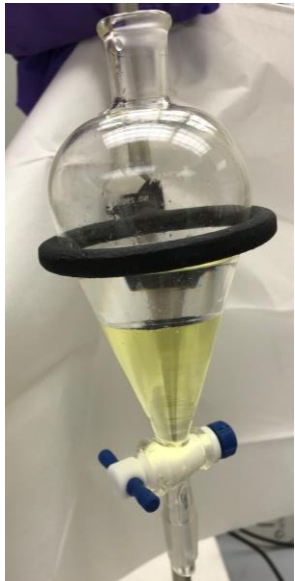
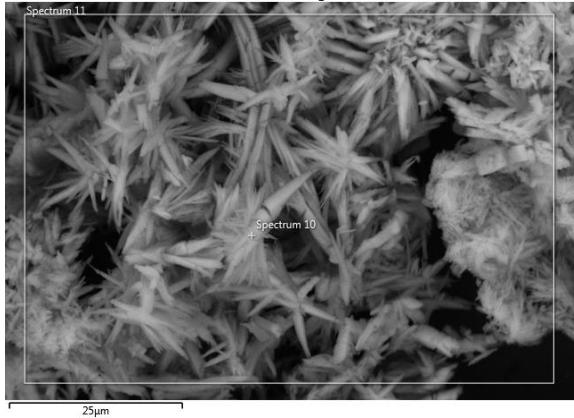


Characterization and Recovery of Rare Earth elements from Powder River Basin Coal Ash

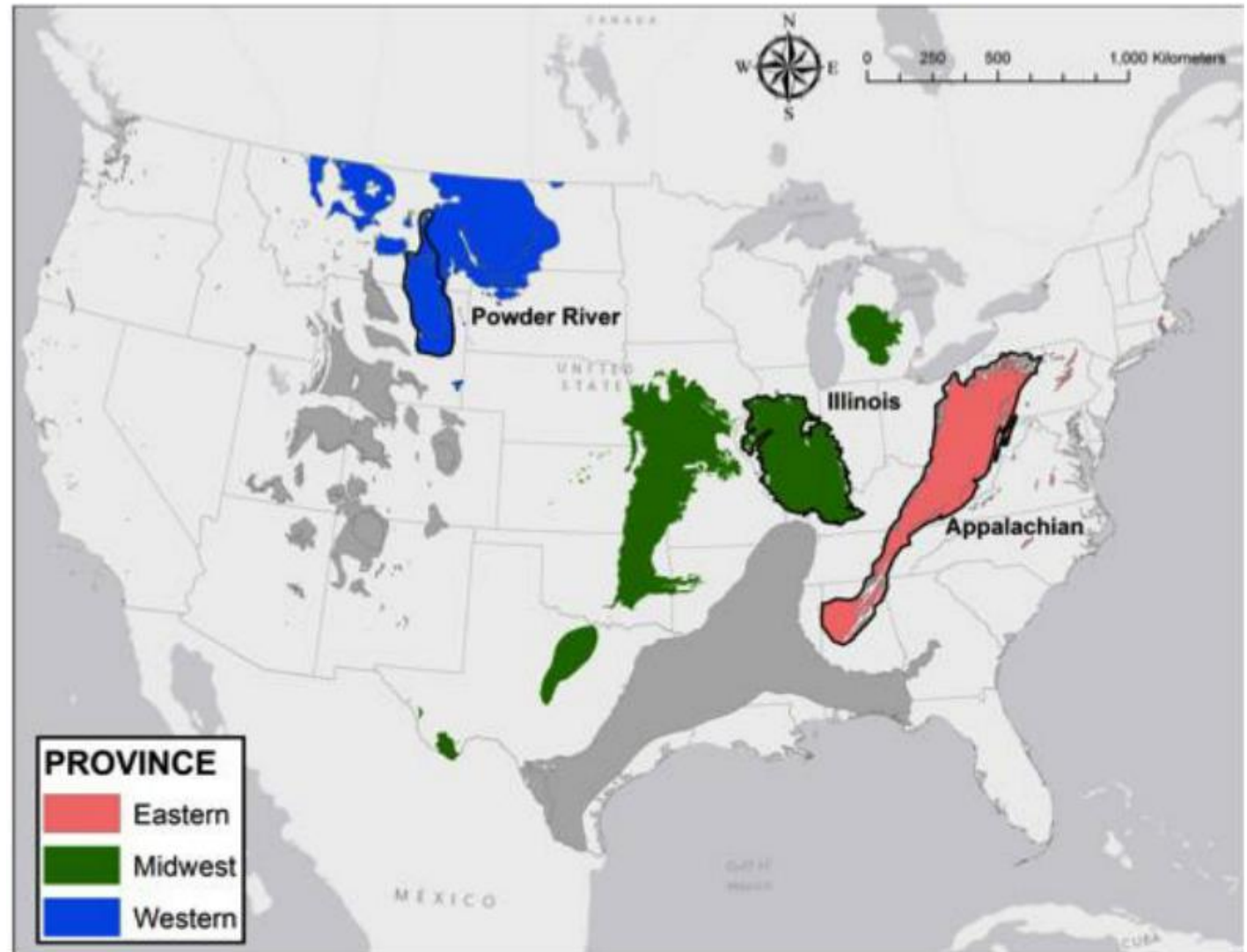
Mengling Stuckman^{1,2}, Christina Lopano², Ben Hedin^{3,4}, Bret Howard², and Evan Granite²

1: Leidos Research Support Team; 2: U.S. Department of Energy, National Energy Technology Laboratory; 3: ORISE; 4: University of Pittsburgh



