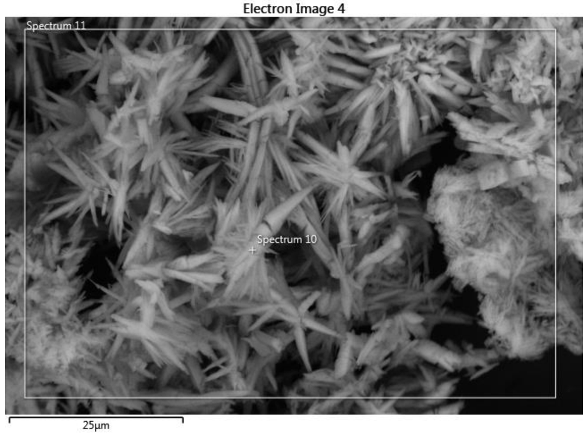
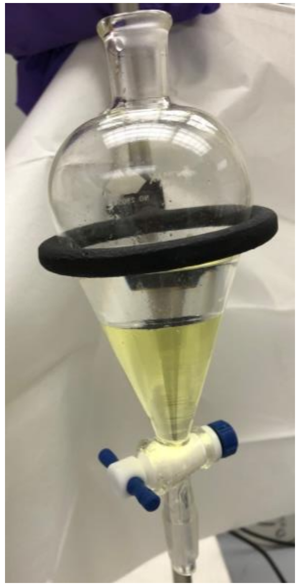




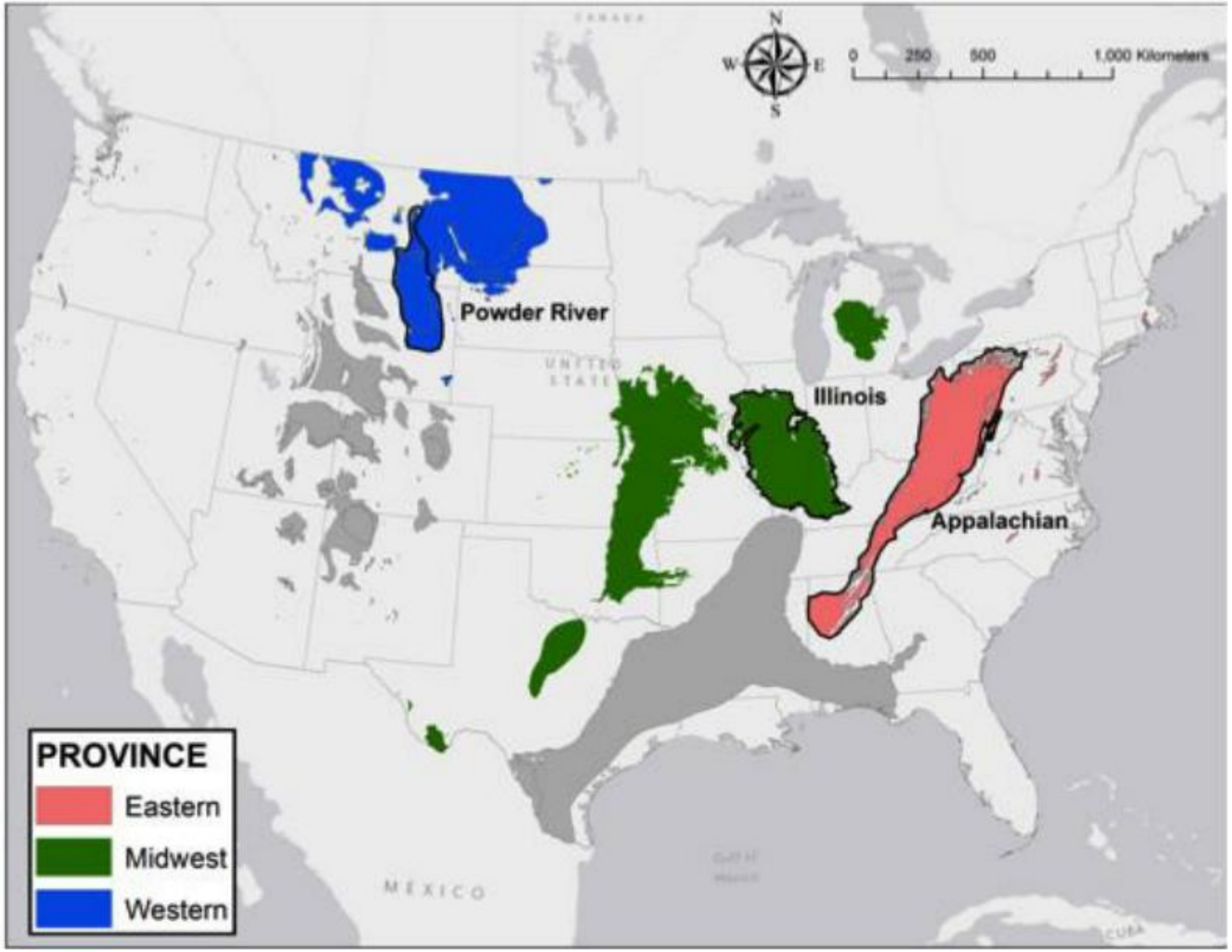
Characterization and Recovery of Rare Earth elements from Powder River Basin Coal Ash

Mengling Stuckman[1,2], Christina Lopano[2], Ben Hedin[3,4], Bret Howard[2], and Evan Granite[2]

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

Powder River Basin

- **<u>Powder River Basin (PRB)</u>** is the largest coal production (36% of total) reservoir in US; est. annual potential 3630 tons REOs



REE recovery potential from PRB Coal byproducts

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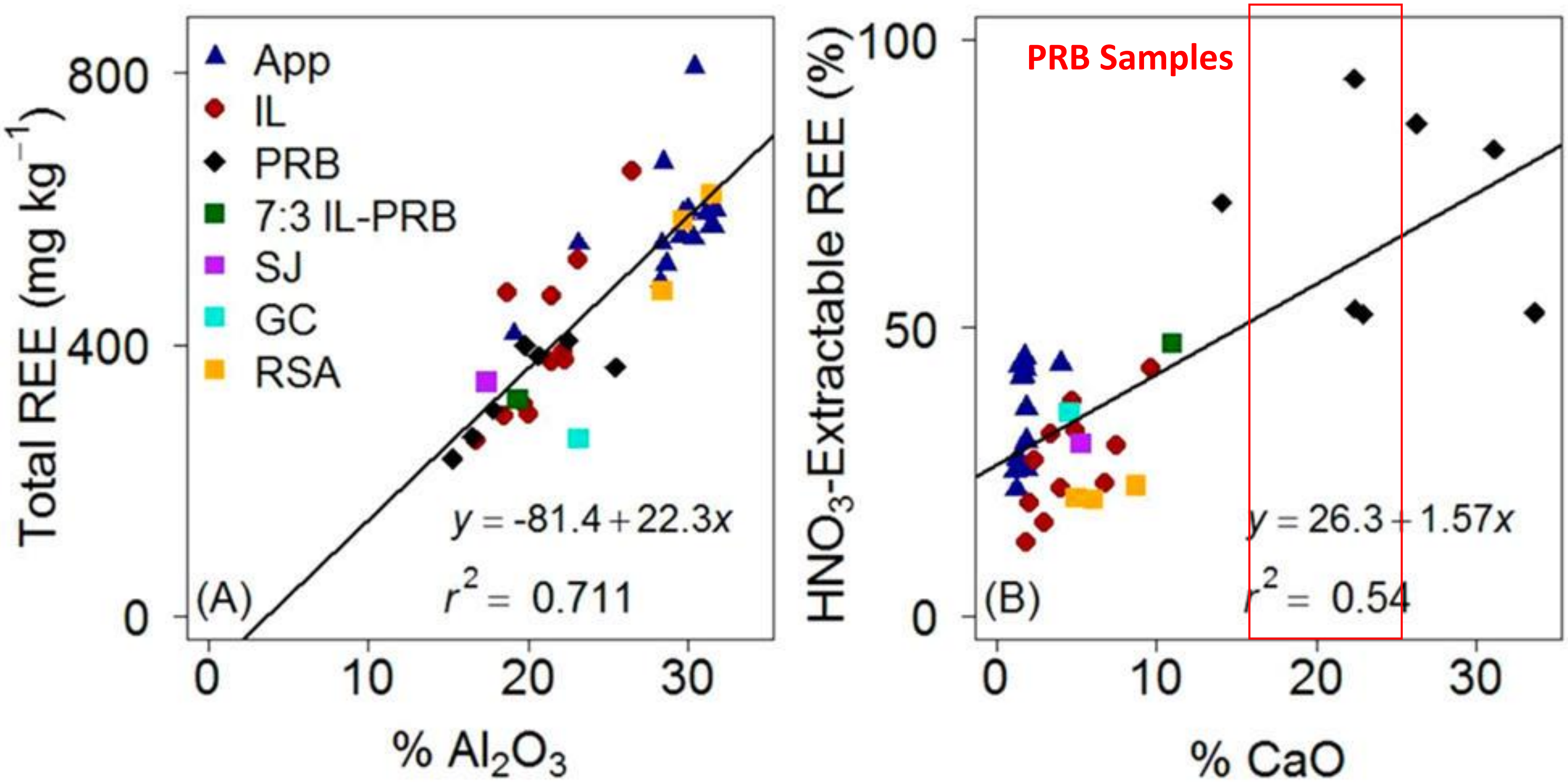
- **Ca-rich Ash samples from Powder River Basin (PRB) content have more mobile REEs compared to Al-rich Appalachian ash, due to different REE deposition environments (Ca/Mg oxides as opposed to glass phase) during coal combustion.**

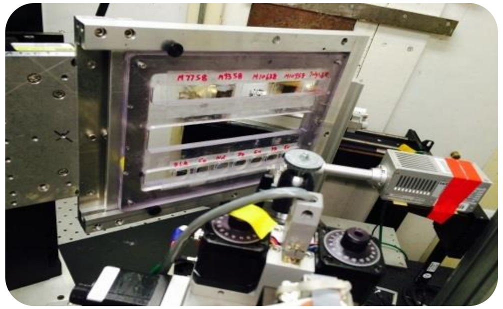


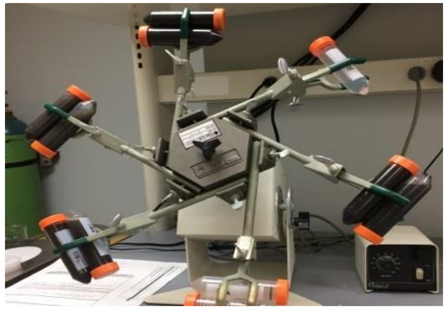
Taggart, R.K., Hower, J.C., Dwyer, G.S., Hsu-Kim, H., 2016. Trends in the Rare Earth Element Content of U.S.-Based Coal Combustion Fly Ashes. Environmental Science & Technology 50, 5919-5926.

Study Goal

Characterization studies to understand the higher REE release (10-30% release from ammonium sulfate) from Ca-Mg rich EPRI ash samples.

Demonstrated approximately 12wt% REE concentrate from fly ash, and 2.7wt% from AMD solids at the lab beaker scale.





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

- Inorganic acid: HNO_3, HCl, H_2SO_4

- Organic acid: Citric, acetic, oxalic, EDTA

- End pH vs. %REY

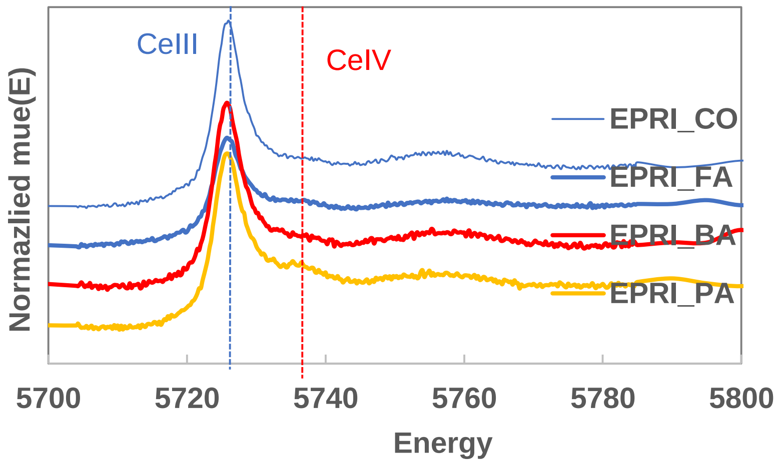
LREE vs. HREE

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	%Ca	%Mg	Ce anomaly	%Ash
ECO	PRB	EPRI Coal	1.9	3	11	24	2.02%	0.34%	0.991	9.01
EFA	PRB	EPRI Fly Ash	26	38	91	264	20.8%	3.46%	0.980	97.40
EBA	PRB	EPRI Bottom Ash	21	32	79	248	17.1%	2.75%	1.001	79.98
EPA	PRB	EPRI Ponded Ash	18	33	87	266	16.3%	2.82%	0.994	93.71
345[1,2]	APP	Fly Ash	141	92	166	524	4.25%	0.53%	1.003	89

EPRI Ce XANES

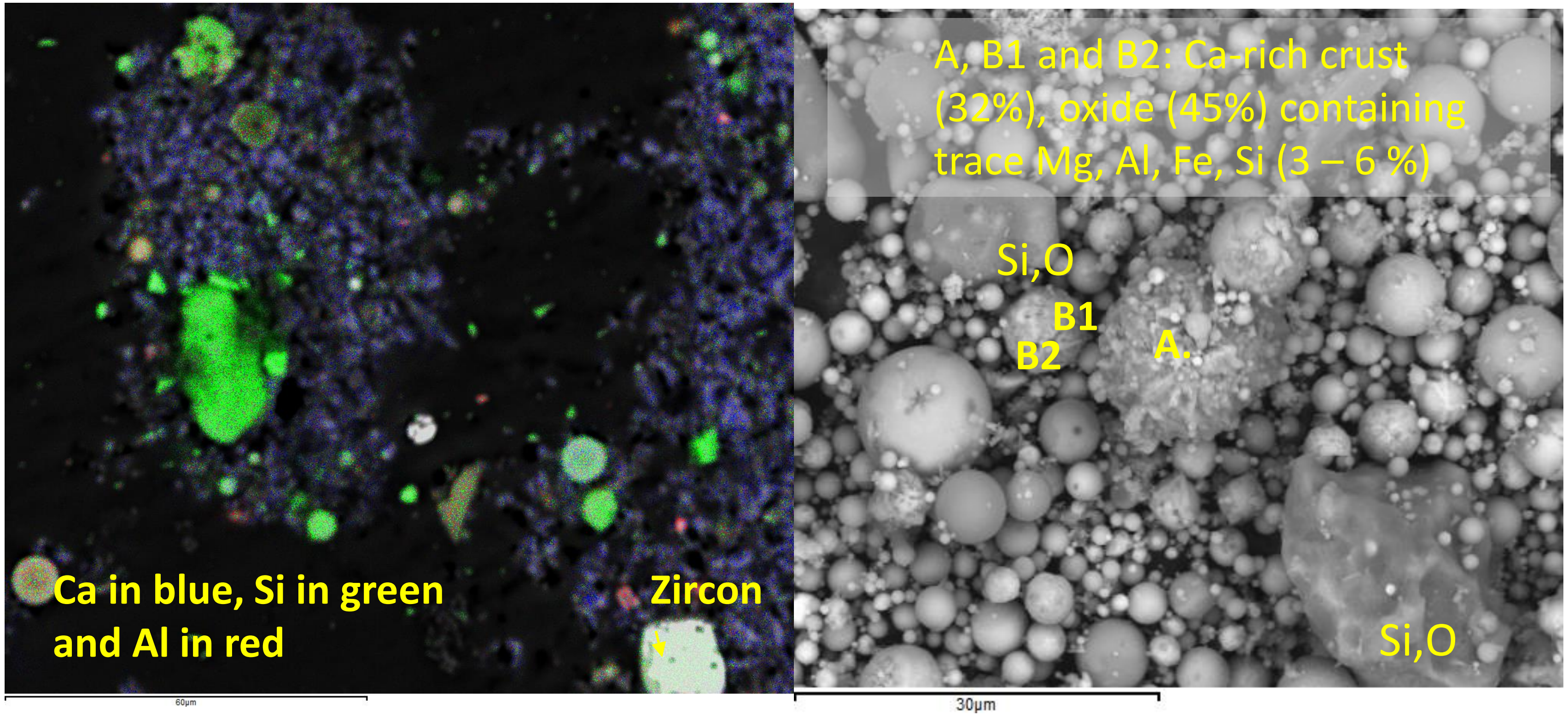


EPRI-BA and EPRI-PA ~10-30% CeIV

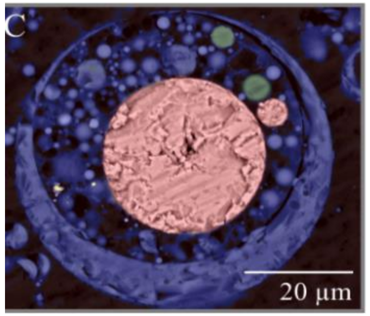
1: M.Y. Stuckman, , et al. (2018), IJCG 195 (2018) 125-138.
2: R. Lin, M.Y. Stuckman, et al. (2018), Fuel, 232 (2018) 124-133.

