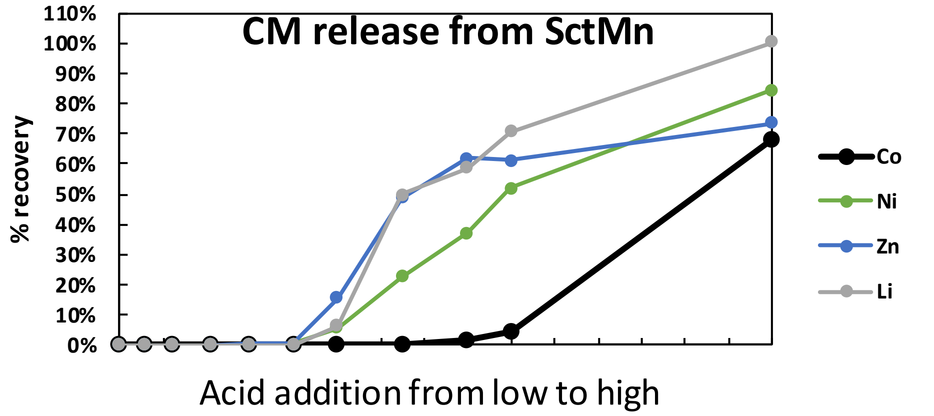
Critical metals (esp. Co) release with Mn

- Substitution into the Mn-O octahedral crystal structure

Can treatment be engineered to optimize these reactions?





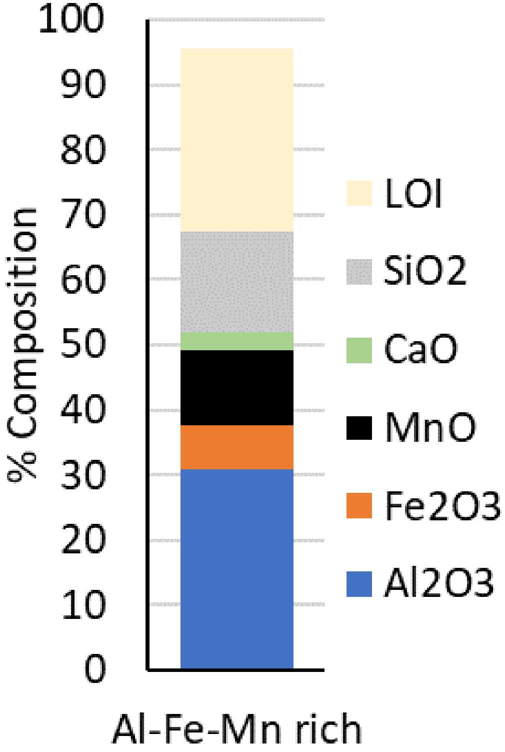


Proof of Concept: AMD Solids

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

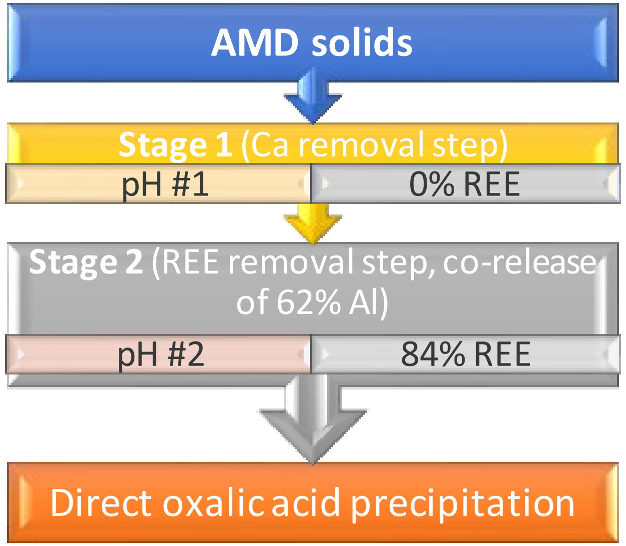
Westbox (Al-, Mn-, Fe-rich)

