# Novel Membrane and Electrodeposition-Based Separation and Recovery of Rare Earth Elements from Coal Combustion Residues

Award #DE-FE0026952

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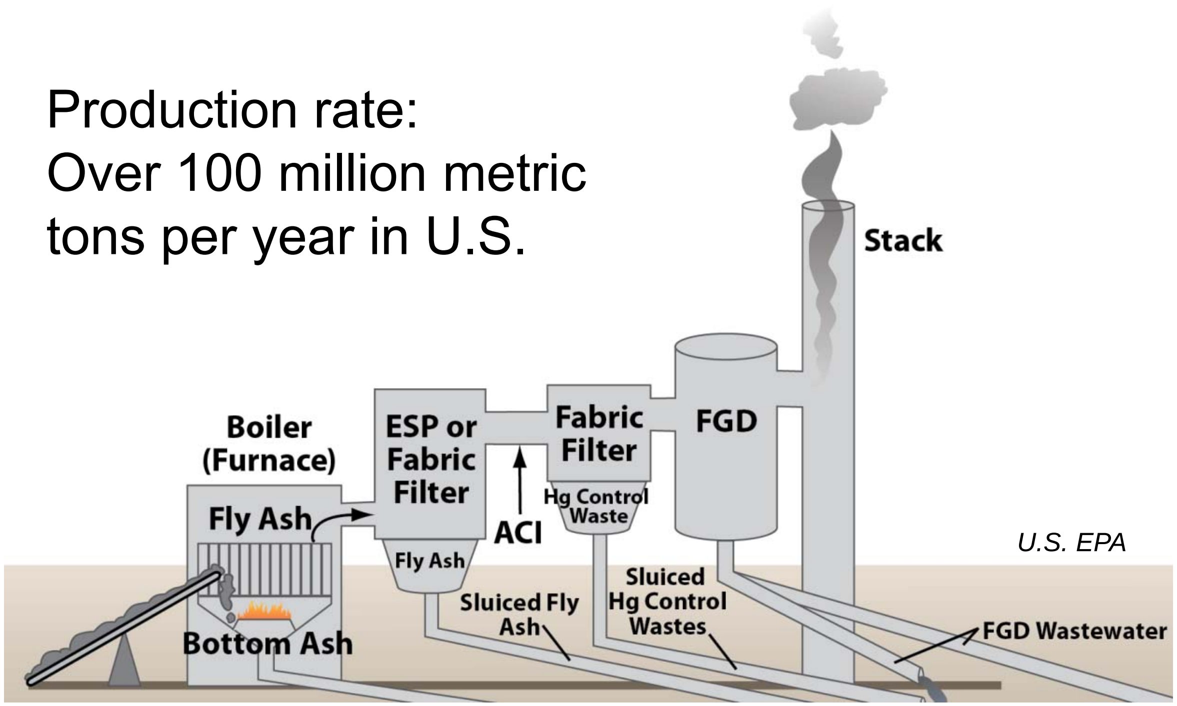
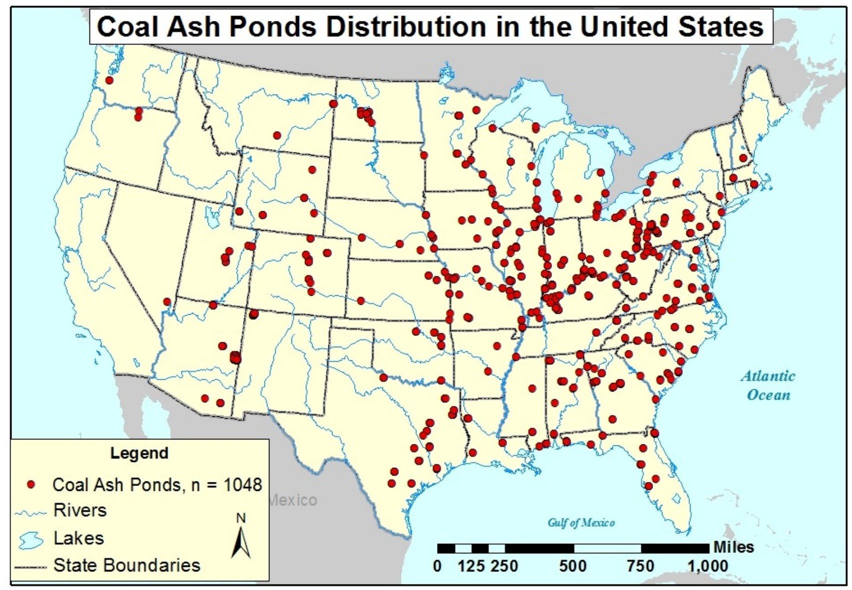
# Coal Combustion Residues

Production rate:
Over 100 million metric tons per year in U.S.



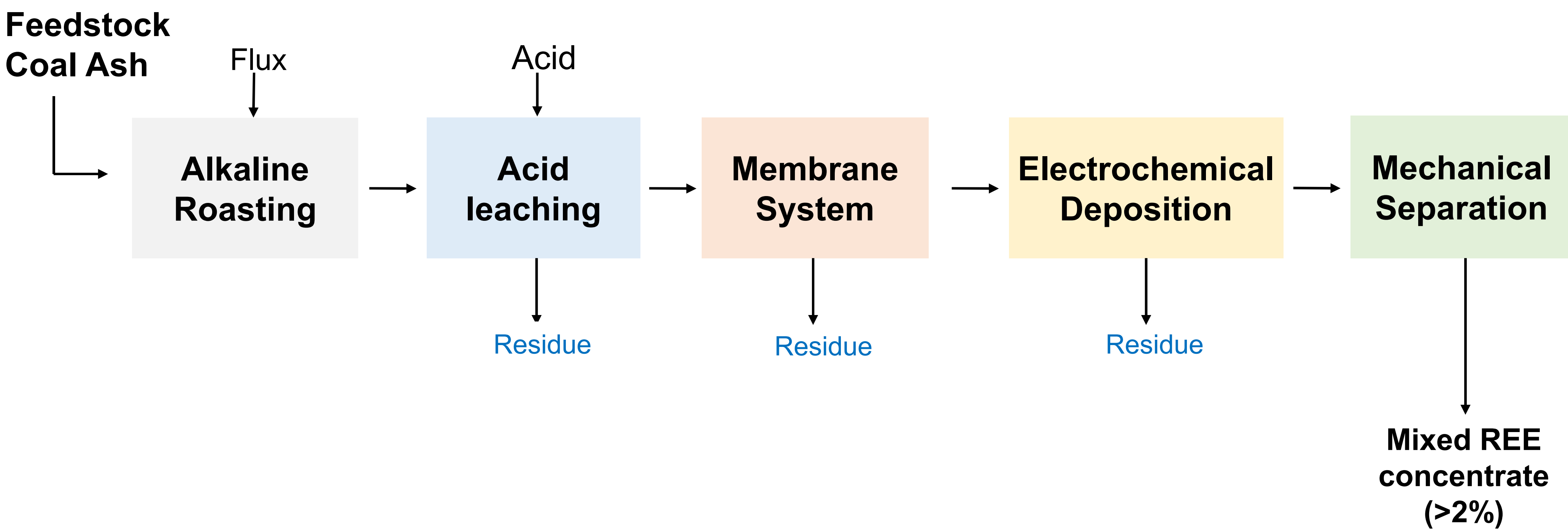




~45% for beneficial use
fly ash - concrete
gypsum - drywall

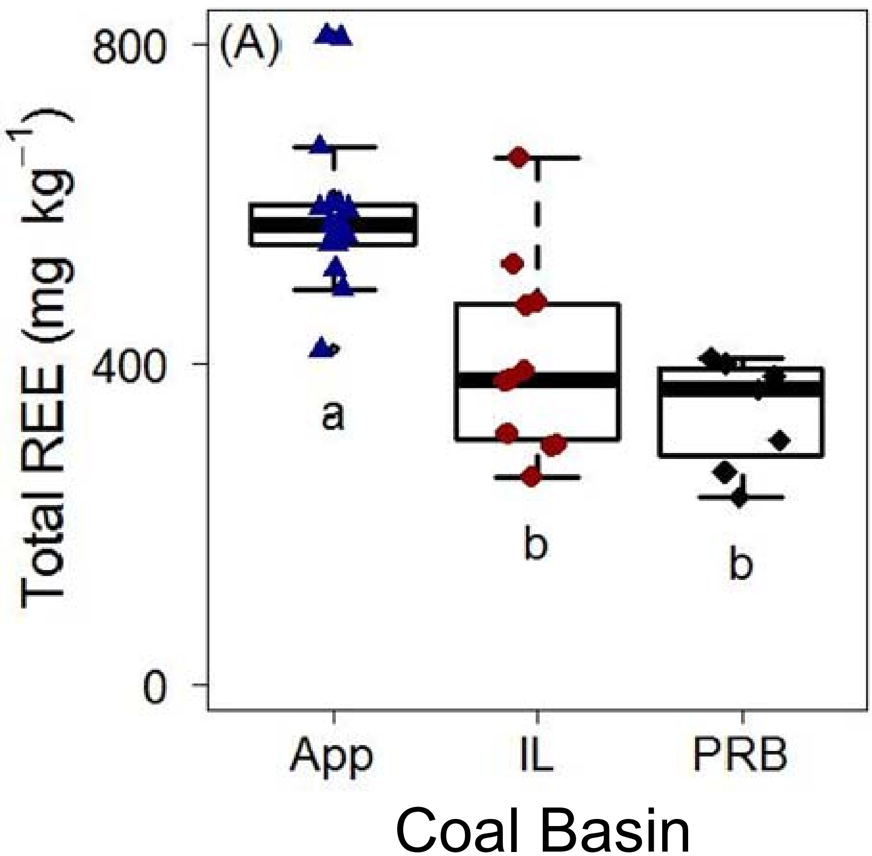
~55% must be disposed as solid waste

(American Coal Ash Association)