Traditional solid characterization

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



345 fly ash



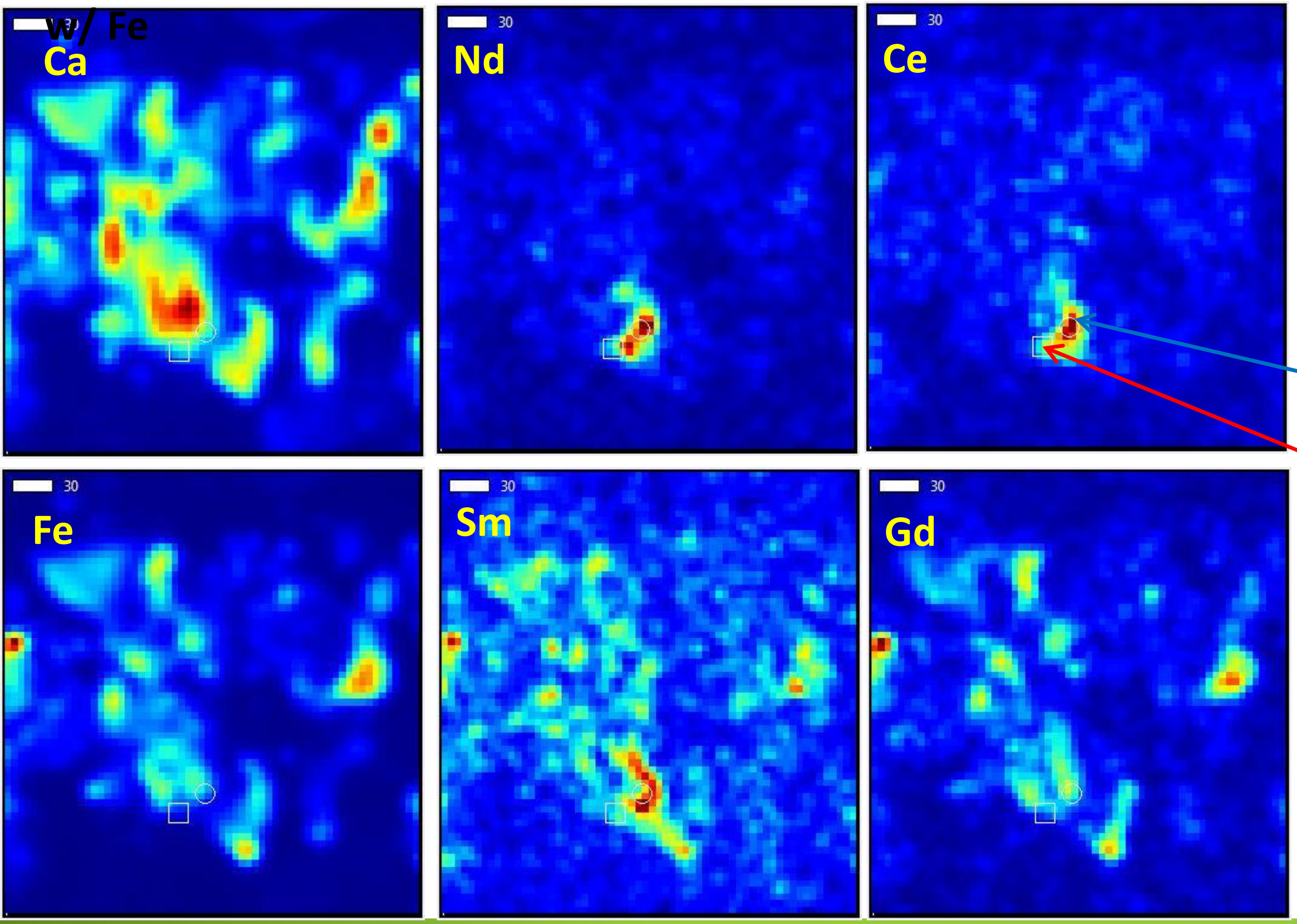
SEM backscatter image of fly ash particle (Montross et al. (2016)). Phases identified:
amorphous Si-Al -purple
Fe-oxide - red
Ca-oxide - green
REE mineral - yellow

- **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**

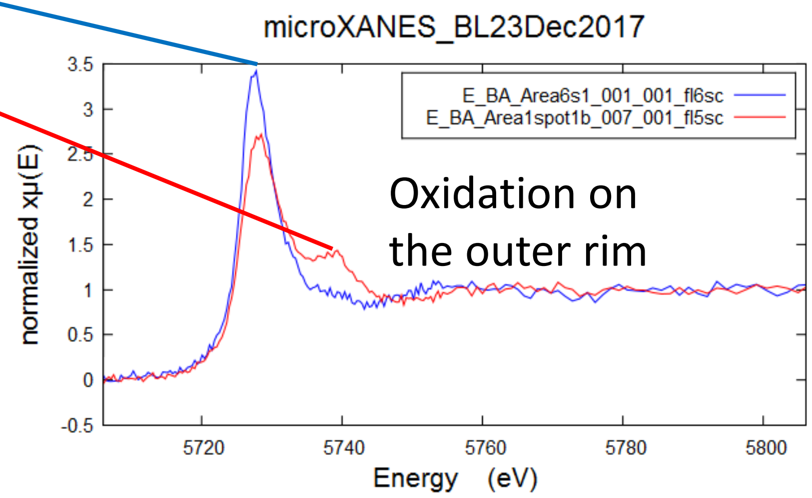
Synchrotron-based Micro-analysis (4 samples 12 mapping areas)

Example: EPRI Ca-, Mg-rich CCBs

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



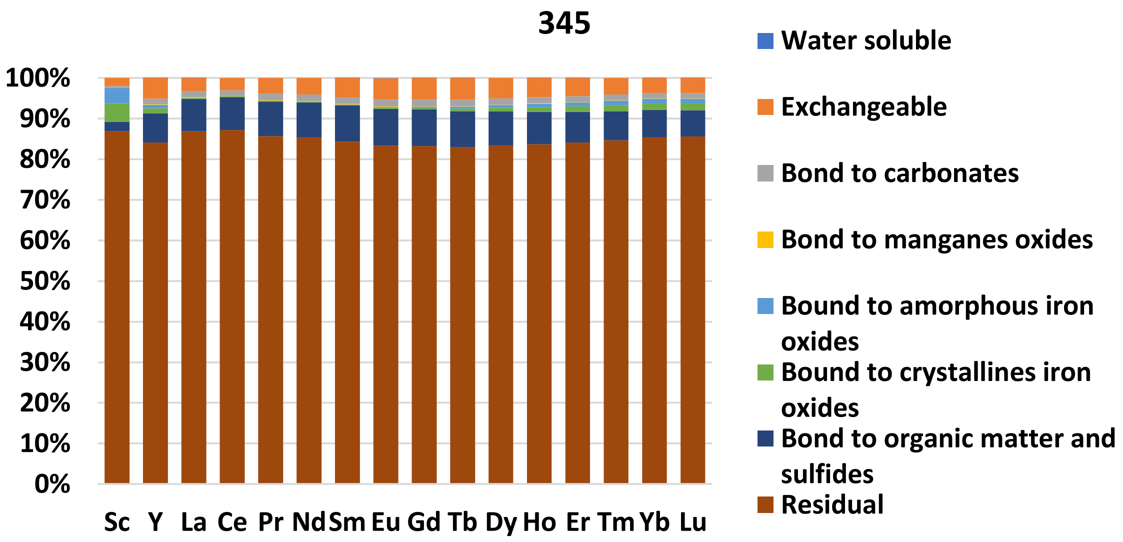
- **During coal combustion, Ce diffused into Ca phases, thus susceptible to Ce oxidation during coal combustion**
- **Ce(III) + O2 = Ce(IV)O2**



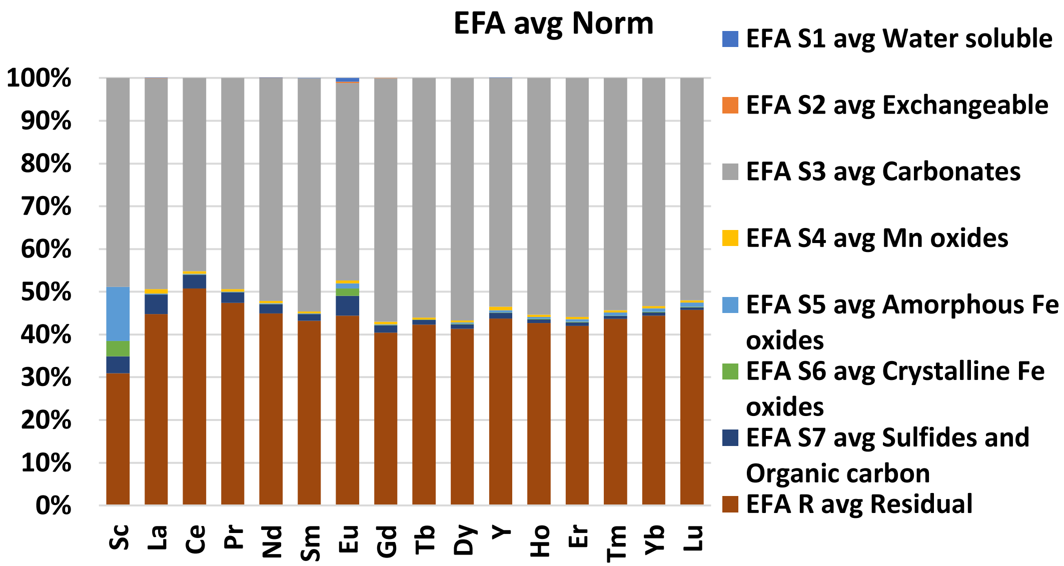
Sequential Extraction for Characterization

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



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.

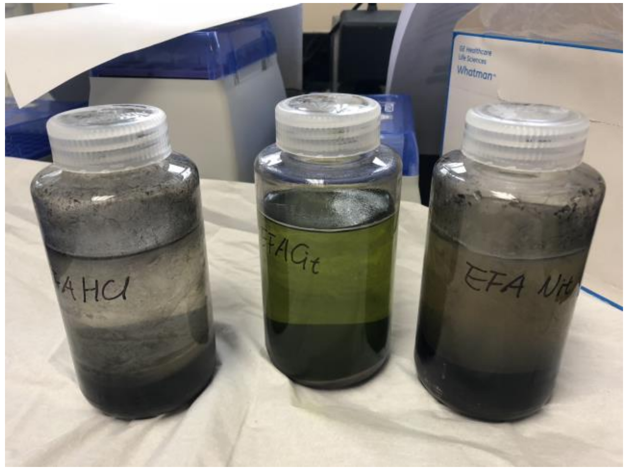
Acid Leaching: Room temperature and mild acid

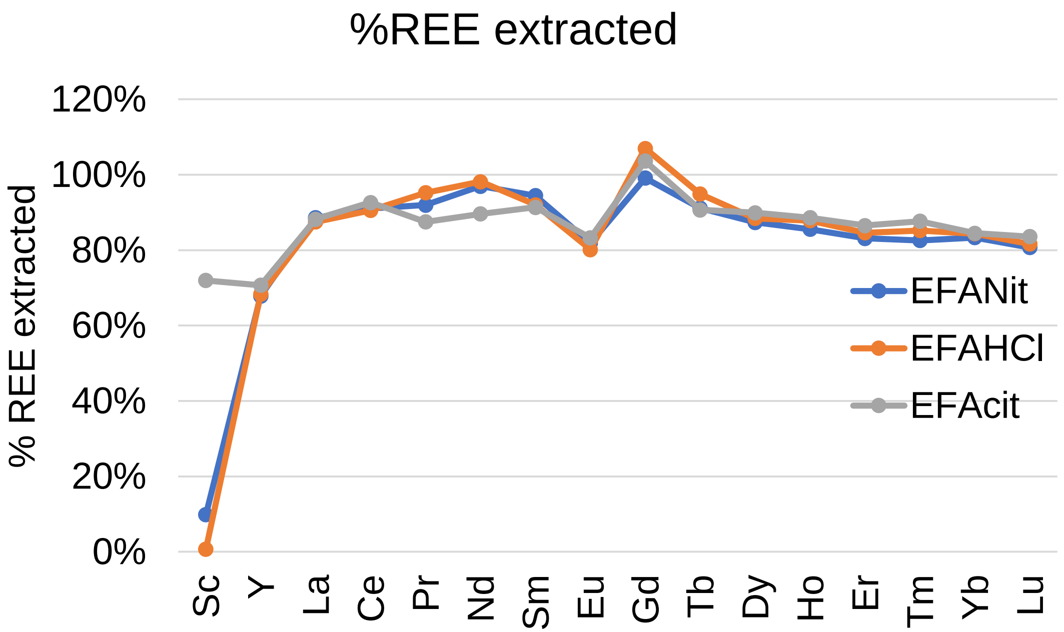
10mL solution/1 g solid, 24hr

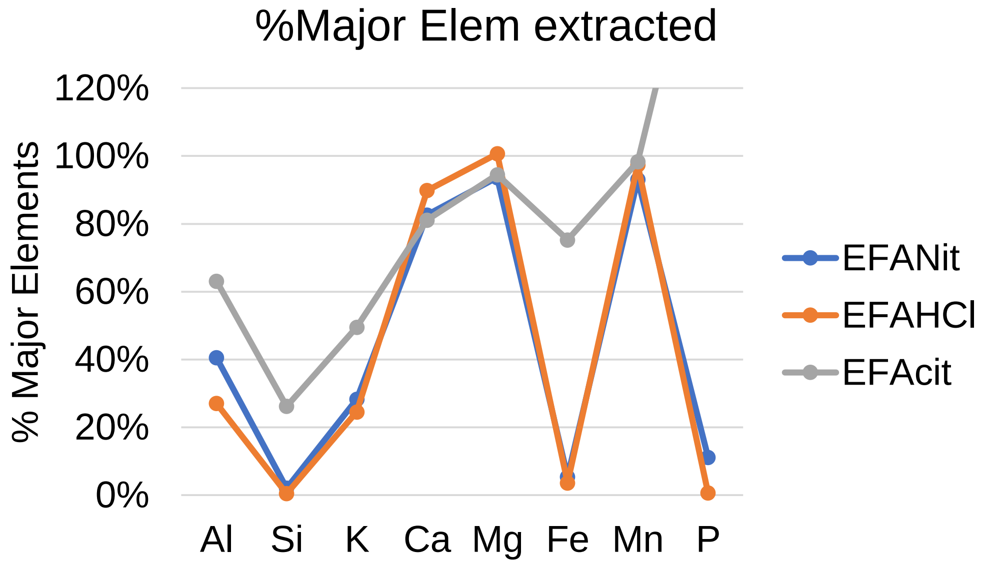
- **Different acid tested**

  1.6 M HNO3, 1.6 M HCl, 1.2 M citric acid

- **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)

