DE-FE0031483: Low Cost Rare Earth Element (REE) Recovery from Acid Mine Drainage Sludge

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Project Objectives and Team

Team Member	Role
RTI International	▪ Prime Recipient ▪ Membrane benchmarking and performance evaluation ▪ Bench-scale parametric studies and performance testing of synthetic and real acid mine sludge/wastewaters ▪ Techno-economic process analyses
Cerahelix	▪ Industrial partner ▪ Selective ion (ceramic) membrane development ▪ Membrane characterization and optimization
Veolia Water/ Montrose	▪ Industrial partners ▪ Access to mine wastewater to validate process performance ▪ Engineering expertise in metals removal from wastewater

Project Objective: Develop a membrane-based, bench-scale system to extract strategic minerals such as rare earth elements (REEs), and other critical minerals, from acid mine drainage (AMD) sludge generated as part of coal mining activities in the United States. The effort will use a staged, membrane-based treatment approach to separate, concentrate, and ultimately recover REEs from AMD.

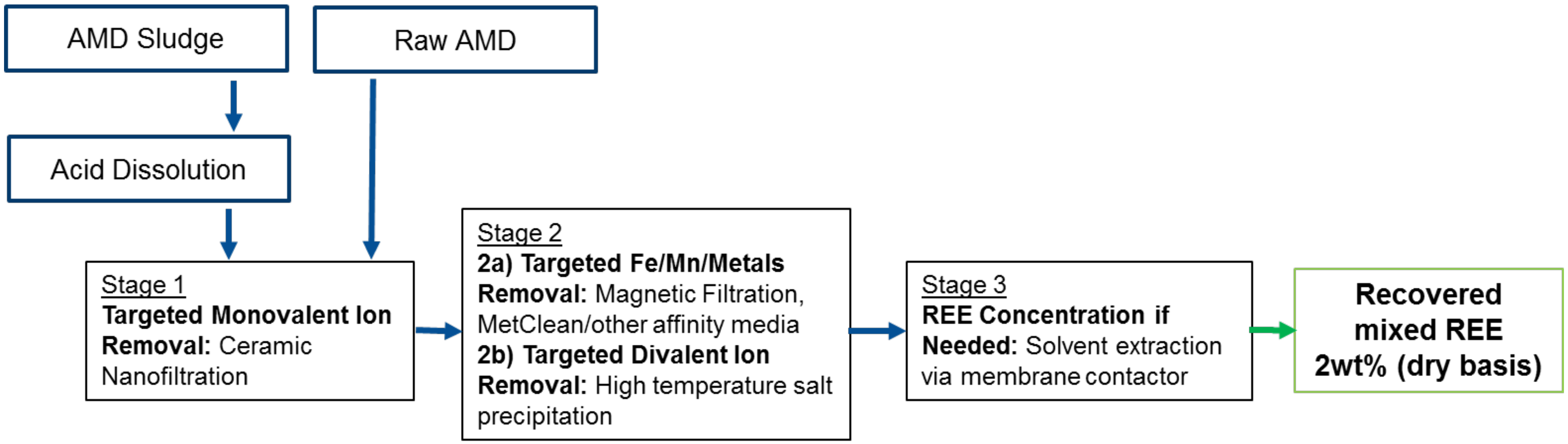
High Variation in Major and Minor Constituents

Analyte	Sample 1[a] Fraction (%)	Sample 2[a] Fraction (%)	Sample 3[b] Fraction (%)	Sample 4[b] Fraction (%)	Sample 5[c] Fraction (%)	Sample 6[c] Fraction (%)
Cl	6.6%	16.9%	NR	NR	NR	NR
NO_3	0.1%	1.3%	NR	NR	NR	NR
SO_4	74.7%	50.3%	3.0%	14.7%	NR	NR
Na	4.2%	18.4%	NR	NR	NR	4.0%
Ca	8.5%	7.5%	43.0%	3.0%	9.3%	28.9%
Mg	3.5%	4.6%	7.0%	12.7%	5.3%	15.0%
K	1.3%	0.8%	NR	NR	0.2%	7.5%
Fe	0.6%	0.0%	33.0%	19.0%	73.6%	1.9%
Mn	0.2%	0.0%	2.9%	8.9%	4.6%	13.5%
Al	0.4%	0.0%	4.5%	29.0%	4.6%	29.2%
Si	NR	NR	6.6%	12.7%	NR	NR
Zn	NR	NR	NR	NR	1.9%	11.3%

NR = not reported
[a] Shanxi Province, China – Zhao et al
[b] Pennsylvania, USA – Ziemkiewicz et al.
[c] Tennessee, USA – Lee et al.

- Both REE and major ion composition varies widely with geography, geology, and specific site characteristics. Also variation in runoff vs. precipitated sludge.
- A flexible and variable treatment approach that accounts for the specific chemical composition of the source AMD is needed.

Multi-stage REE Recovery from AMD - Overview



We are evaluating several approaches as part of a staged membrane- and sorbent-based approach to recovery REE from AMD.

- Each process stage is considered interchangeable, and the selection and order of the unit operations will be dictated by AMD characteristics.
- Nanofiltration (NF) membrane selectivity between REE and other major dissolved constituents will be assessed.
- We will also evaluate sorbent or affinity media for REE/major ion selectivity.
- Both total REE recovery and individual REE element recovery will be evaluated

Target Performance Metrics

Target removal/recovery goals for each enrichment stage

Process Stage:	Stage 1 – NF Filtration	Stage 2a Target Metal Removal	Stage 2b – Target REE Recovery	Stage 3 – REE Solvent Recovery
Target Performance Metric:	1) >95% rejection of total dissolved REE 2) <30% rejection of monovalent ions	1) >90% removal target metal(s) 2) <10% removal of total REE	1) >90% removal REE 2) <10% removal of target bulk metal(s)	1) >90% recovery of total REE 2) <30% recovery other dissolved species

Framework for Project

Key Focus Areas

- Ceramic nanofiltration membranes for REE enrichment (Task 3)
- Electrochemically assisted deposition for direct REE capture (Tasks 5)
- Dendrimer based sorbents for REE affinity (Task 4)
- Preliminary Techno-Economic and Feasibility Assessment (Task 6)