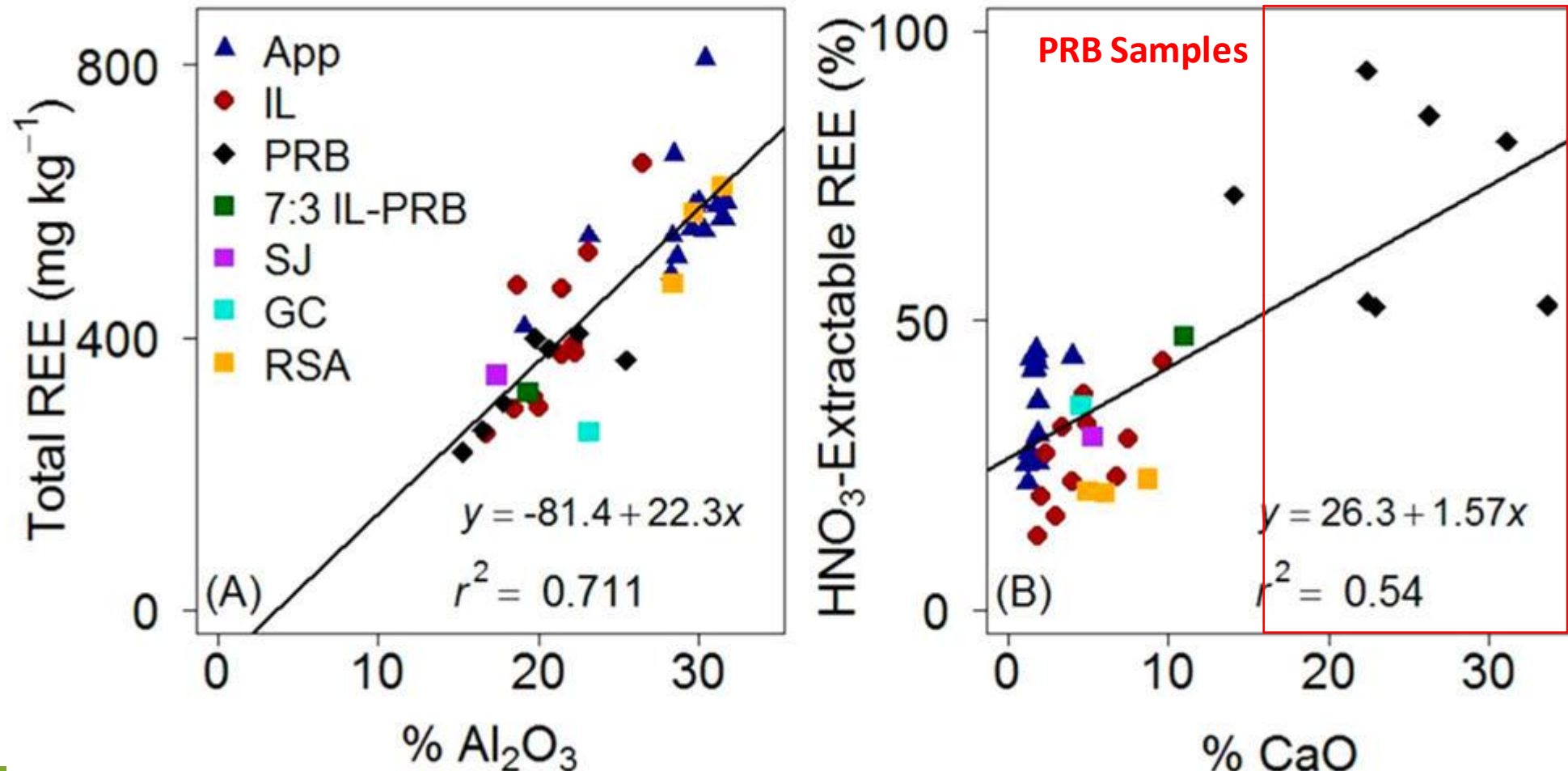
Powder River Basin

- Powder River Basin (PRB) is the largest coal production (36% of total) reservoir in US; “sub-bituminous” coal
- Annual ash production: 8.9 million metric tons; est. annual potential 3630 metric tons REOs (38% of US annual demand)



REE recovery potential from PRB Coal byproducts

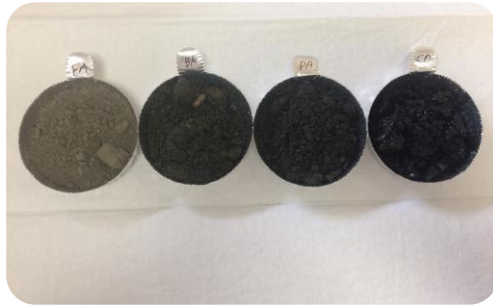
- Ca-rich Ash samples from Powder River Basin (PRB) content have more mobile REEs compared to Al-rich Appalachian ash, due to different REE deposition environments (Ca/Mg oxides as opposed to glass phase) during coal combustion.



Study Goal

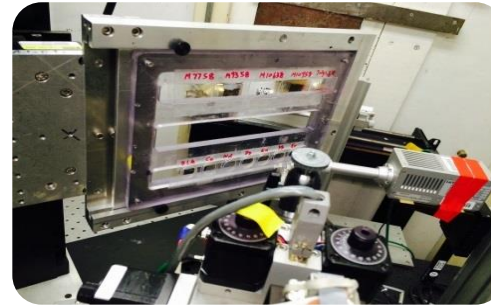
Characterization studies to understand the higher REE release from **Ca-Mg rich PRB** ash samples.

Demonstrated approximately **12wt% REE concentrate** recovered from PRB fly ash.



Solid Characterization

- 4 PRB sample vs. 1 APP fly ash
- Elemental Composition: ICP-MS, C and S content
- **Mineralogy**: XRD and SEM



Elemental Distribution

- Synchrotron micro-XRF mapping and micro-XANES for Ce(III) and Ce(IV)
- 7-step sequential extraction



Acid Leaching

- Rotator 24hr, 10:1 L:S ratio
- Inorganic acid: HNO₃, HCl, H₂SO₄
- Organic acid: Citric, acetic, oxalic, EDTA

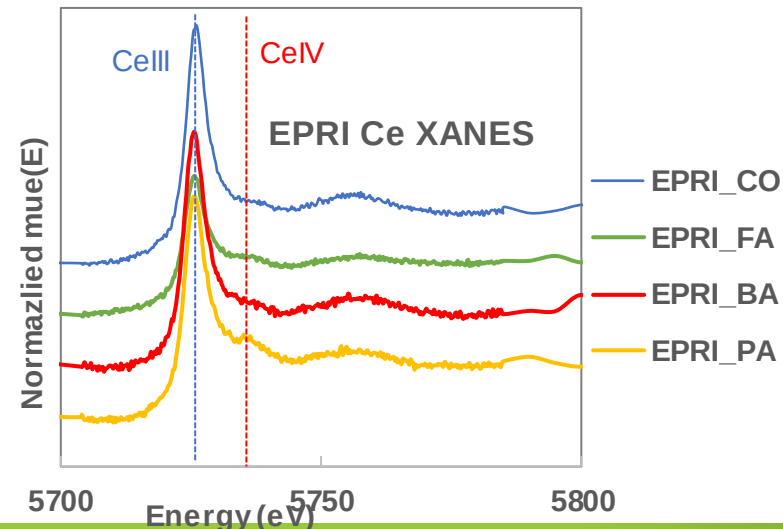
Ash samples (PRB vs. APP)

Powder River Basin (PRB), MO plant, High Ca, Mg content, from Electric Power Research Institute (EPRI)