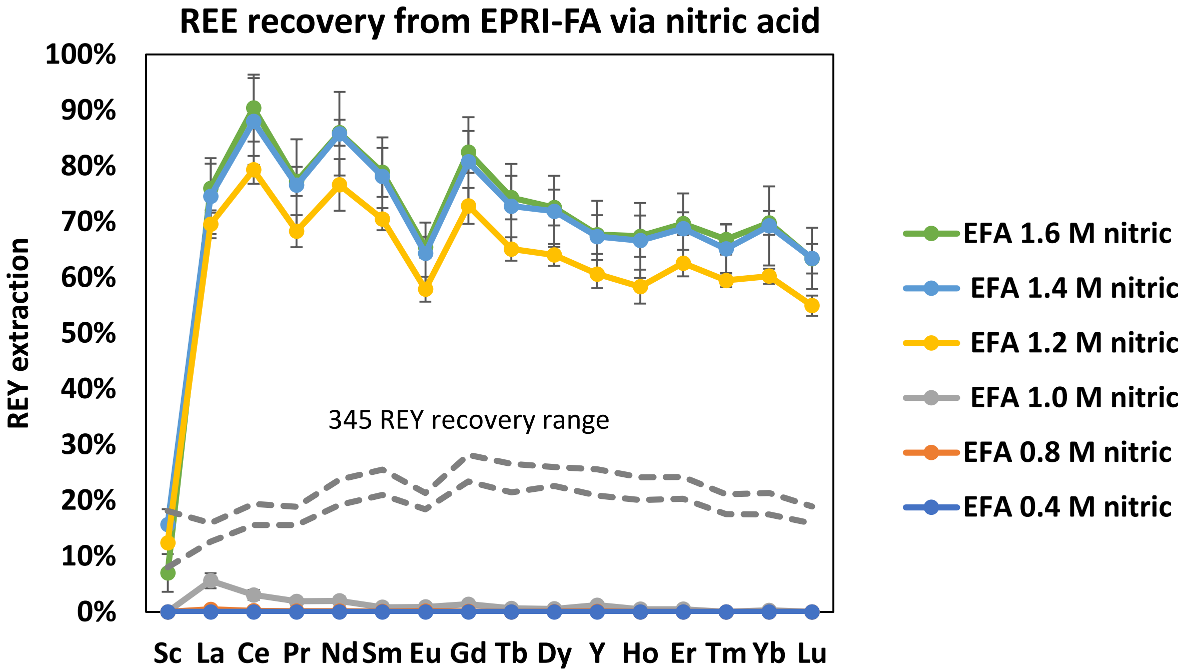


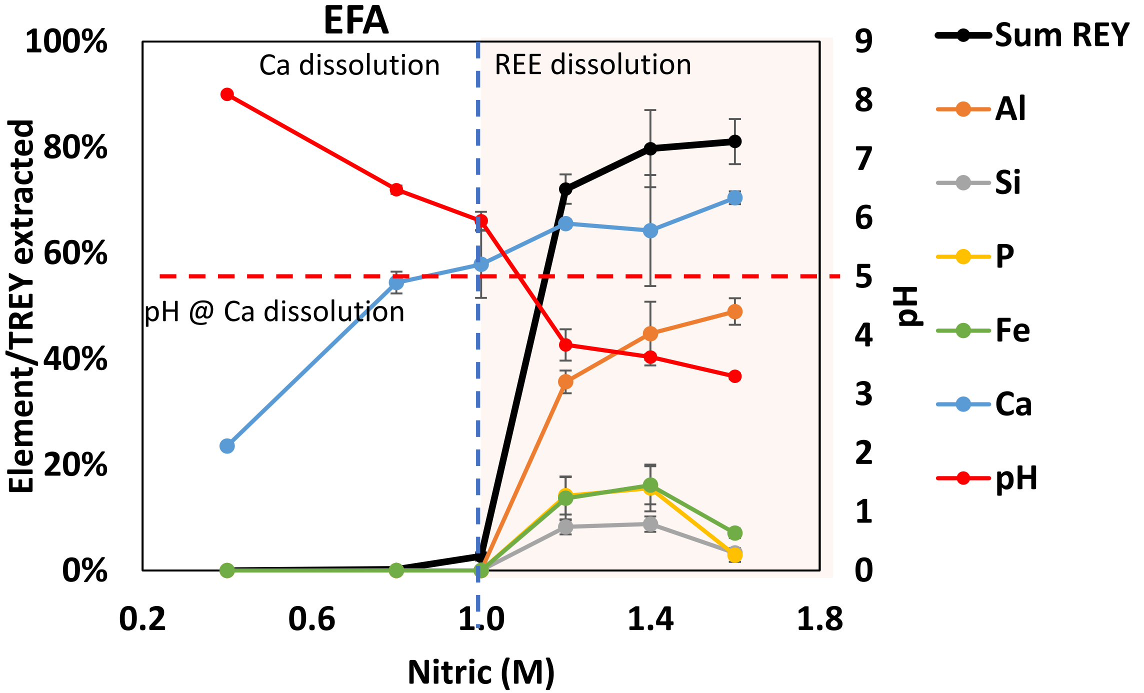




Inorganic acid extraction

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)
- Total 1.6M HNO3 will recover 80% REYs from PRB ash

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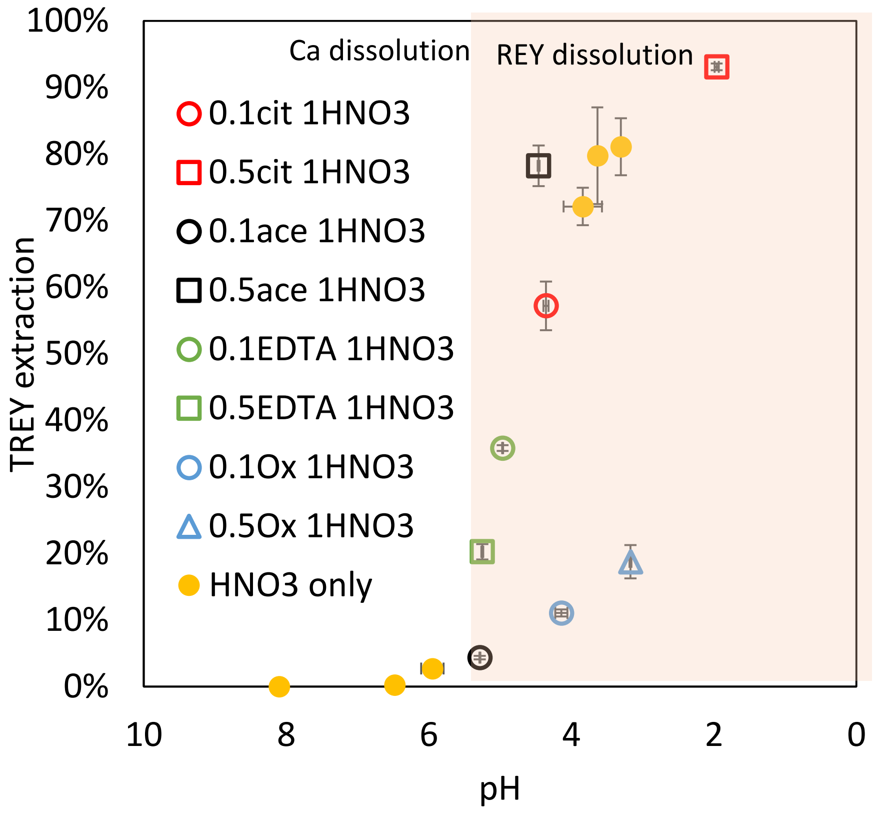
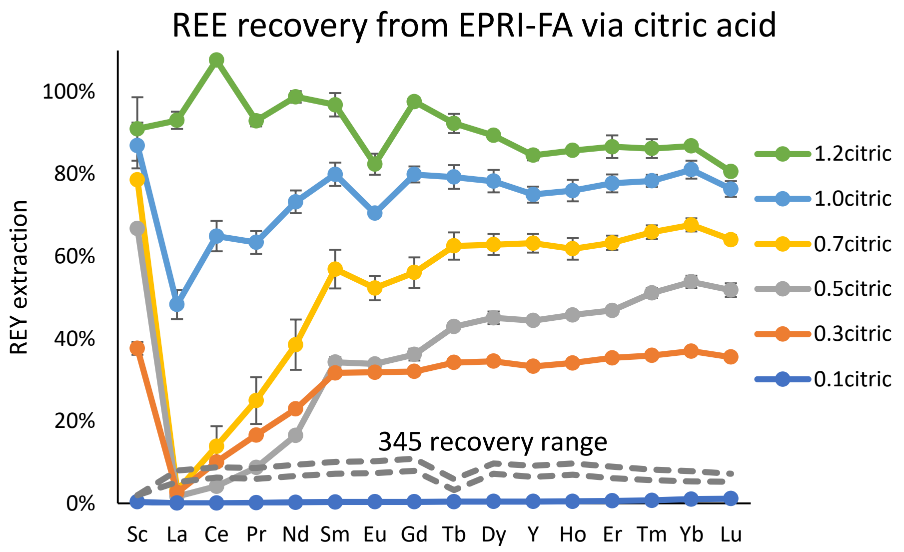
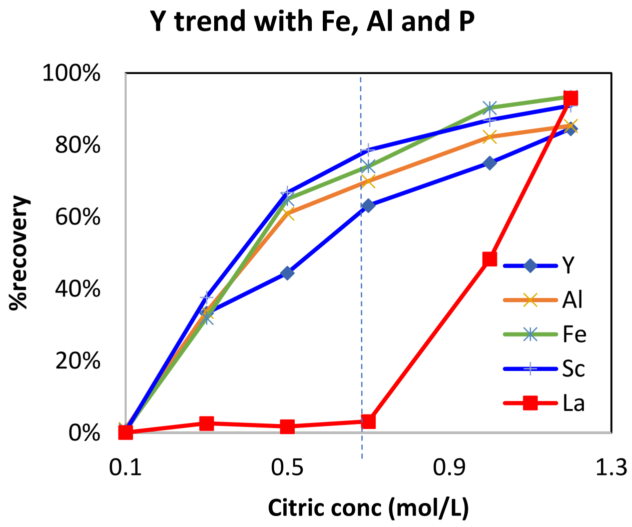
Organic extraction

pH based extraction independent of organic acid selection



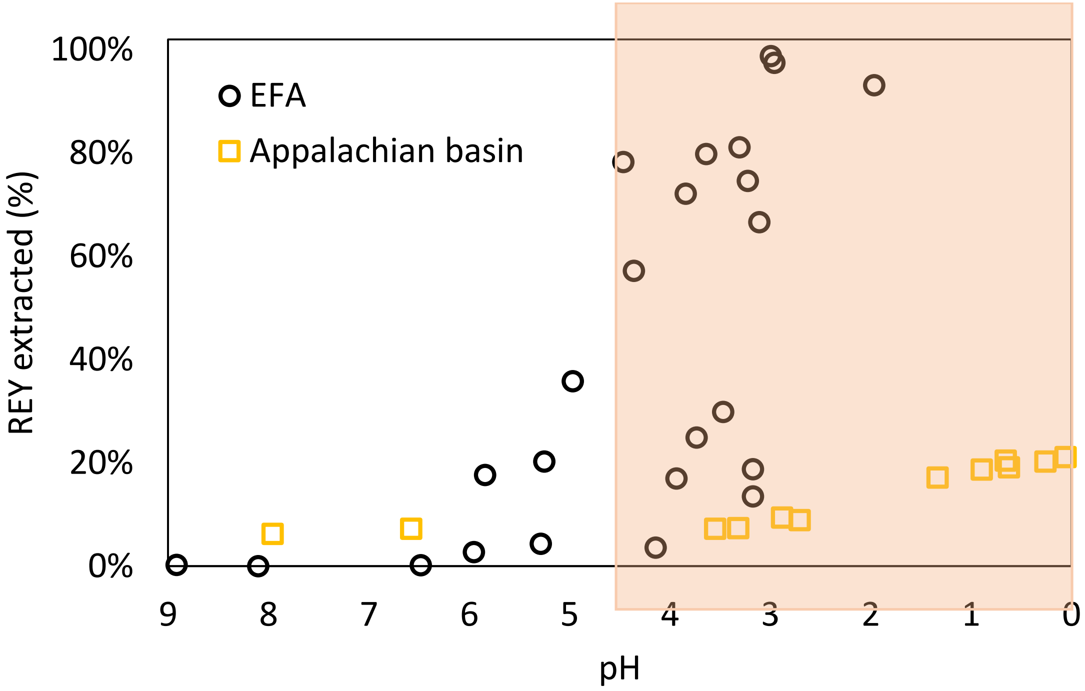
- **Citric acid will first extraction MHREEs (Eu-Lu) via chelating Fe**



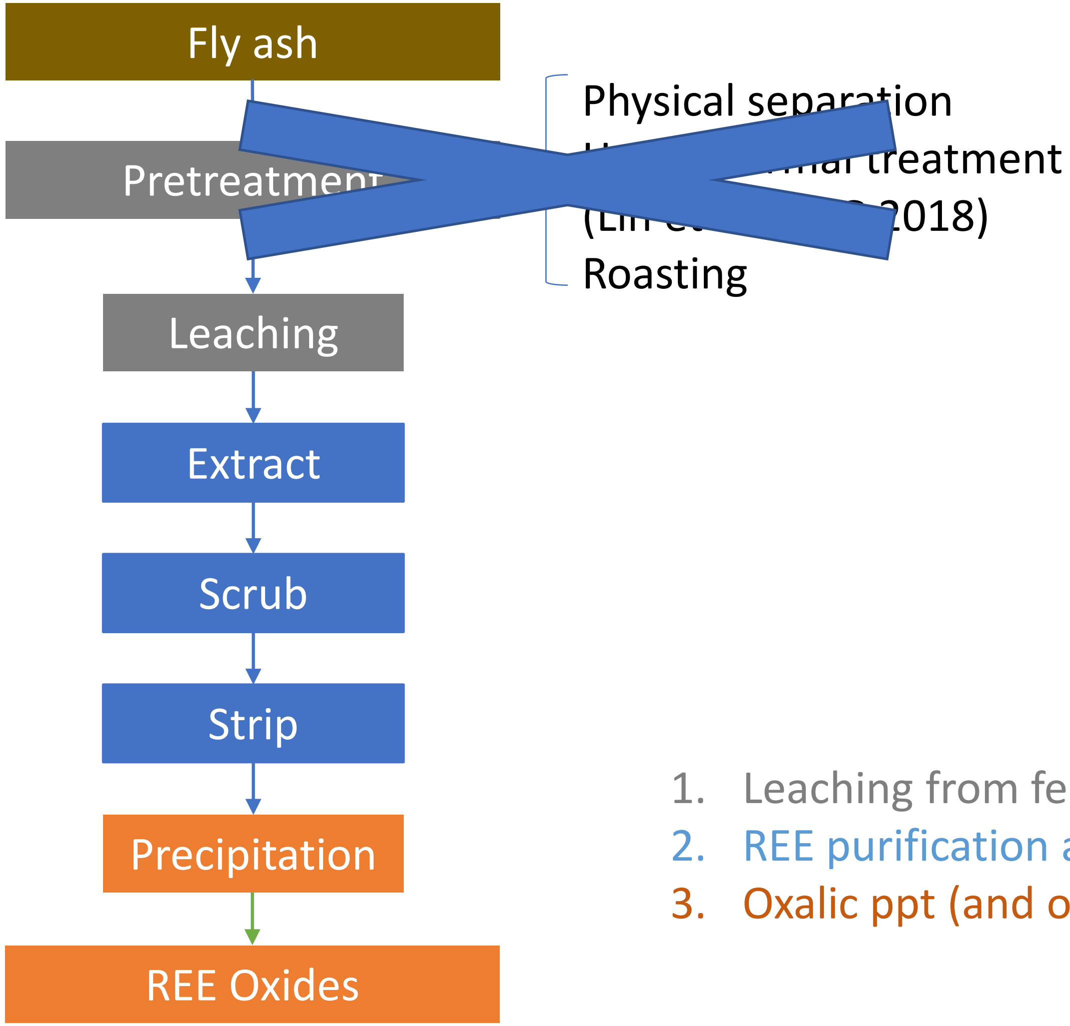


Highlights

- pH vs. %REE: pH < 4 for efficient %REE from EPRI samples
- REE released due to mineral phase dissolution: Al, P, Fe dissolution for HREEs vs. Ca dissolution for LREEs
- 1.2M citric acid results in %100 REE extraction with end pH 3.05, final solution 20ppm REE+Y



Implication 1 for REE separation: Traditional vs. EPRI Fly Ash



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)

REEE Enrichment

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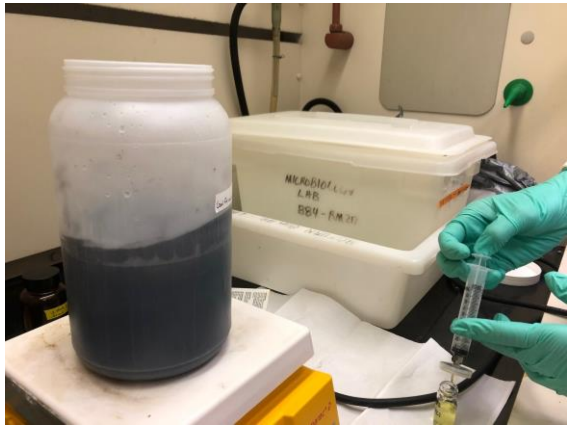
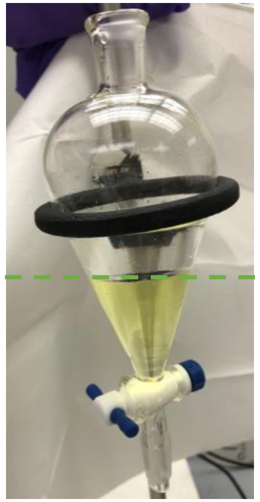
EPRI fly ash