Project Management Overview

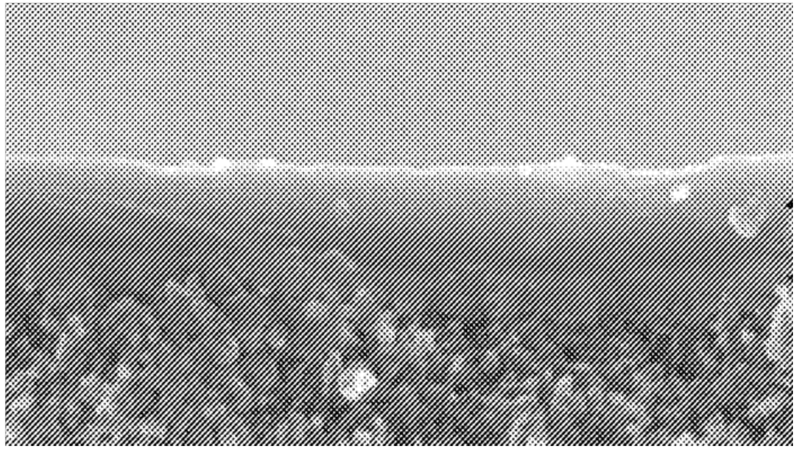
- Project making good technical progress
- Delays and loss of access to AMD site has delayed the verification of technology components with actual AMD samples
  - Sampling agreement with Montrose signed in February 2019 for AMD from 4 sites
  - First samples arrived April 2019
  - PMP and milestones have been updated to account for 3-month NCE
- All necessary resources available
- On track with all the technical and financial reporting requirements
- Investigating commercial interest for REE recovery with varying sources

Milestone Table

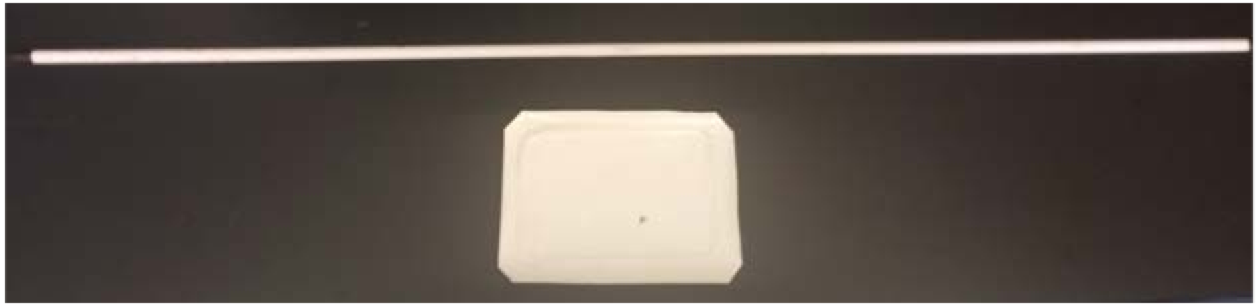
#	Description	Planned completion date	Updated completion date	% Complete
1	Project Kickoff Meeting	December 20, 2017	January 25, 2018	100%
2	Experimental performance feasibility of NF membranes to enrich major REE constituents in AMD sludge by <30% rejection (R) of target monovalent ions and >90% rejection of REE ions.	February. 28, 2019	April 30, 2019	90%
3	Experimental performance verification of metal affinity media to further enrich REE constituents in AMD sludge through >80% selective removal of other competing metals and target divalent ions	March. 31, 2019	June 30, 2019	90%
4	Experimental validation of final polishing technology to achieve project's final T-REE enrichment concentration of 2 wt% targeted	April. 30, 2019	August 30, 2019	20%
5	Submission of Final Technical Report	July 31, 2019	October 31, 2019	0%

Task 3: REE Membrane Enrichment Technology Evaluation and Optimization

- **Objective: Evaluate ceramic nanofiltration membranes for REE recovery**
- Commercially available tubular membranes from partner Cerahelix
- Testing performed in our single tube membrane module as well as the 7-channel monolith at Cerahelix facilities
- Testing covered the typical operating conditions for each pore size
- Results show excellent performance of REE separation from mono-valent ions and also showed potential for Fe separation
- Validate using AMD samples from field



Ceramic Nanofiltration Membranes used for REE Recovery

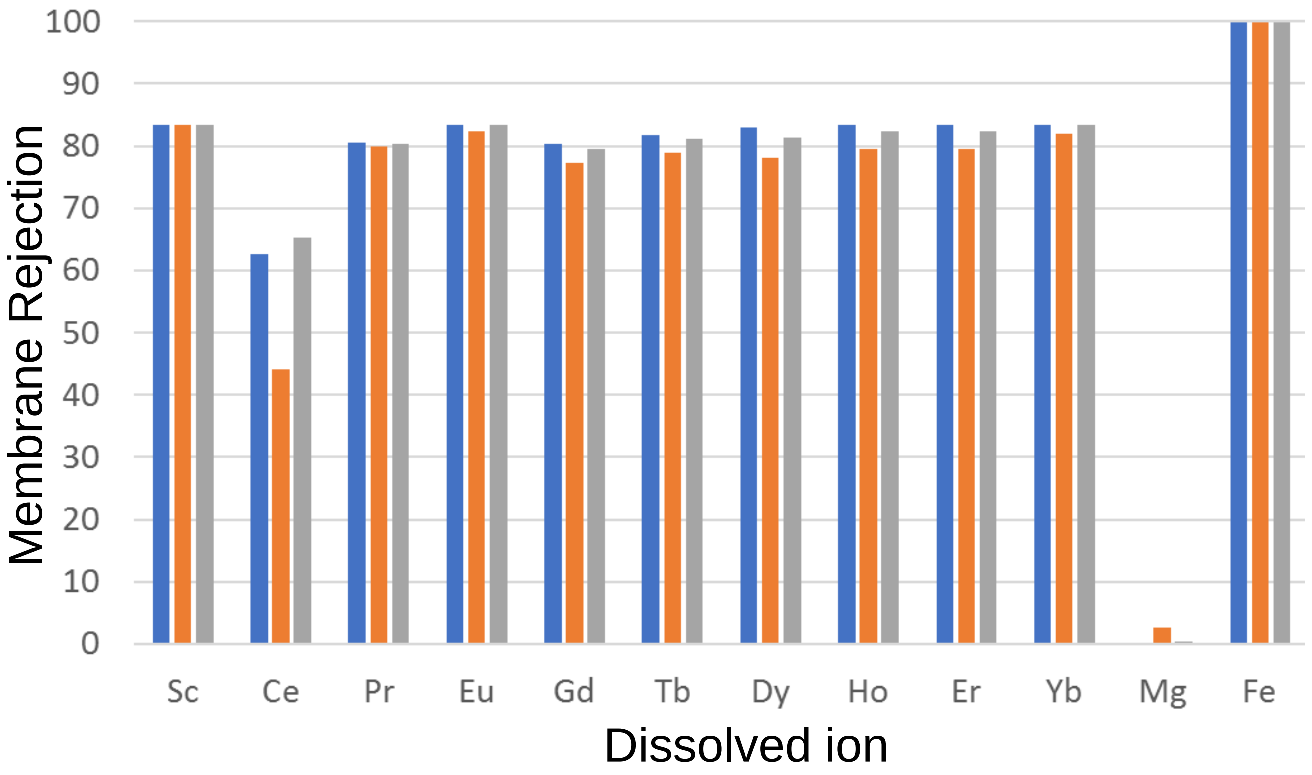


Membrane	Material	Form Factor	MWCO (Da)	Surface Area (m^2)
PH	Ceramic	Tube	400	0.019
NH	Ceramic	Tube	800	0.019
UH	Ceramic	Tube	1200	0.019