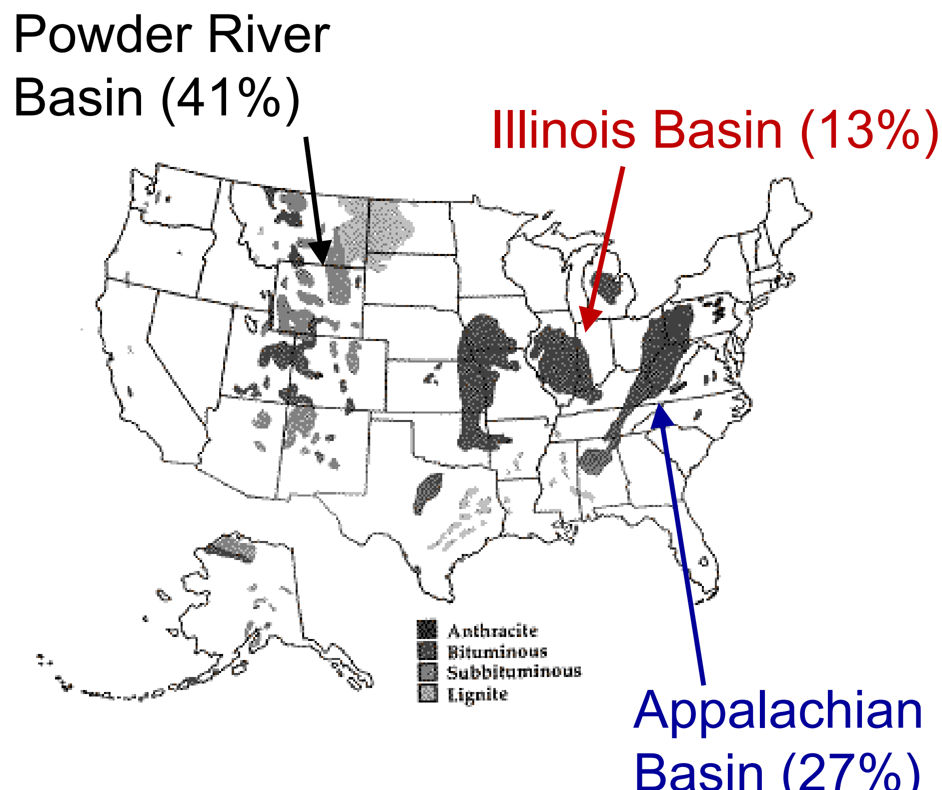
# Technological Approach



# Feedstock Coal Ash



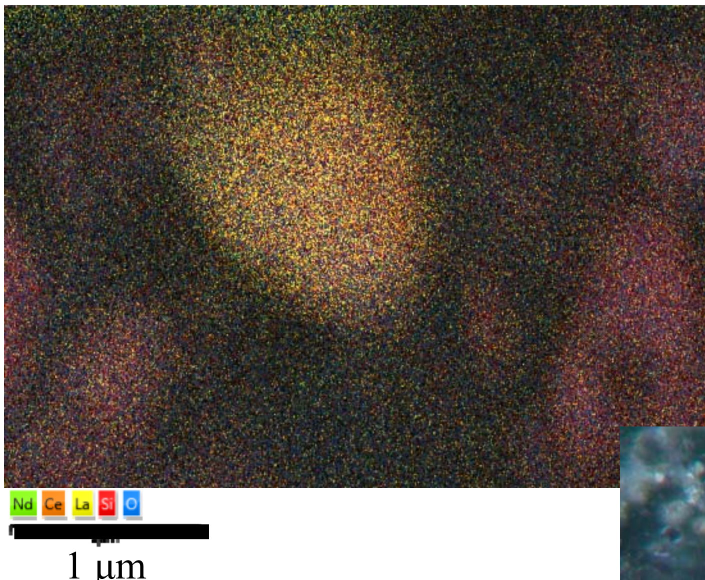

Coal Production in the U.S.



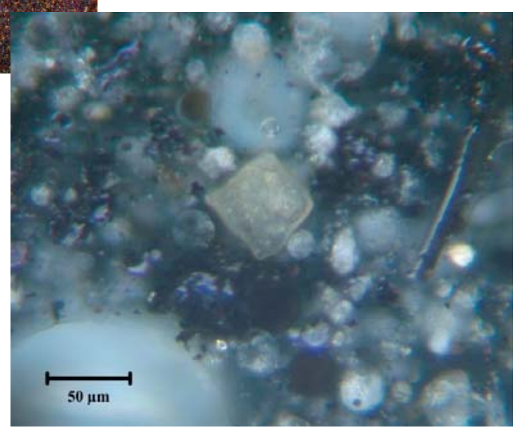

Taggart *et al.*, *Env. Sci. & Technol.*, 2016

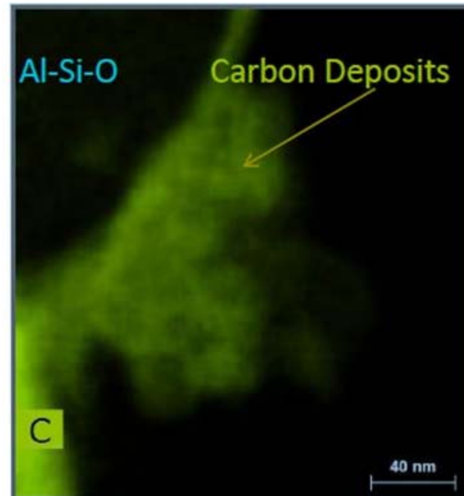
# REEs: Modes of Occurrence in Fly Ash

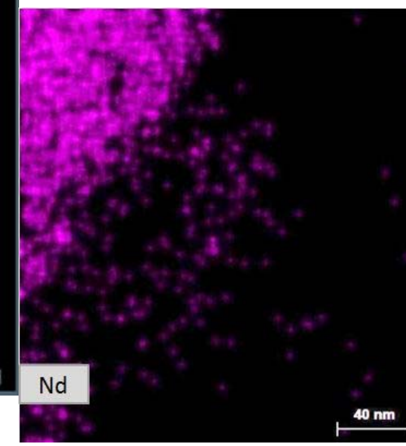
aluminum-oxide particle with Ce, La, Ca, Nd, Ba

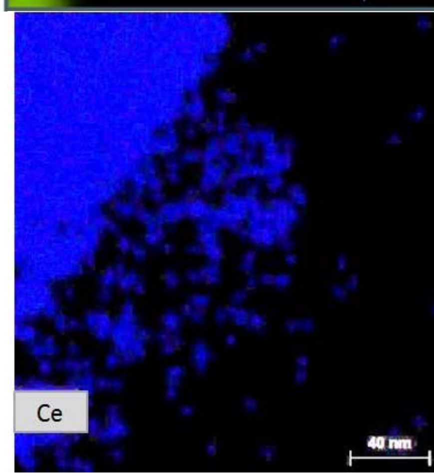



discrete monazite particle



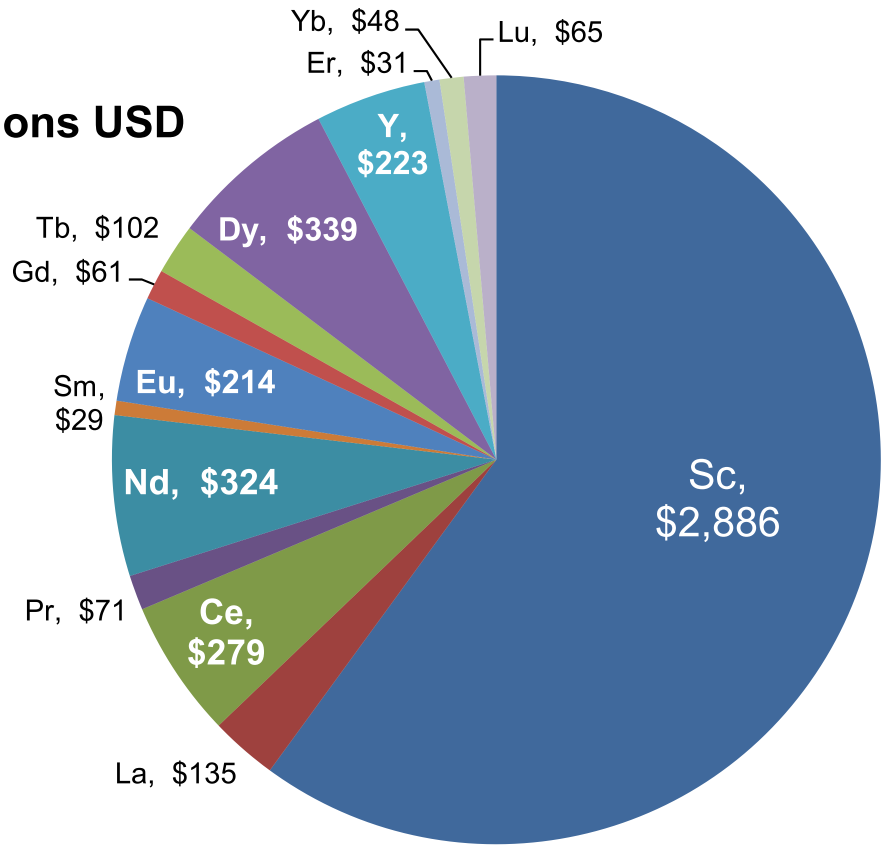




Nanoscale inclusions in amorphous carbon

# Feedstock Coal Ash

## Total Annual Value in Unused Fly Ash

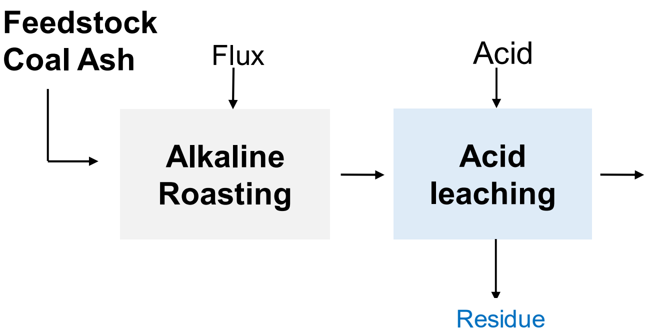



Total:
$4 billion per year

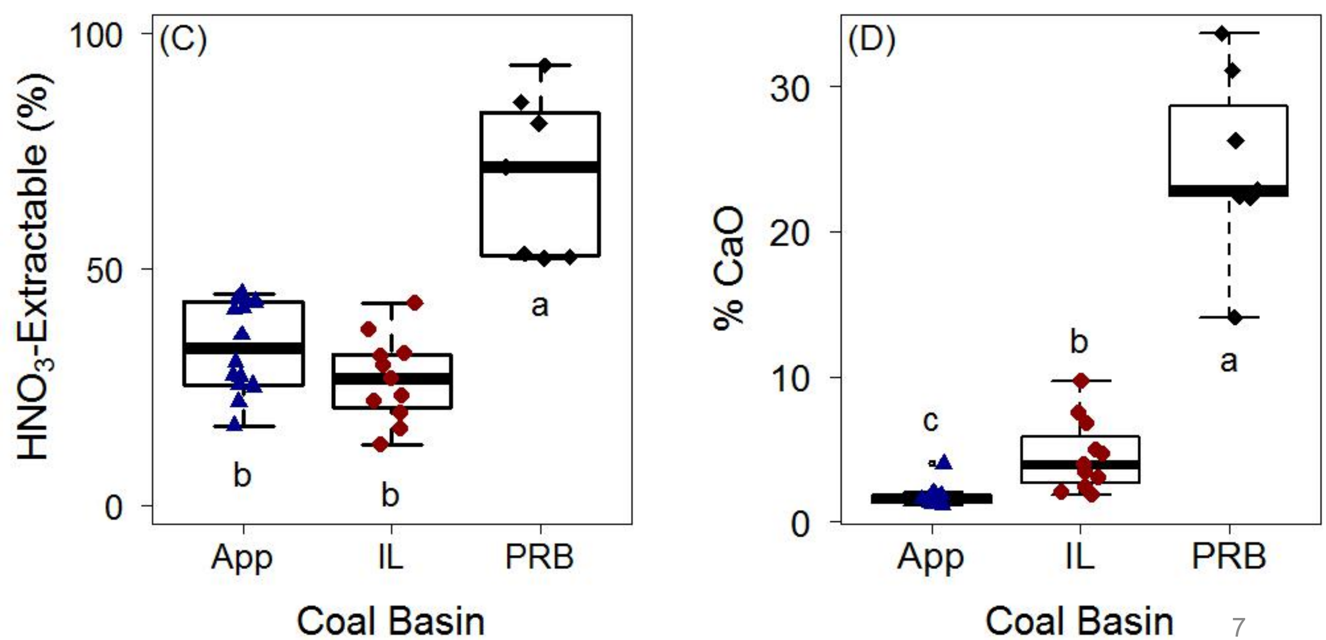
(Basis: 2011 prices for high purity rare earth oxides)