Leaching with HCl



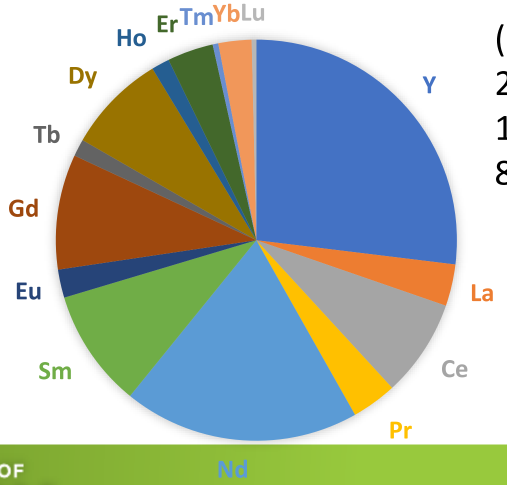
Organic Phase

Aqueous Phase: Fe and HREE+Y

L:L extraction

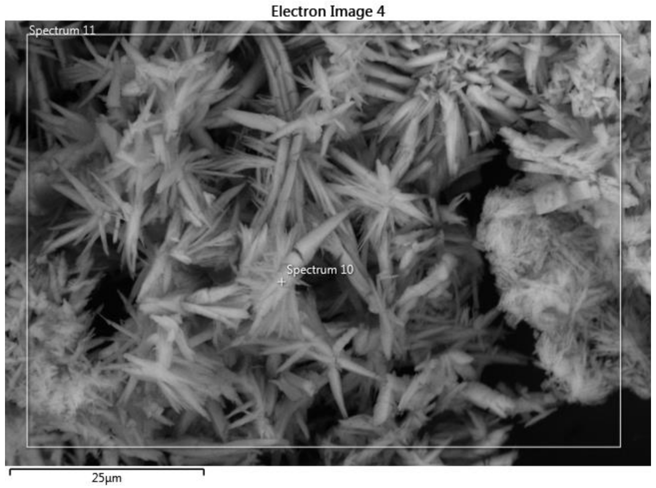
Oxalic acid precipitation

FLY ASH OXALATE PRECIPITANTS, 12%WT REE, WITH 22% IRON AND 6% SODIUM



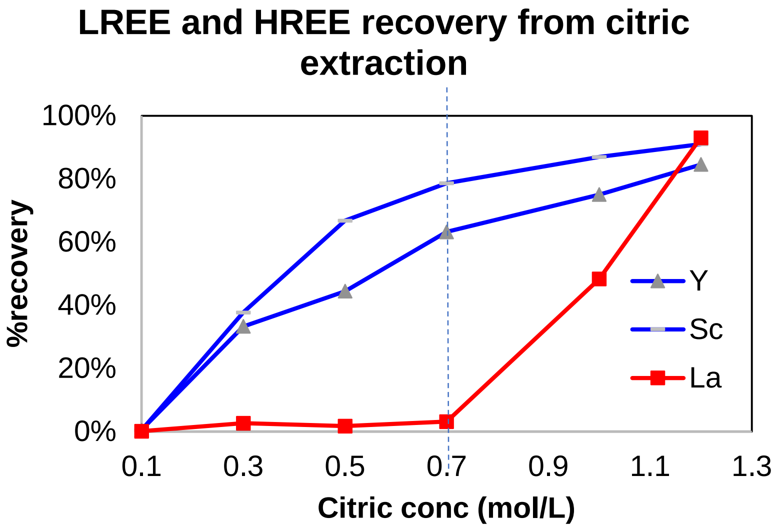
(Mostly HREEs: 27% Y, 19% Nd, 10% Sm, 9% Gd, 8% Dy)

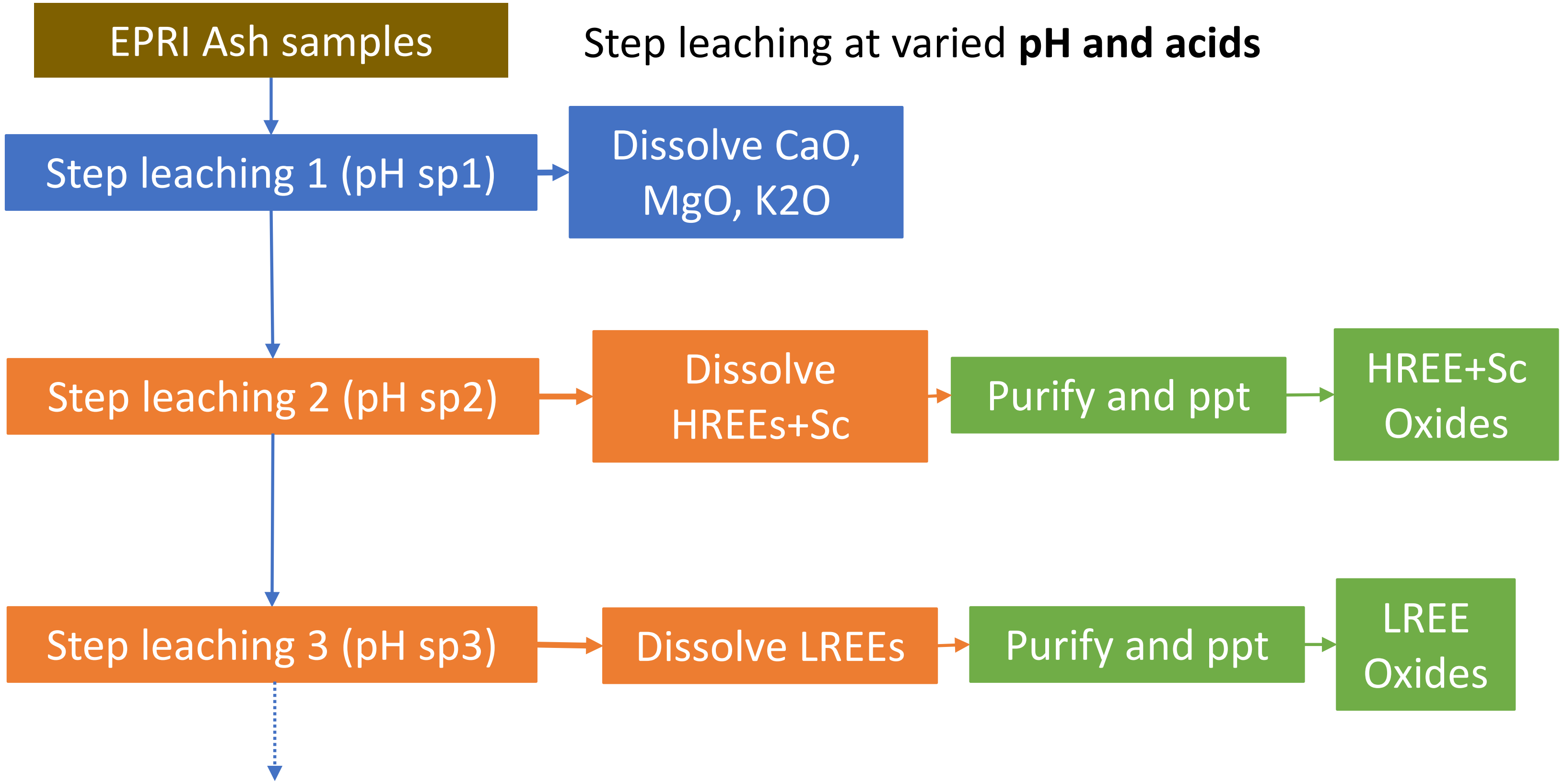
HREE+Y oxalate precipitates (~12%wt REY)



Implication 2: Step leaching via characterization

More dilute acids, leachate with less TDS, less organic solvent for later stage





Conclusions

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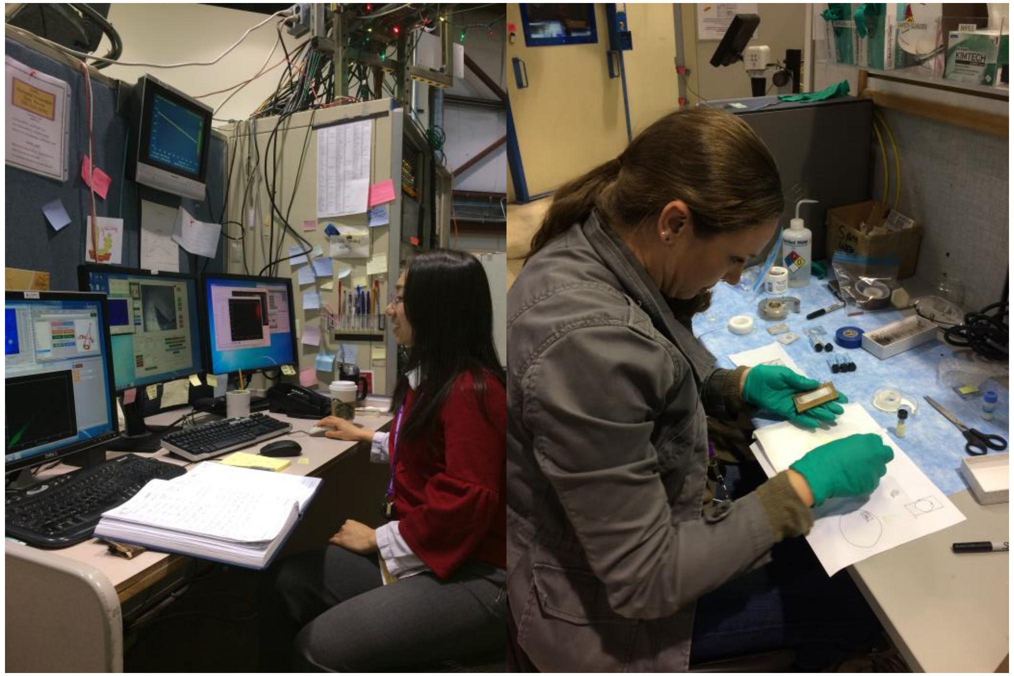
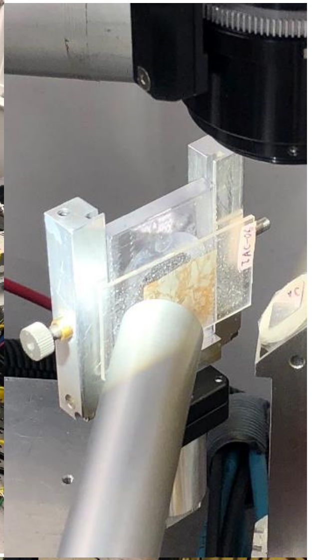
- The preliminary results demonstrate 100% REE extractability from PRB ash using dilute acids at room temperature in short period of time.
- Heavy REEs and light REEs can be leached from the fly ash separately using different acid conditions sequentially extracting Ca phases and Fe phases.
- Information will provide guidance of type of acids and acid amount for future effective REE extraction from PRB ash samples

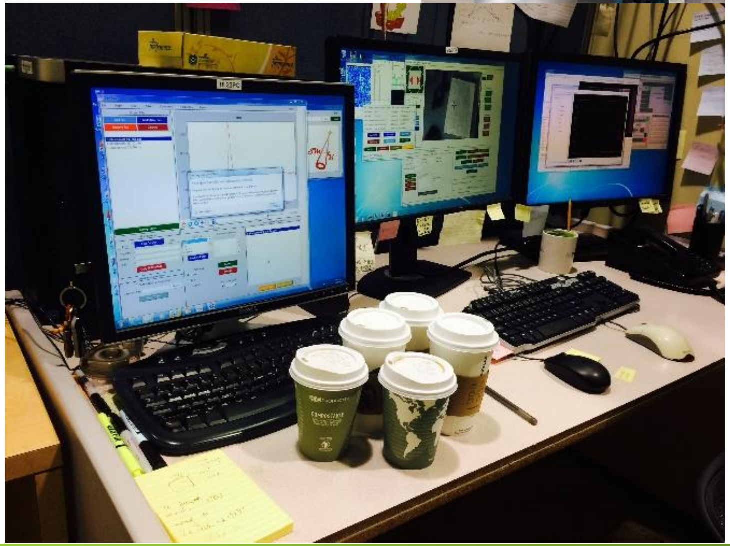


Acknowledgements

Coffee is your friend!

- **REE Research Team and Management**
- **Scott Montross (Leidos) for SEM imaging**
- **Sam Webb, Nick Edwards and Courtney Roach (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 Elment 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.**





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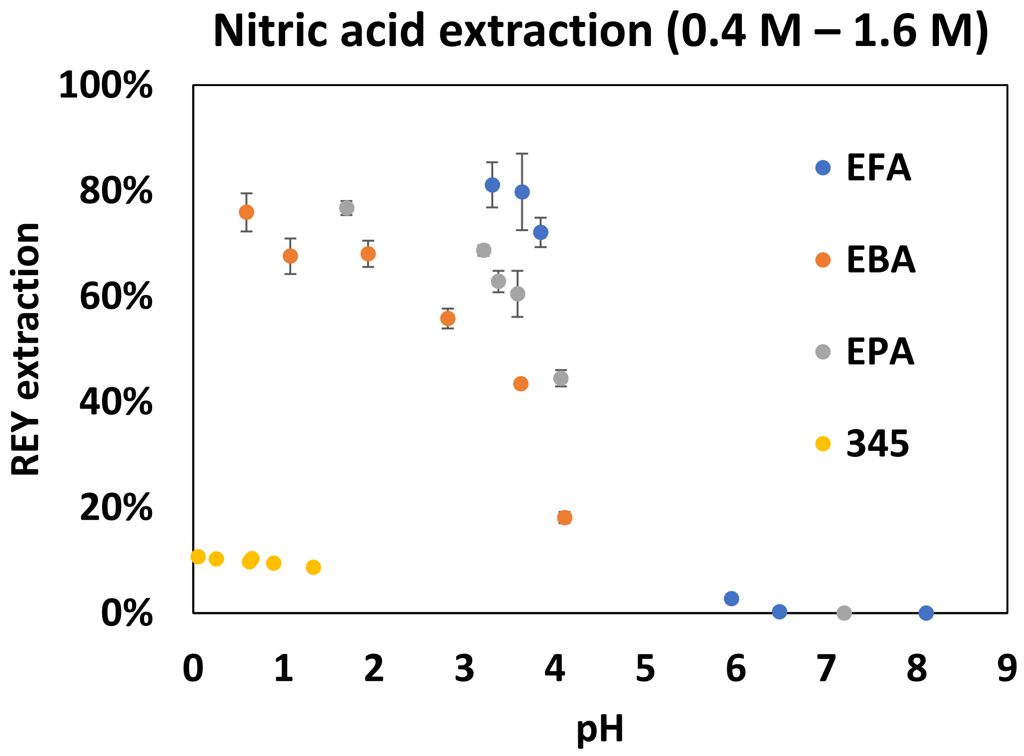
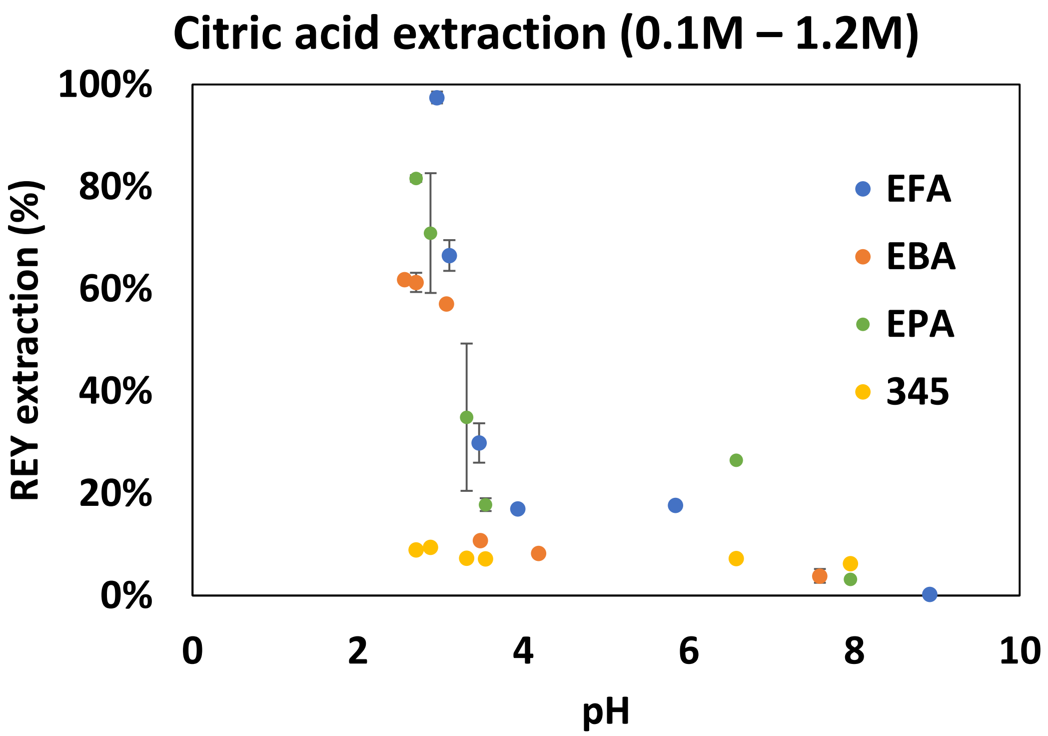
Information Slides

