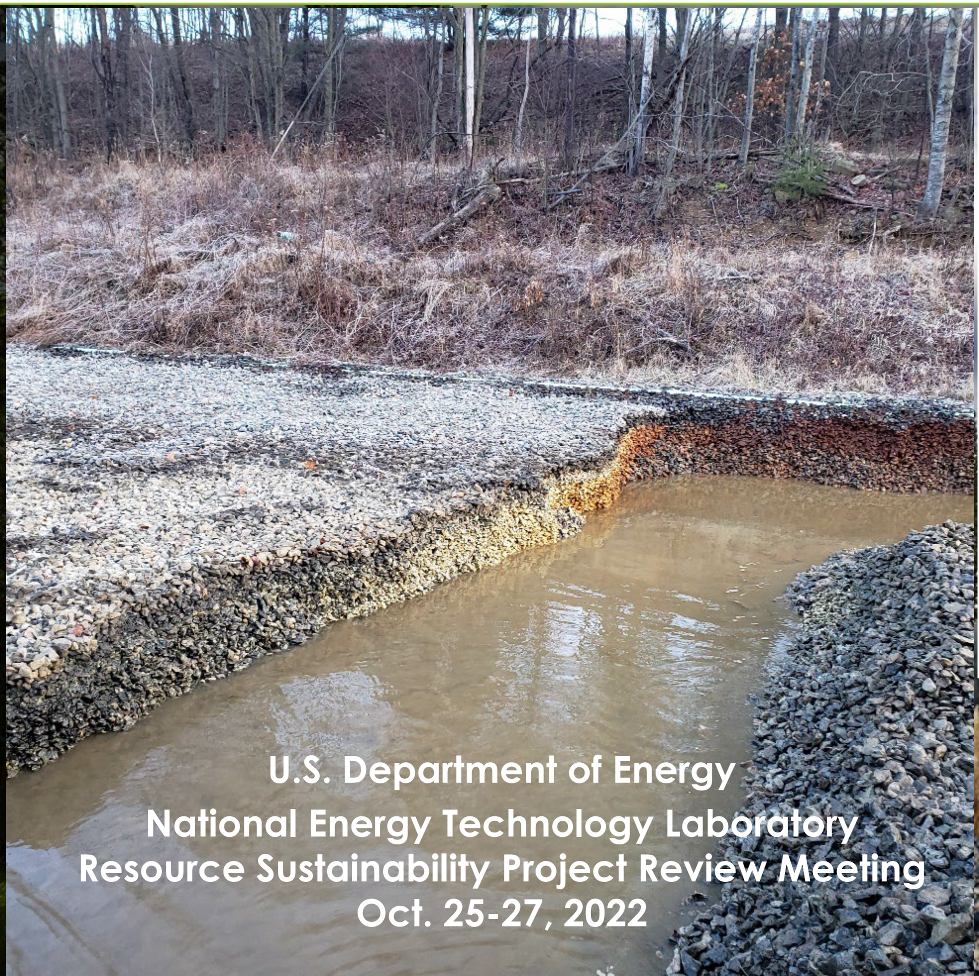
# Characterization-Informed Recovery of Critical Minerals from Acid Mine Drainage Treatment Solids

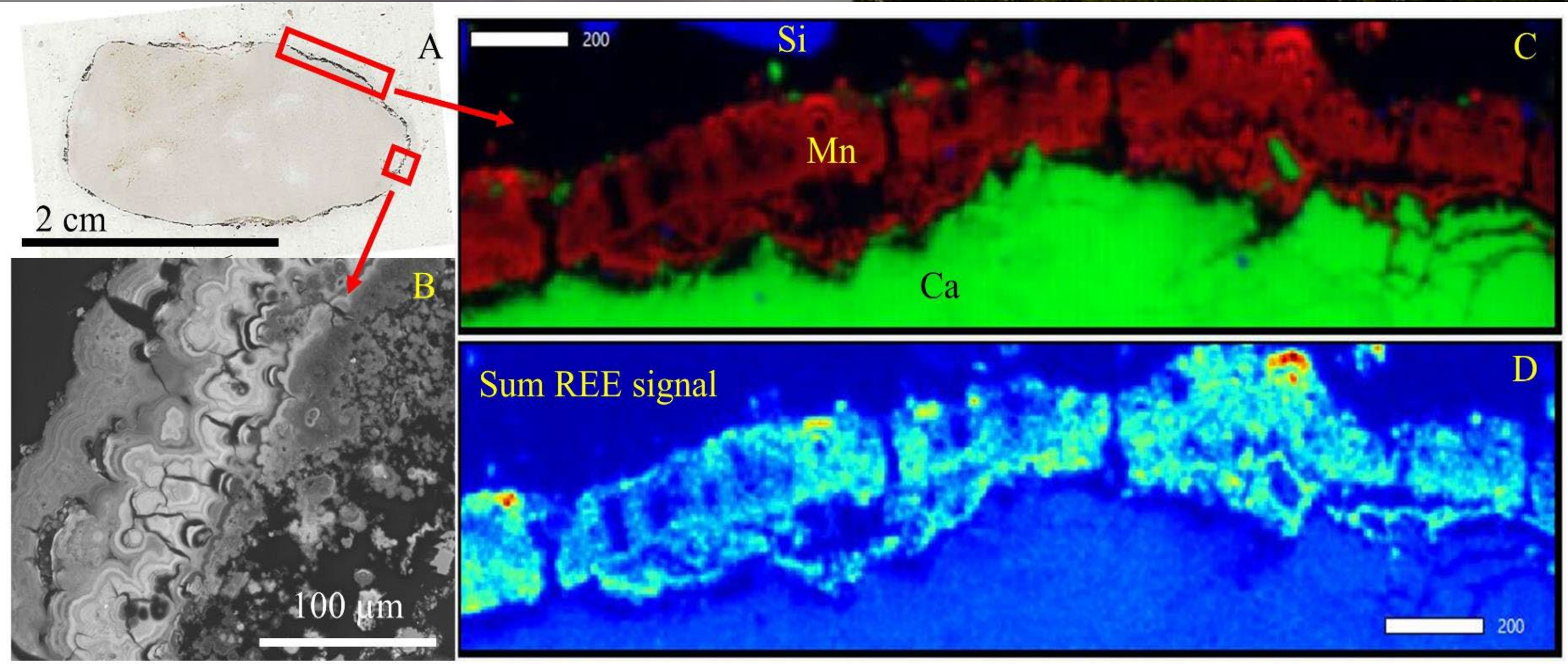
## FWP-1022420

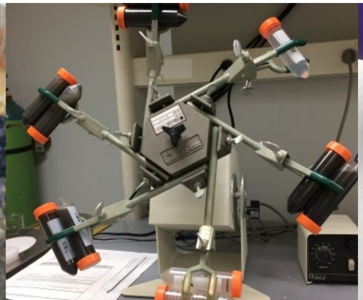

***Mengling Stuckman, Ph.D.***

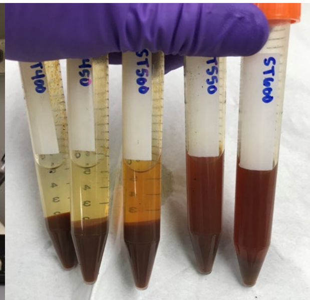
*National Energy Technology Laboratory (NETL), NETL Support Contractor*

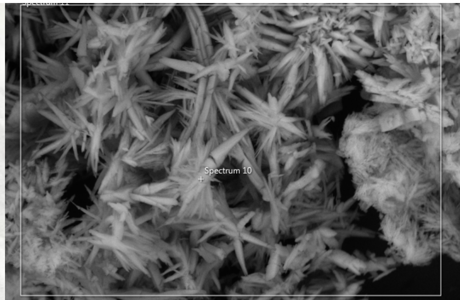



U.S. Department of Energy
National Energy Technology Laboratory
Resource Sustainability Project Review Meeting
Oct. 25-27, 2022







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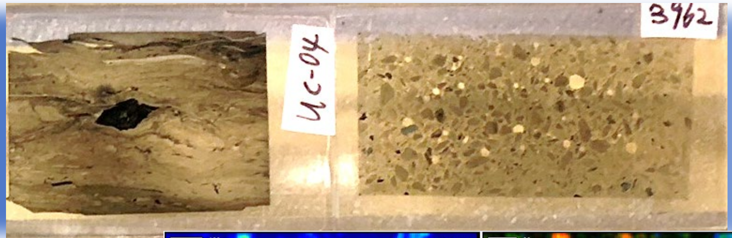
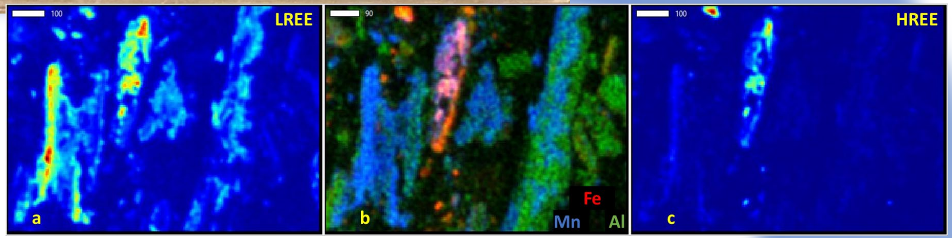
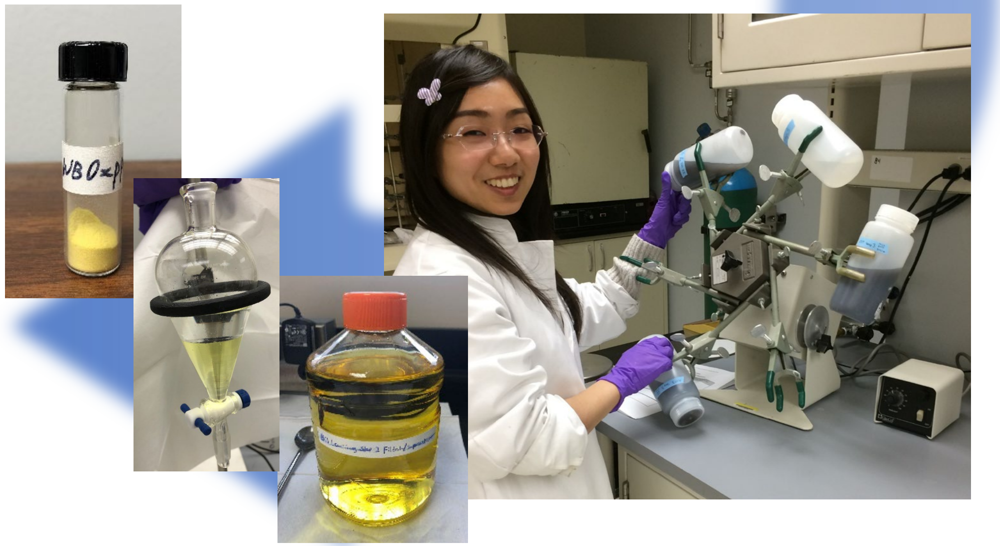
# Project Overview

**Funding from NETL Critical Mineral  Research Field Work Proposal: $365k for EY2022, TBD for EY2023 and 2024; Overall Project Performance Dates: EY2022-2024**





**Goal:** Utilize **advanced characterization** techniques on acid mine drainage treatment solids (AMD) to inform critical minerals (CM), including rare earth elements (REE), Co/Ni/Zn and Li, binding conditions in these materials, and to **innovate targeted extractions** for efficient and economical CM recovery.