- Three pore sizes evaluated, designated by molecular weight cut-off (MWCO)
- pH range from 2 to 5.8; pressure from 80-150 psi
- 12L feed recirculated, 1.5-2.2 L/min
- 80% target recovery
- Mass balance on feed, permeate, retentate to determine precipitative loss

- 7-chanel membrane is similar to full scale
- pH range from 2-5; pressure range from 250-450 psi
- 30L feed recirculated, 3-8 L/min
- 80% target recovery

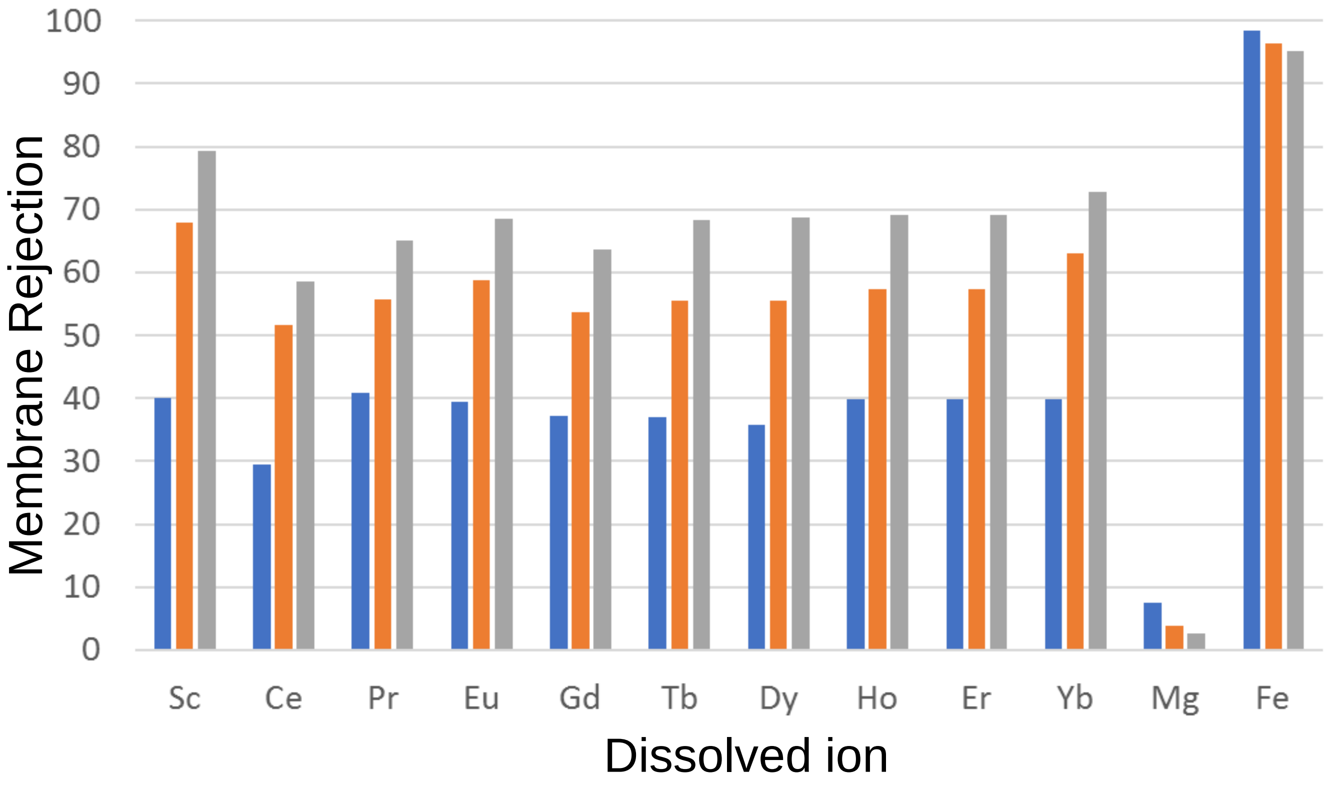
REE Rejection and Recovery with Nanofiltration



REE and Mg/Fe rejection values for the 4070 membrane at pH 4 blue = 5.46 LMHB, orange = 4.26 LMHB, gray = 3.89 LMHB. Note LMHB = L/m2/hr/bar (80% recovery)

Element	Feed Concentration (mg/L)
Sc	30
Ce	30
Pr	30
Eu	30
Gd	30
Tb	30
Dy	30
Ho	30
Er	30
Yb	30
Mg	191
Fe	4832
Na	964