pH effect for other ash samples

- **End pH < 4 has higher extractability**





REE Extraction from a Powder River Basin Fly Ash

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REE concentrate after acid extraction of EPRI-FA (>20ppm, pH3, 40g/L TDS)

pH adjusted to 1 by HCl

Liquid: liquid extraction

Organic extractant with HREE+Y

Aqueous phase with high TDS

Acid stripping via 3M HCl

Ca fertilized soil supplement or for LREE extraction

Recycled organic phase

Aqueous phase with REYs

pH adjusted to 1-2 by NaOH

Oxalic acid addition

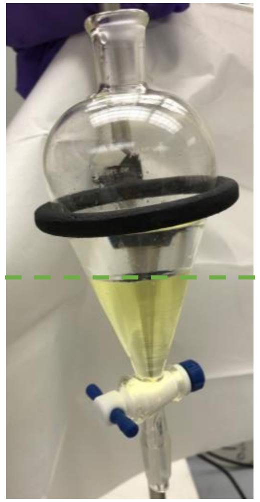
REY oxalate↓

1. Acid Leaching
2. L:L Extraction
3. REE stripped to Aq
4. Oxalic ppt

Organic Phase: <u>Fe and HREE+Y</u>

Aqueous Phase Most TDS

L:L Extraction using CYANEX



Organic Phase

Aqueous Phase: <u>Fe and HREE+Y</u>

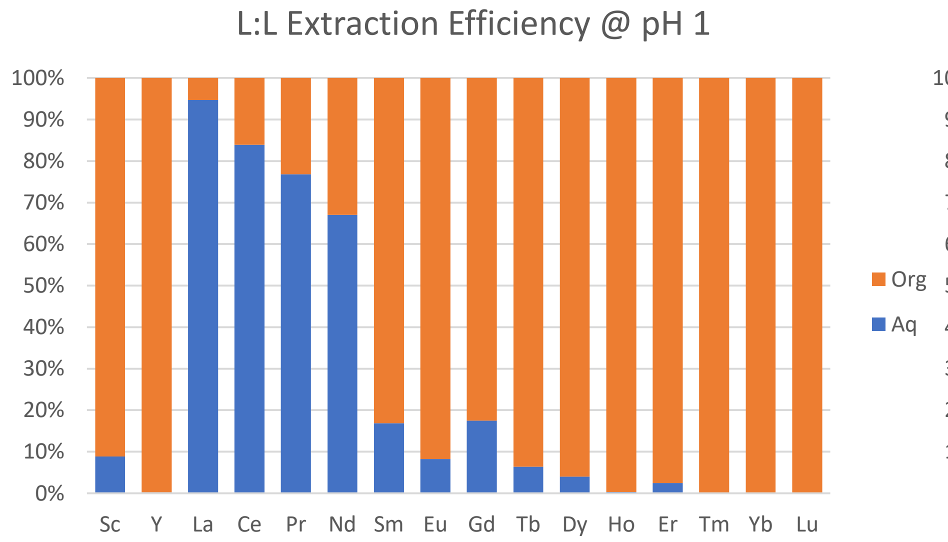
Acid stripping via 3M HCl

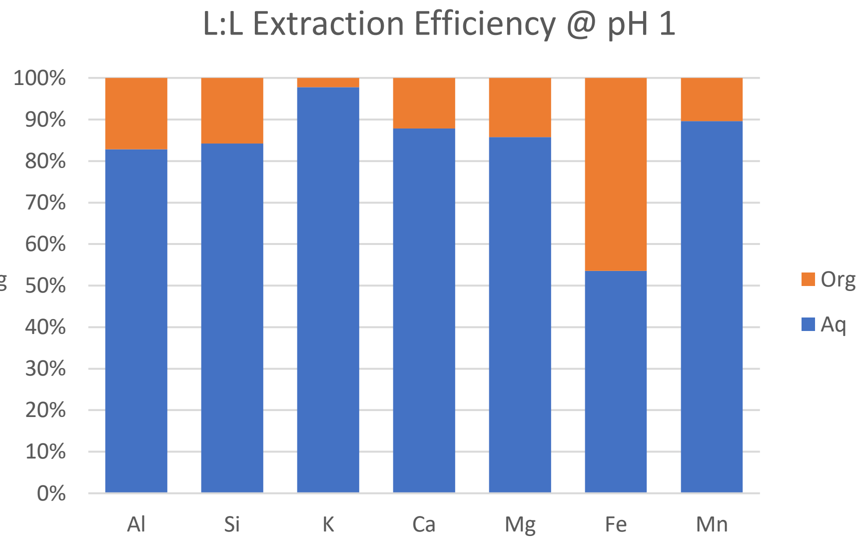
L:L extraction @ pH 1 for HREE

0.3mL conc. HCl into 50mL REE leachate to reduce pH to 1

50mL 20% CYANEX 572 and 80% Pentane was used for L:L extraction

Mix and Stir for 20 min, before settling for 1hr for separation



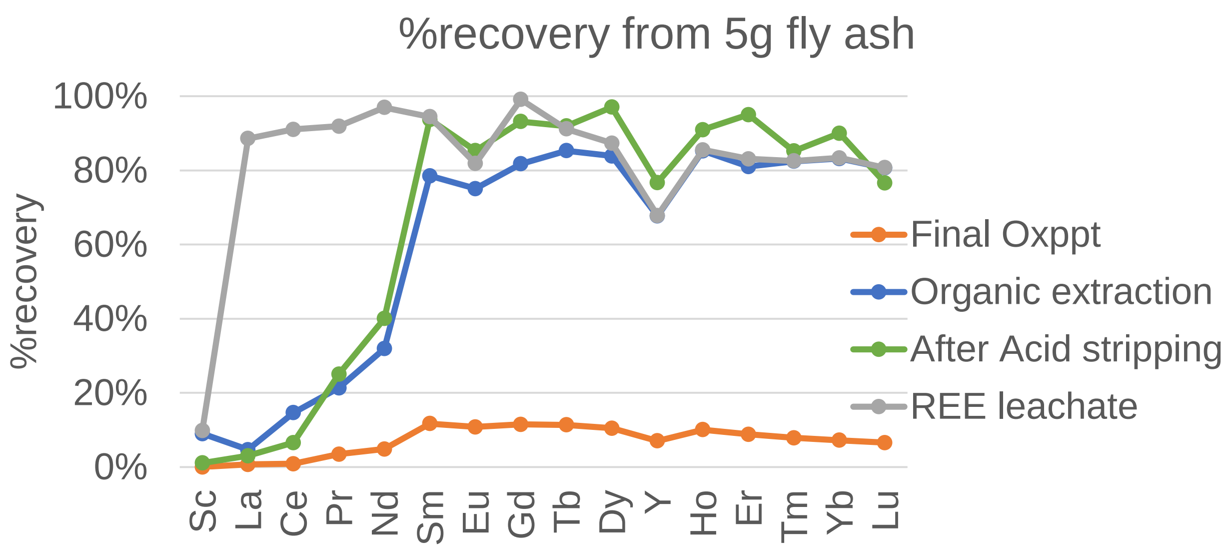


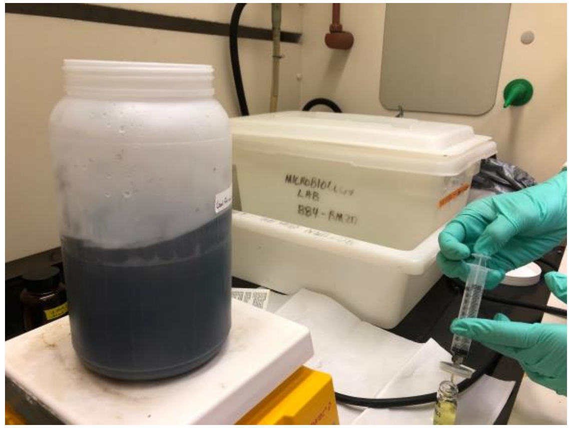
L:L Extraction using CYANEX

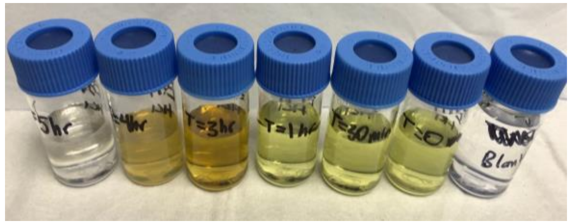
- **Successful: >90% HREE and 46% Fe into organic phase**

Current stage

Optimize these steps, on a 5 gram basis, 10% recovery rate, final product 0.42mg







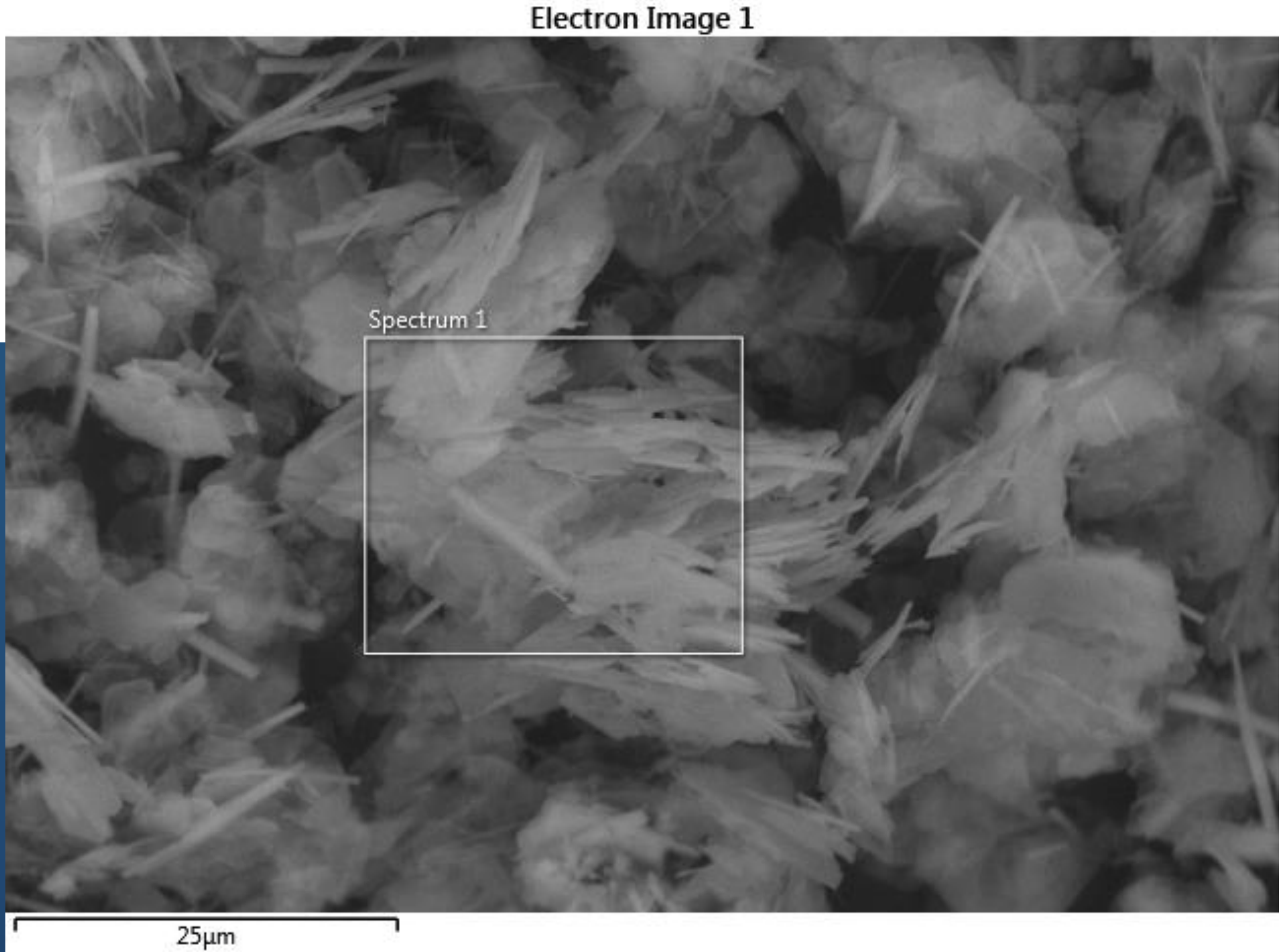
Scale-up, March 2019

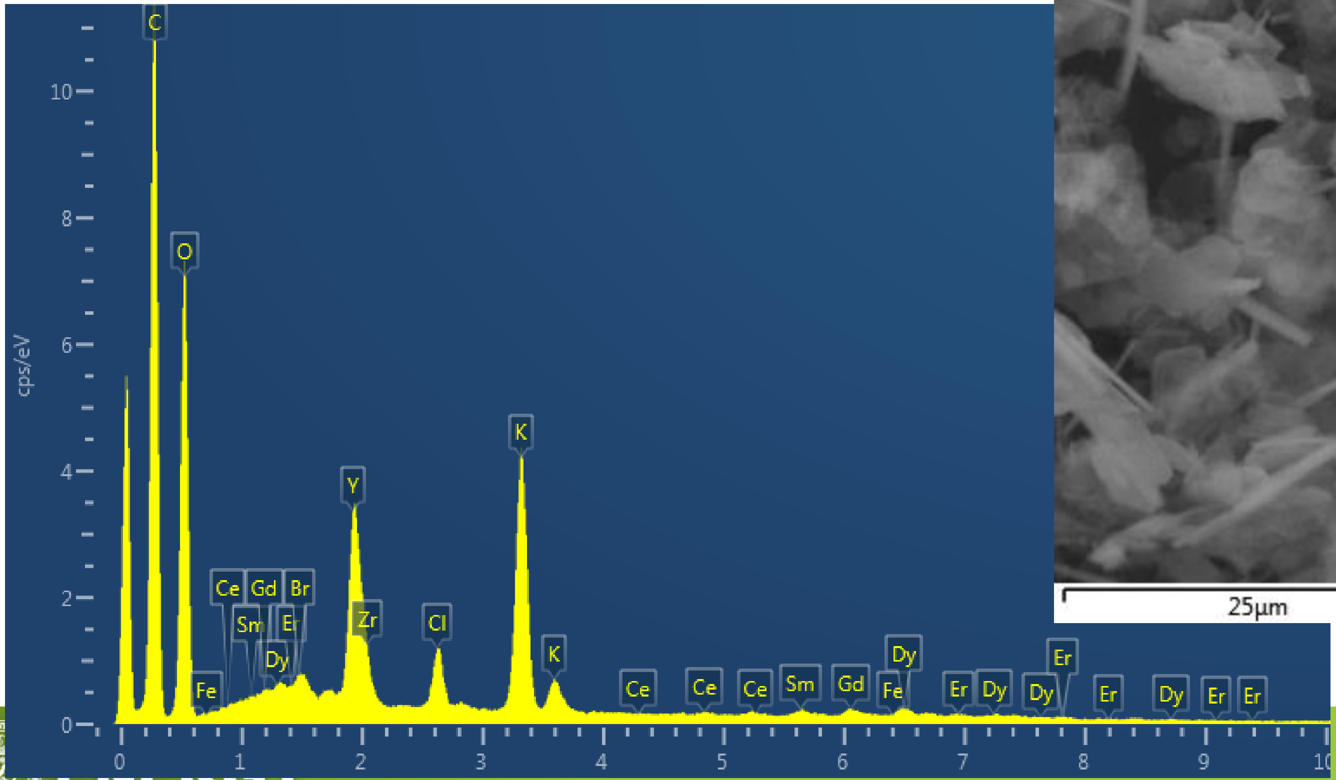
1. <u>100gram fly ash with 1L 1.6M HCl, kinetics conducted (expected final product: 8mg REOs)</u>
2. 1/3 leachate for L:L ex at pH3 (result pending)
3. 1/3 leachate for L:L ex at pH1 (result pending)
4. 1/3 leachate for sorbent testing, not efficient (probably due to high Chloride contamination?)