**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 wastes.

# Project Current Status

## Chemically-Informed CM Recovery from AMD Solids

- Technical advances:
  - **Expand CM focus: REE, Co/Ni/Zn, Mn, Al, Fe, Li, etc.**
  - **80% reduction** in reagents, reaction time
  - Reduction in process steps/complexity: **sequential leach of different CMs**
  - Reduction in process intensity: **ambient temperature and pressure**
  - Techno-economic analyses in progress to further explore process performance
- Fundamental and lower technical readiness level (TRL) for innovations:
  - **<u>Work smarter, not harder</u>**
  - Fine-tune extractions to target certain CM
  - Novel reagents and extractions: Different acids, different agents, cocktails, waste streams
  - Modeling to improve design of treatment
- Industry input/validation:
  - Regular communication with industry partners
  - Active discussions on technology licensing and industry needs

# Background: Acid Mine Drainage (AMD) is Enriched in CM

## Domestic Source of CM

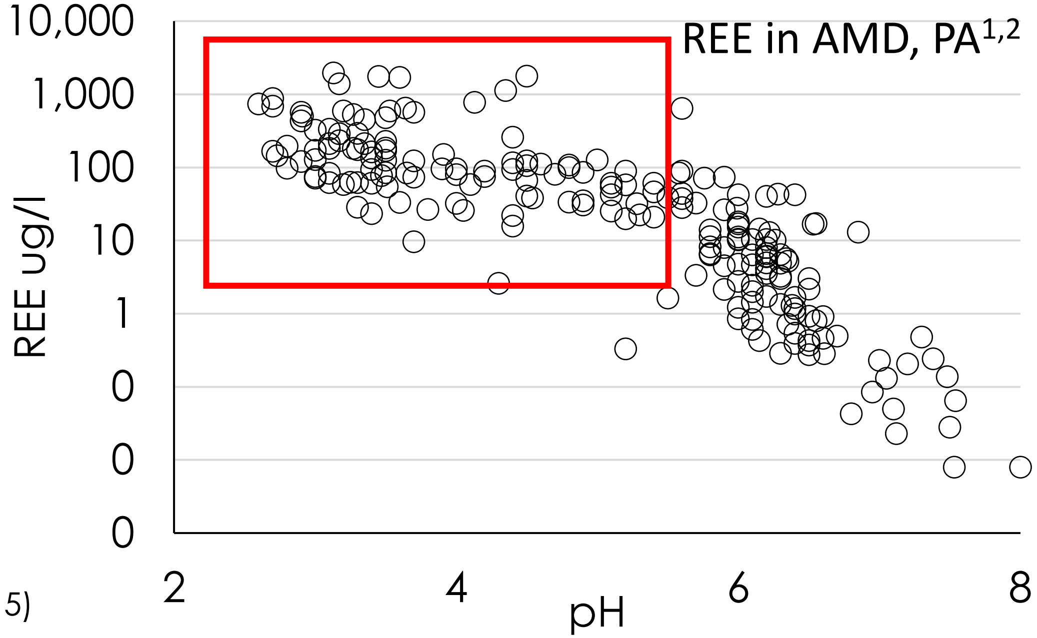
**Pyrite ($FeS_2$) oxidation** releases hydrogen ions

- Decreases pH, mobilizes metals (e.g., Fe, Mn, Al)
- Need to treat toxic levels of metals that negatively effect the water, including REE, Co and Ni under acidic conditions



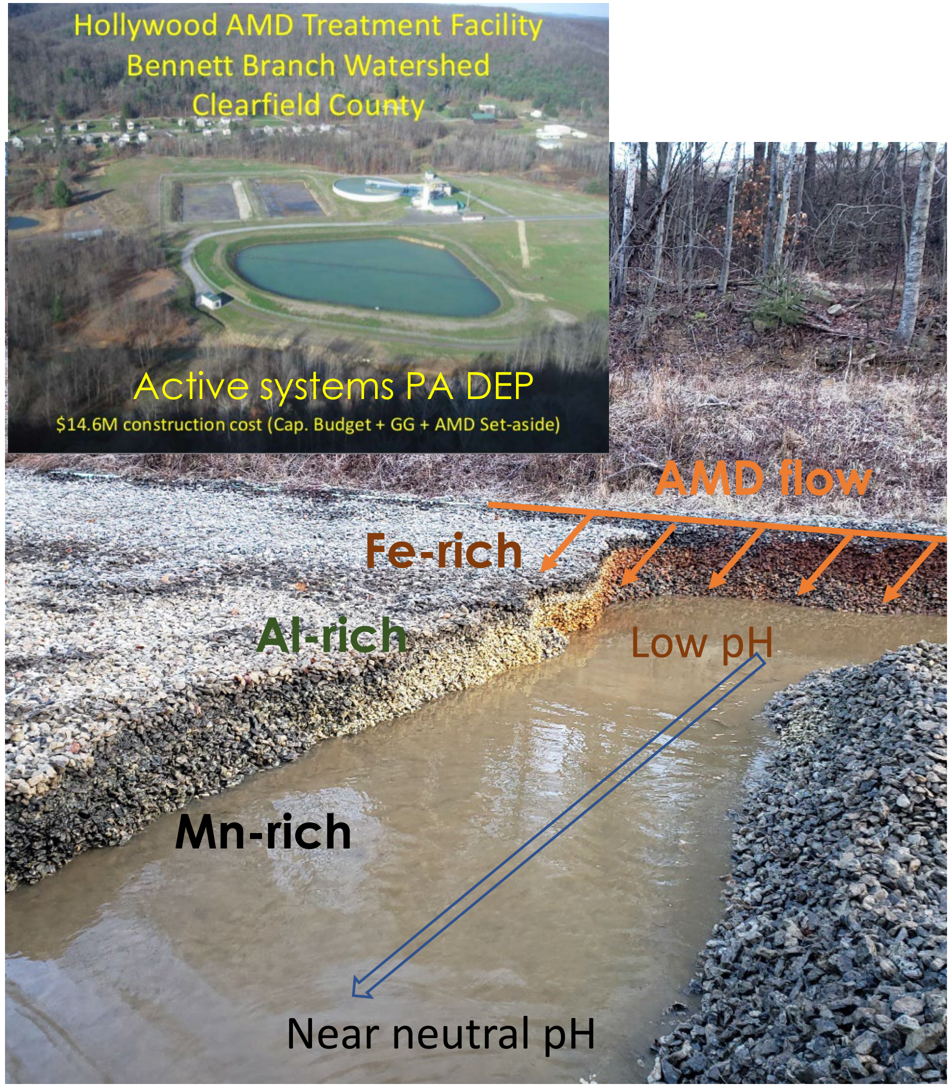
### CMs from 140 discharges across Pennsylvania[2]

| Element | Max conc. (ug/L) | Min conc. (ug/L) | Max loading (kg/year) | Min loading (kg/year) |
|---|---|---|---|---|
| Mg | 210,000 | 3,600 | 3,541,140 | 40 |
| Mn | 74,000 | 19 | 215,522 | 4.5 |
| Sr | 3,600 | 27 | 83,321 | 0.23 |
| **Ni** | 3,200 | 2.6 | 10,428 | 0.3 |
| **REE** | 1,765 | 0.4 | 7,364 | <0.01 |
| **Co** | 3,100 | 0.3 | 6,952 | 0.1 |
| Cu | 190 | 0.4 | 2,086 | <0.1 |
| Li | 390 | 11.0 | 4,513 | 0.2 |




1: Hedin et al. (2019); Stewart et al. (2017); 2: Cravotta (2008); Cravotta and Brady (2015)