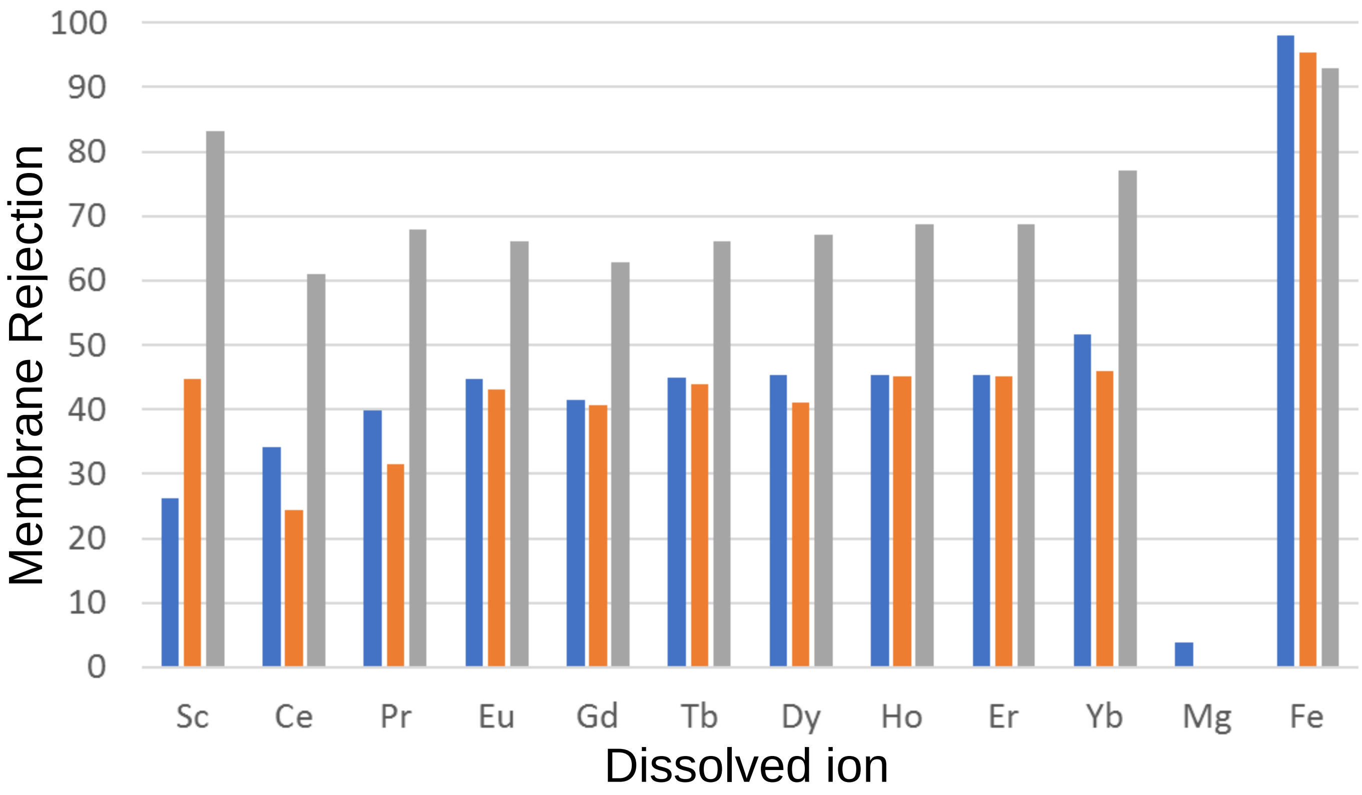
REE Rejection and Recovery with Nanofiltration



REE and Mg/Fe rejection values for the 4388 membrane at pH 4 blue = 3.47 LMHB, orange = 2.52 LMHB, gray = 1.34 LMHB. Note LMHB = L/m^2/hr/bar. (80% recovery)

Element	Feed Concentration (mg/L)
Sc	30
Ce	30
Pr	30
Eu	30
Gd	30
Tb	30
Dy	30
Ho	30
Er	30
Yb	30
Mg	191
Fe	4832
Na	964

REE Rejection and Recovery with Nanofiltration



REE and Mg/Fe rejection values for the 4388 membrane at pH 3 blue = 3.47 LMHB, orange = 2.52 LMHB, gray = 1.34 LMHB. Note LMHB = $L/m^2/hr/bar$. (80% recovery)

Element	Feed Concentration (mg/L)
Sc	30
Ce	30
Pr	30
Eu	30
Gd	30
Tb	30
Dy	30
Ho	30
Er	30
Yb	30
Mg	191
Fe	4832
Na	964

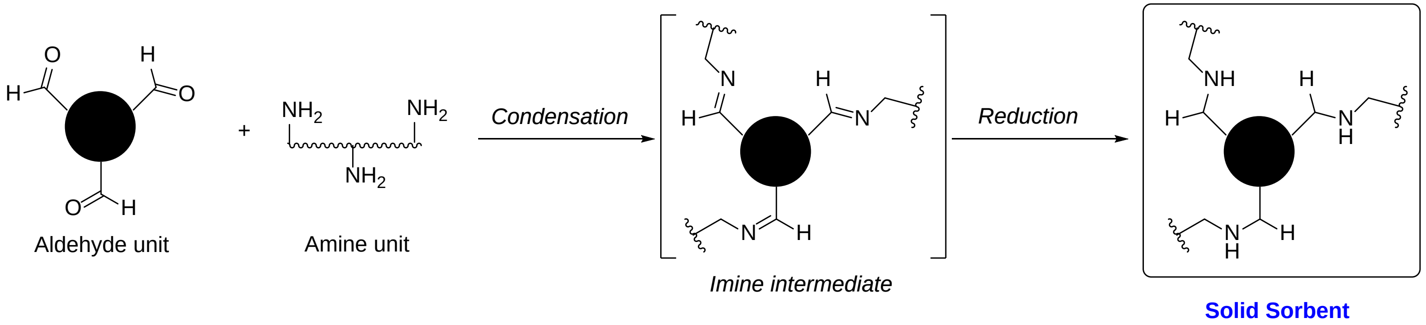
Task 4: Metal Affinity Technology Evaluation and Optimization

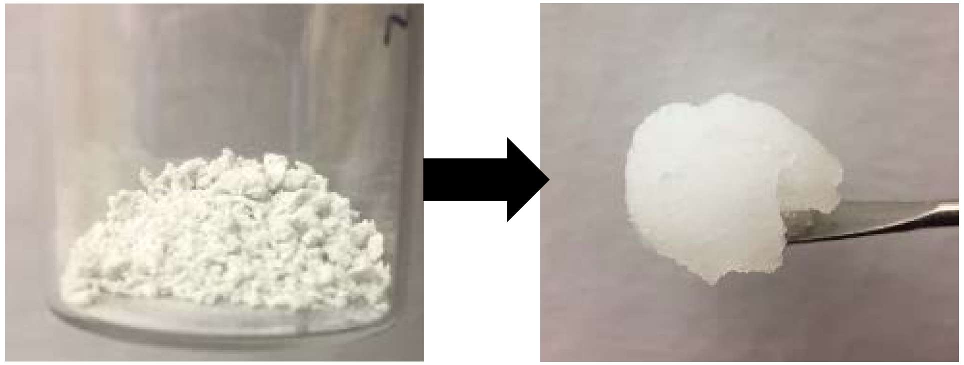
- **Objective: Evaluate solid affinity media for the capture of REE or the targeted removal of bulk metals present in AMD**
- Evaluated dendrimer sorbents (previously used for CO_2 scrubbing) for metal chelation
- Investigate kinetics, sorbent loading, and pH effects on ion selectivity

- Determine optimal conditions for REE selectivity
- Evaluate continuous flow format (sequencing batch, sorption column)
- Determine recovery/recycle for continuous use
- Validate using AMD samples from coal-mine sites