Preliminary characterization of new end-product 1

End product extracted at pH1

- Appears to consist of Y-enriched REE oxalate and residual KCl



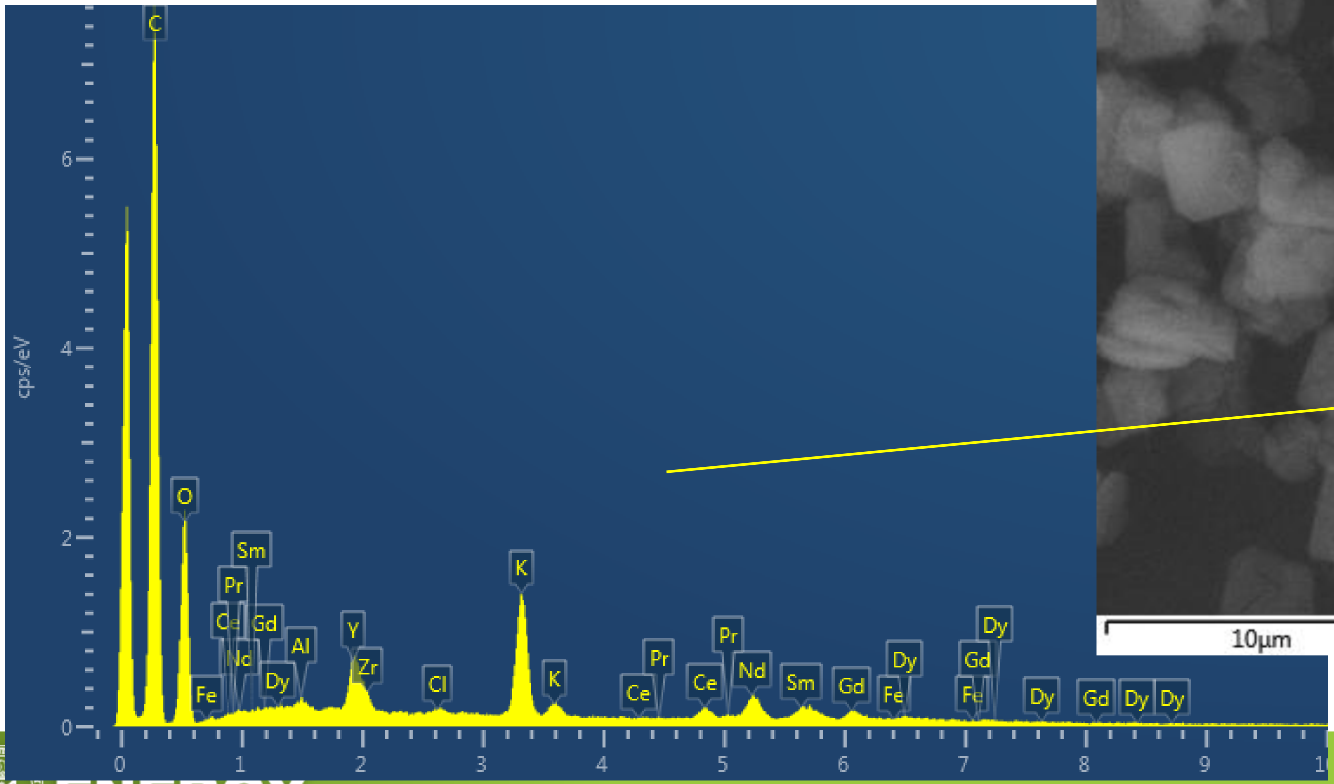


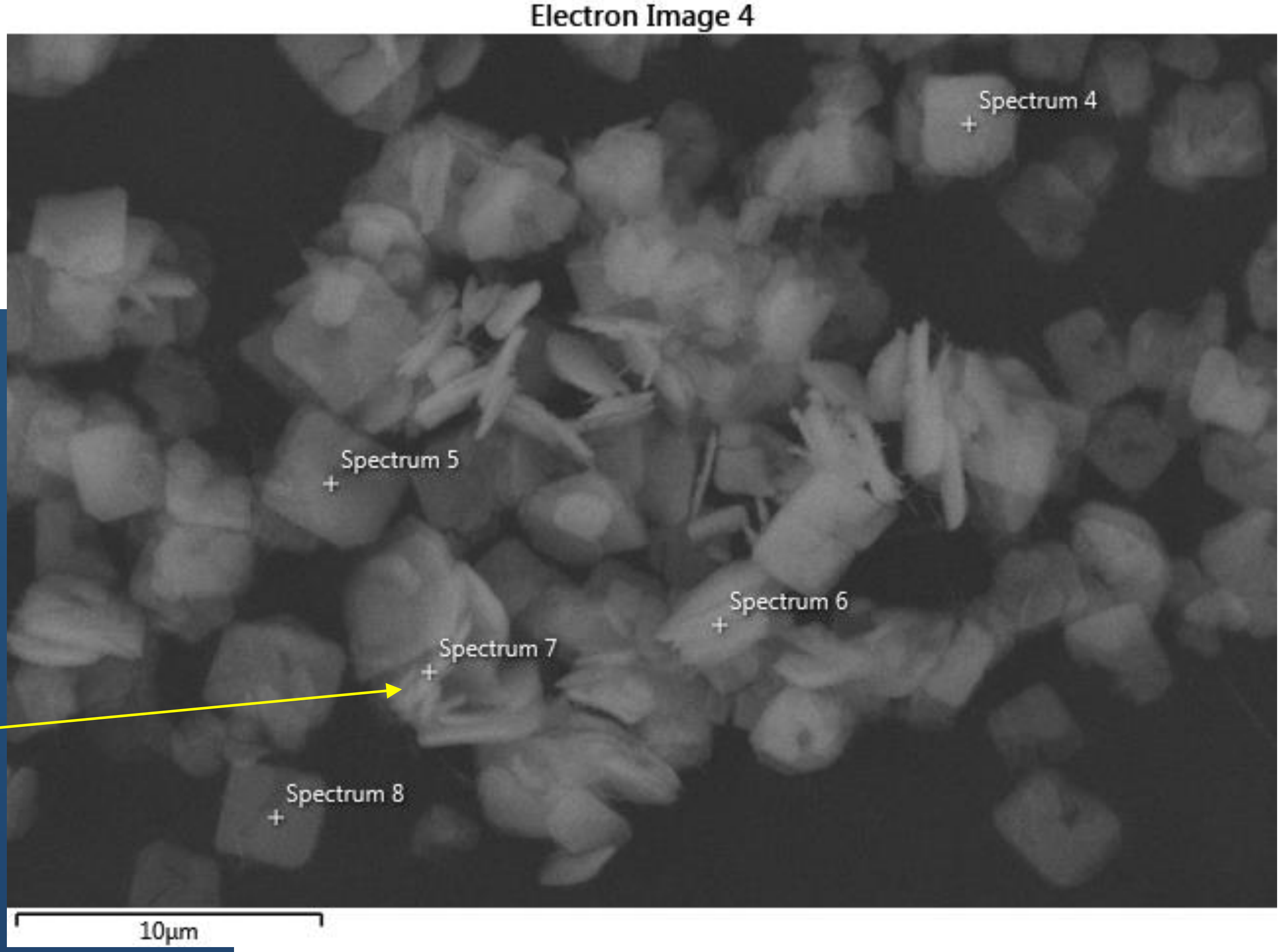
SEM provided by Bret Howard

Preliminary characterization of new end-product 2

End product extracted at pH3

- **In addition to REY-oxalate, possible Y-enriched K-REE oxalate phases as suggested by the low Cl content**





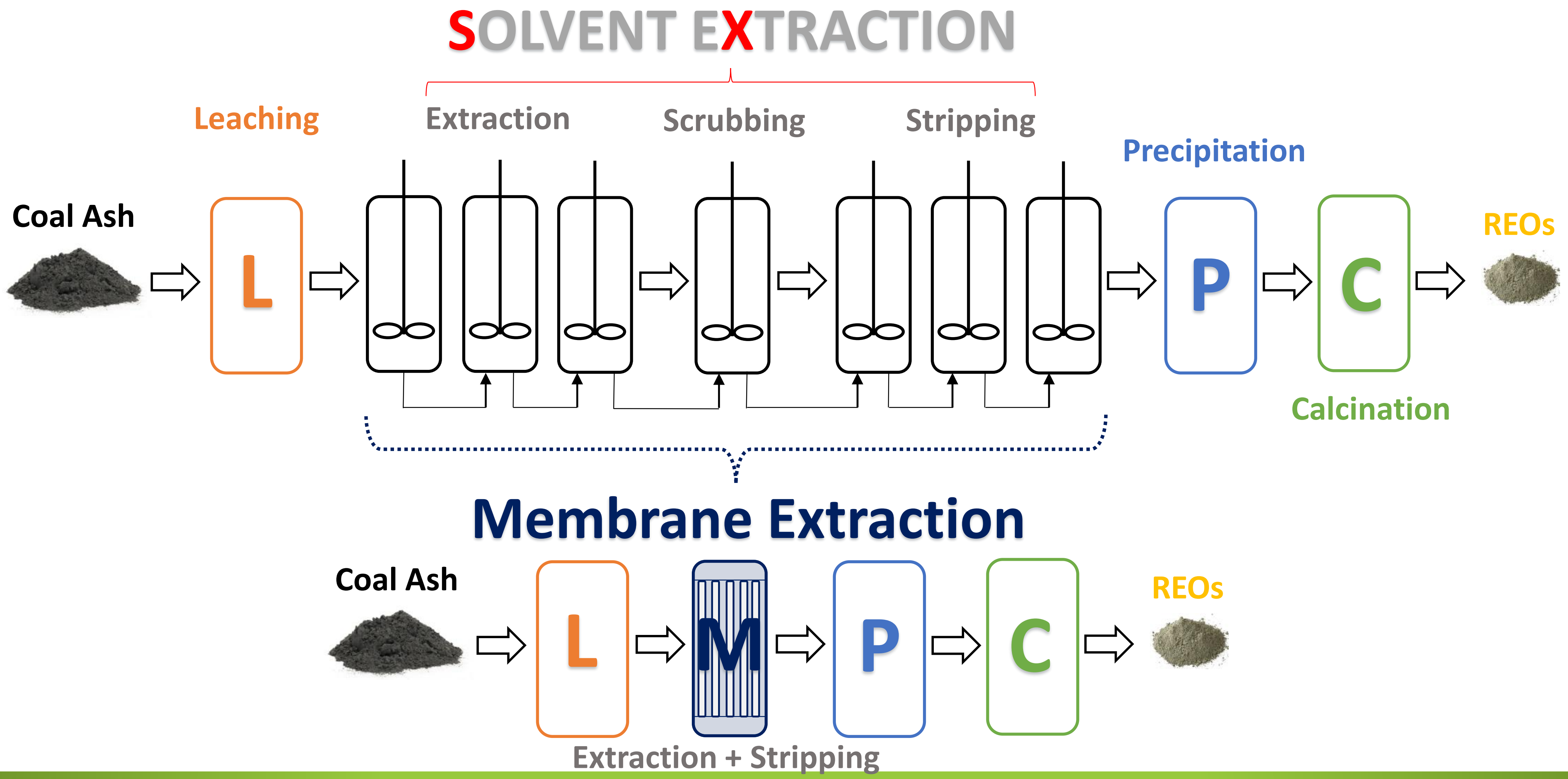
SEM provided by Bret Howard

Future tasks

1. Reduce acid usage and reaction time, and identify selective leaching solution (e.g., citric acid for HREE + HCl/H2SO4 for LREE)
2. Identify efficient purification and REE separation steps (L:L extraction membrane extraction, or sorbent extraction)
3. Optimize oxalic acid ppt step (critical, currently low efficiency for harvesting, despite >80% REE removed from solution after oxalic ppt)
4. Separately develop Sc processing chain (behave very differently in all steps)

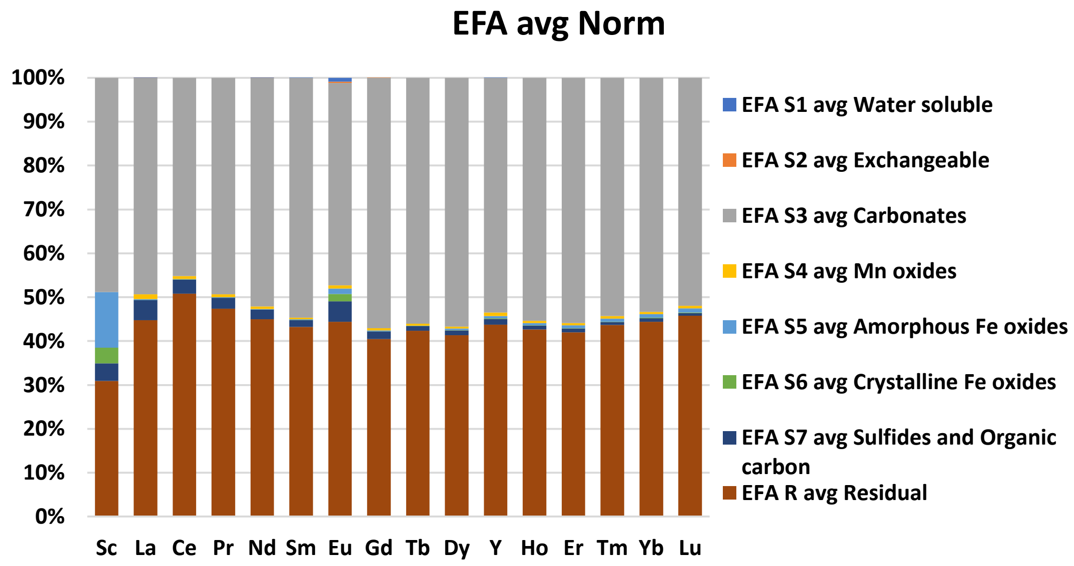
Questions and more work from Dr. Daejin Kim