# AMD Treatment Systems and REEs




## Passive Remediation Treatment: No chemical added, >200 systems in PA

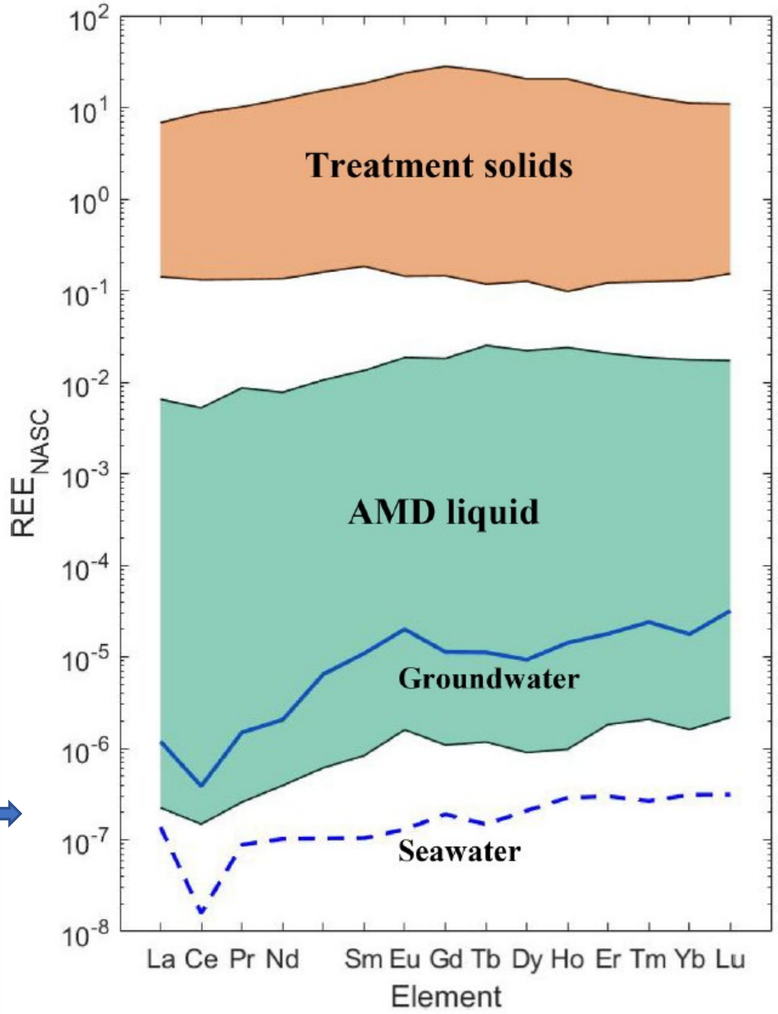
~85 billion gallons/year AMD treated

Raises pH of water (Limestone beds)

Precipitate dissolved metals

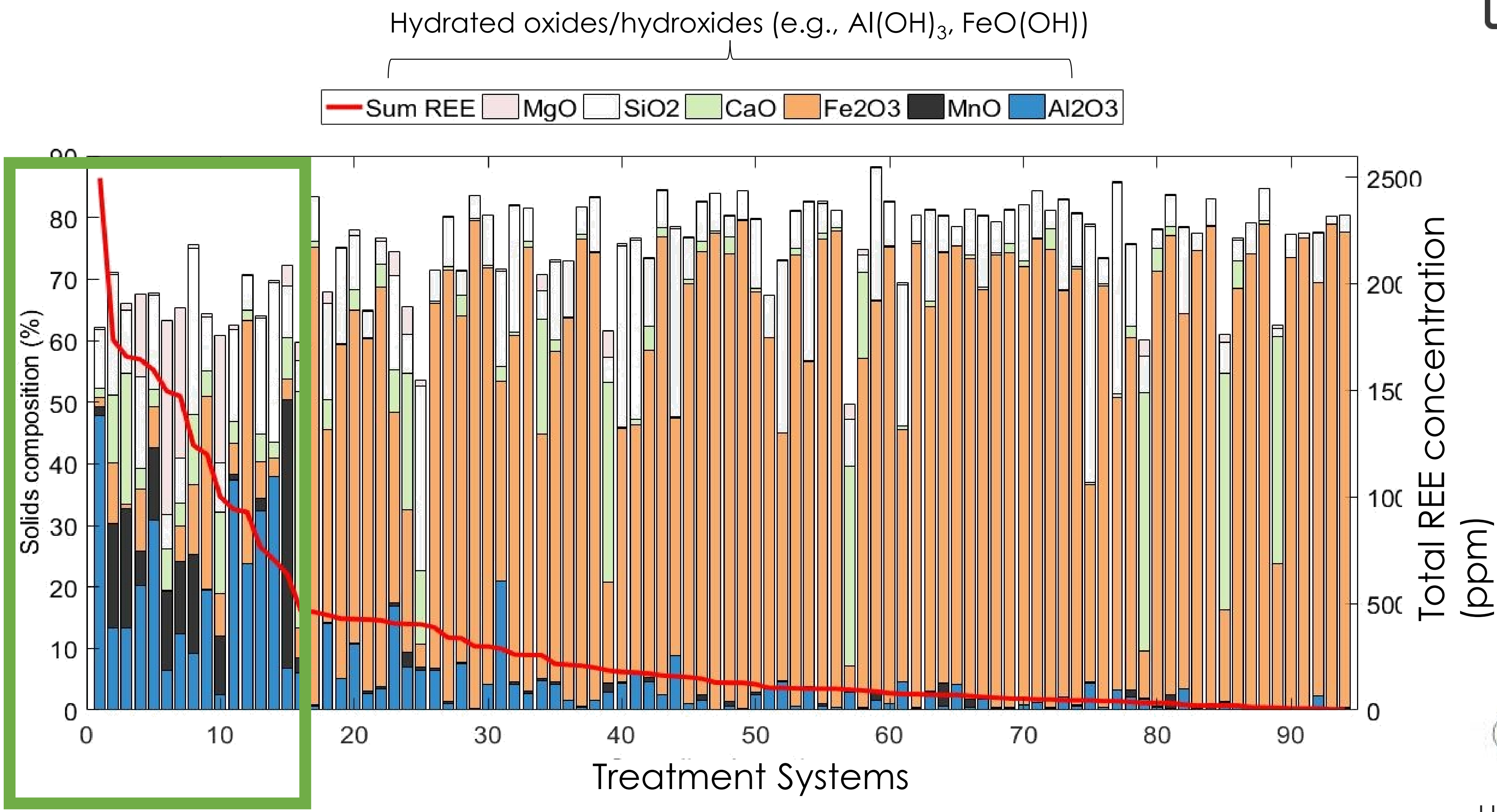
- 90% REE sequestration REEs precipitate with Fe, Mn, Al

~18,000 tons/year treatment solids produced: AMD solids


*Hedin et al. (2019 & 2020), IJCG*

# Approximately 100 AMD Solids from Passive Systems in PA




- ~50% critical REE (Eu, Nd, Tb, Dy, and Y)
- <50 ppm U, Th
- \$3 to \$400 REE value and \$0.04 to \$217 Co value/metric ton dry solid

Hedin et al., IJCG, 2020

# Challenge of the Project: Chemical Diversity

NATIONAL ENERGY TECHNOLOGY LABORATORY

Unit: wt% for major elements and mg/kg for trace elements

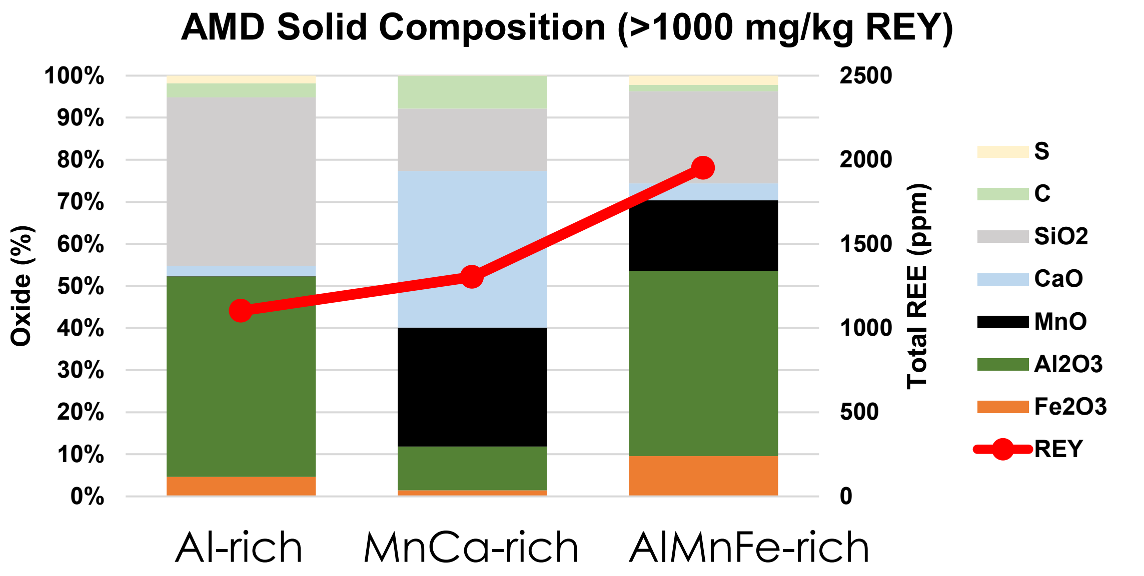
| | C | S | Al | Si | Fe | Mn | Mg | Ca | K | Ti | **REE** | Li | Co | Ni | Cu | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Al-rich solid | 2% | 2% | **18.0%** | 19.3% | 2.1% | 0.1% | 0.2% | 1.2% | 0.7% | 0.3% | **1113** | 38 | 22 | 50 | 106 | 315 |
| MnCa-rich solid | 4% | ND | 3.5% | 6.1% | 0.5% | **18.1%** | 0.6% | 16.8% | 0.4% | 0.1% | **1590** | 108 | 6026 | 8889 | 89 | 13585 |
| AlMnFe-rich solid | 1% | 1% | **15.4%** | 9.7% | **5.2%** | **8.5%** | 0.2% | 2.8% | 0.3% | 0.1% | **1900** | 440 | 2059 | 3002 | 518 | 5812 |

The transition metal contents are sometimes higher than REE; Lithium content is also reasonably high MnCa-rich solid has higher accumulation of Co, Ni and Zn


Al-rich solids

MnCa-rich solid


Al-, Mn-, Fe-rich solid



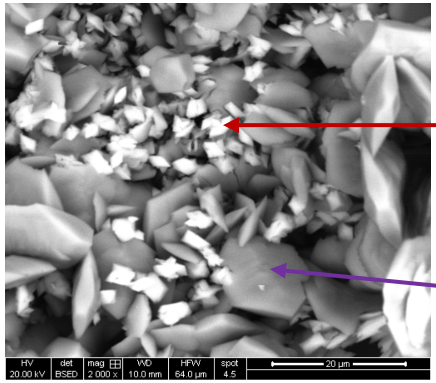

**Stuckman, PIOGA Tech seminar, 2021**

**Hedin et al., IJCG, 2019**

# Research Success Metric in Previous Years

## Yearly Progression Demonstrated

- AMD waste solids
- Est. 1102 metric tons REO/yr
- 12% of U.S. 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<br>Additional AMD solid field sampling (early 2020) |
| 2020 | 95% (mg scale) | 2 – 3 | >80% | **ROIs in prep**; By-product recovery in development;<br>Upscaling and optimization of lab scale processes |
| 2022-2024 | Co, Ni, Zn | 3 - 4 | >80% | Collaboration with Hedin Environmental, Inc.;<br>Explore biotechnologies to sequester, recover and purify REEs and critical elements in planning |