Dendrimer based sorbents for REE affinity

The solid sorbent is cross-linked polyamine polymer





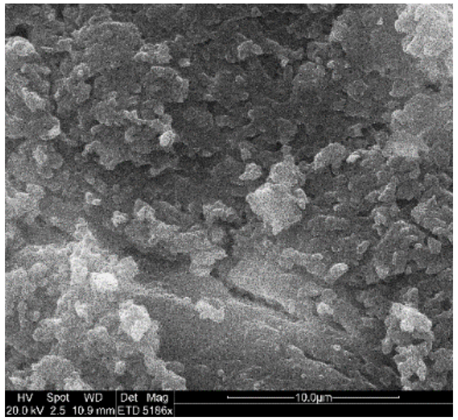
Swells with H_2O

Up to 12.8 g H_2O / g Sorbent

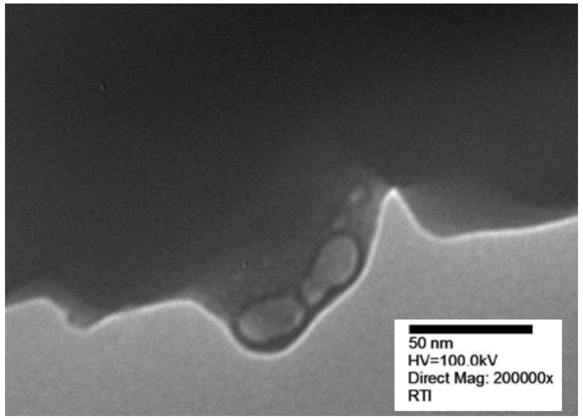
Particle Information
▪ Produced in bulk as irregular particles >350 µm
▪ Material can be sieved to ~10-15 µm
▪ Packed density: 0.22 g/mL
▪ Non-porous solid
▪ Hydrophilic solid

Stability
▪ Thermally stable up to 200 ^oC
▪ Insoluble in organic/aqueous media
▪ Stable in 50 wt% aq. NaOH and 12N HCl
▪ Sulfuric acid does not degrade material