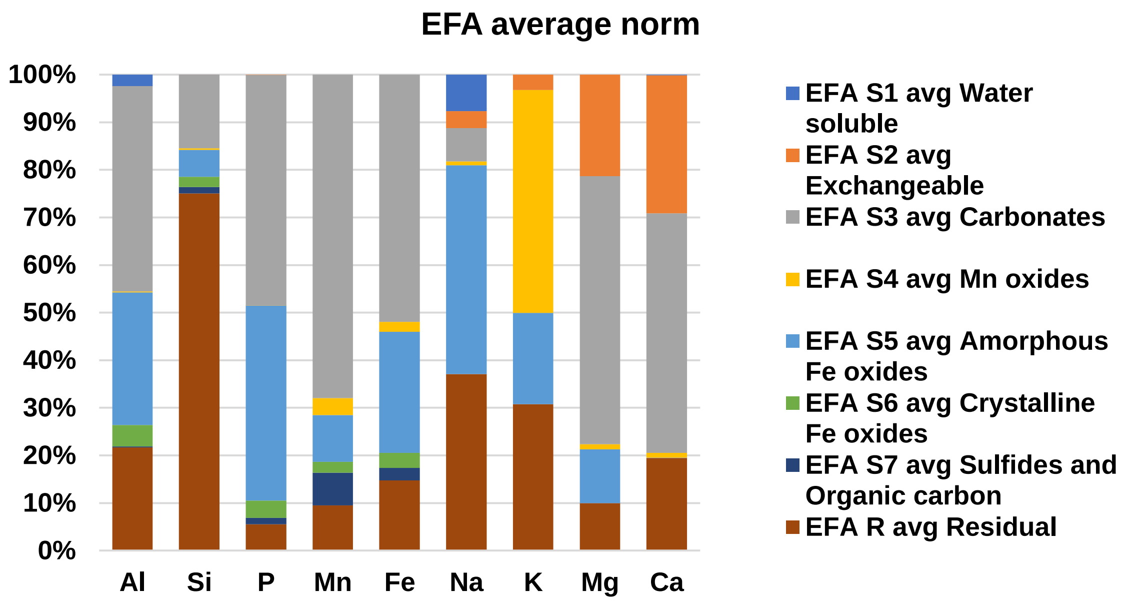
Slide provided by Daejin Kim



Sequential extraction

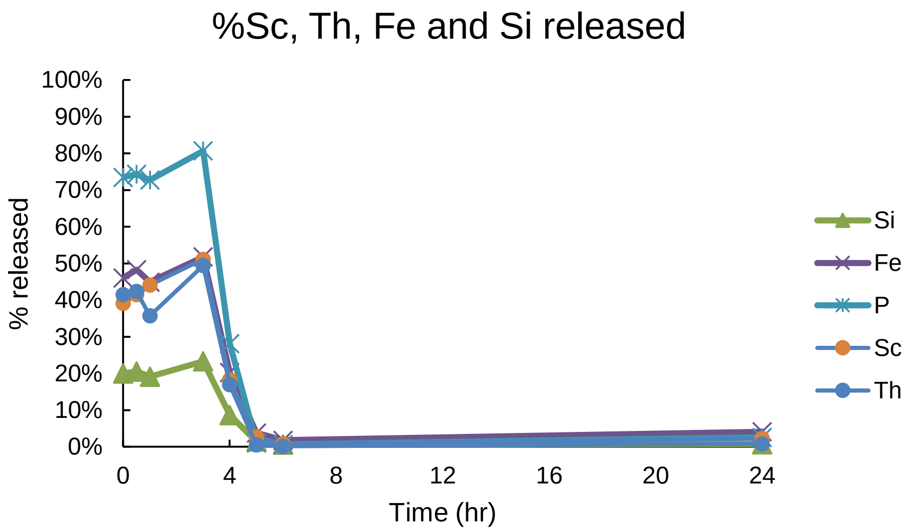
S3: 0.1M acetic acid at pH 2.88

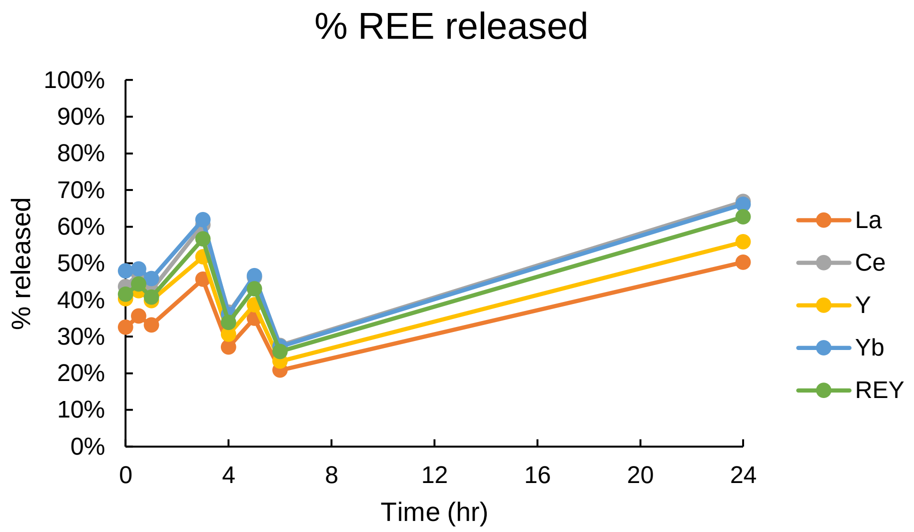


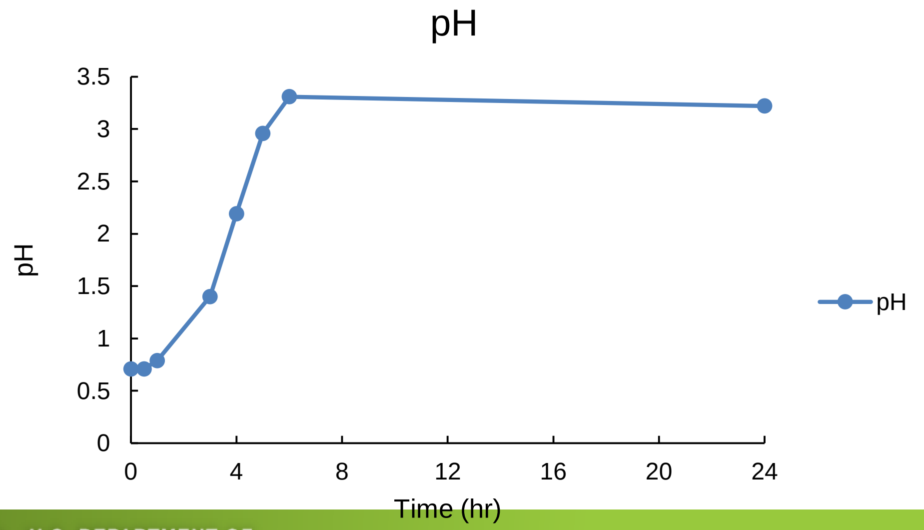


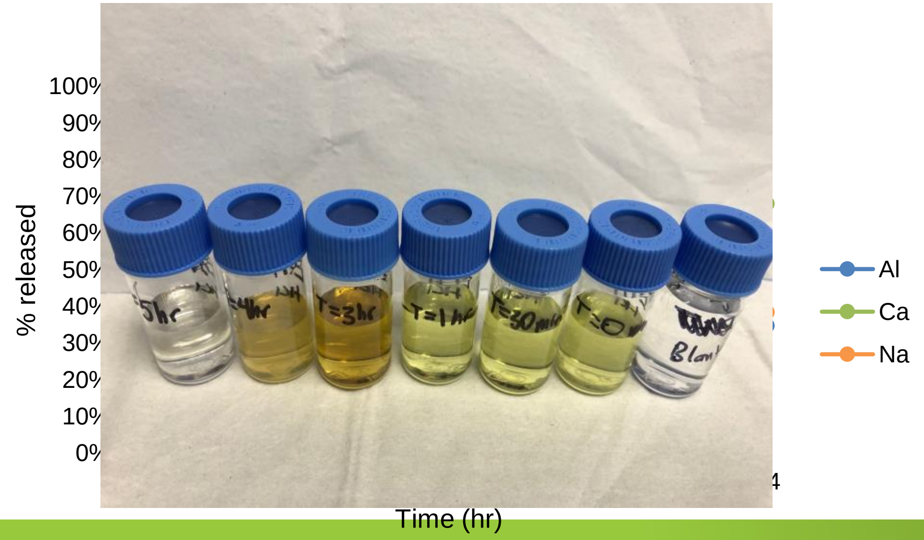
Kinetics: EFA HCl Leaching

Sc associated with Fe and P release; lanthanides associated with Al, Ca release



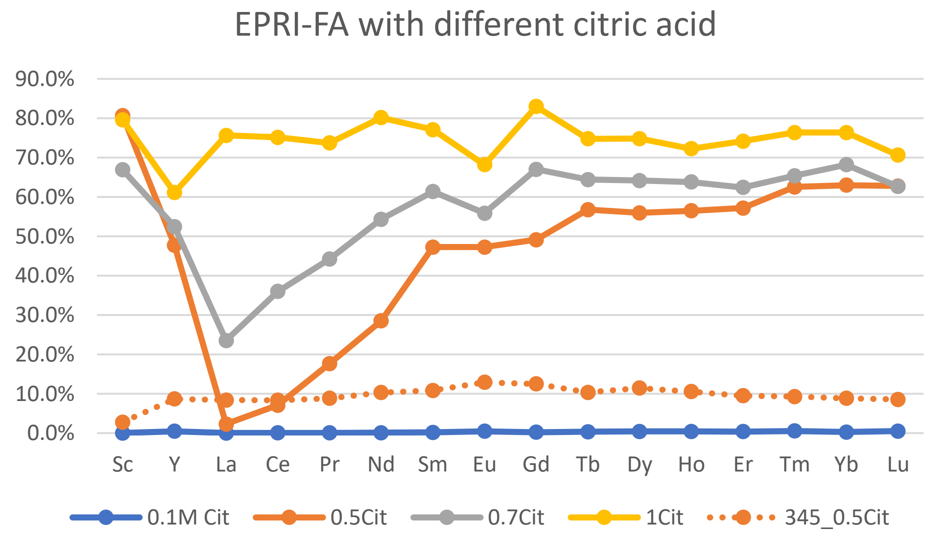






Future Work for acid leaching

- **Test L:S ratio to reduce reagent and leachate quantity**
- **Test extraction time to reduce reaction time**
- **Test more acids or acid mixture**
  - Sulfuric acid: preliminary test successful and less Ca and Mg dissolution
  - First citric to extract HREE and Sc, later HCl/H2SO4 for LREE



REE purification (L:L Ex or Sorbent)

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- **Starting leachate, pH 3.19 for EFA Nit acid leachate**

	Unit	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Sum REE+Y
EFANit	mg/L	0.25	2.61	4.17	8.29	0.98	3.82	0.77	0.17	0.81	0.11	0.67	0.12	0.35	0.05	0.31	0.05	23.28

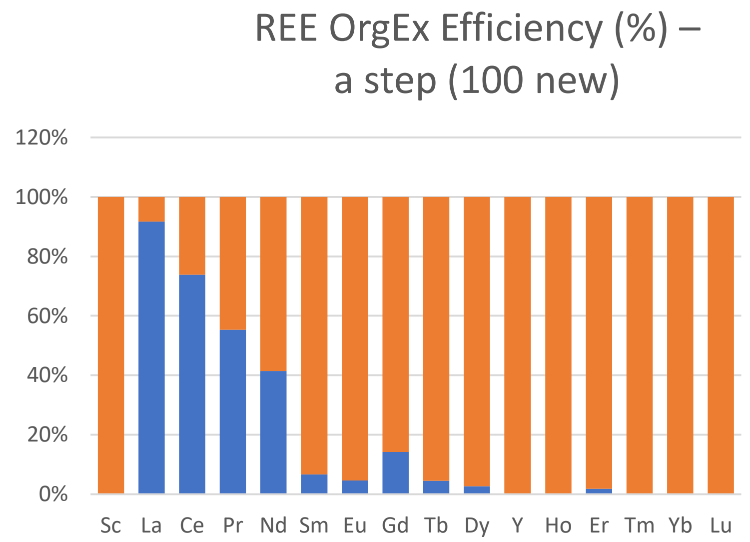
Al	Si	K	Ca	Mg	Fe	Mn	P	Sr	Zr		As	Pb	Ba
3830	333.9	108.2	16659.5	3298.5	219.1	8.5	28.4	211.9	#VALUE!	0.0	0.2	0.1	6.8

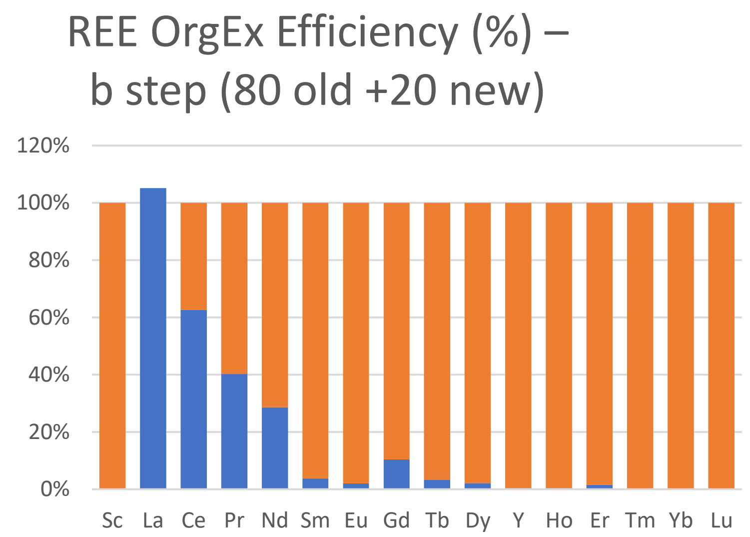
Recyclable Organic extraction

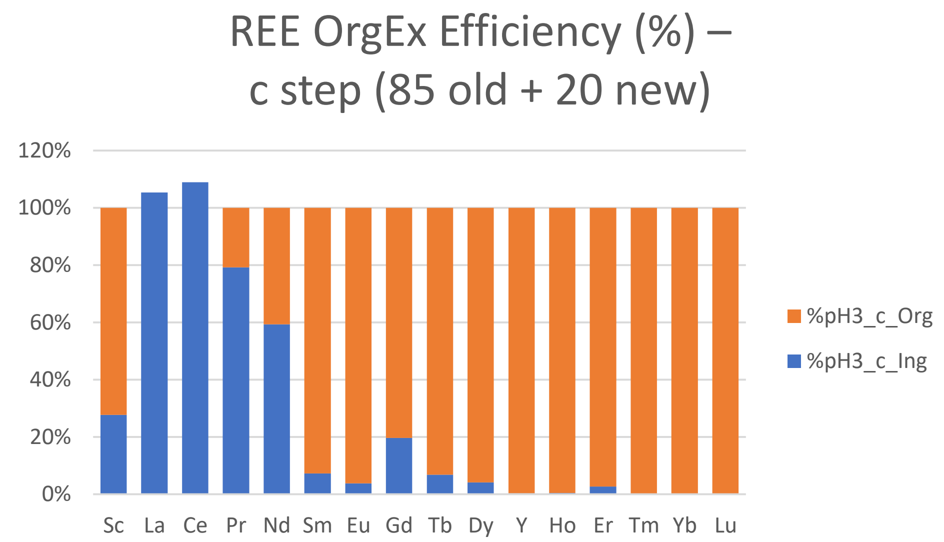
Step a: 100mL EFAHCl + 100mL Organic Solvent

Step b: 100mL EFAHCl + 100mL Organic Solvent (80mL old + 20mL new)

Step c: 100mL EFAHCl + 100mL Organic solvent (85mL old + 20mL new)





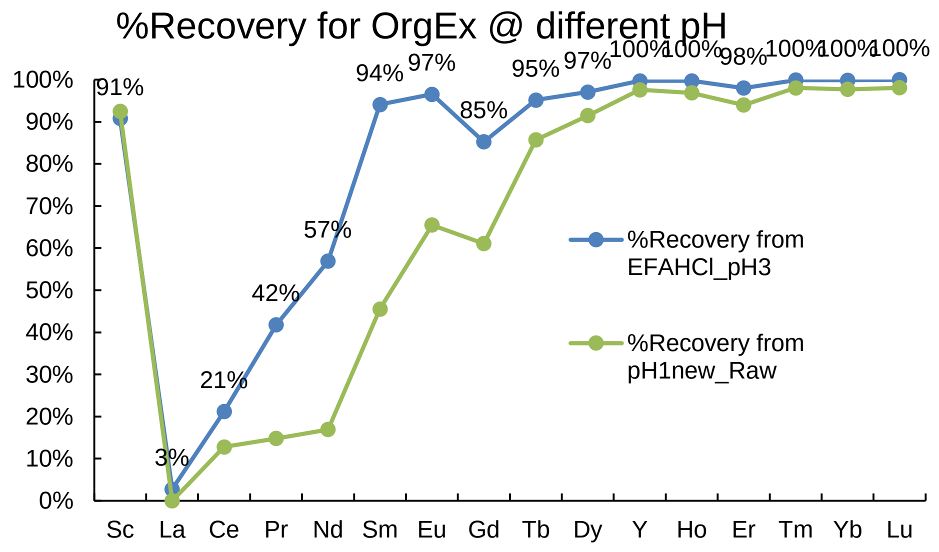


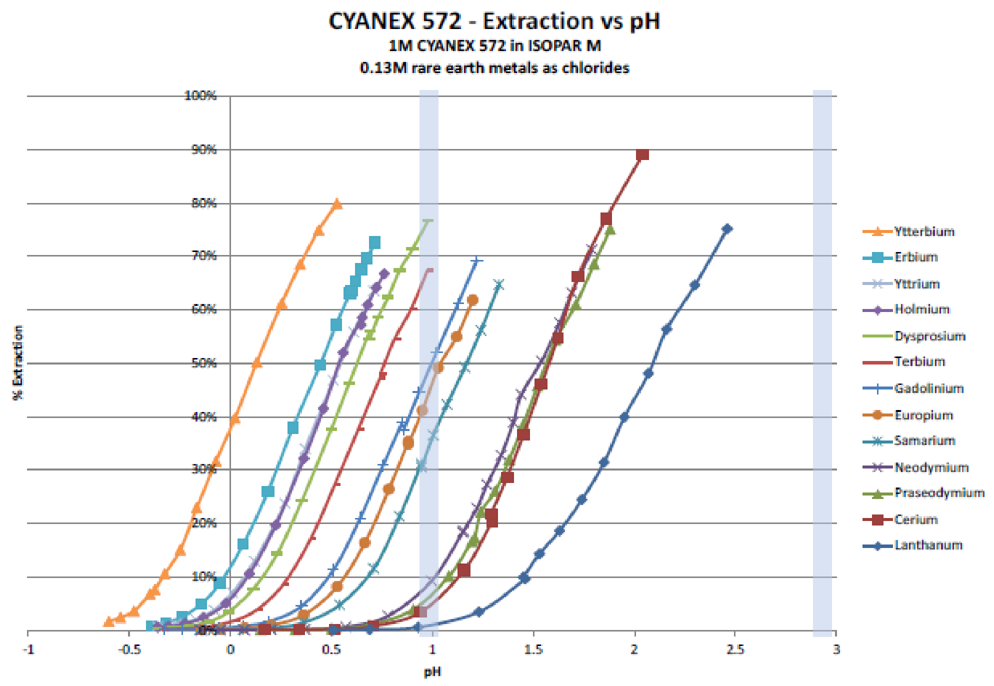
- **Every step generate similar extraction efficiency, indicating solvent can be reused or less solvent can be used (e.g., 140mL solvent for 300mL EFAHCl leachate)**