# Technical Approach/Project Scope

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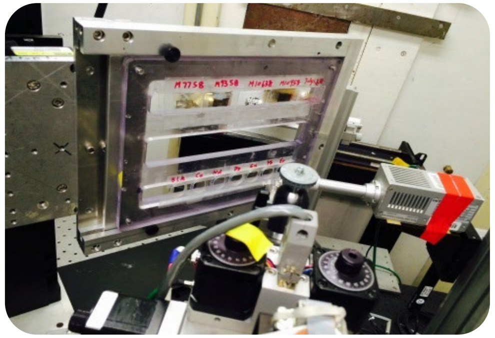
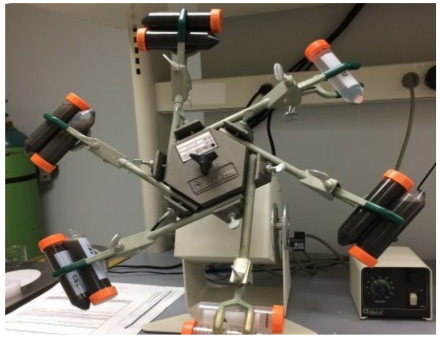
## Characterization Informed Recovery






### EY22 Characterization of CM Binding

- CM distribution:

In-house SEM, XRD, Raman, **synchrotron-based spectroscopy, seven-step sequential extraction**

- Geochemical modeling (**PHREEQ-N-AMDTreat** from USGS)

### EY23 Optimized Targeted Extraction

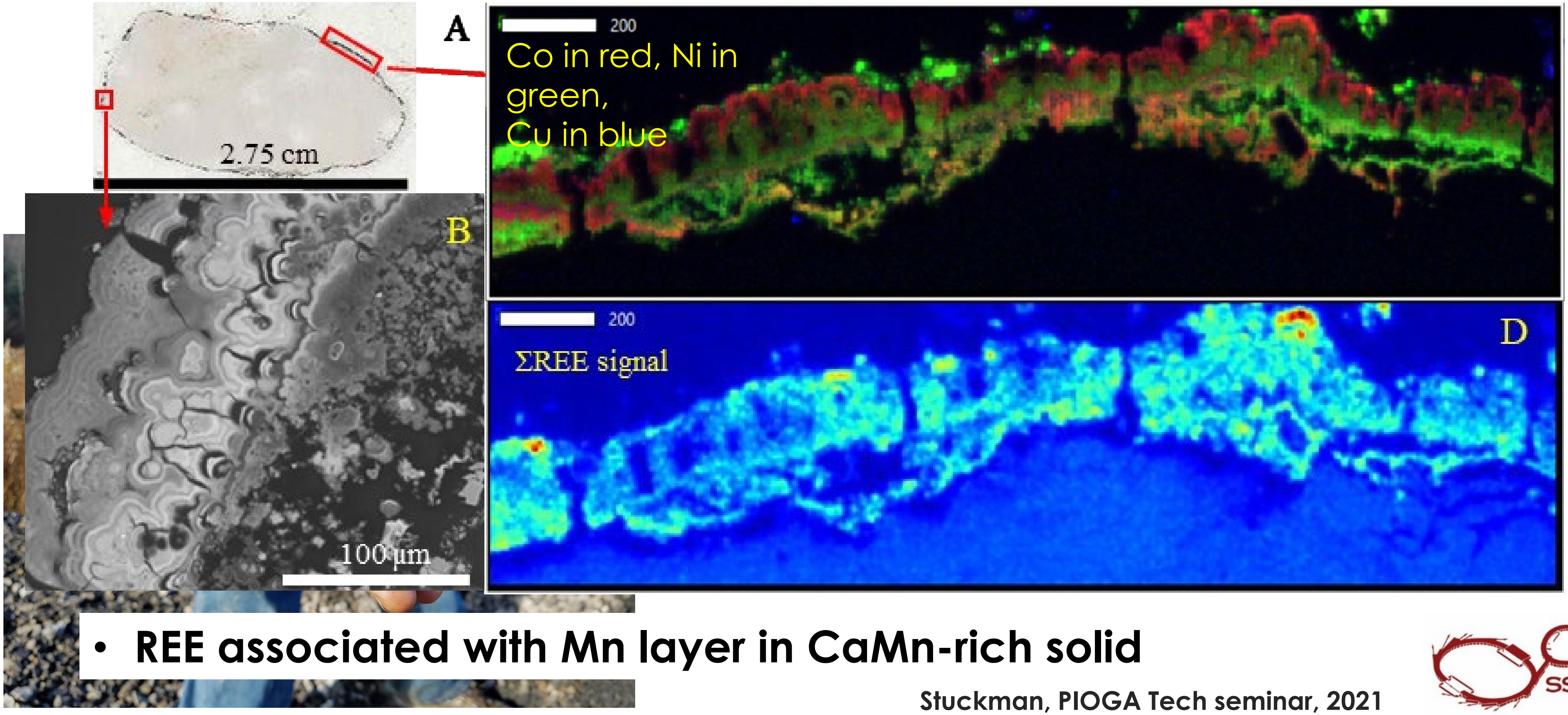
- Sequential leach
- Innovative leaching strategies

### EY24 Downstream Optimization and Operation Optimization

- Optimization of the extraction
- Explore to bypass costly traditional solvent purifications further downstream

# Progress: The REE and CM Binding in MnCa Solid

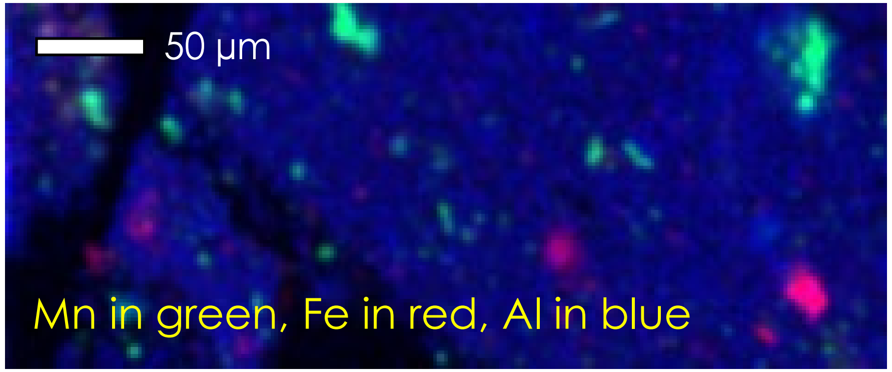
Synchrotron µXRF

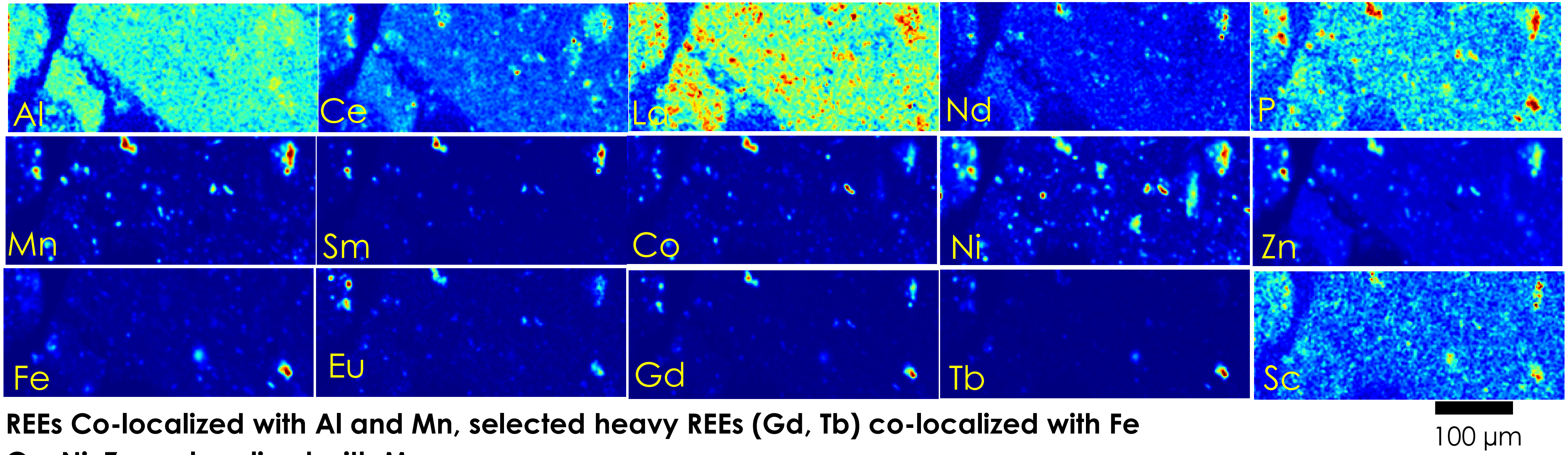



- **REE associated with Mn layer in CaMn-rich solid**

Stuckman, PIOGA Tech seminar, 2021

# Progress: The REE and CM Binding in Al-Rich Solid



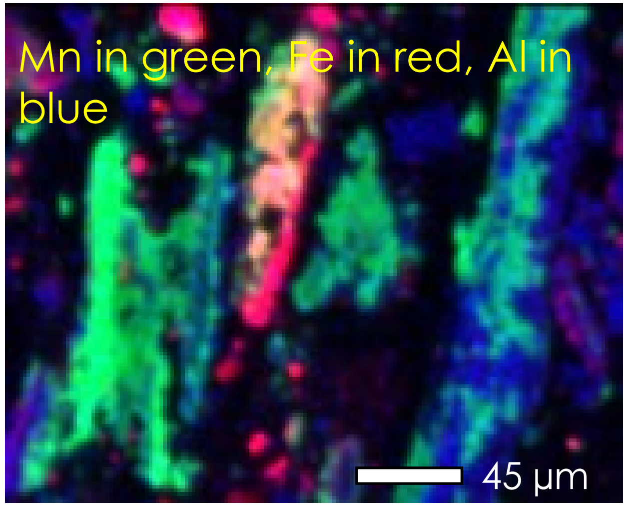

- **REEs Co-localized with Al and Mn, selected heavy REEs (Gd, Tb) co-localized with Fe**
- **Co, Ni, Zn co-localized with Mn**