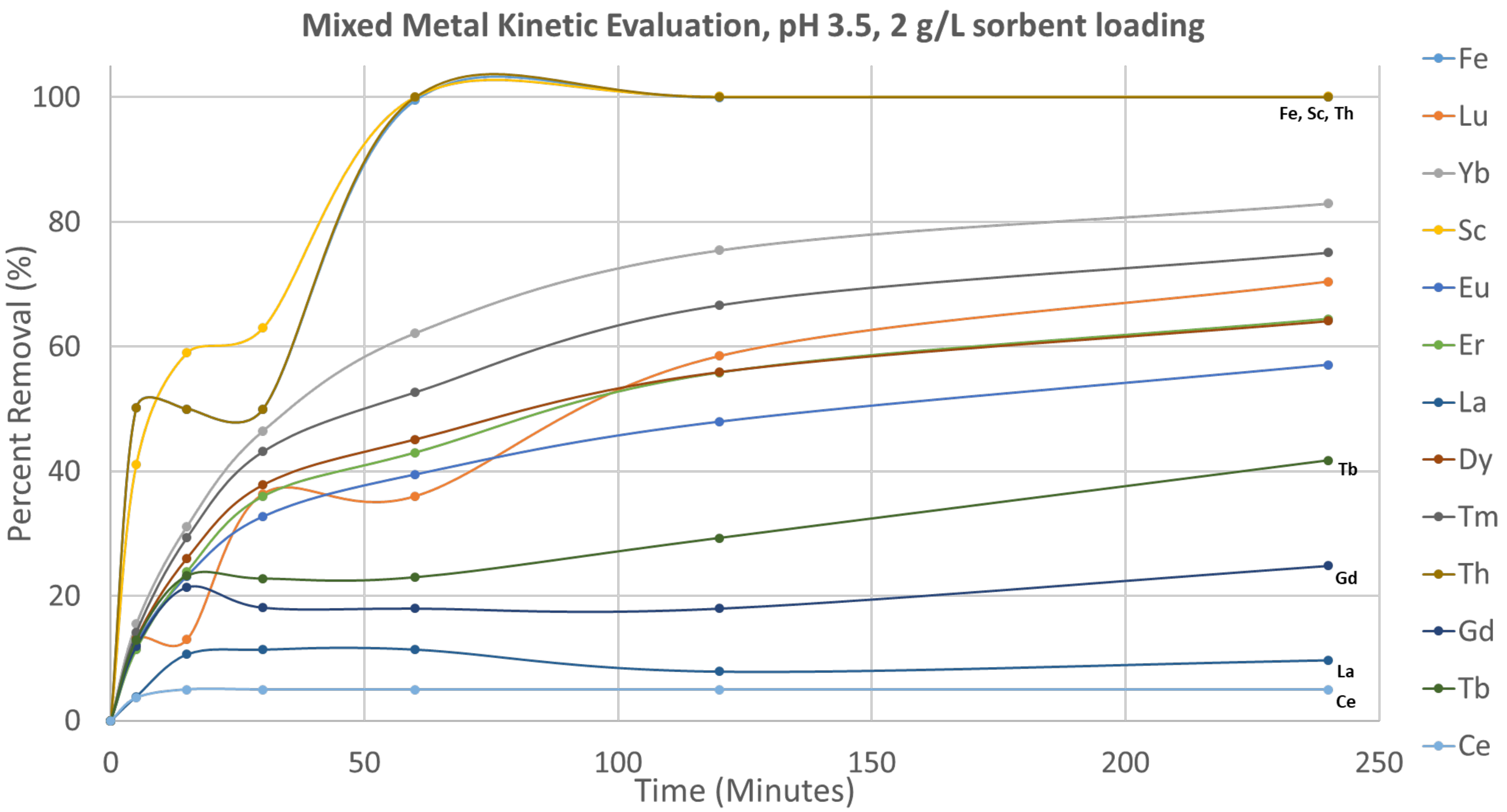
SEM Imaging



TEM Imaging



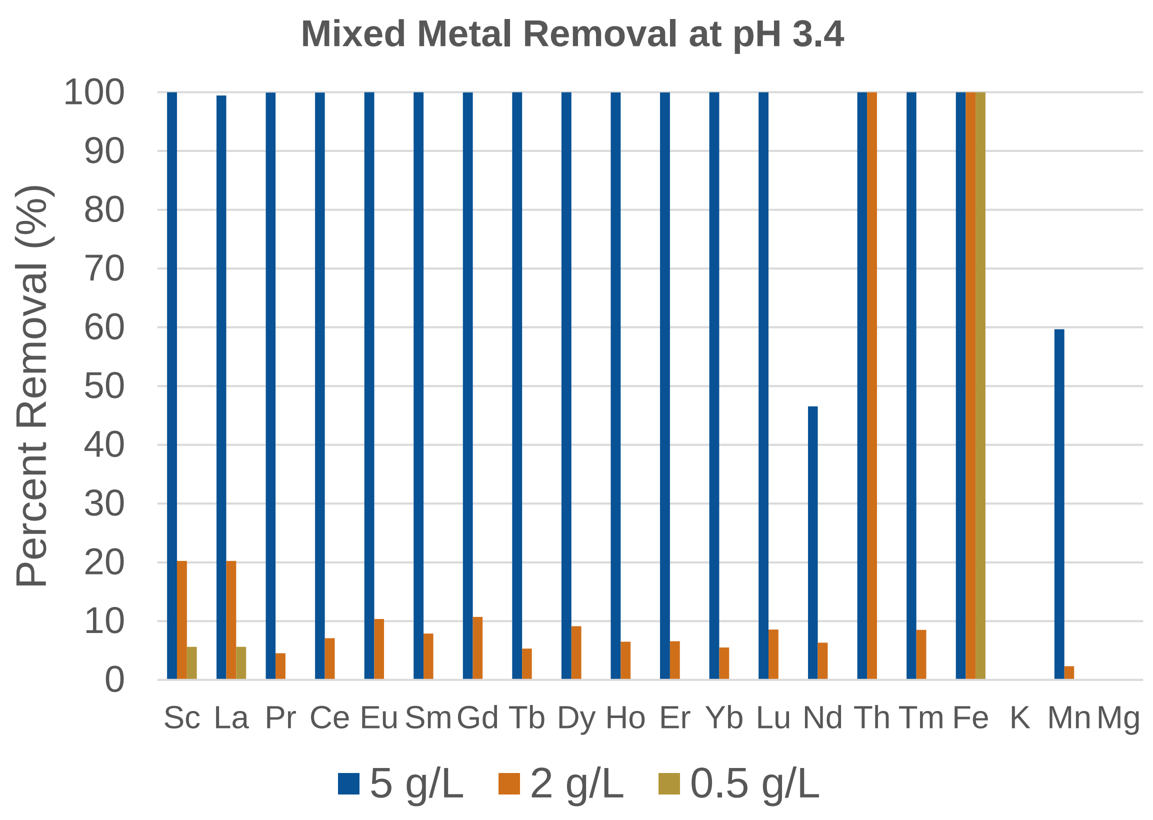
Kinetics of Metal Update with Sorbent Media

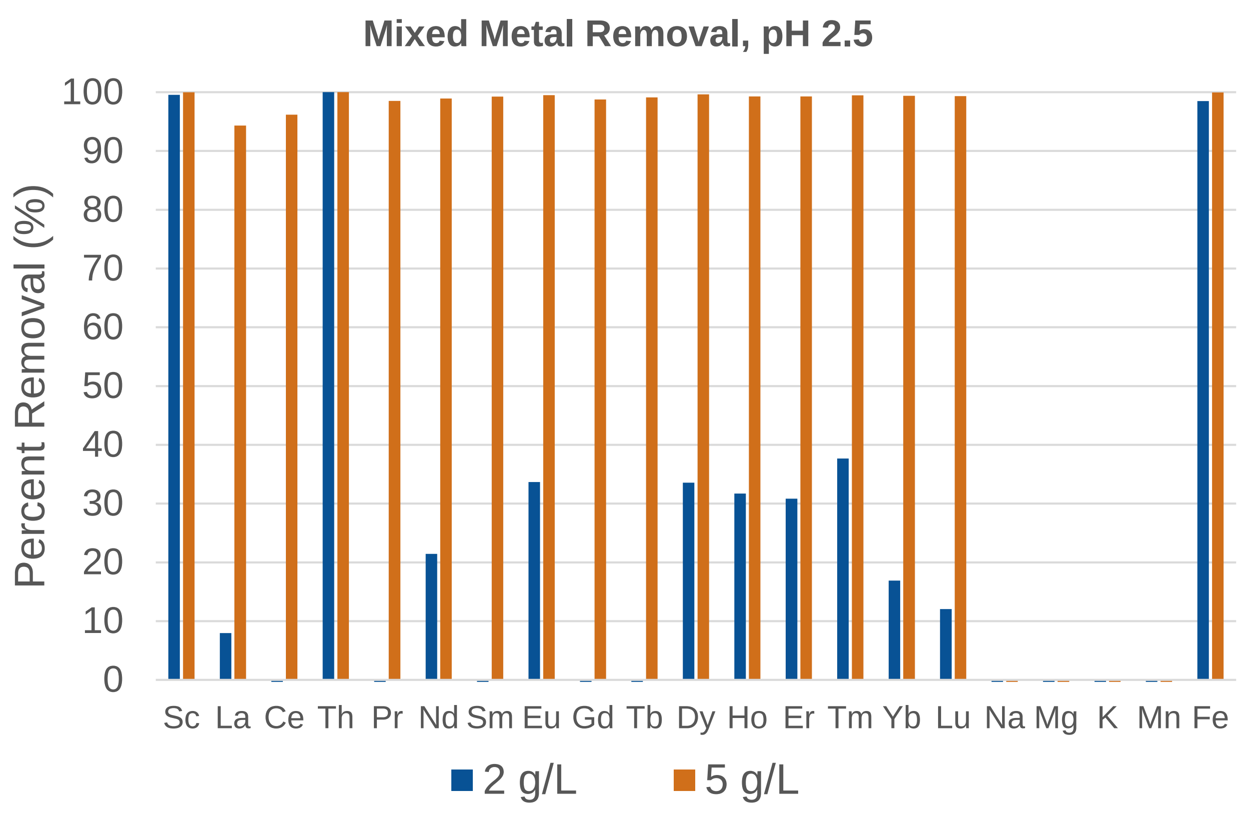


30 ppm all metals

Element	Ksp (25°C)of X(OH)y
Ce	2.0 x 10^-20
Er	3.5 x 10 ^-20
Eu	9.38 x 10^-27
Gd	1.9 x 10^-23
Ho	4.0x 10 ^-19
La	2.0 x 10^-21
Lu	1.8 x 10^-20
Pr	3.4 x 10^-24
Sm	2.0 x 10^-21
Sc	2.2 x 10^-31
Th	3.0 x 10 ^-51
Y	1.0 x 10^-22
Fe	4.0 x 10^-38
Mg	5.6 x 10^-12

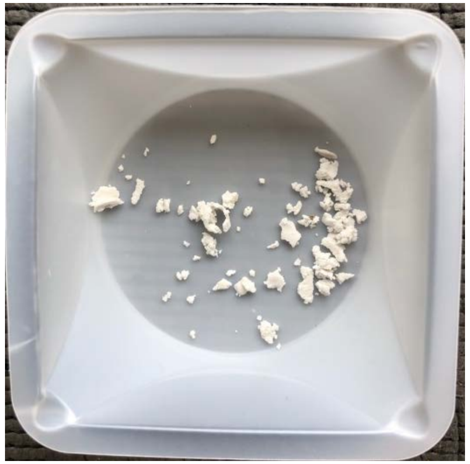
Selectivity for Metals with Sorbent Media