L: L extraction: pH effect

New findings: pH 3 is better than pH 1

- **More extraction pH study needed for EFA acid leachate**



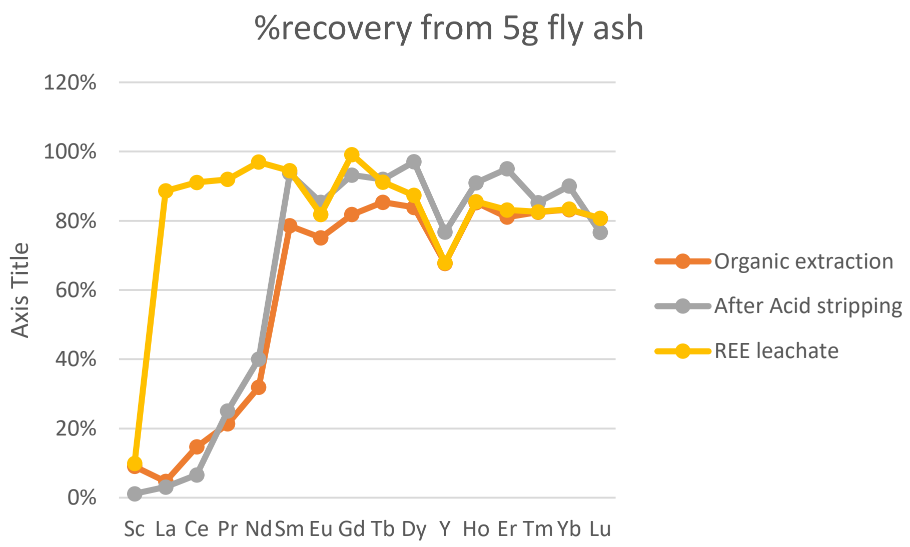


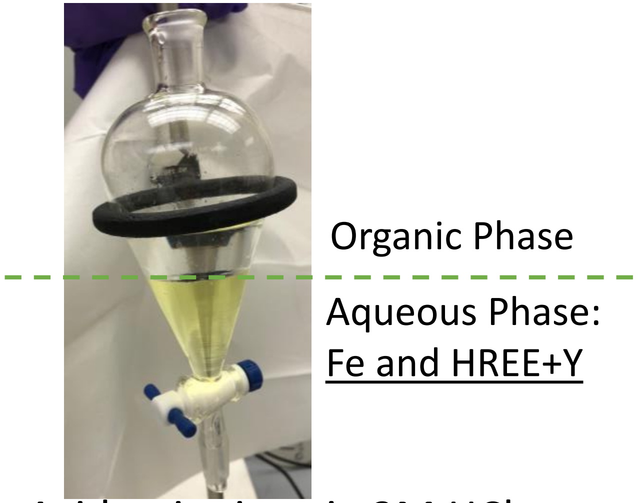
Info data sheet of Cytec Cyanex 572

Acid stripping and oxalate precipitation

Add 25mL 3M HCl into ~50mL organic phase, mix and settle to separate the Aq phase

- **More data coming**
- **Reduced acid amount (1:1 ratio to 2:1 ratio)**

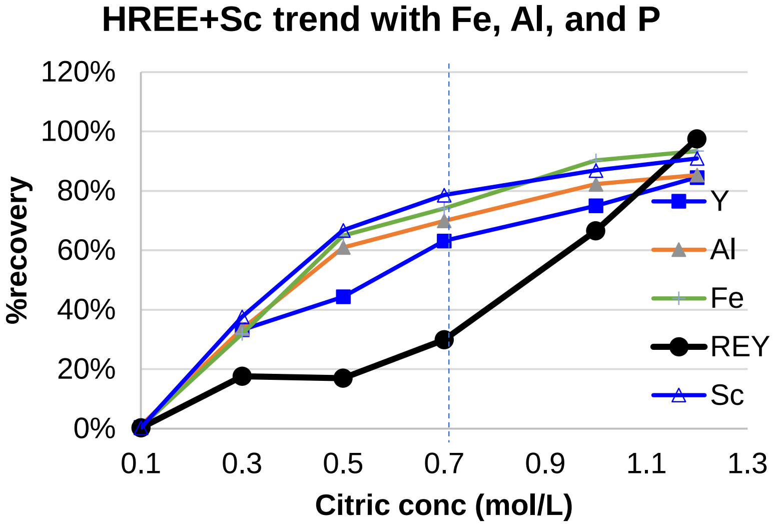


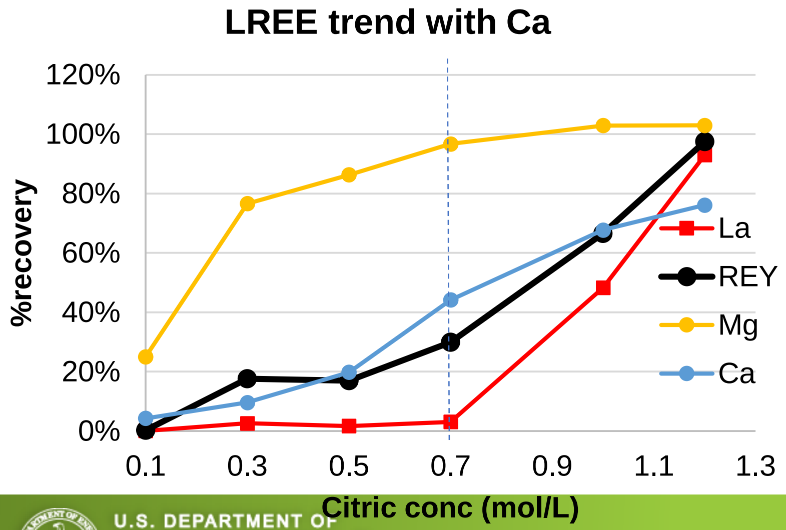


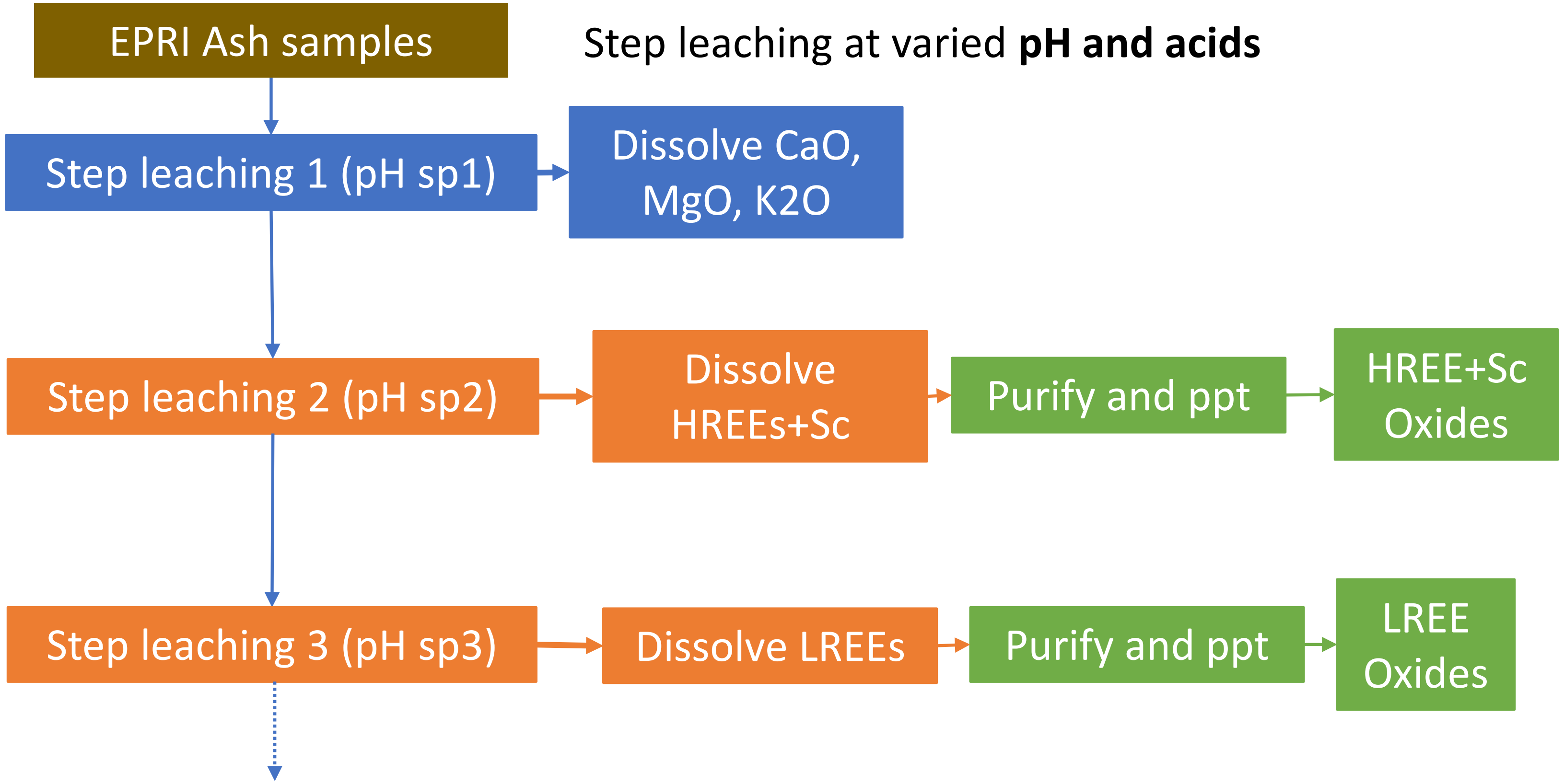
Acid stripping via 3M HCl

Future tasks: Step leaching

More dilute acids, leachate with less TDS, less organic solvent for later stage







Future work for REE purification and separation

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- Use sorbent for REE purification
- Use efficient apparatus for L:L extraction https://www.zaiput.com/
- Optimize L:L extraction conditions
  - pH of organic extraction, separate LREE vs. HREE, using actual acid leachate
  - Reduce the amount of organic solvent
  - Check recycle and reuse of organic solvent
  - Reduce amount of acid used for acid stripping
  - Recued reaction time
- New solvent for separating REEs (Cyanex 923)

Staged REE separation and stripping

ENHANCED SEPARATION OF RARE EARTH ELEMENTS 2016 International Mineral Processing Congress K. Lyon, M. Greenhalgh, R. S. Herbst, T. Garn,A. Welty, M. D. Soderstrom, B. Jakovljevic

- **Saponification:**

Solvent + Feed mix

- **Extraction: Remove other cations to purify REE**
- **Scrub: separate different REEs under different pH**
- **Strip: strip different REEs under different pH**

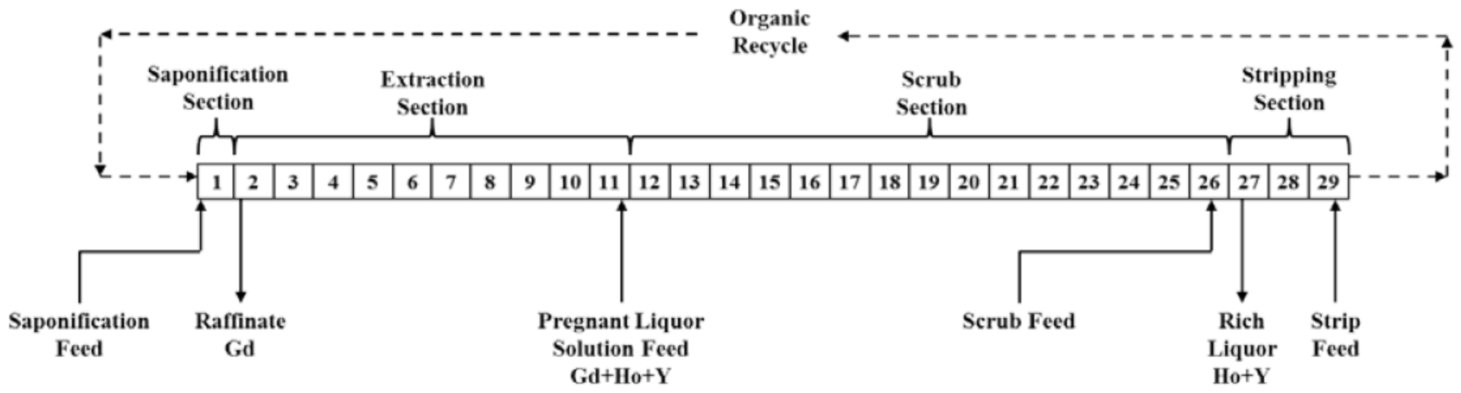
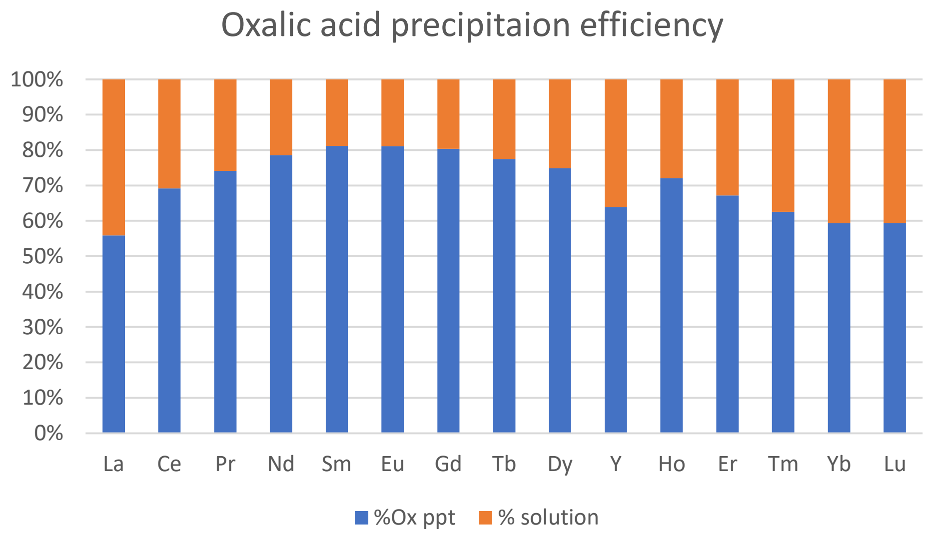


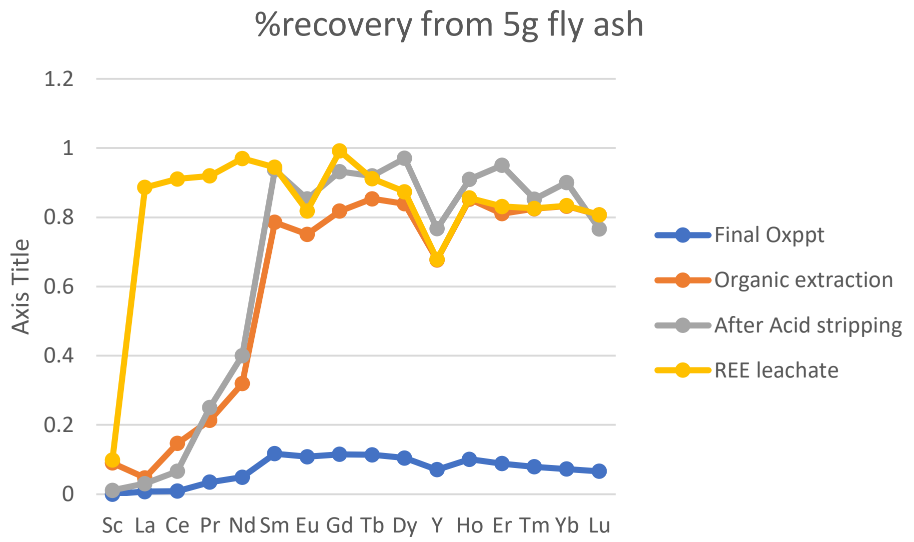
Figure 3- Proposed flowsheet for the separation of Ho and Y from Gd.

Oxalic acid precipitation efficiency

Precipitation has 56% - 81% efficiency to remove lanthanides from solution

The final Oxppt may have been not collected enough





Future work for Oxalic acid ppt (and oxidation)

5 gram fly ash yielded 0.42mg oxalates, only about 10% recovery rate

- **Major loss from (1) <u>incomplete oxalic ppt ;</u> (2) <u>incomplete oxalate precipitant collection; (3) inefficient final rinse</u>**
- **Future work:**
  - Optimize oxalic acid ppt conditions
    - pH
    - quantify amount of Ox needed (modling)
    - identify competing ions (Fe, Ca, etc.)
  - Further oxidation (750 Celsius for 2 hr)
    - REE oxalate to REE oxides