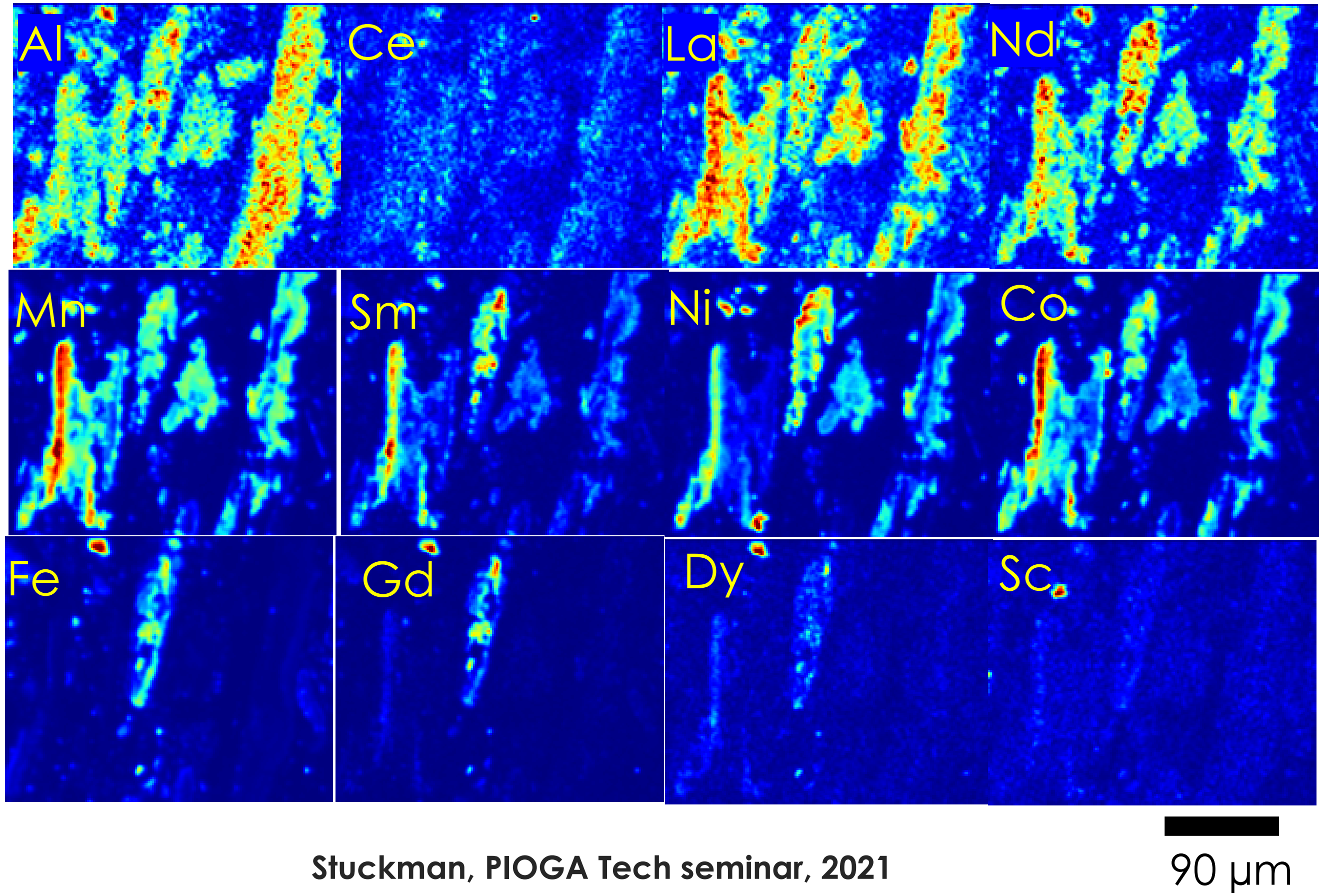
**Stuckman, PIOGA Tech seminar, 2021**

# Progress: The REE and CM Binding in AlMnFe-Rich Solid

- **REEs Co-localized with Al and Mn, selected heavy REEs (Gd,Dy) co-localized with Fe**
- **Co, Ni, Zn co-localized with Mn**