Taggart *et al.*, ES&T, 2016

# Extraction of REEs from Feedstock Coal Ash

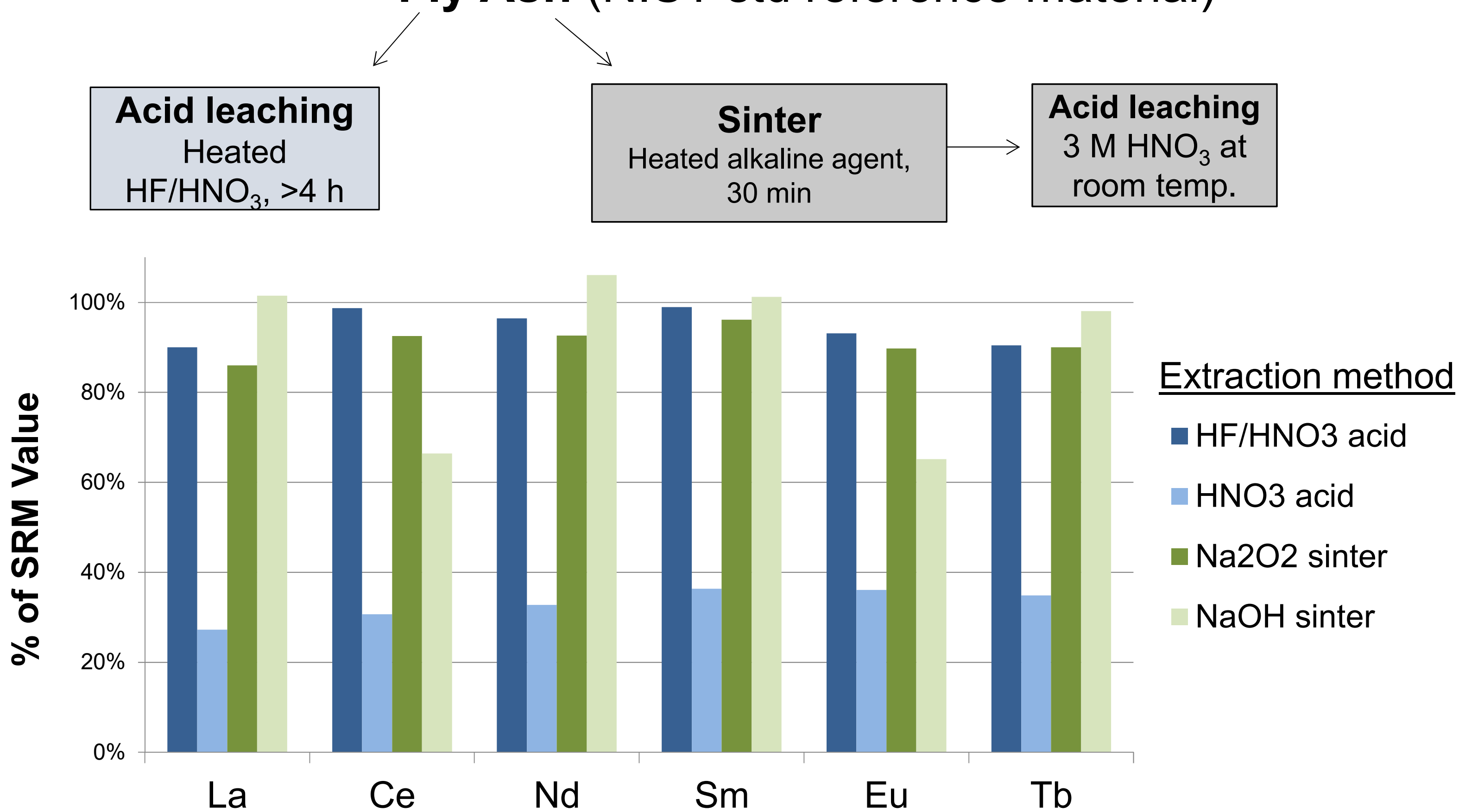



- Much higher calcium content of PRB ashes may account for higher extractability
- Greater susceptibility to leaching

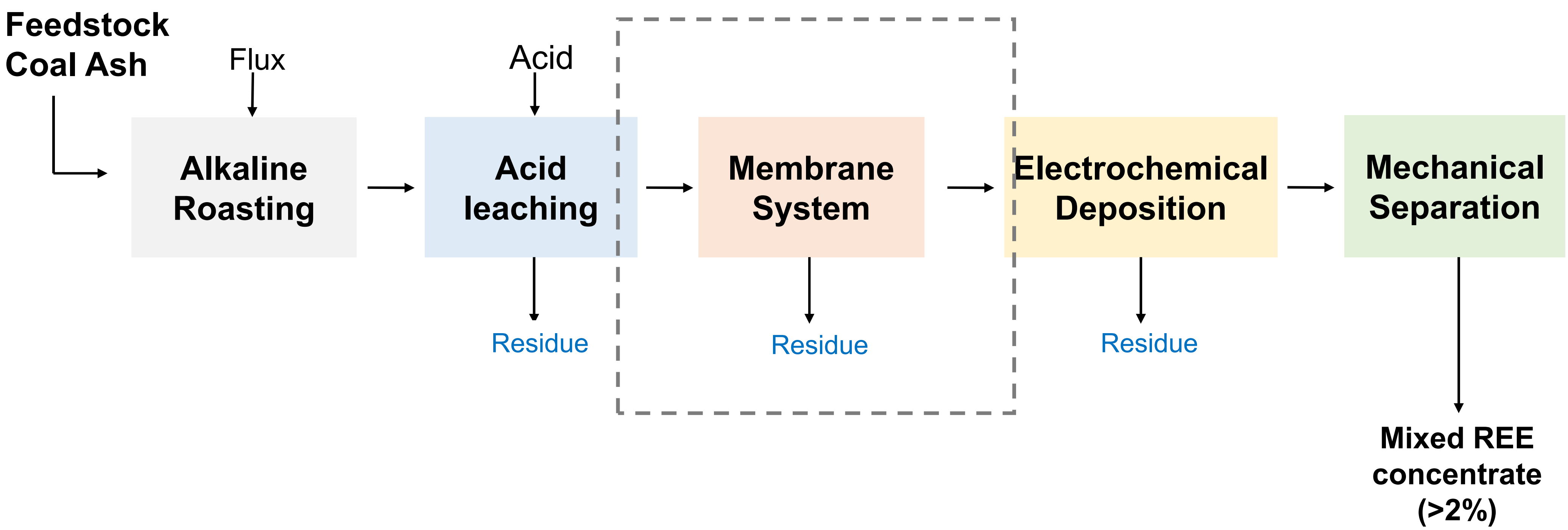


# Extraction of REEs from Feedstock Coal Ash

**Fly Ash** (NIST std reference material)



# Membrane Separations



## Synthetic Leachate

| Element | Concentration (mg $L^{-1}$) |
|---|---|
| $Na^{+}$ | 6270 |
| $Mg^{2+}$ | 10 |
| $Ca^{2+}$ | 33 |
| $Al^{3+}$ | 271 |
| $Fe^{3+}$ | 90 |
| $Si^{4+}$ | 590 |
| $Y^{3+}$ | 0.15 |
| $Tb^{3+}$ | 0.15 |
| $Er^{3+}$ | 0.15 |
| $Dy^{3+}$ | 0.15 |
| $Nd^{3+}$ | 0.15 |
| $Eu^{3+}$ | 0.15 |

1% v/v $HNO_3$ → Initial pH= 0.95

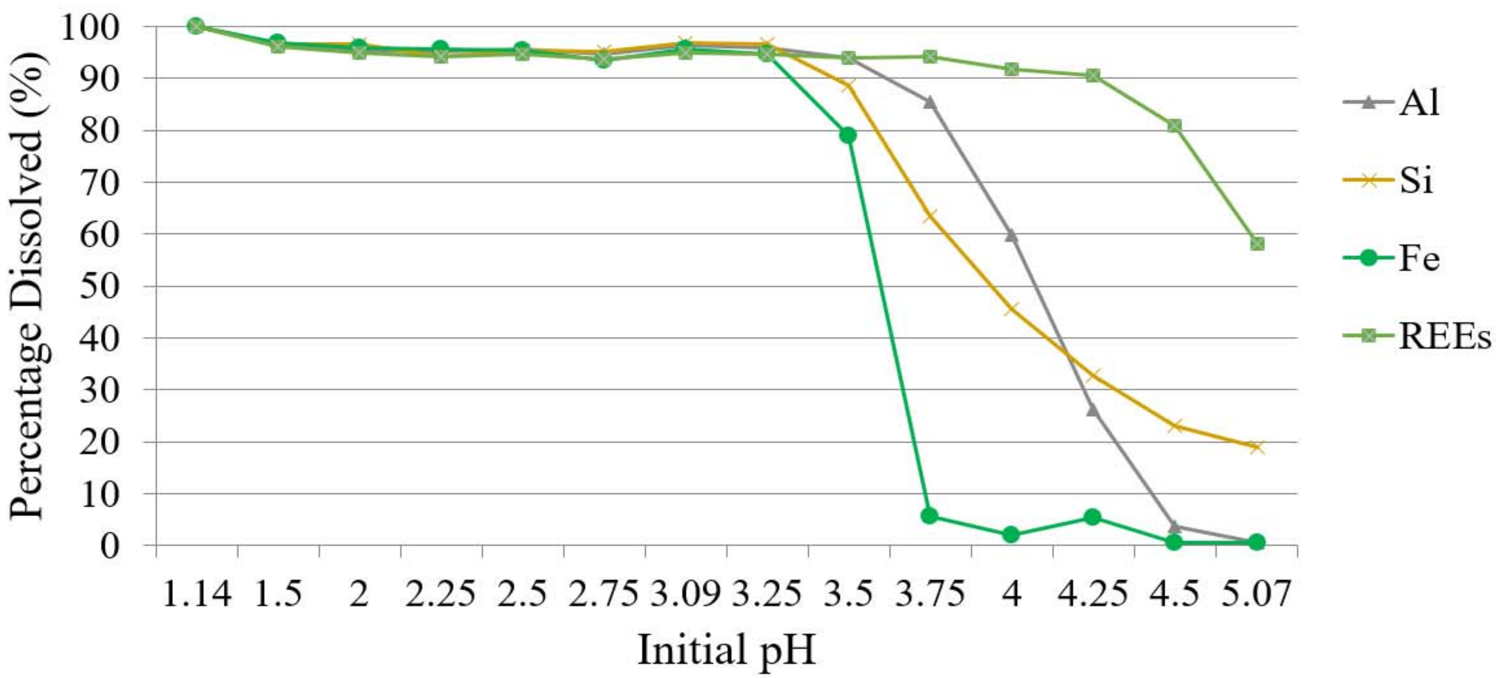
Separations:

- Chemical Precipitation & Nanofiltration
- Micelle-enhanced ultrafiltration
- Liquid film emulsion membranes
- Electrochemical deposition

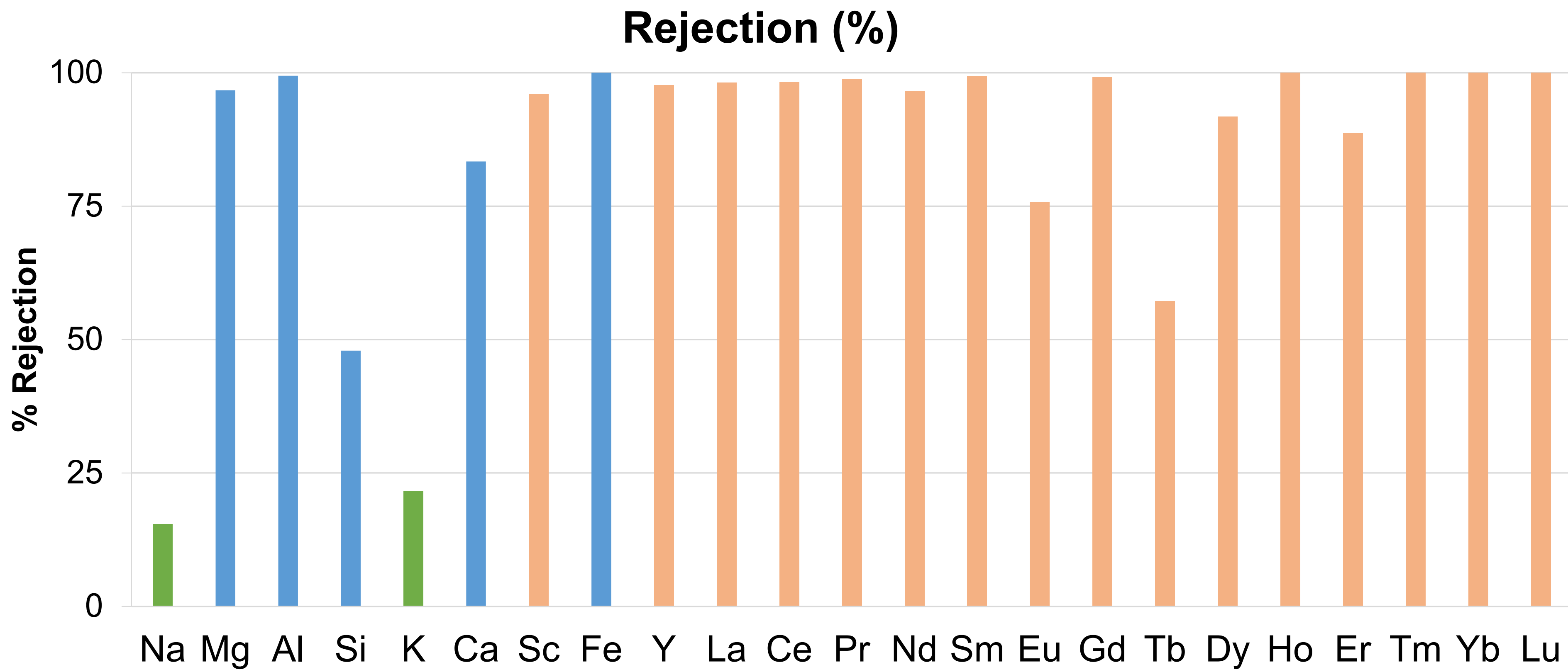
# pH-adjusted chemical precipitation

- pH adjustment with NaOH
- Precipitation time (20-90 min)
- Filter particles (0.45 μm pore size)

At pH 4.5:
- Substantial removal of Fe, Al and Si
- ~12% loss of REEs
- No removal of Na, Ca, and Mg

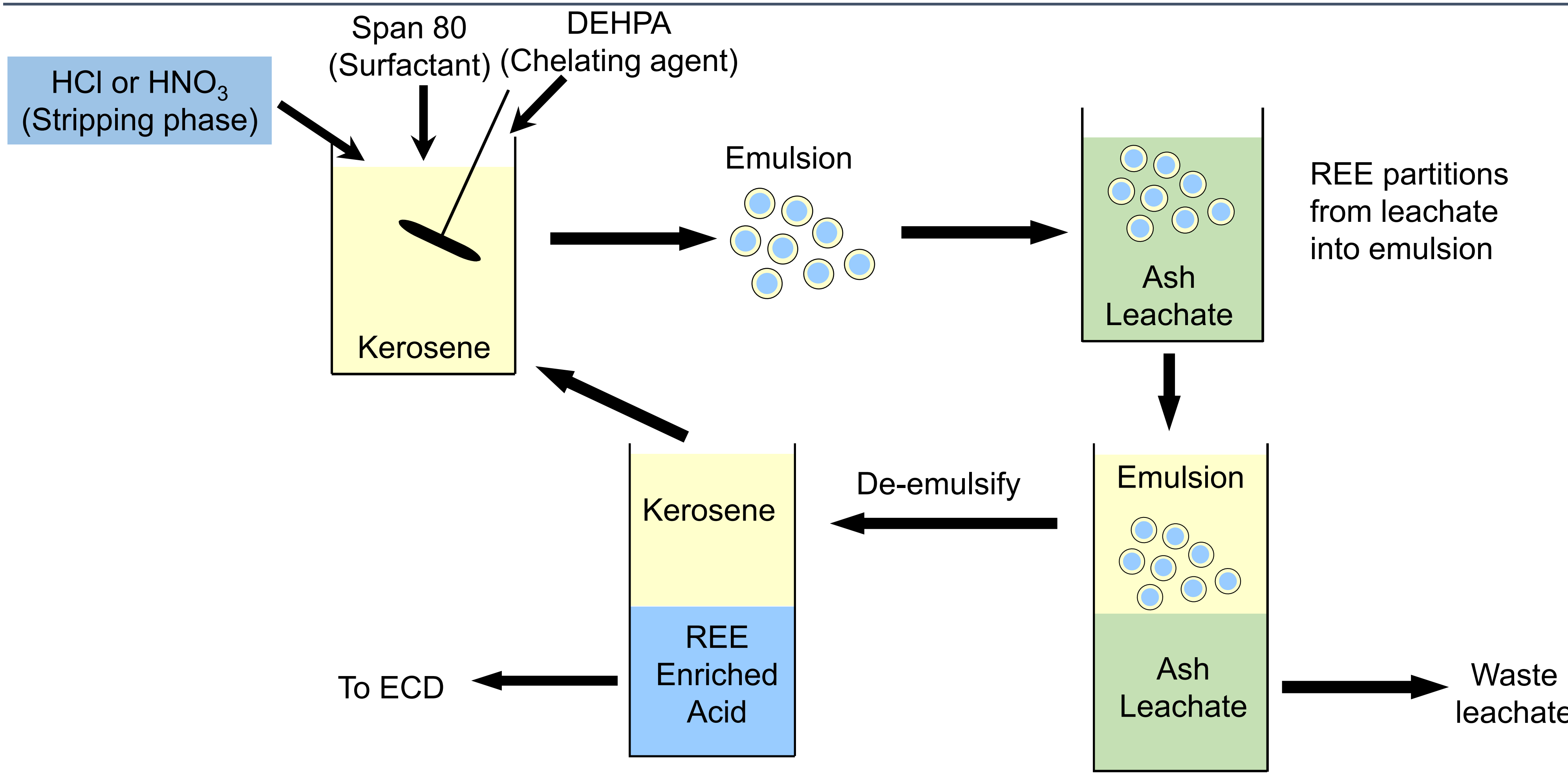


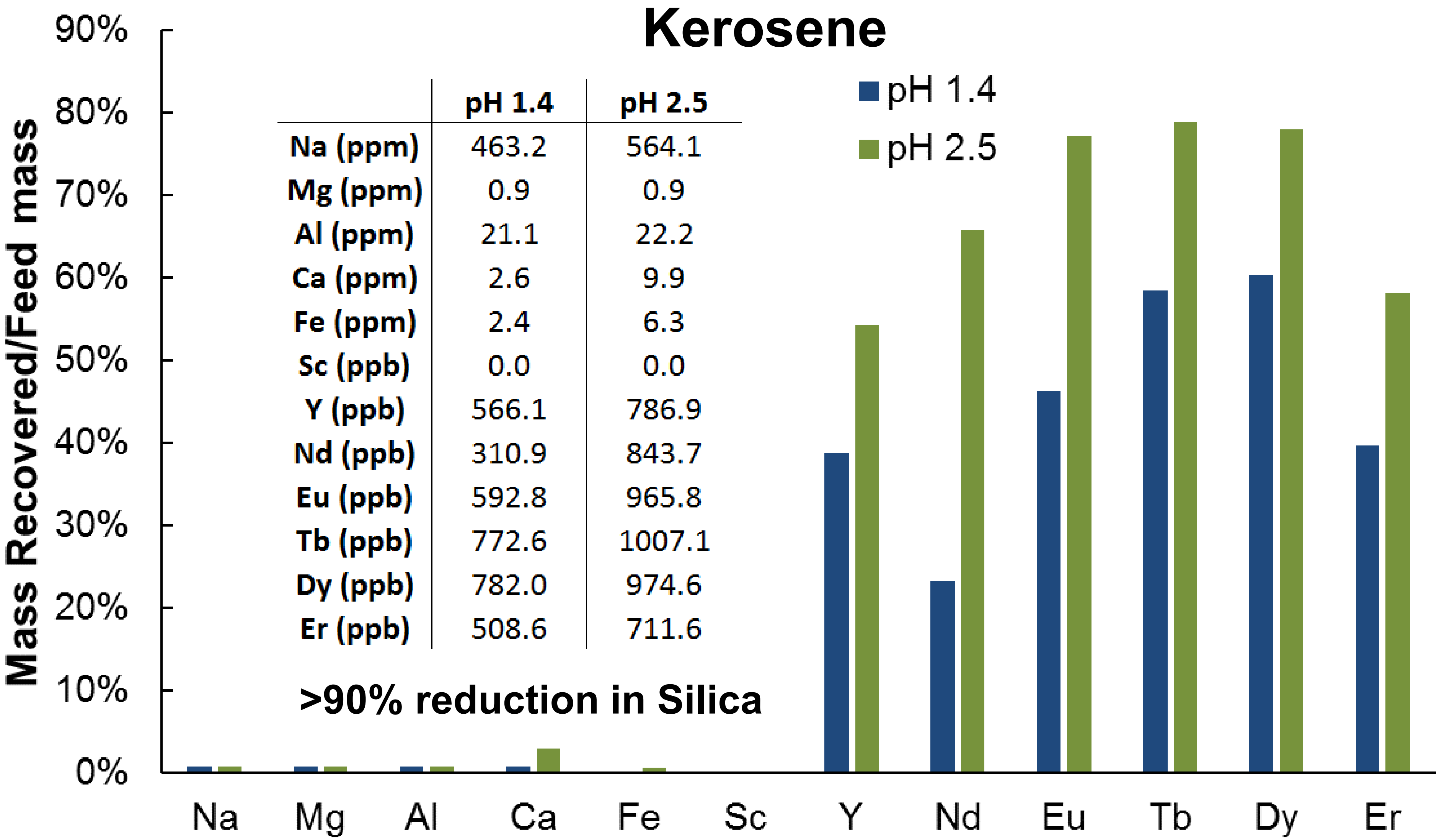
# Nanofiltration after chemical precipitation