Ca content in fly ash 345 from Appalachian basin (APP), OH plant: 4.25%

All units in ppm as whole-basis, unless stated otherwise

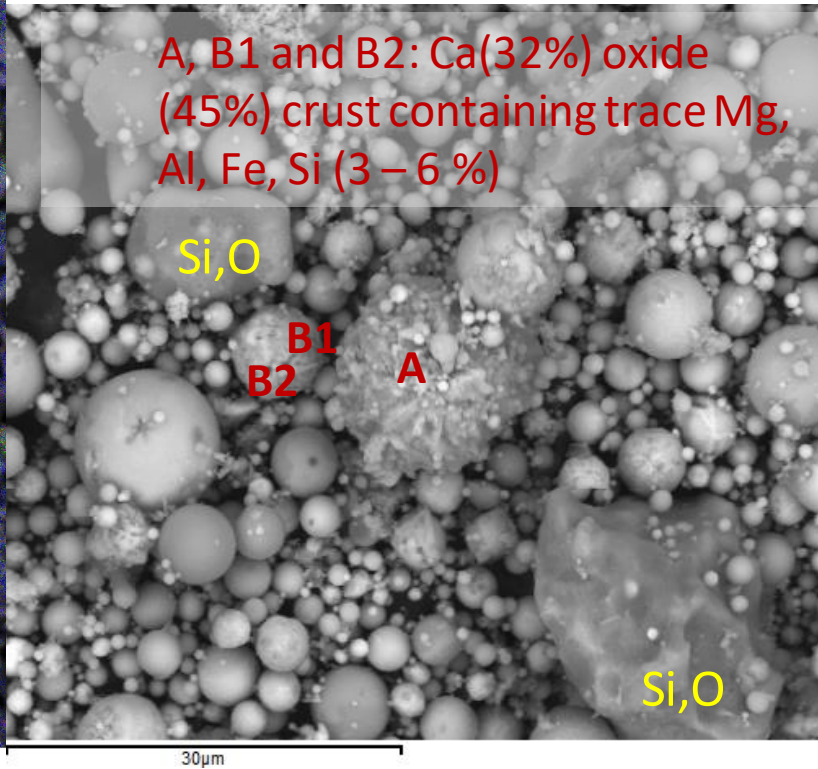
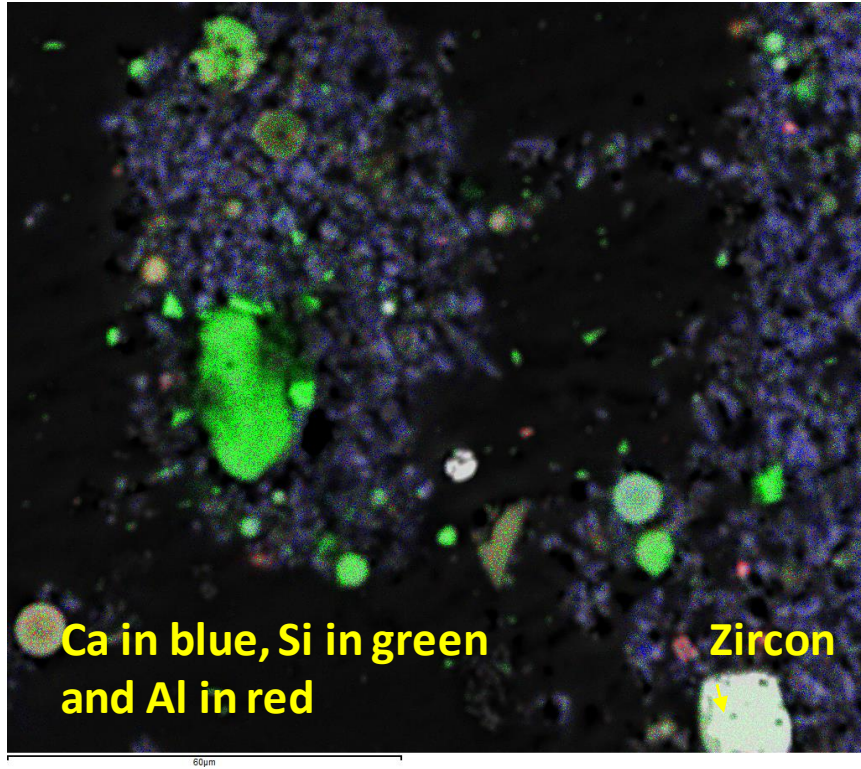
Sample Label	Coal basin	Description	Sc	Y	Ce	REY	%Al	%Ca	%Mg	Ce anomaly	%Ash
ECO	PRB	EPRI Coal	1.9	3	11	24	0.59%	2.02%	0.34%	0.991	9.01
EFA	PRB	EPRI Fly Ash	26	38	91	264	9.45%	20.8%	3.46%	0.980	97.40
EBA	PRB	EPRI Bottom Ash	21	32	79	248	8.16%	17.1%	2.75%	1.001	79.98
EPA	PRB	EPRI Pondered Ash	18	33	87	266	8.29%	16.3%	2.82%	0.994	93.71
345 ^{1,2}	APP	Fly Ash	141	92	166	524	11.3%	4.25%	0.53%	1.003	89



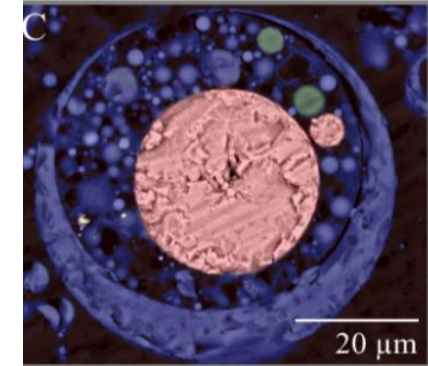
EPRI-CO and -FA:
95%CeIII, <5% CeIV
EPRI-BA and EPRI-PA
~10-30% CeIV

Solid characterization

EPRI fly ash SEM backscatter image (left) and SEM-EDS analysis (right)



345 APP fly ash



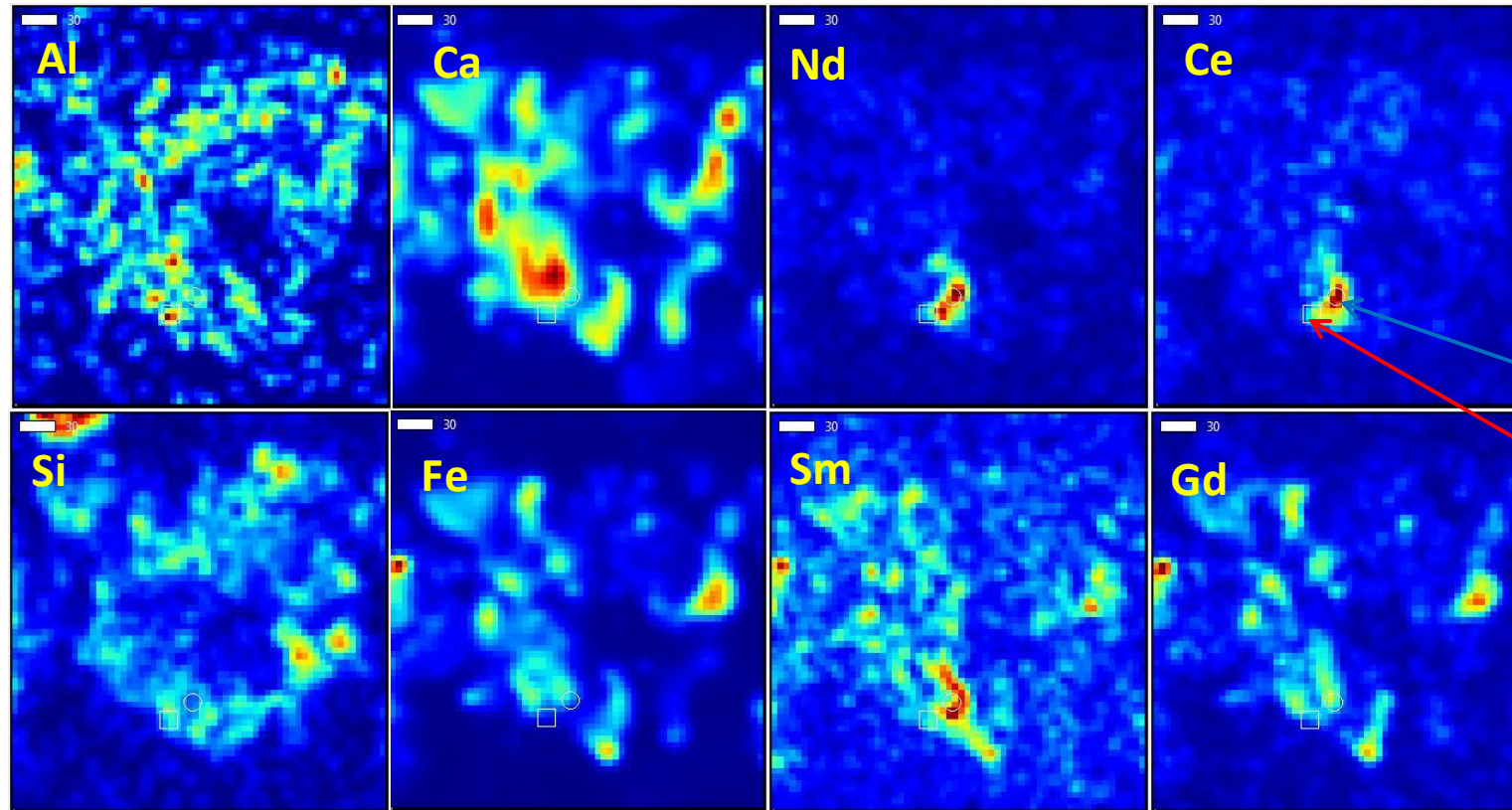
SEM backscatter image of fly ash particle (Montross et al. (2016)). Phases identified:
Si-Al phase - purple
Fe-oxide - red
Ca-oxide - green
REE mineral - yellow