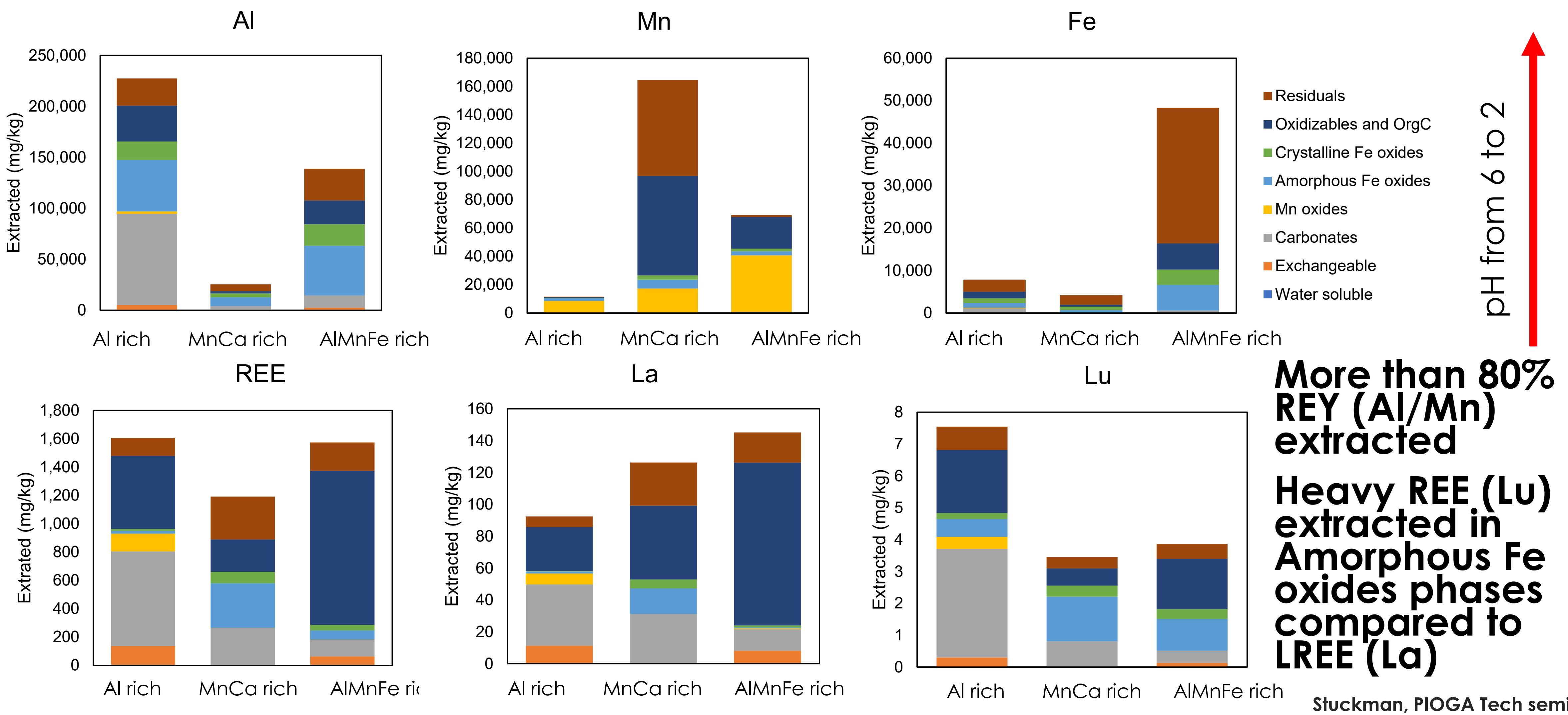
Al-, Mn-, Fe-rich solid




Stuckman, PIOGA Tech seminar, 2021

# Progress: REE Sequential Extractions (Total Exacted vs. Residuals)

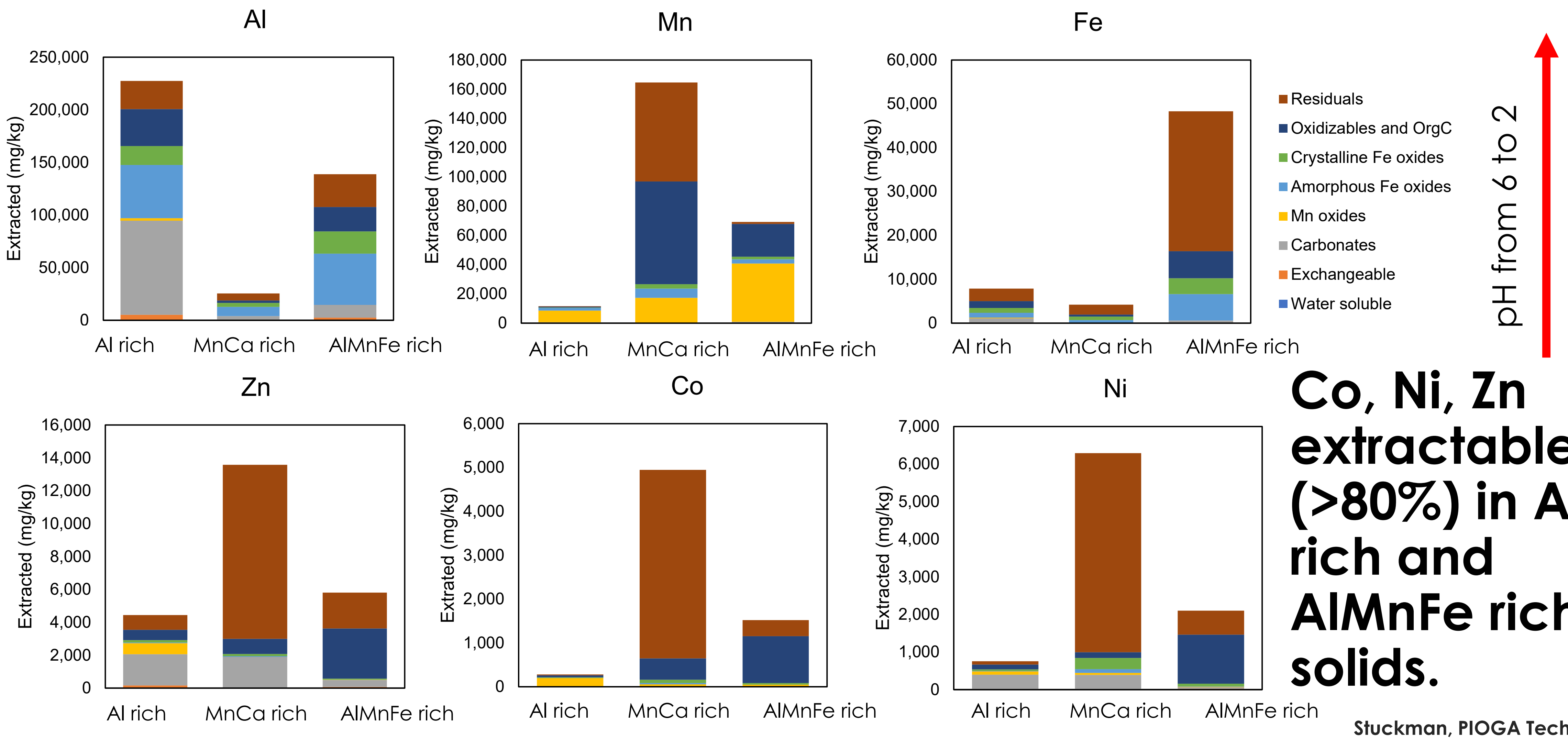



**More than 80% REY (Al/Mn) extracted**

**Heavy REE (Lu) extracted in Amorphous Fe oxides phases compared to LREE (La)**

Stuckman, PIOGA Tech seminar, 2021

# CM Sequential Extractions (Total Exacted vs. Residuals)



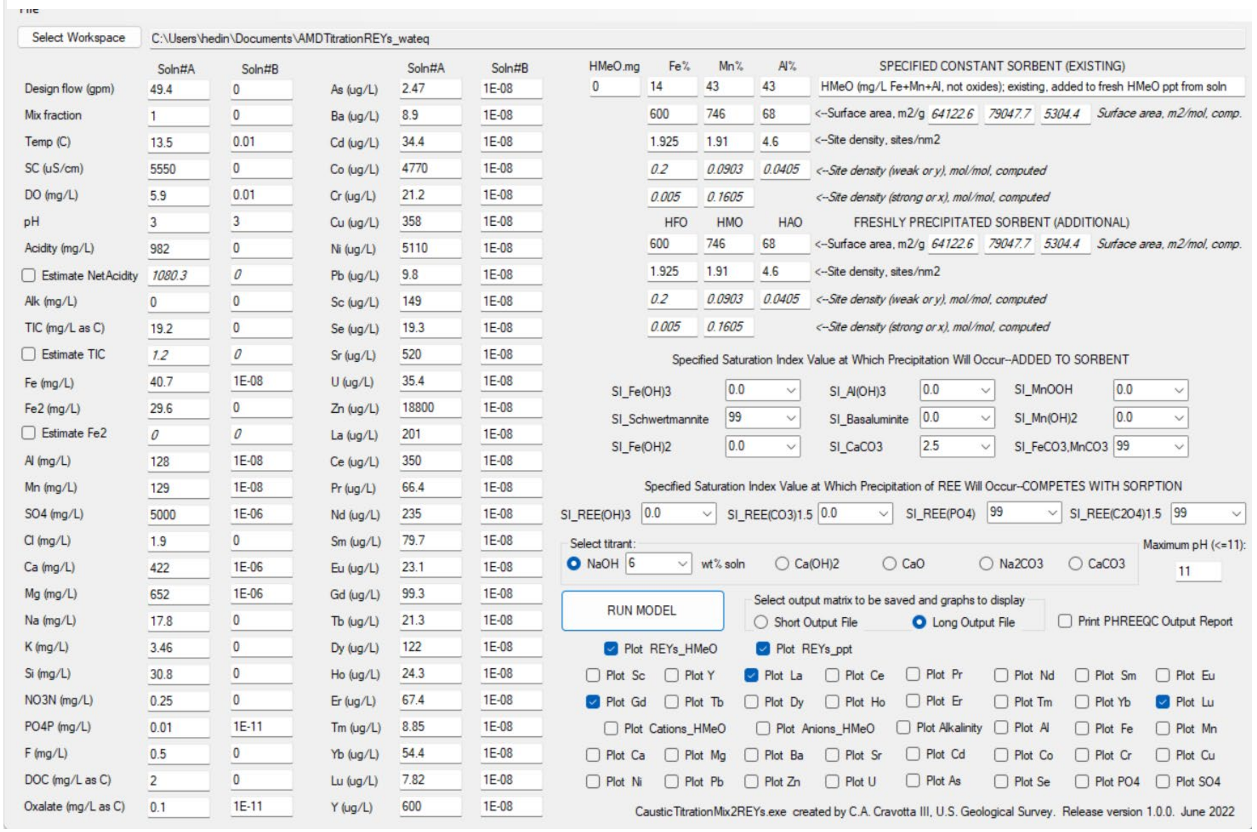

**Co, Ni, Zn extractable (>80%) in Al rich and AlMnFe rich solids.**

Stuckman, PIOGA Tech seminar, 2021

# Progress: Geochemical Modeling

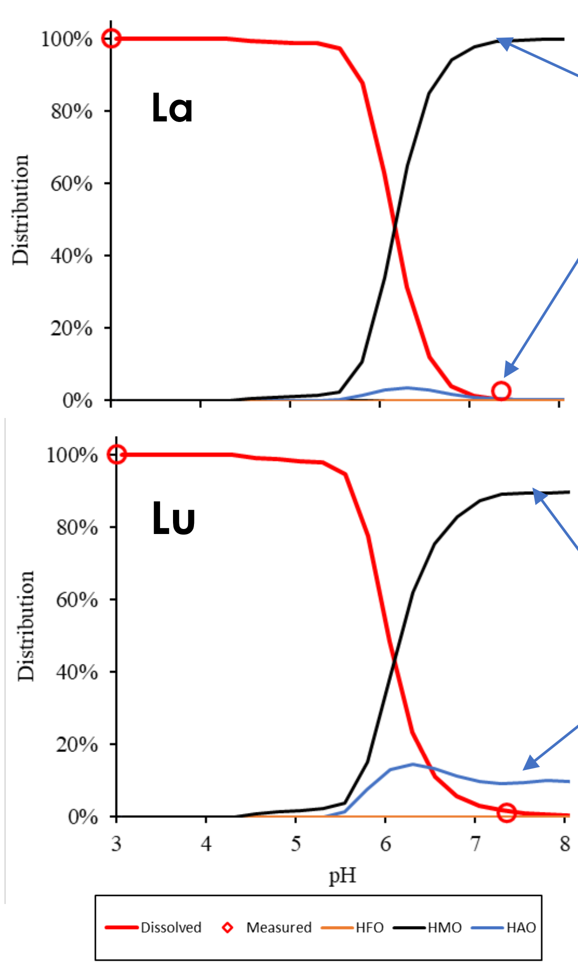
**PHREEQ-N-AMDTreat developed by C. Cravotta (2022)**

- **Current focus on REE prediction for one type of treatment system**
- **Future efforts will incorporate other CMs in existing modeling**




https://code.usgs.gov/water/phreeq-n-amdtreat

**Different sorption for La and Lu**




100% precipitated at effluent pH Adsorbed mainly on $MnO_2$ (HMO)

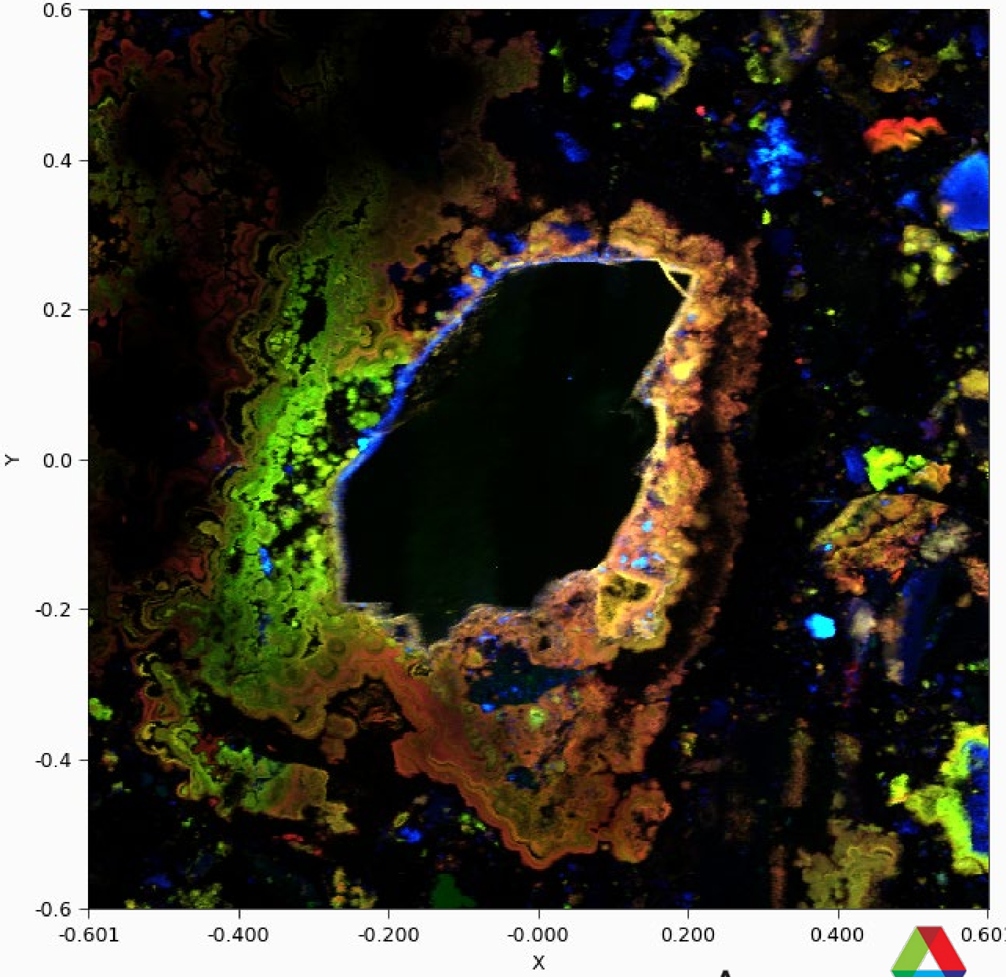
100% precipitated at effluent pH Adsorbed mainly on Mn hydroxides (HMO) and Al hydroxides (HAO)