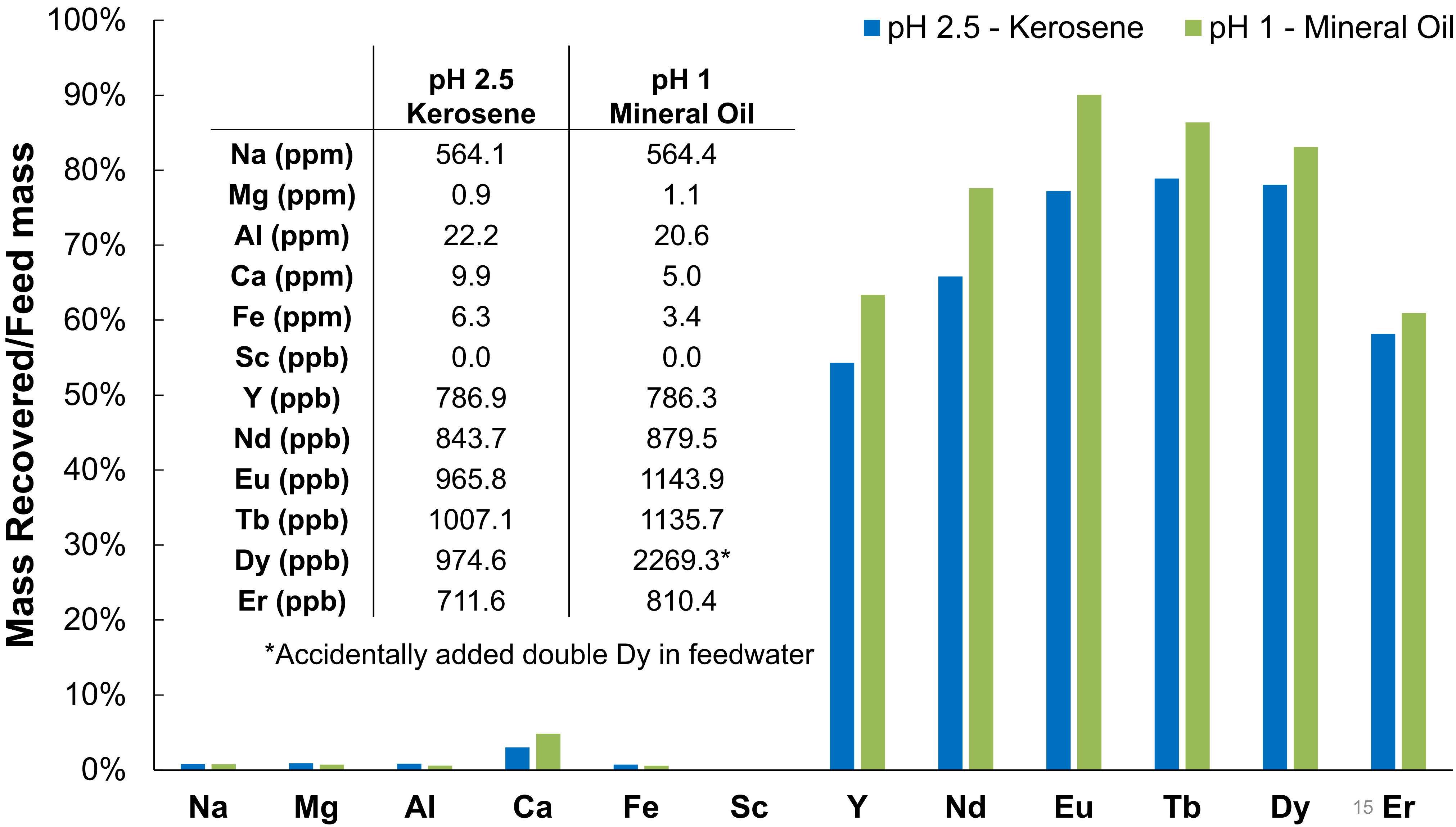

Separation of monovalent ions ($Na^+$, $K^+$) from others

# Liquid Film Emulsions





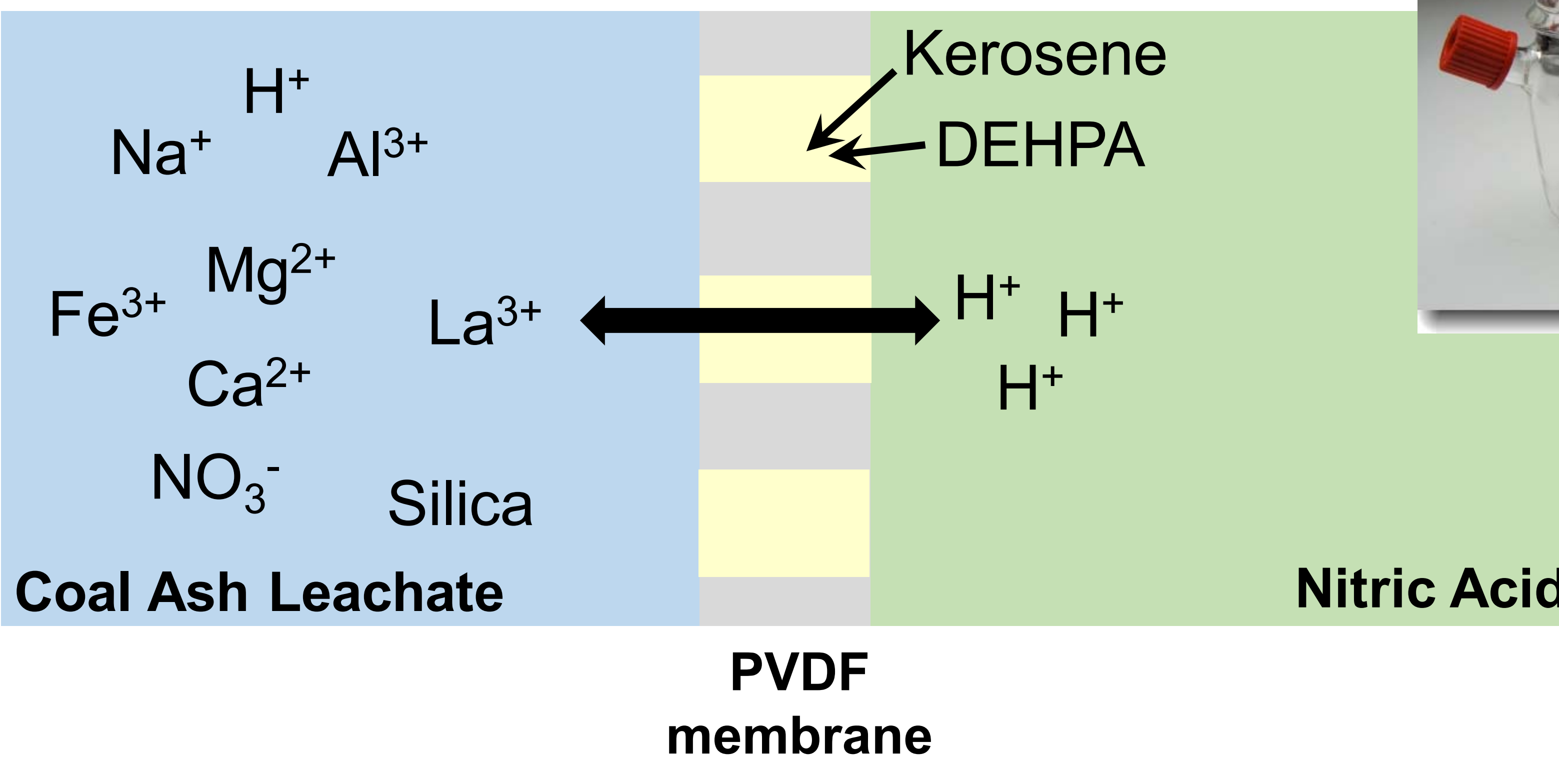

| | pH 1.4 | pH 2.5 |
|---|---|---|
| Na (ppm) | 463.2 | 564.1 |
| Mg (ppm) | 0.9 | 0.9 |
| Al (ppm) | 21.1 | 22.2 |
| Ca (ppm) | 2.6 | 9.9 |
| Fe (ppm) | 2.4 | 6.3 |
| Sc (ppb) | 0.0 | 0.0 |
| Y (ppb) | 566.1 | 786.9 |
| Nd (ppb) | 310.9 | 843.7 |
| Eu (ppb) | 592.8 | 965.8 |
| Tb (ppb) | 772.6 | 1007.1 |
| Dy (ppb) | 782.0 | 974.6 |
| Er (ppb) | 508.6 | 711.6 |