- Preliminary XRD results found that PRB while predominantly amorphous, generally consists of Ca,Mg-rich mineral phases (e.g., lime, periclase, anhydrite, merwinite, calcite and brownmillerite), in contrast to the aluminosilicate phases (e.g. mullite) commonly found in APP ash.
- SEM results showed amorphous glass phases with Ca-rich crusts in EPRI fly ash

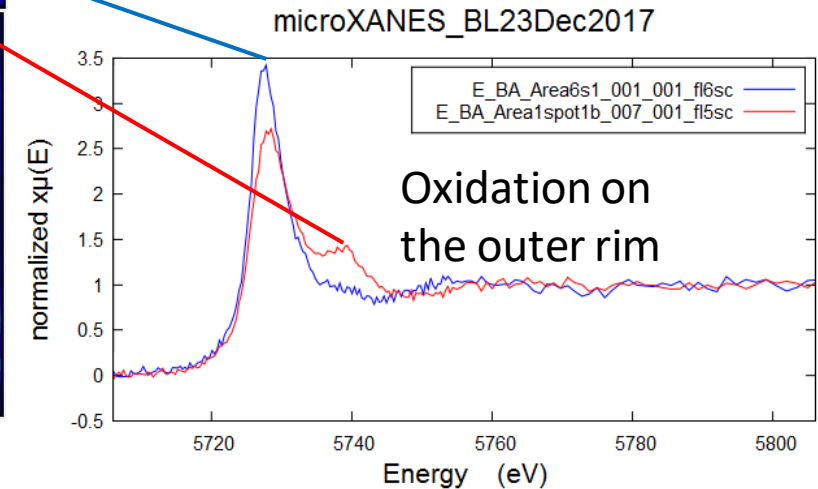
Synchrotron-based Micro-analysis (3 samples 6 mapping areas)

Example: EPRI Ca-, Mg-rich Bottom Ash

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



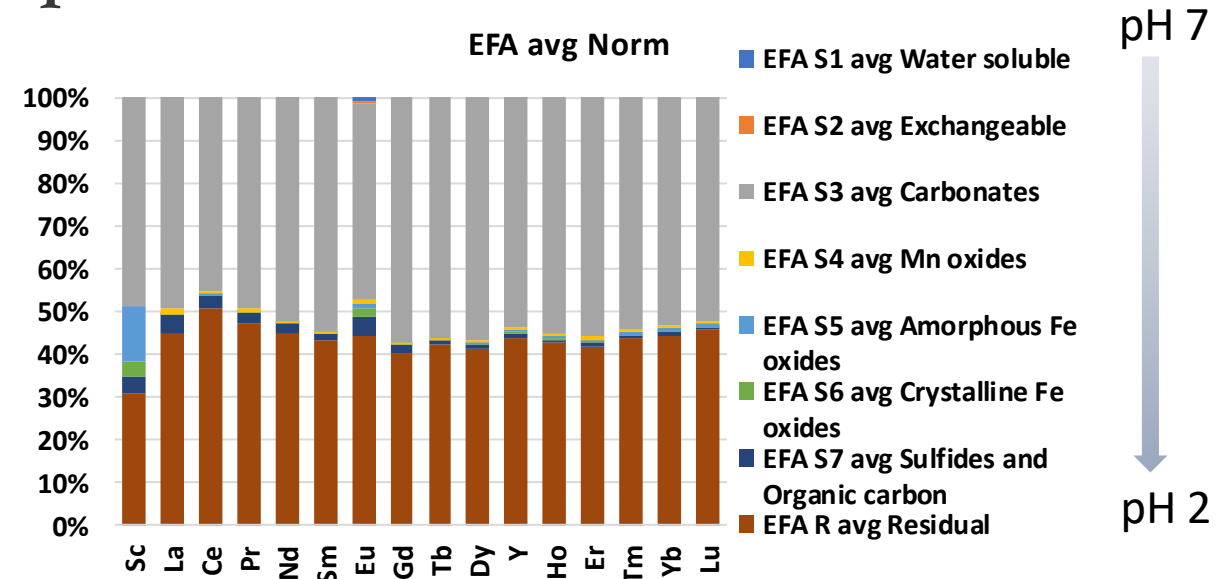
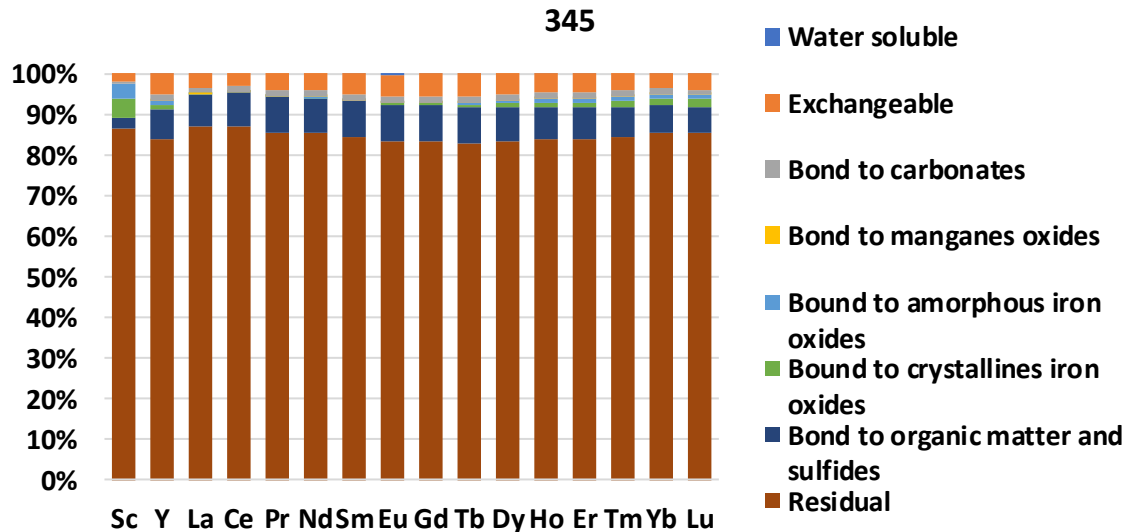
- During coal combustion, Ce diffused into Ca phases, thus susceptible to Ce oxidation during coal combustion
- $\text{Ce(III)} + \text{O}_2 = \text{Ce(IV)O}_2$



Sequential Extraction for Characterization

Informing extractability of REEs associated with different mineral fractions

- Fly Ash 345 (313ppm REE+Y) derived from Appalachian Basin coal (4%wt Ca)
- REE associated mainly with Residual phase (aluminosilicates)
- EPRI-FA (264ppm REE+Y) derived from Powder River Basin coal (20%wt Ca)
- >60% REE released in “carbonate” phase extraction