**Hedin et al., ICARD, 2022**

# Characterization Summary

**Mn in red, Ni in green, Co/Fe in blue**

Image 1.2 mm x 1.2 mm, 2 mm spot (APS GSECARS, Sector 13)




Argonne NATIONAL LABORATORY

- **AMD solids have diverse chemical composition, so extractions may need to be tailored toward different chemical compositions.**
  - REEs mostly co-localized with Al and Mn, selected HREEs (Gd/Dy) co-localized with Fe
  - Regardless of composition, Co, Ni, Zn mainly co-localized with Mn (hydr)oxides in AMD solids
- **Disseminate results**: 4 peer review journals published, 3 in prep, report(s) of invention in progress

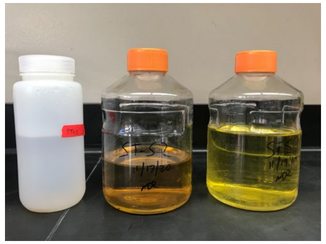

- Hedin, B., Stuckman, M., Lopano, C., Cravotta, C., and Capo, R. "Characterization and modeling of REE binding behaviors in passive acid mine drainage remediation solids" In preparation for submission to *Applied Geochemistry*
- Miller, J.D., Stuckman, M.Y., Means, N., Lopano, C.L., and Hakala, J.A. (2022) "Determination of transition metal ions in fossil fuel associated wastewaters using chelation ion chromatography" *Journal of Chromatography A*, 1668, 462924. https://doi.org/10.1016/j.chroma.2022.462924
- Stuckman, M., Lopano, C.L., and Tarka, T. (2022) "Step Leaching Process of Rare Earth Elements from Ash Materials Using Mild Inorganic Acids at Ambient Conditions", *U.S. Patent: US 2022/0017992 A1*. https://patents.google.com/patent/US20220017992A1/en
- Fritz, A. G., et al. (2021). "Technoeconomic Assessment of a Sequential Step-Leaching Process for Rare Earth Element Extraction from Acid Mine Drainage Precipitates." *ACS Sustainable Chemistry & Engineering* 9(28): 9308-9316.
- Hedin, B. C., et al. (2020). "Critical metal recovery potential of Appalachian acid mine drainage treatment solids." *International Journal of Coal Geology* 231: 103610.
- Hedin, B. C., et al. (2019). "The evaluation of critical rare earth element (REE) enriched treatment solids from coal mine drainage passive treatment systems." *International Journal of Coal Geology* 208: 54-64.

# Progress: Optimized Targeted Extraction

## Update: Innovative Extractions

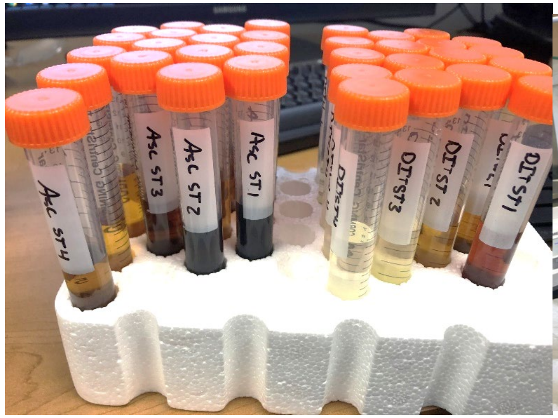
- <u>Optimized sequential leach</u>
  - Targeted Rare Earth Extraction (TREE)*
  - 90% REE and up to 70% Co recovered in separate, targeted steps

AMD solids Fly ash TREE process



*Stuckman, M.Y., Lopano, C.L. and Tarka, T. (2021) U.S. Patent: US 2022/0017992 A1, https://patents.google.com/patent/US20220017992A1/en

- <u>Extraction utilizing REDOX</u>
  - Preliminary results showed up to 80% CM recovery in one extraction using neutral pH extractant, report of invention in preparation
  - Optimization of conditions needed

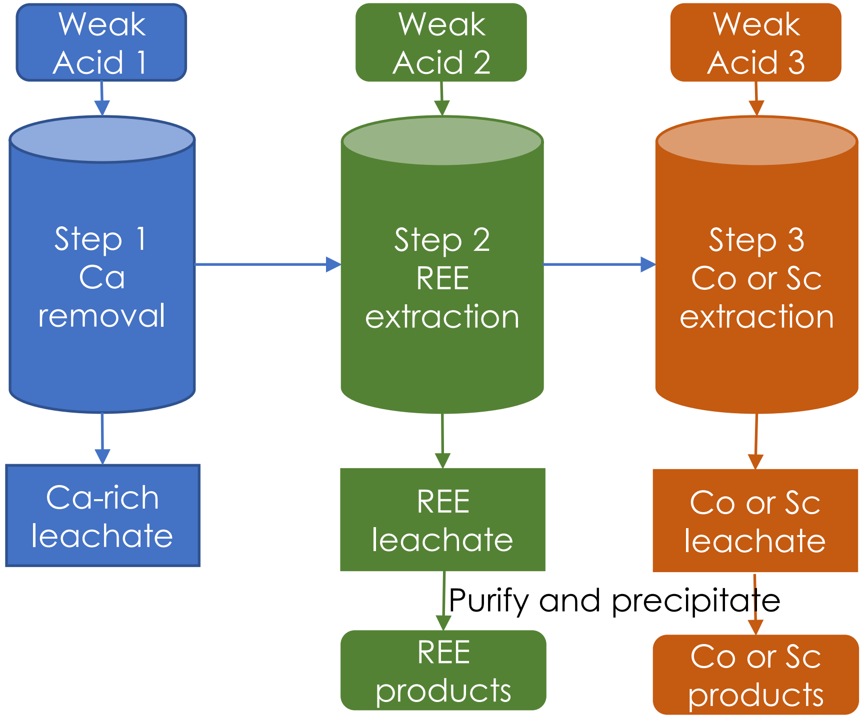



# Achievement: TREE

## Reduce Extraction Steps and Conditions

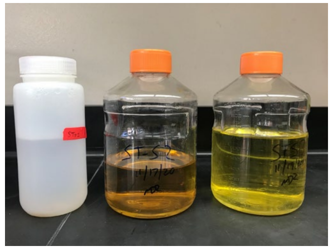
### TREE Advantages over REE mining:

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

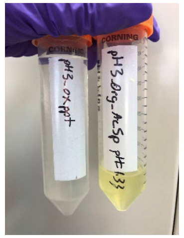


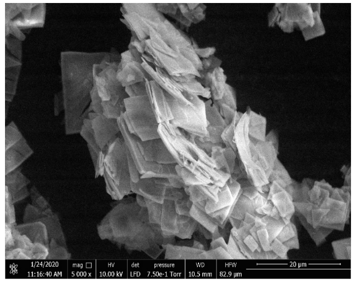

2022 R&D 100 FINALIST

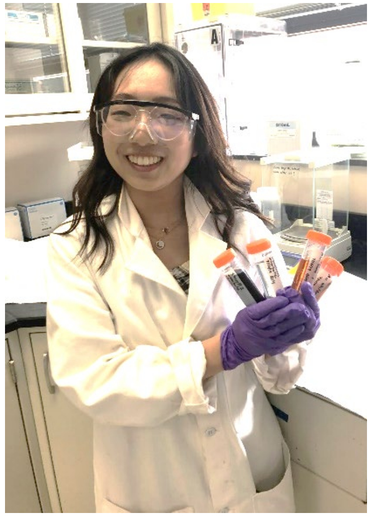
AMD solids Fly ash TREE process



3 step leachates







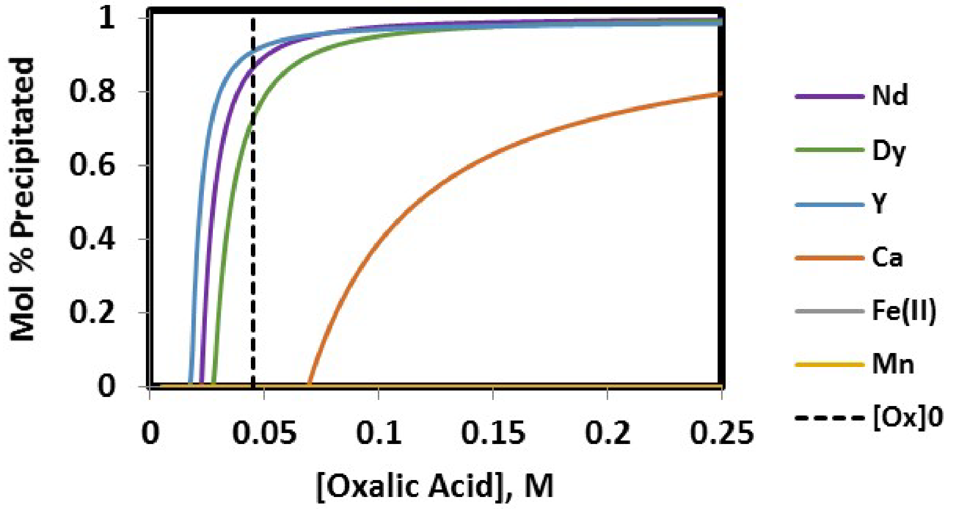
*Stuckman, M.Y., Lopano, C.L. and Tarka, T. (2021) U.S. Patent: US 2022/0017992 A1, https://netl.doe.gov/node/10318