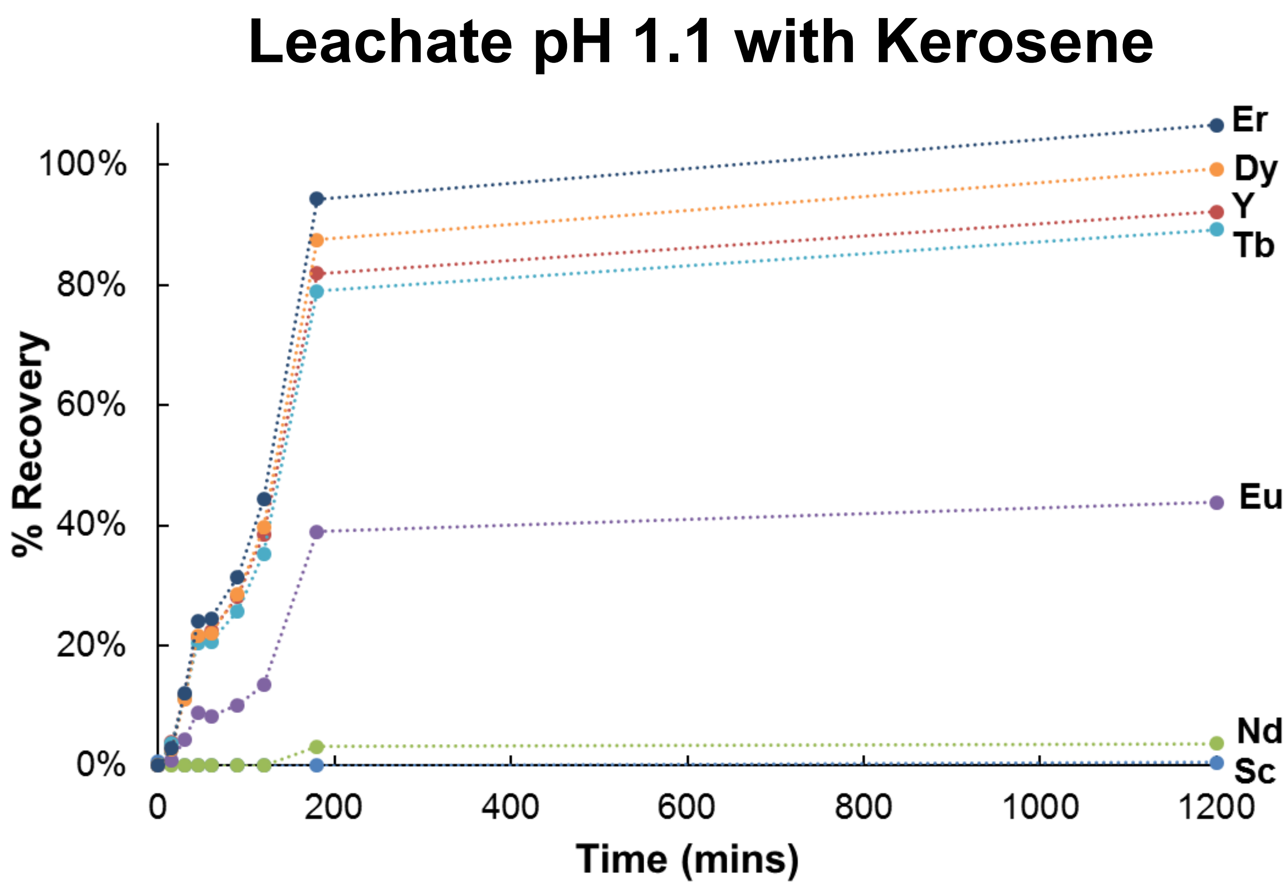

| | **pH 2.5 Kerosene** | **pH 1 Mineral Oil** |
|---|---|---|
| **Na (ppm)** | 564.1 | 564.4 |
| **Mg (ppm)** | 0.9 | 1.1 |
| **Al (ppm)** | 22.2 | 20.6 |
| **Ca (ppm)** | 9.9 | 5.0 |
| **Fe (ppm)** | 6.3 | 3.4 |
| **Sc (ppb)** | 0.0 | 0.0 |
| **Y (ppb)** | 786.9 | 786.3 |
| **Nd (ppb)** | 843.7 | 879.5 |
| **Eu (ppb)** | 965.8 | 1143.9 |
| **Tb (ppb)** | 1007.1 | 1135.7 |
| **Dy (ppb)** | 974.6 | 2269.3* |
| **Er (ppb)** | 711.6 | 810.4 |

*Accidentally added double Dy in feedwater

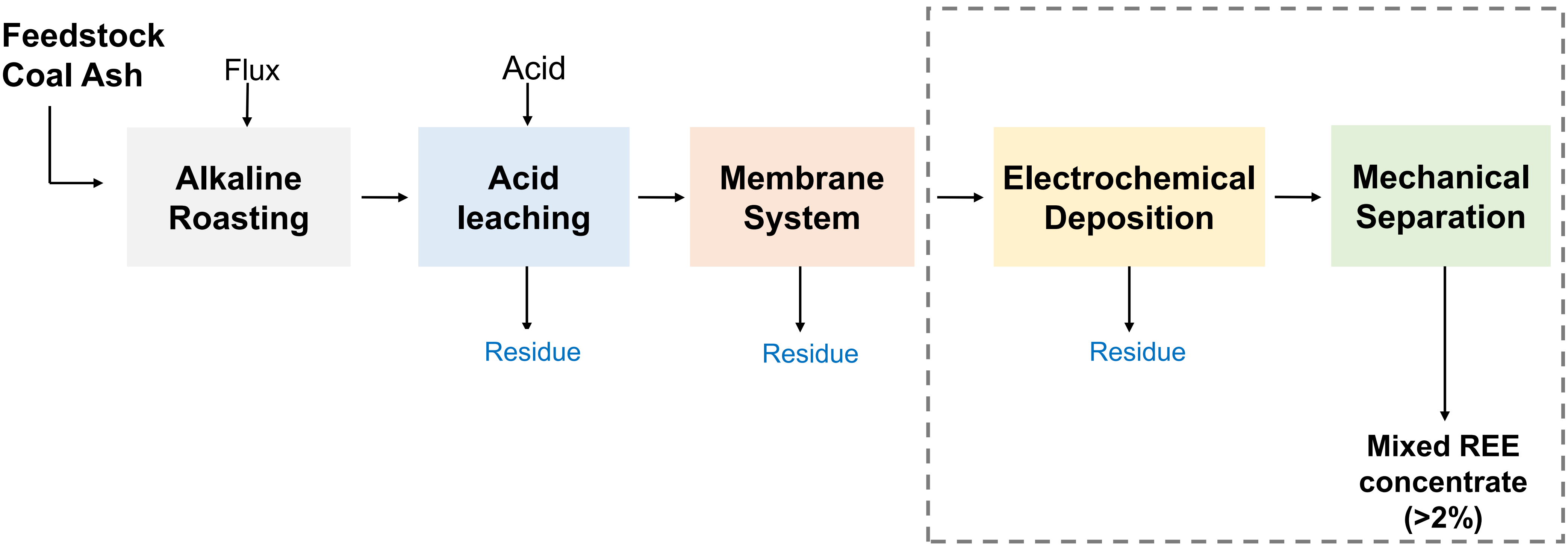
# Supported Liquid Membranes




# Supported Liquid Membranes



# Electrochemical Deposition



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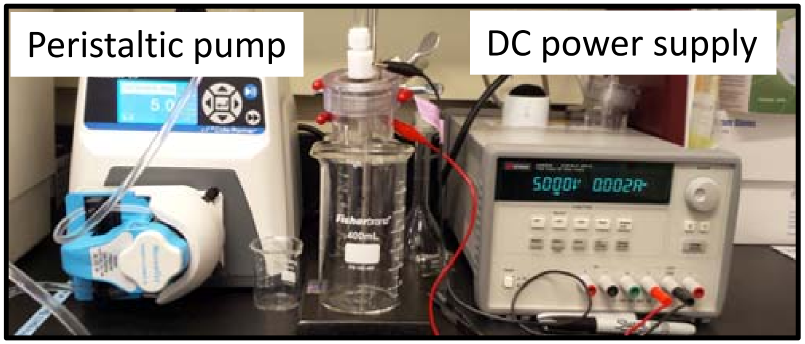
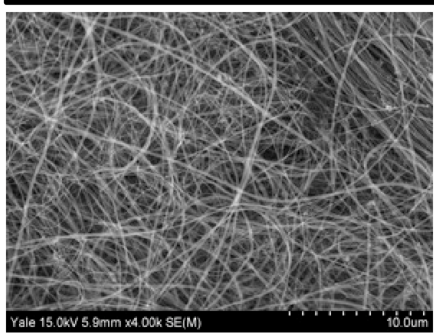
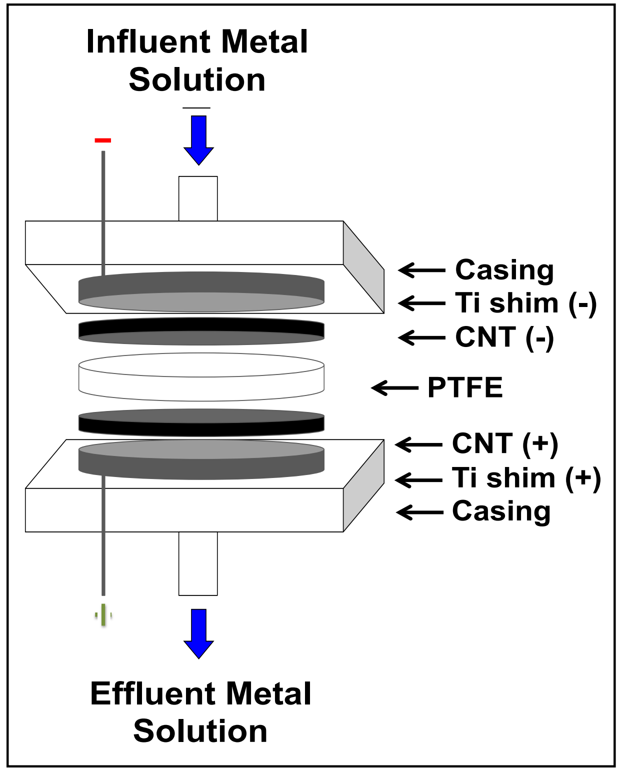
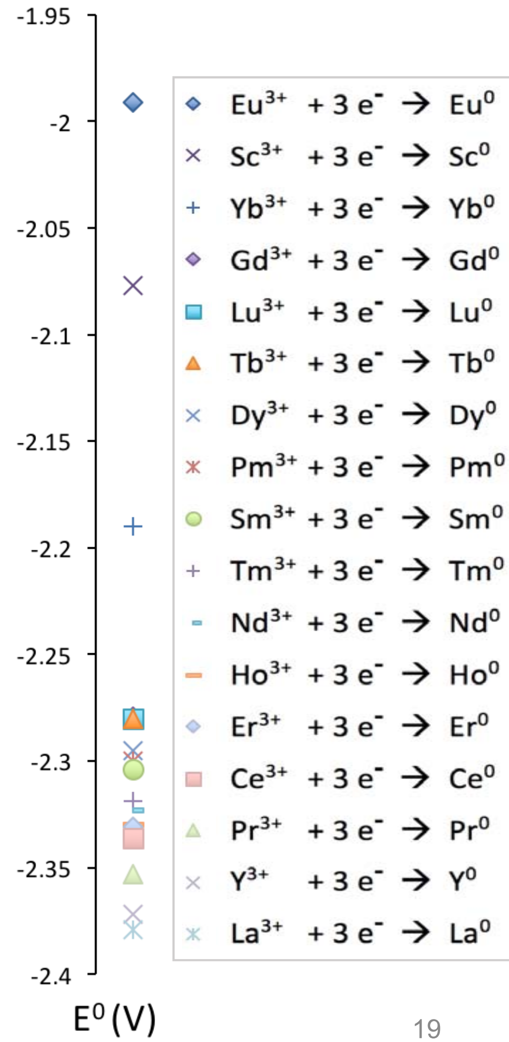