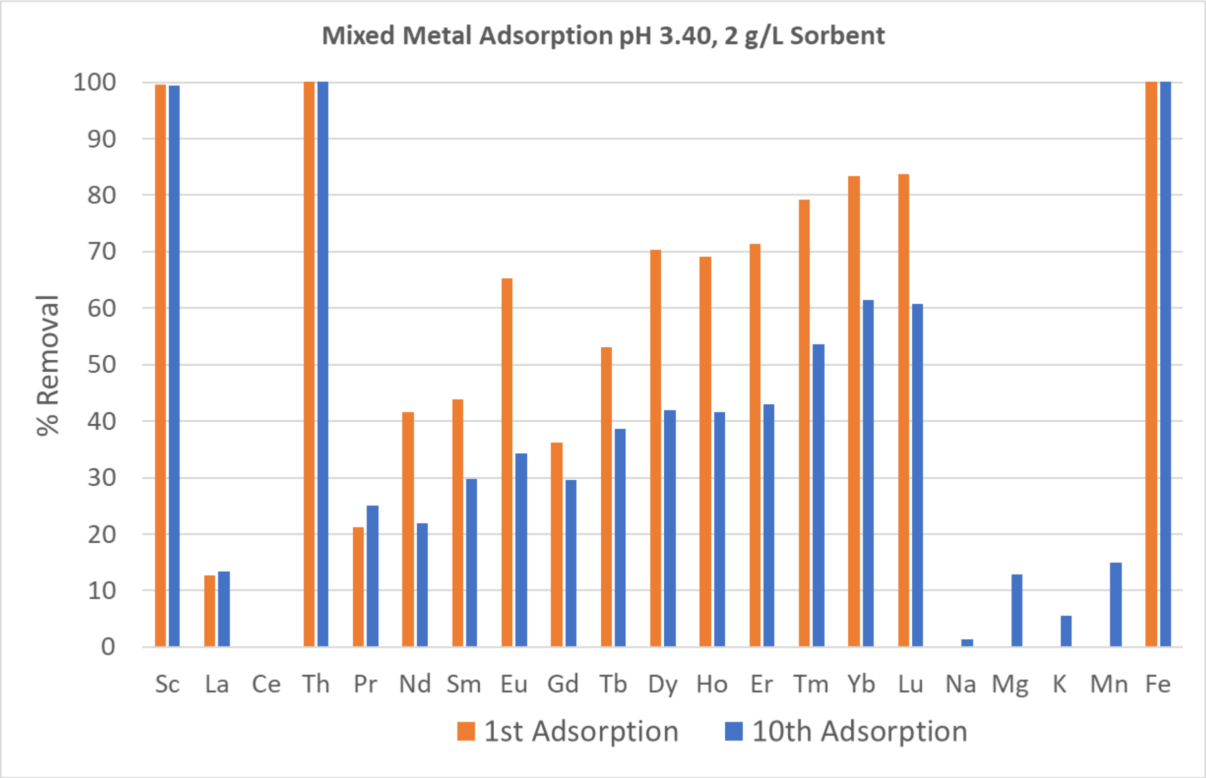
- Selectivity between REE and Fe demonstrated using sorbent (>99% Fe to REE) for some elements
- Sc, Th, and Fe removed faster than other metals, but selectivity observed at lower sorbent loadings
- Still need demonstrate for relevant concentrations (Fe >>> REE)

Sorbent Media Regeneration



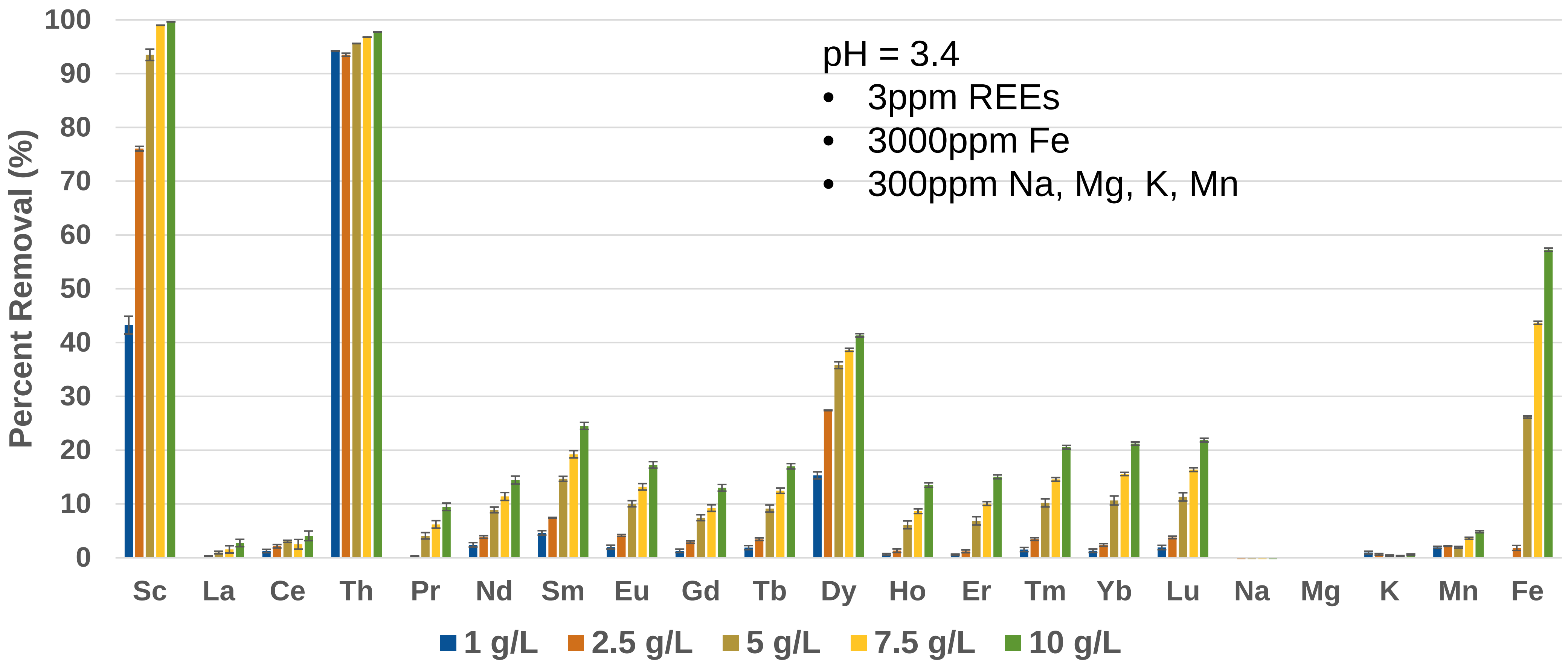
Mixed metal adsorption

Acid/base washing (1 M HCl/ 10% NaOH)



The polyamine groups of the sorbent depend on protonation to chelate metals. Flooding saturated sorbent with strong acid removes metal from surface. The sorbent's N groups can be deprotonated again via base wash.