1,800 ppm REE

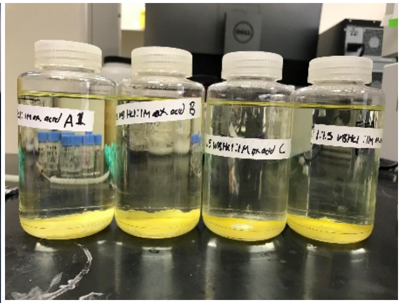


Hedin et al (2019) International Journal of Coal Geology

Hedin et al (2021) in preparation

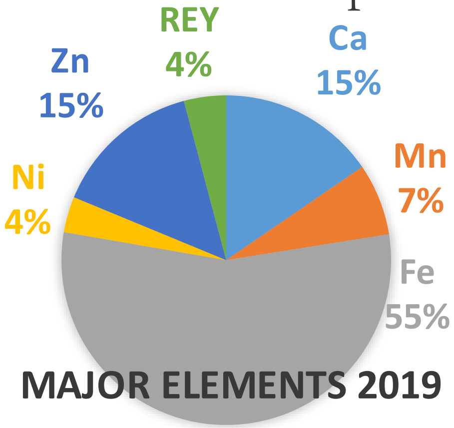


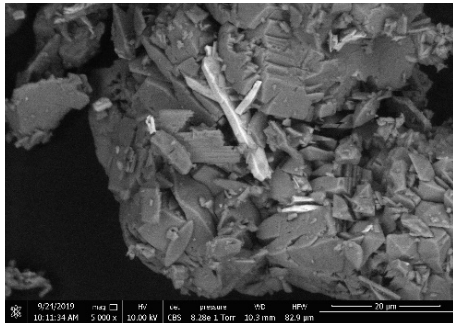
Large scale leachate



Ox precipitation

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





Stuckman, M.Y., Lopano, C.L. and Tarka, T. (2020) U.S. Provisional Application Serial No.: 63/053,925

Sequential Leaching: Benign & Economical

Fly ash ⟷ Ca-rich fly ash

Pretrea…

- Physical separation
- …drothermal treatment
- (… IJCG 2018)
- Roasting

Leaching ⟷ Step Mild Acid Leaching

Extract

Scrub

Strip

Precipitation

REE Oxides

AMD solids

Pretreatm…

- Physical separation
- …thermal treatment
- (… …CG 2018)
- Roasting

Leaching ⟷ Step Leaching

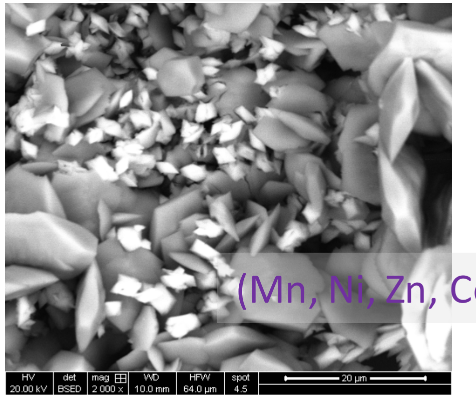
Extract

Strip

Precipitation

REE Oxides ⟷ REEs and By-products

REY oxalates



(Mn, Ni, Zn, Co)Ox

1. Leaching from feedstock (e.g., Fly ash, AMD solids, or underclay)
2. REE purification and separation (e.g., L:L extraction, or sorbent)
3. Oxalic ppt (and oxidation)

Conclusions To-Date

Status of REE Extraction Research

- Utilize advanced characterization to develop innovative extraction and enrichment technologies to unlock the potential of coal to create a domestic REE/CM industry.
- RIC Separations technologies have exhibited the potential to dramatically reduce reagent consumption, process complexity/intensity, and therefore cost compared to existing REE production pathways

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, Fe, P

On-Going and Future Work:

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

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
  - Campbell County, Wy; City of Gillete, Wy; Energy Capital Economic Development
- University of Chicago & Argonne National Lab – approached NETL researchers (Lopano & Stuckman) for support 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 & and detector testing is underway)

Acknowledgements

It takes a village – and coffee

- Dr. Mengling Stuckman (LRST-NETL) – CO-PI
- Tom Tarka – RIC REE Technical Portfolio Lead (NETL)
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- Brianna O'Neal-Hankle (MLEF-NETL)
- Dr. Scott Montross (LRST-NETL) - SEM
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