Acid Leaching: Room temperature and mild acid

10mL solution/1 g solid, 24hr

- **Different dilute acids tested (~ 0.1 – 1.7 M)**

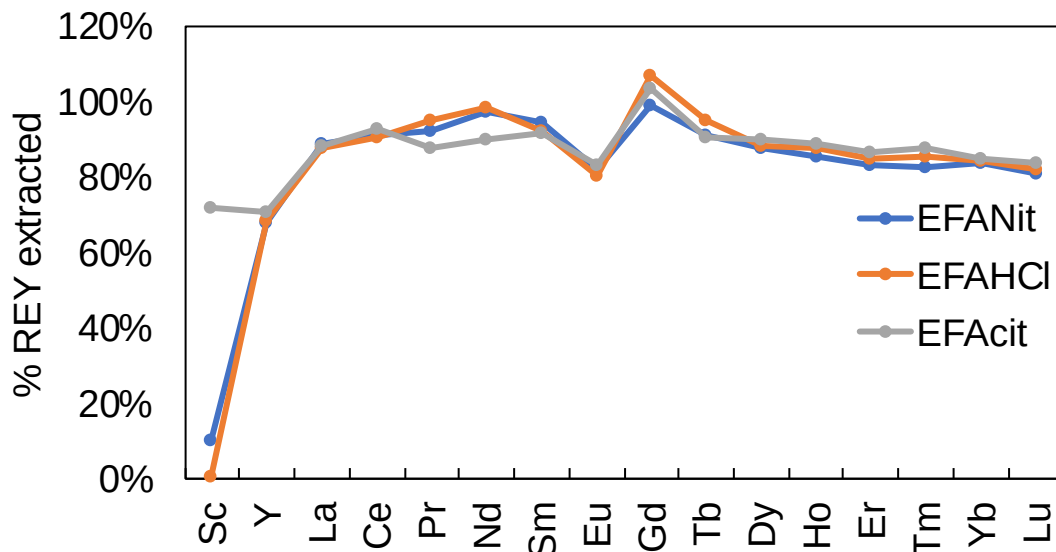
- HNO₃, HCl, citric acid, and sulfuric acid (inefficient due to gypsum coating)

- **Observations:**

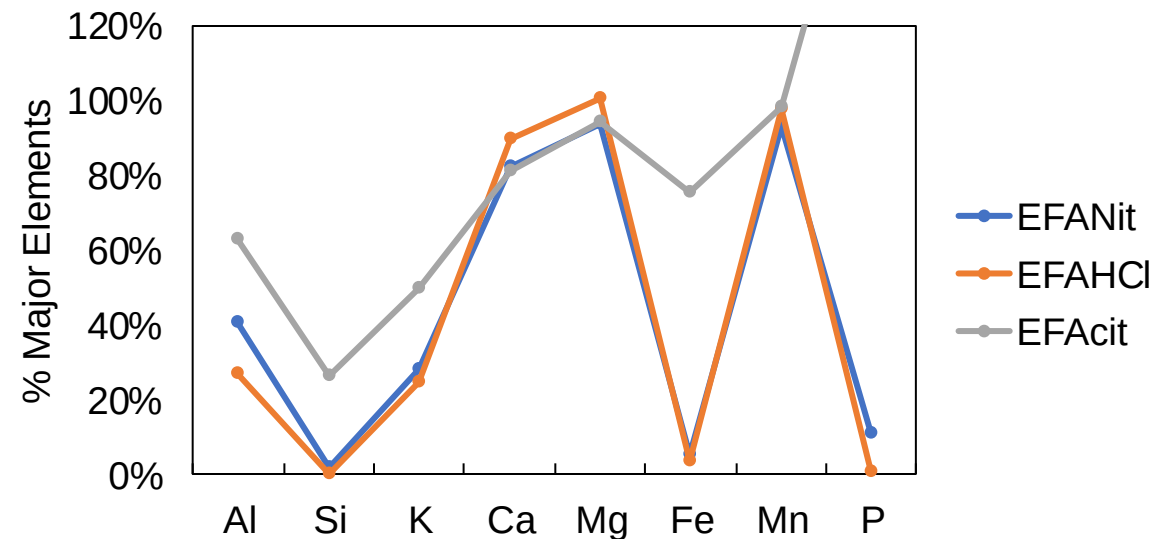
- Other than Sc, about 90% REE extracted by different acids
 - 100% Ca, Mg and Mn were extracted during acid leaching
 - Citric acid extracted more Fe and P, slightly more Al and Si (gel formed)



%REE extracted

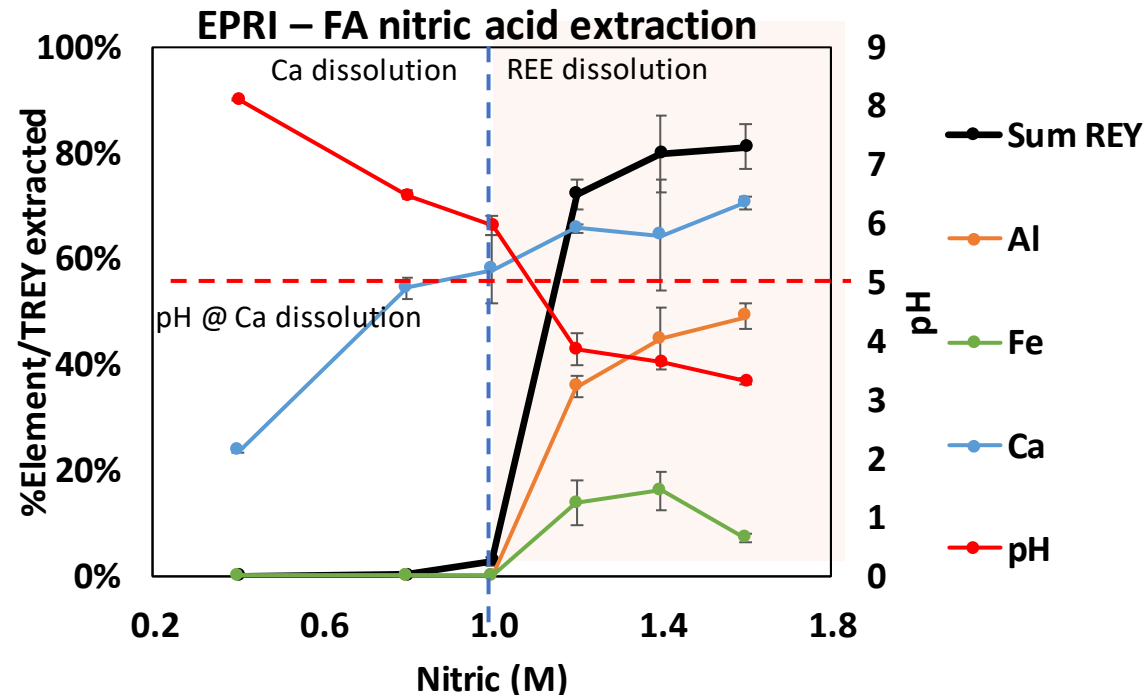
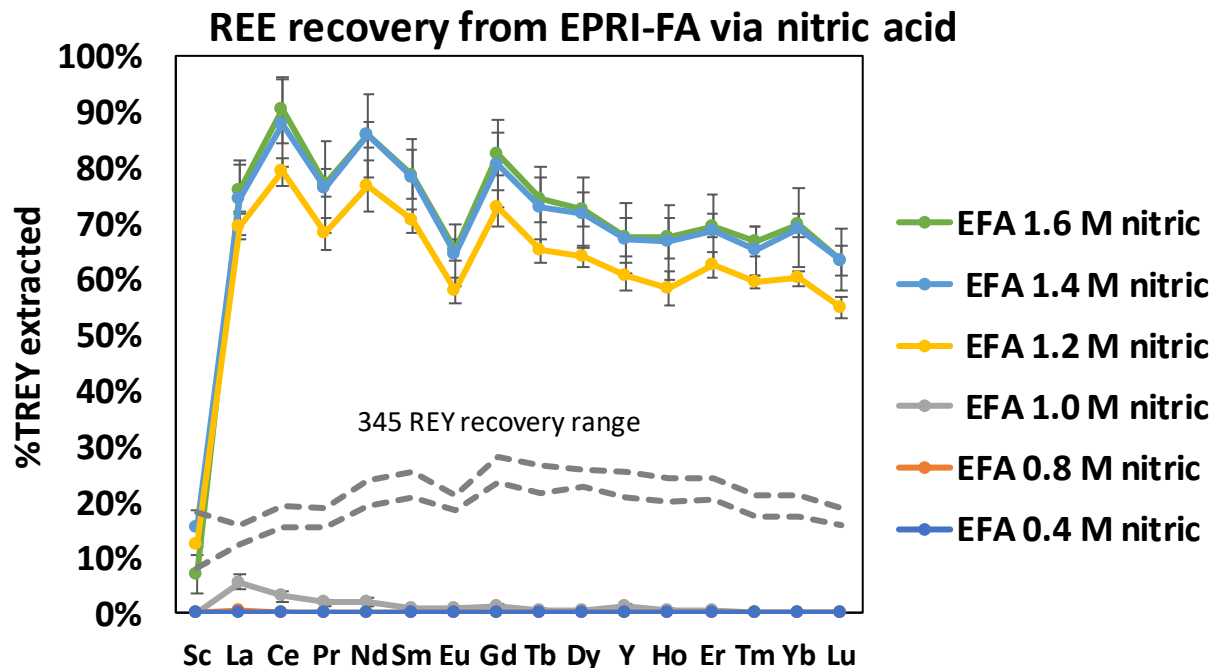