SEM image of carbon nanotube filter

Filter housing



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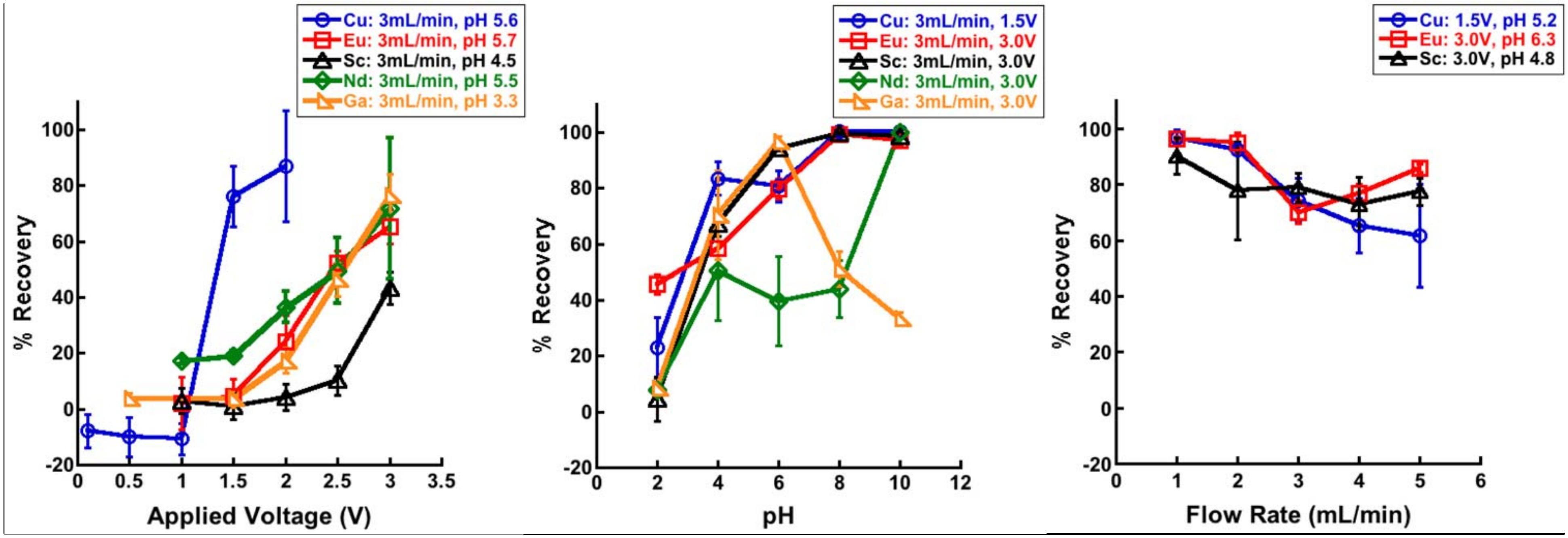
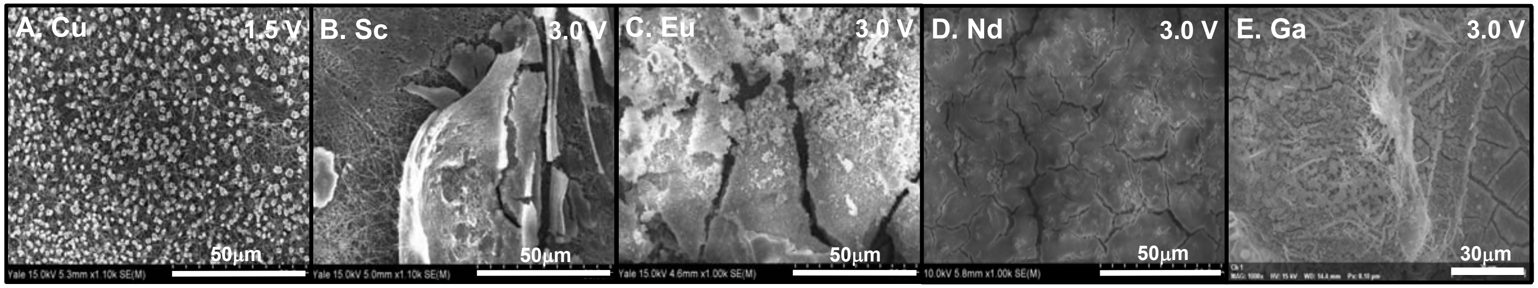
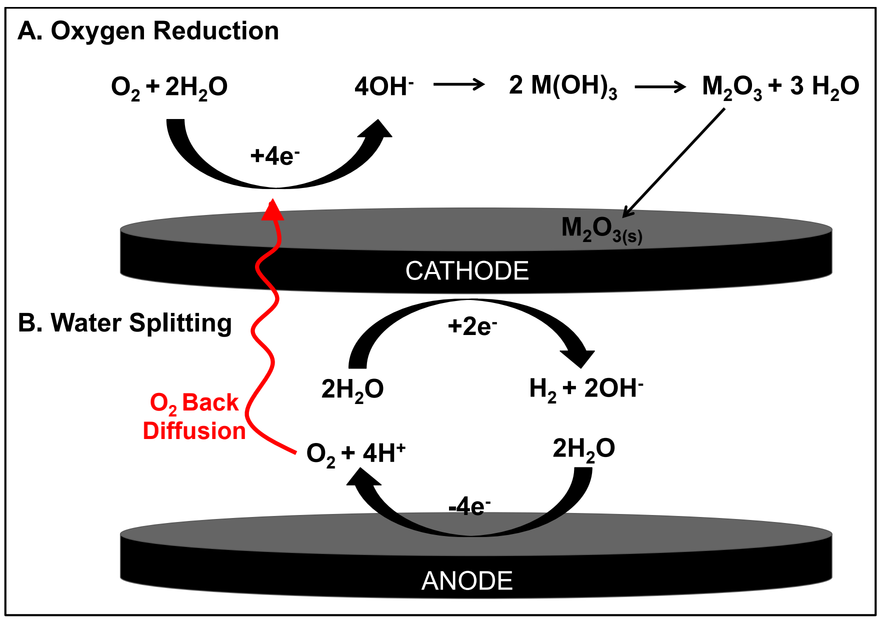
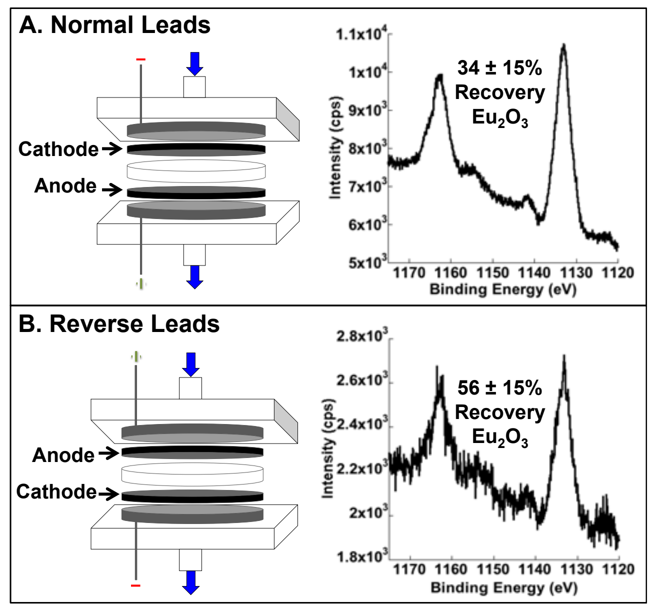



- Voltage-mediated recovery confirmed, but not at theoretical reduction potentials
- Significant pH sensitivity
- Minor influence of flow rate

# Electrochemical Deposition



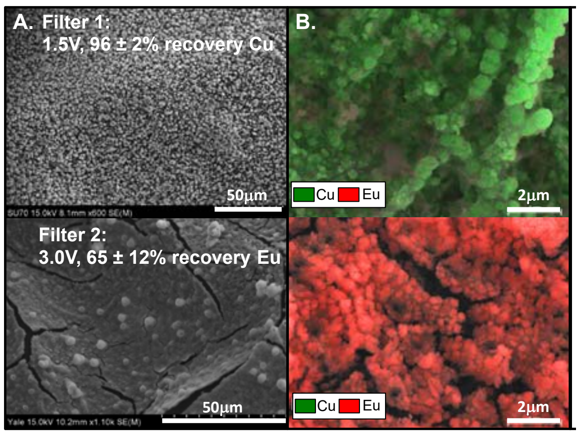




- Reduced metal crystals for easy-to-reduce metals
- Oxide recovery of REE
- Oxygen sources: both dissolved and electrochemical

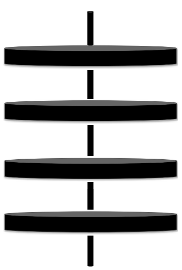
# Electrochemical Deposition

Relatively pure samples: great separation

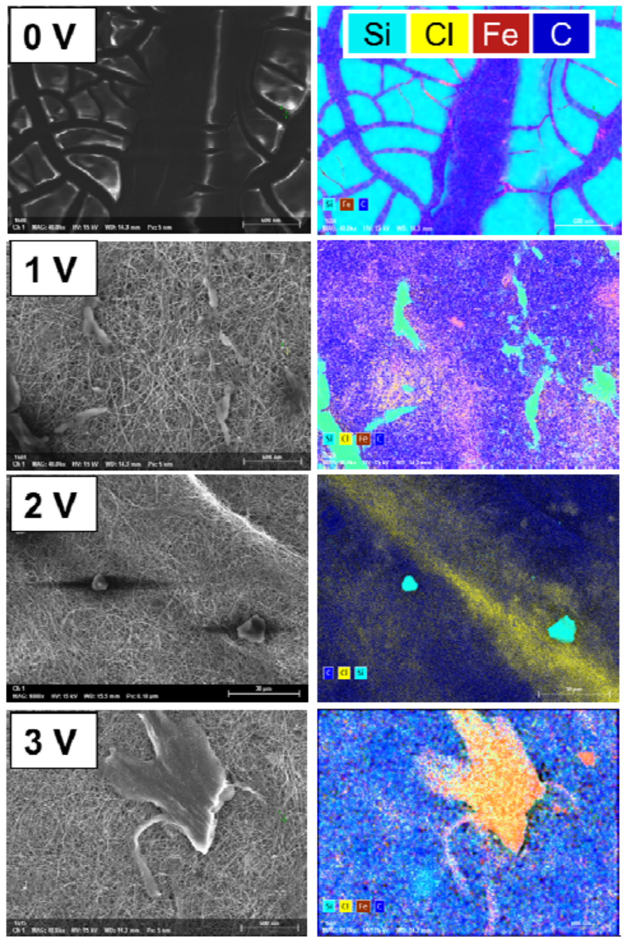



Cu Eu

Stacked filters

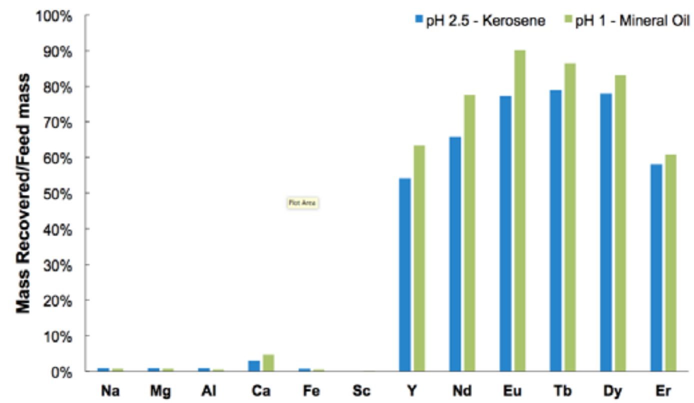


Real leachate: Si, Fe, Al breakthrough




**Pre-treatment required!**

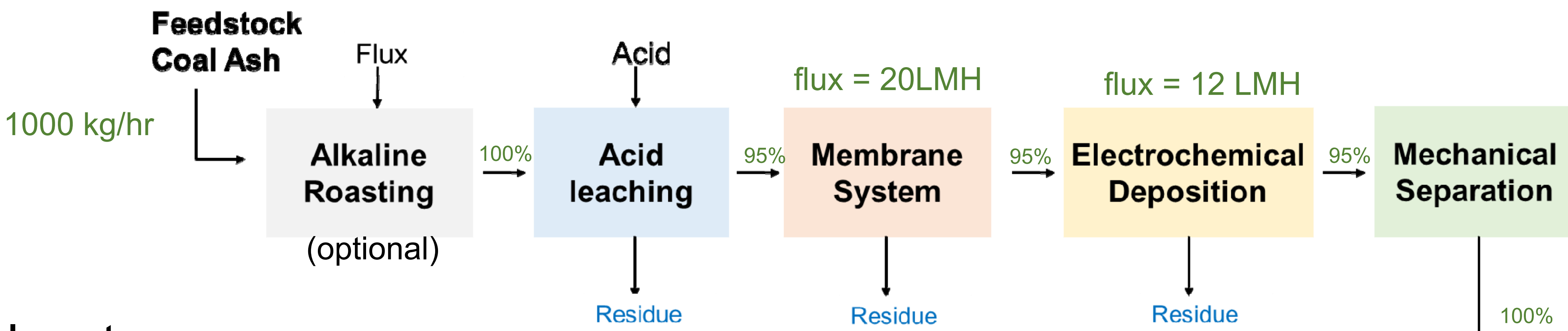
Recall LFE enrichment step:




Currently: testing combination of LFE pretreatment for mixed REO capture

# Techno-Economic Model Overview

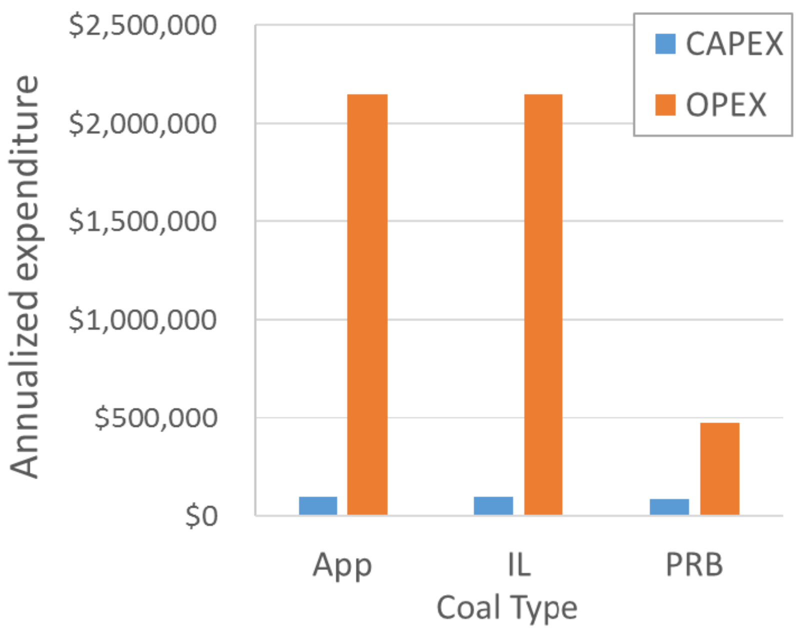
## Key Assumptions

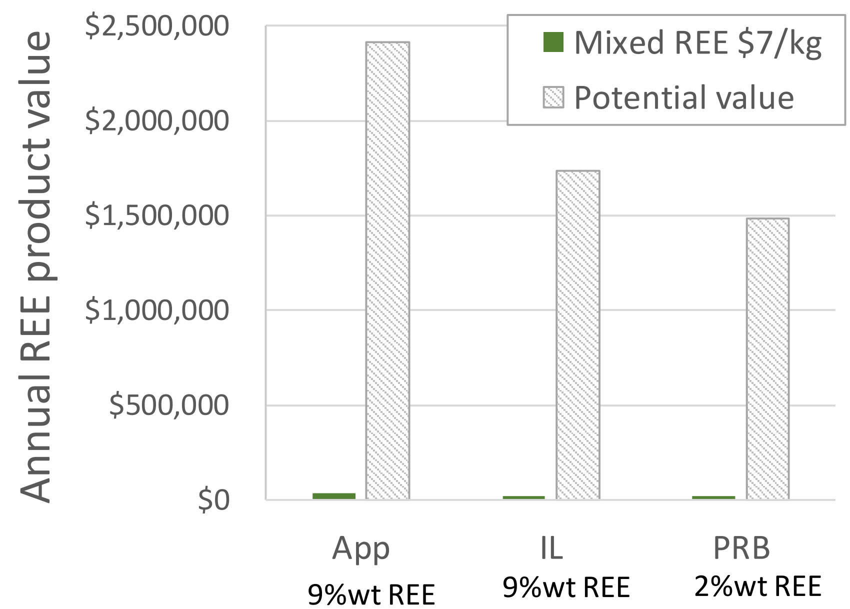



- Inputs:
  - type of CCR: based on geographical regions.
  - Select alkaline roasting conditions (if any).
  - Select membrane system concentration approach: nanofiltration (NF), micelle enhanced ultrafiltration (UFM), or liquid emulsion membrane recovery (LEM).
- Model output: CAPEX and OPEX costs as well as final REE mass and concentration.

# TE Analysis Results

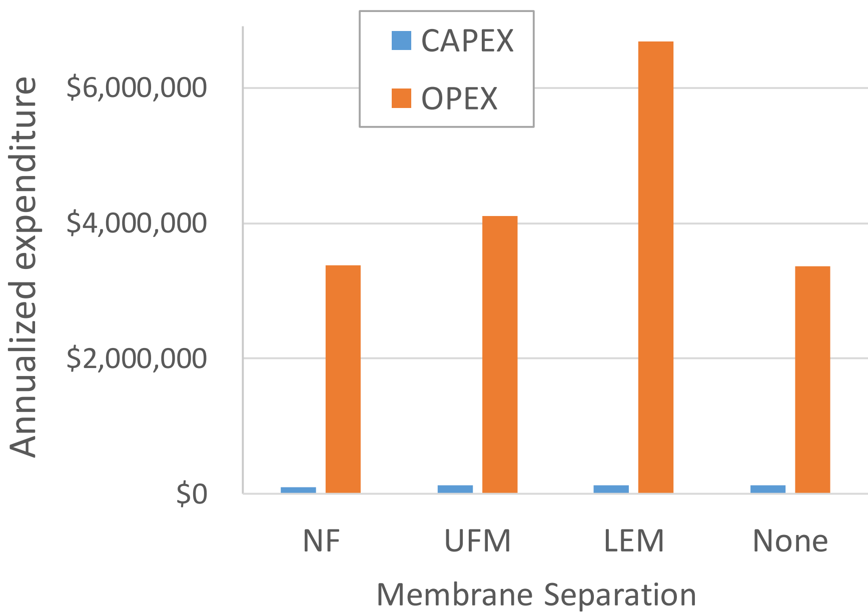
**<u>Scenario 1: NF as REE concentration step</u>**. (NF@ 80% water recovery; 90% rejection of multi-valent ions; 25% rejection of monovalent ions)

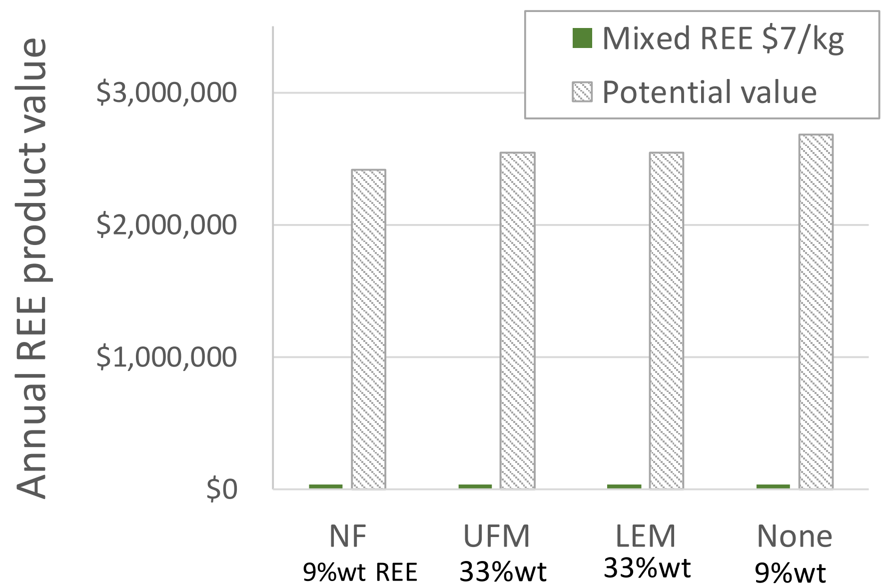



- **Costs are driven by OPEX over CAPEX** – required chemicals consumed and disposal costs are the dominant factors. These have high uncertainty at this stage of project.
- **Potential value** – is determined from individual REE recovered value.

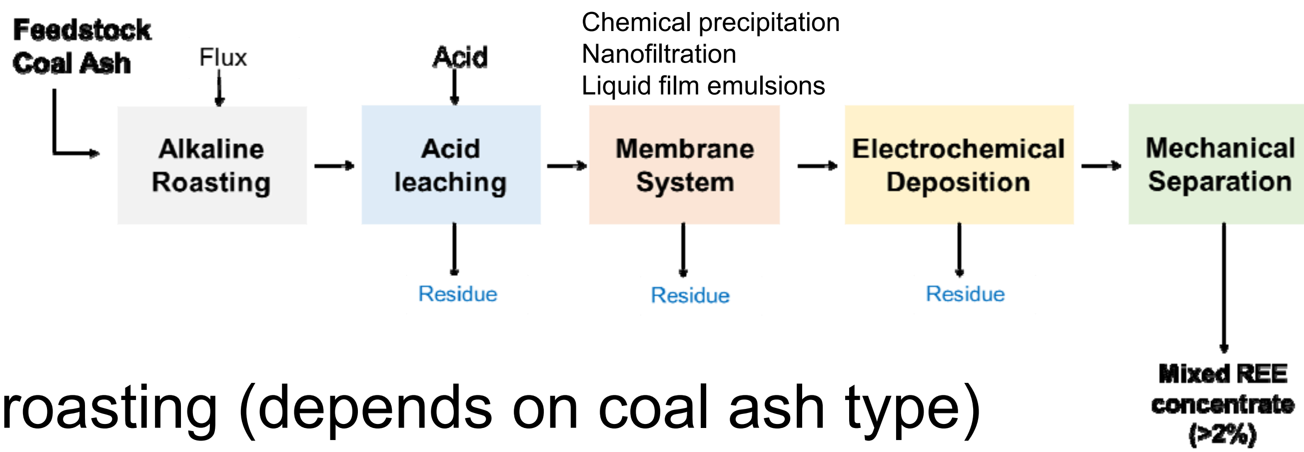
# Impact of Process Selection – Concentration Step




- **Highest to lowest costs:** LEM > UFM > NF > No concentration step.
- Consumption of chemical inputs drive the operation cost for each concentration option.
- The "none" option may not be a true option if a minimum REE concentration is required for recovery in the final step.

# Summary




Extraction from coal ash:
Acid leaching or alkaline roasting (depends on coal ash type)

Leachate separations:
Requires selectivity of desired metals from majors (Fe, Al, Si, Ca)

Techno-economic feasibility:

- Focus research on reducing chemical consumption, disposal
- Added value: Aluminum, Scandium

# Thanks!

Research Team:

Duke University: Ross Taggart, Ryan Smith, Borte Mutlu, Beatrice Cannoli

Yale University: Riley Coulthard, Megan O’Connor

University of Kentucky: Kevin Henke, Uschi Graham, Madison Hood

RTI International: Nandita Akunuri