# Progress: Downstream Optimization-Bypass Solvent Extraction

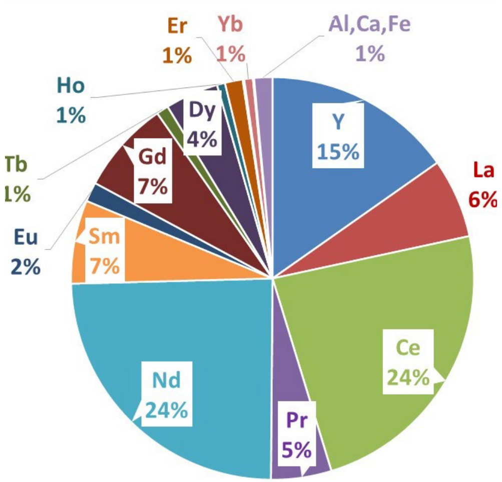
## Direct Oxalic Precipitation from Select TREE Leachate

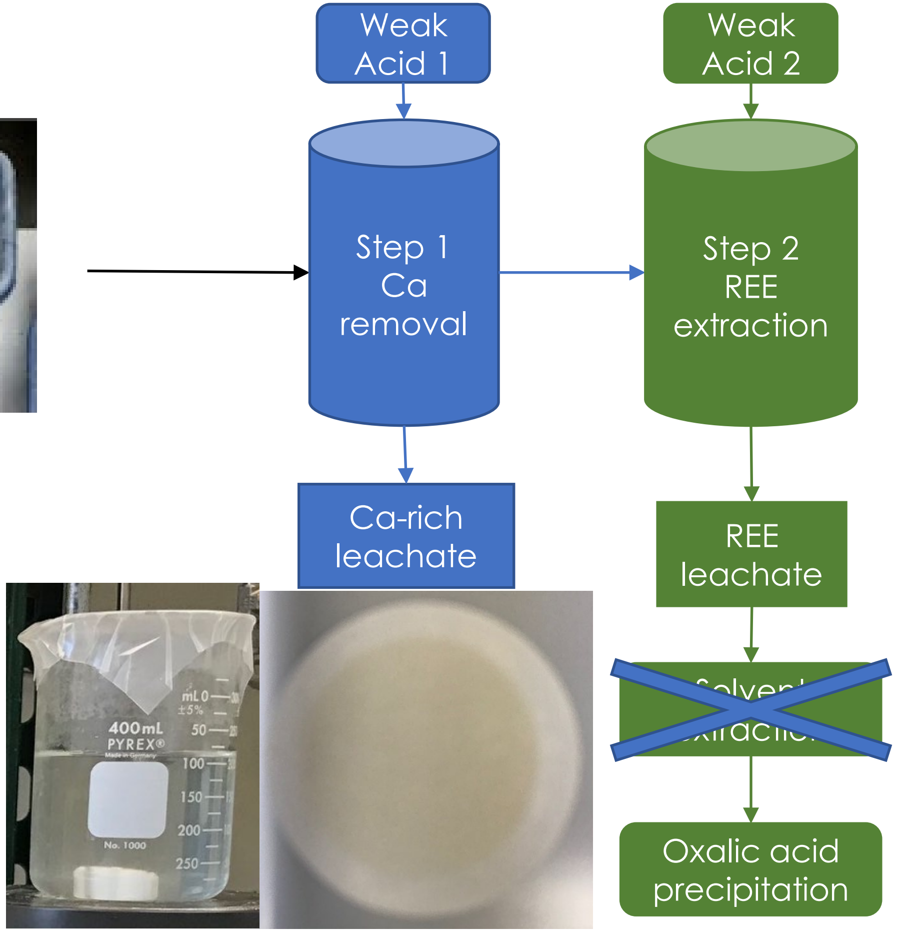
**After TREE process, precipitation modeling guided oxalic acid precipitation**

- Minimized oxalic acid use
- Successful rejects of Ca
- 99%wt REE oxalate recovered




*AMD solid*



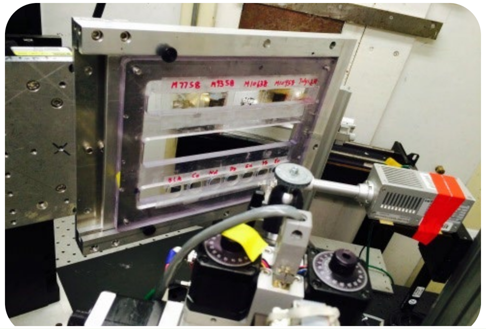

*REE Oxalate, 99%wt*

# Partners, Outreach and Workforce Development

- **Outside Organizations/Funds Engaged in Research**
- Critical Minerals Task 4: Biological Recovery of Critical Materials from Acid Mine Treatment Solids
- Critical Mineral Task 16: Sorbent for Li Recovery Derived from Acid Mine Drainage (AMD) Treatment Solids
- Hedin Environmental: Previous collaboration with Hedin Environmental will be leveraged to access AMD treatment solids to characterize CM recovery potential and develop deployable technology.
- University of Pittsburgh: Collaboration with the isotope geochemistry group at Pitt and their students to better understand AMD geochemistry.
- Synchrotron sources: University of Chicago & Argonne National Lab; Stanford University and Stanford Linear Accelerator Lab.
- **Outreach:** Pennsylvania Independent Oil and Gas Association (PIOGA) Tech seminar (2021 and 2022), Stony Brook University, University of Pittsburgh, Leidos headquarter, and Brazilian Coal Association
- **Workforce Development:** 3 ORISE and Mickey Leland summer interns, Ph.D. students or gradates from University Pittsburgh and Duke University

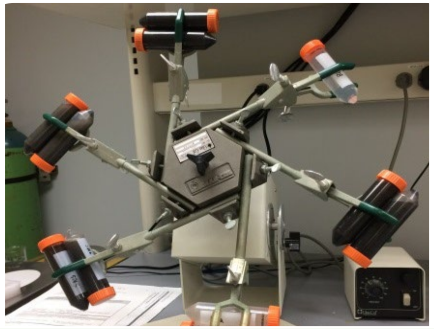
# Summary

- **Characterization-Informed Recovery**



### EY22 Characterization of CM Binding (On track)

- REE complete
- Co, Ni, Zn in progress



### EY23 Optimized Targeted Extraction (In progress)

- Demonstrate sequential leach of REE and Co/Ni from multiple AMD solids
- Demonstrate 80-100 % CM recovery via different acids, and/or reducing agents

### EY24 Downstream optimization and operation optimization (In progress)

- Direct oxalic acid precipitation modeling established
- Optimized of the extraction, such as liquid: solid ratio, kinetics and temperature

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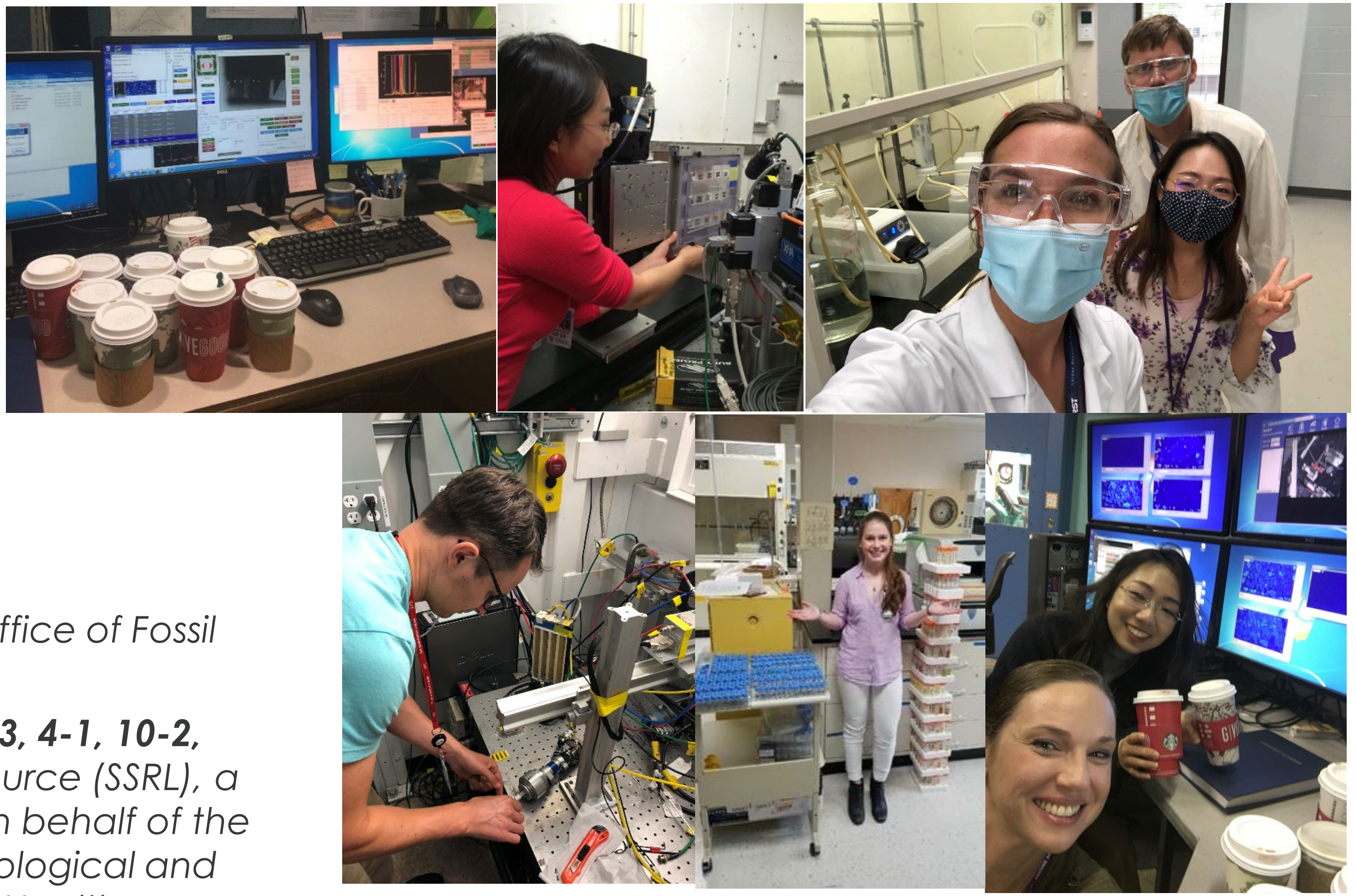

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