%Major Elem extracted



Inorganic acid extraction

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

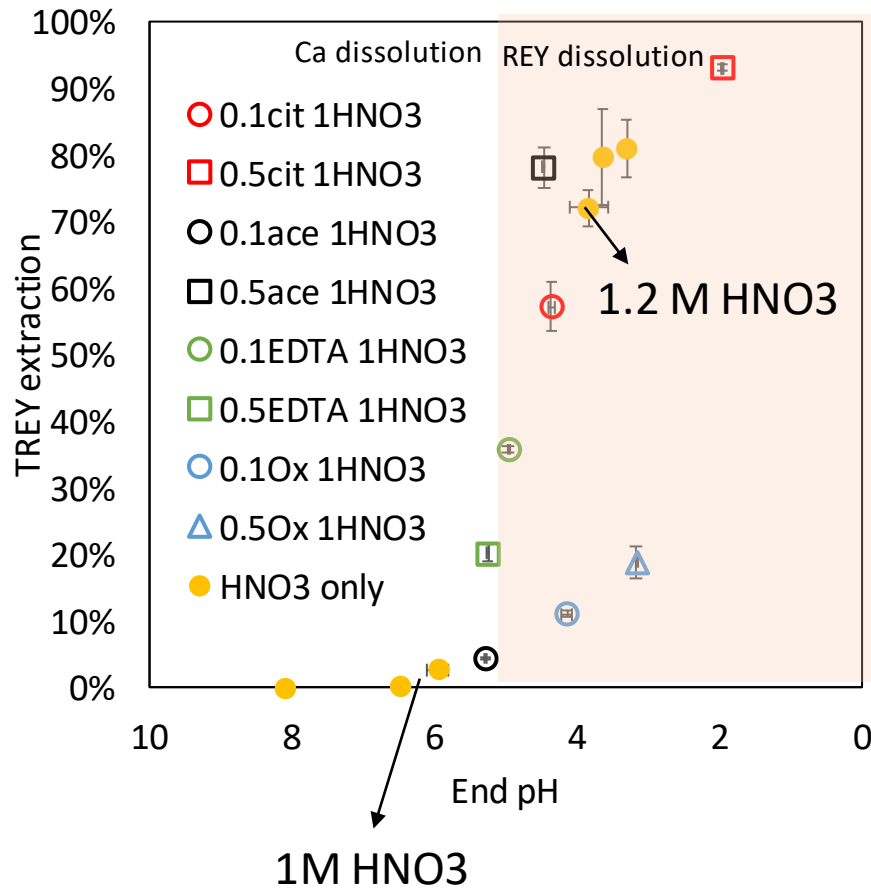


- Compared to 345, REY from PRB ash samples can be mobilized
- Acid will first dissolve **Ca phases** (End **pH** > 5, @ 1M HNO₃ for EFA) and then REYs together with **Al** and **Fe** (End **pH** < 5)

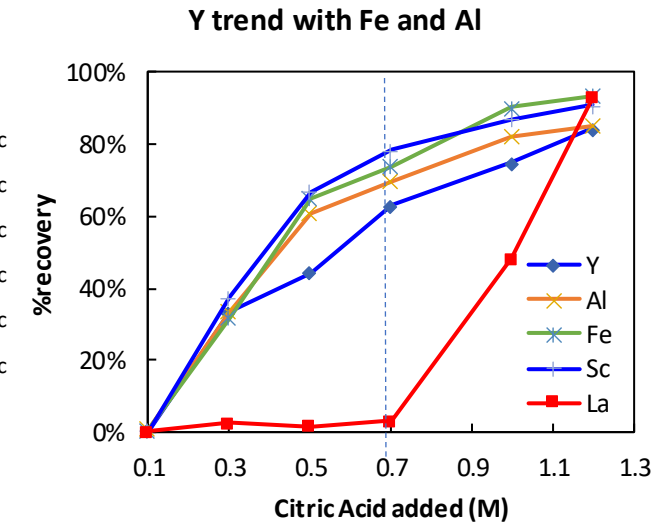
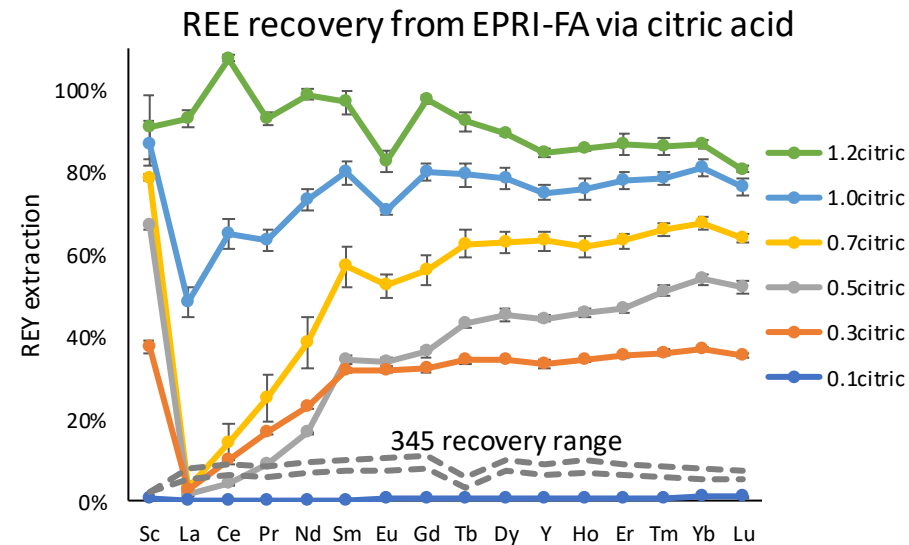
Organic extraction

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

REY dissolution occurs @ End pH<5

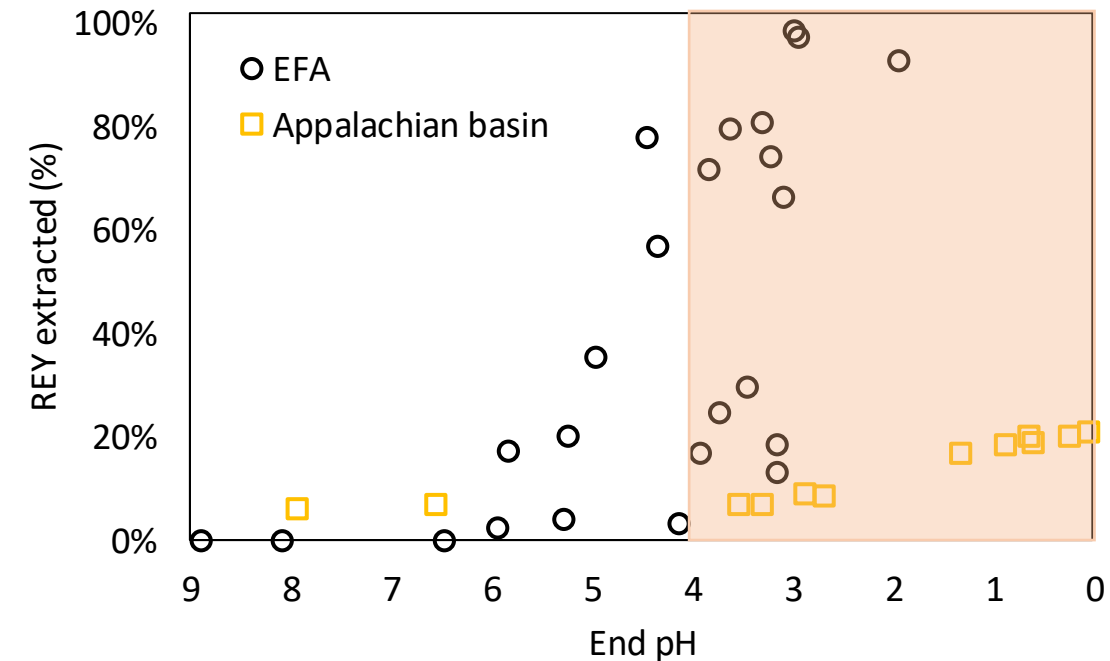


- Citric acid will first extraction MHREEs (Eu-Lu) via chelating Fe

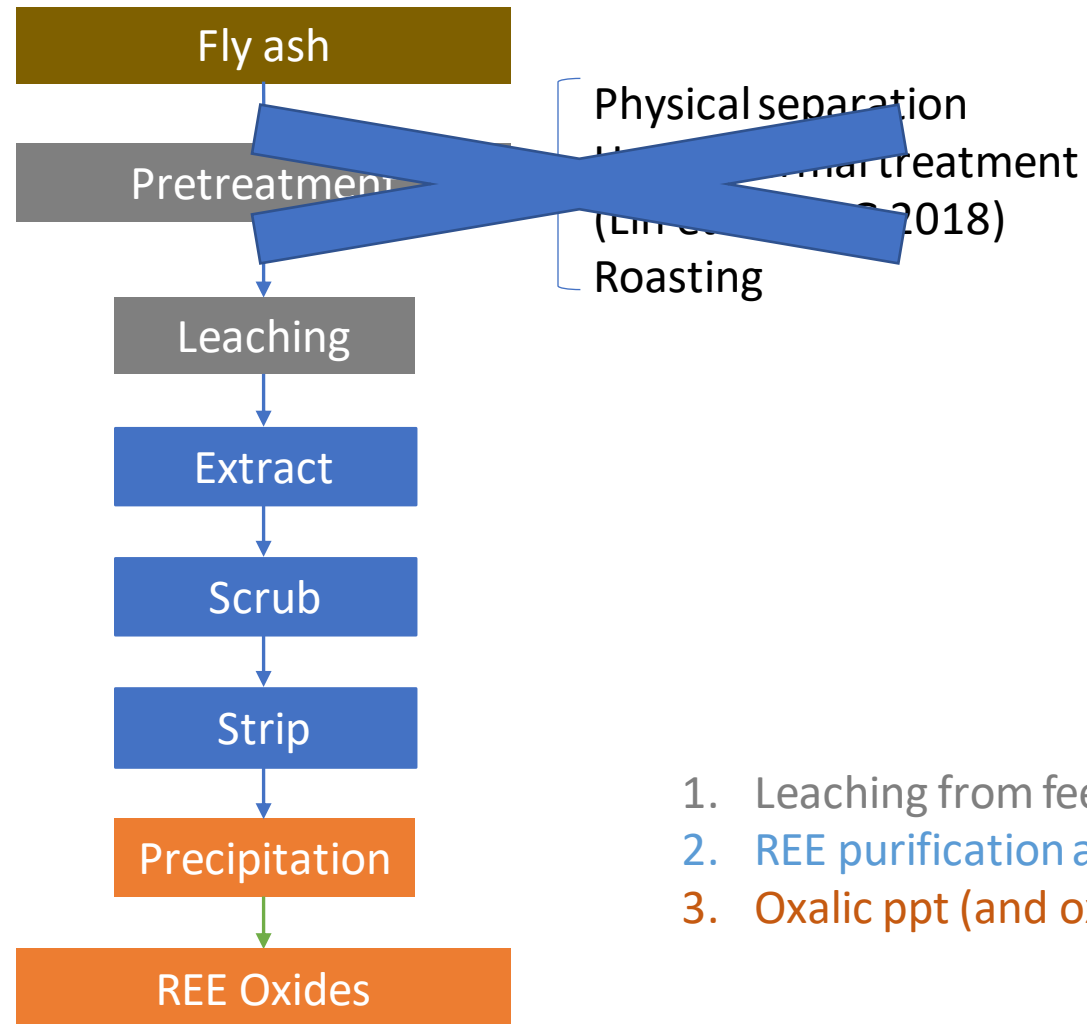


Highlights

- End pH vs. %REE: pH < 4 for efficient %REE from PRB EPRI samples
- REE released due to mineral phase dissolution: Ca dissolution threshold for LREEs; Fe and Al dissolution for HREEs
- Dilute acid extractions results in 100% REE extraction with end pH 3.05, final solution 20ppm REE+Y



Benefit for REE separation: Traditional vs. PRB Fly Ash



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

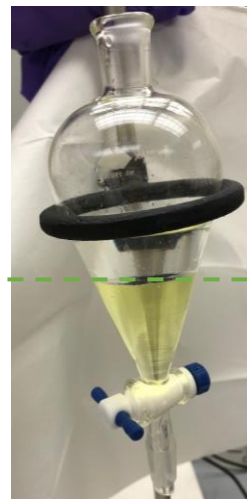
REE Enrichment



EPRI fly ash



Acid Leaching



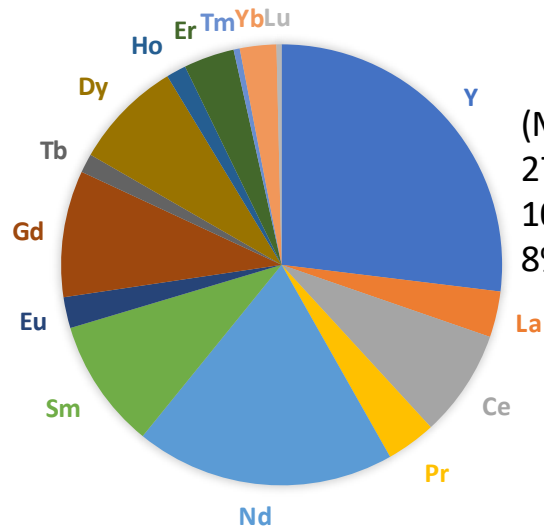
L:L extraction

Organic Phase
Aqueous Phase:
Fe and HREE+Y



Oxalic acid precipitation

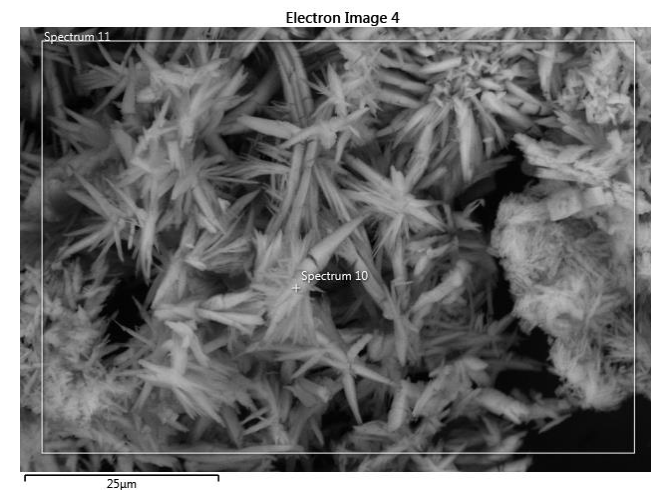
FLY ASH OXALATE PRECIPITANTS, 12%WT REE



(Mostly HREEs:
27% Y, 19% Nd,
10% Sm, 9% Gd,
8% Dy)



HREE+Y oxalate
precipitates (~12%wt REY)



Conclusions and Implications

The preliminary results demonstrate 100% REE extractability from PRB ash using dilute acids at room temperature.

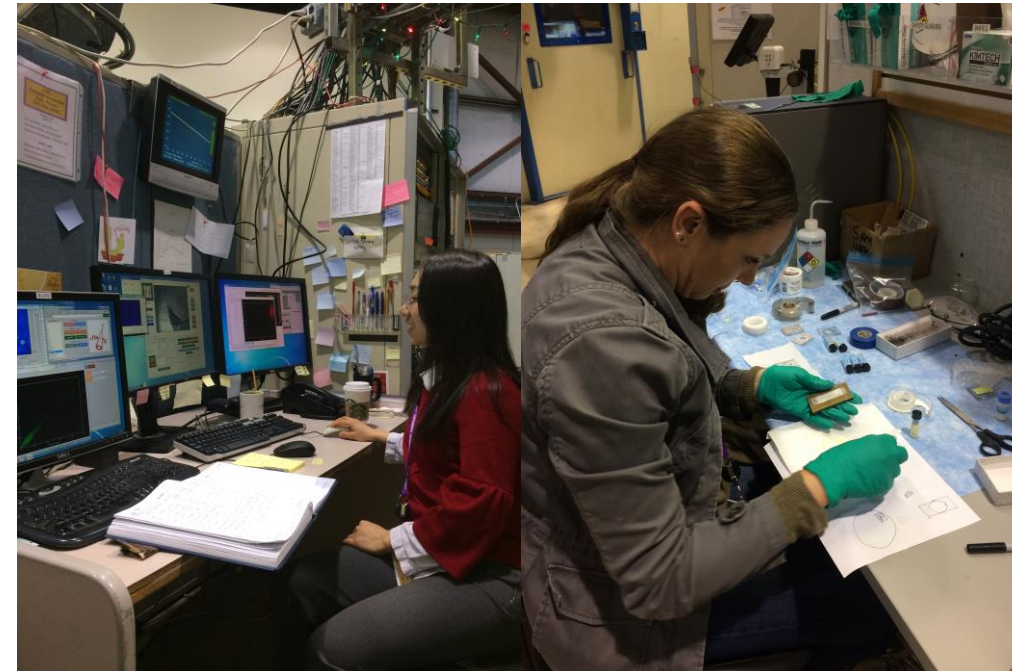
- Possible organic acid extraction for PRB ash samples
- Dilute acids will save the cost for REE extraction from ash samples.

End pH @ 3 -4 for efficient REE extraction

- Leachate will be more environmental friendly and save the cost for later REE purification
- Demonstrated high REY recovery (12wt%)

Heavy REEs and light REEs can be leached from the fly ash separately using different acid conditions sequentially extracting Ca phases and Fe phases.

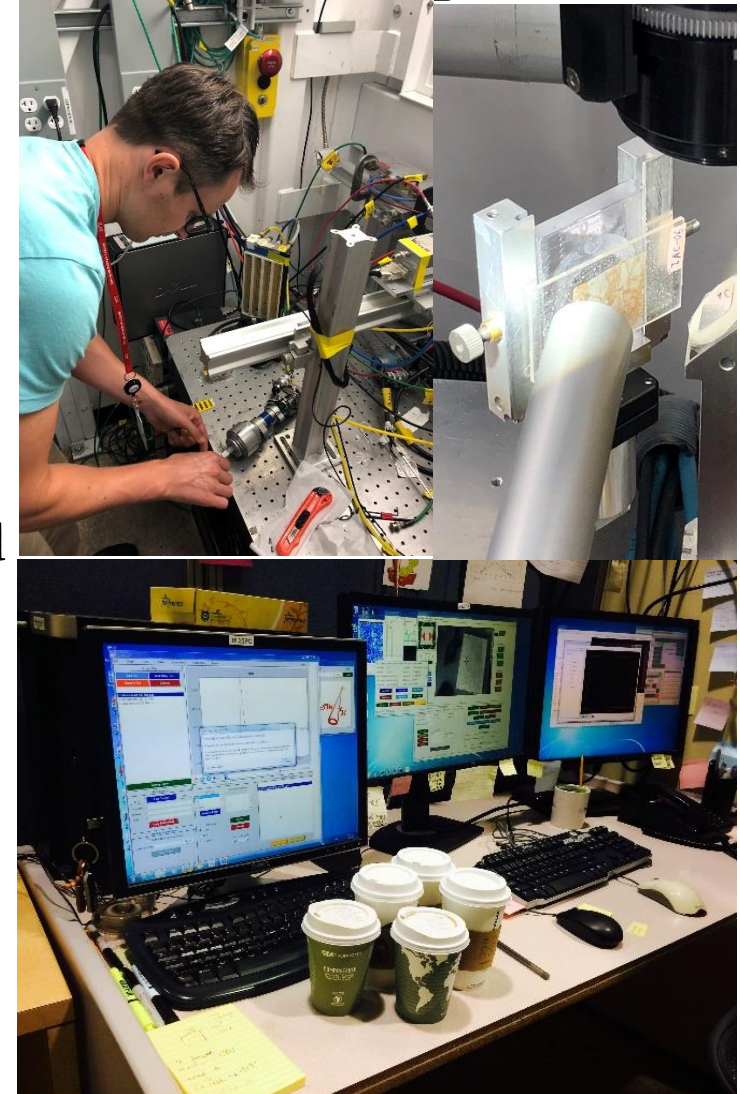
- Step leaching for fly ash for initial separation of LREE and HREE
- Save the cost for REE purification and separation



Acknowledgements

Coffee is your friend!

- REE Research Team and Management at NETL
- Scott Montross (Leidos) for SEM imaging
- Sam Webb, Nick Edwards and Sharon Bone (SSRL)
- This work was performed in support of the US Department of Energy's Fossil Energy Crosscutting Technology Research Program. The Research was executed through the NETL Research and Innovation Center's Rare Earth Element Research performed by Leidos Research Support Team staff was conducted under the RSS contract 89243318CFE000003.
- The synchrotron work was conducted on beamlines 2-3, 4-1 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.



Disclaimer

This work was funded by the Department of Energy, National Energy Technology Laboratory, an agency of the United States Government, through a support contract with Leidos Research Support Team (LRST). Neither the United States Government nor any agency thereof, nor any of their employees, nor LRST, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.