Selectivity for Metals with Sorbent Media in Excess Iron



pH = 3.4

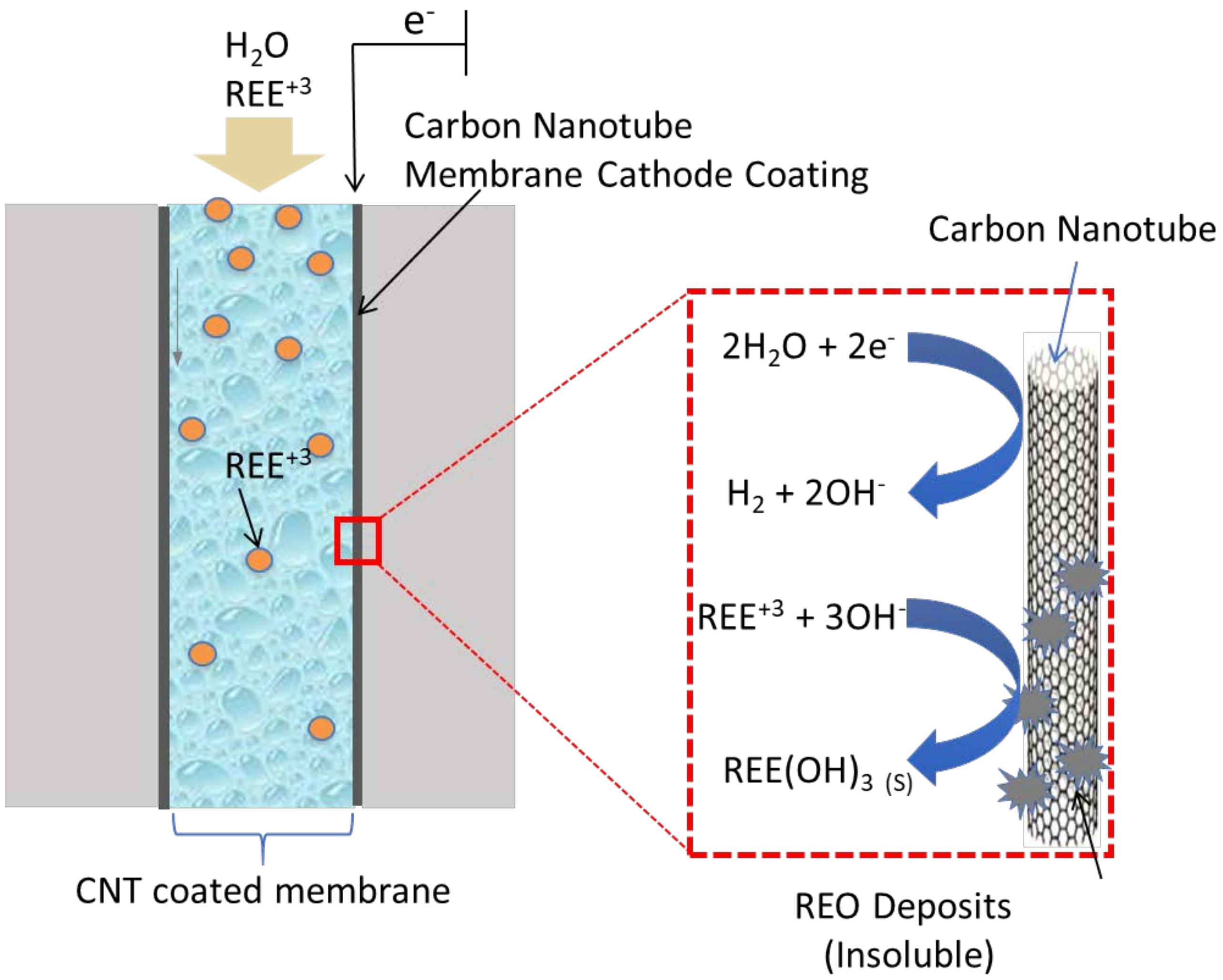
- 3ppm REEs
- 3000ppm Fe
- 300ppm Na, Mg, K, Mn

Task 5: Electrochemically Assisted Deposition for Direct REE Capture

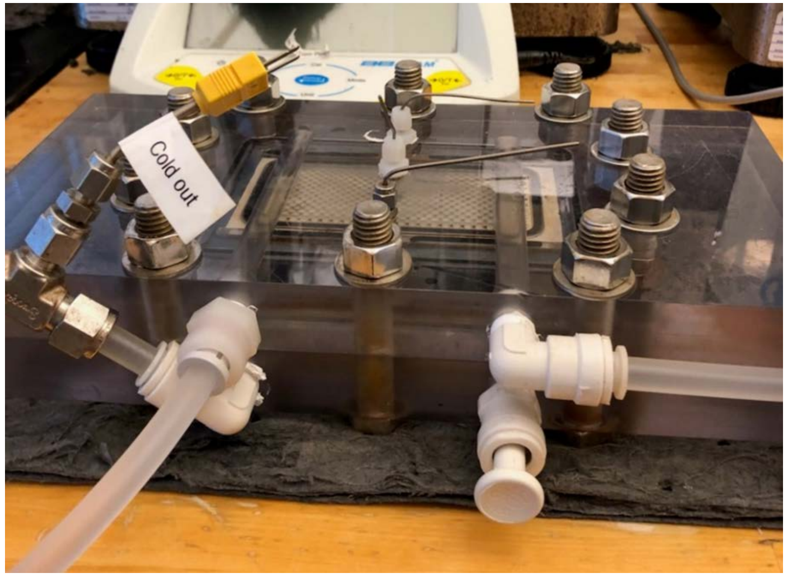
- **Objective: Develop a targeted REE enrichment method that can be used as polishing step (if needed) to meet 2wt % goal**
- Evaluated electrochemical assisted deposition with bench-scale membrane cell
- Investigate operating voltage and starting pH on ion selectivity

- Determine membrane capacity for REE capture
- Determine approach for final dry MREO recovery (mechanical vs acid wash)
- Evaluate alternative electrically conductive coatings for compatibility
- Validate using effluent from upstream fed AMD samples from coal-mine sites

Electrochemical REE Deposition Concept

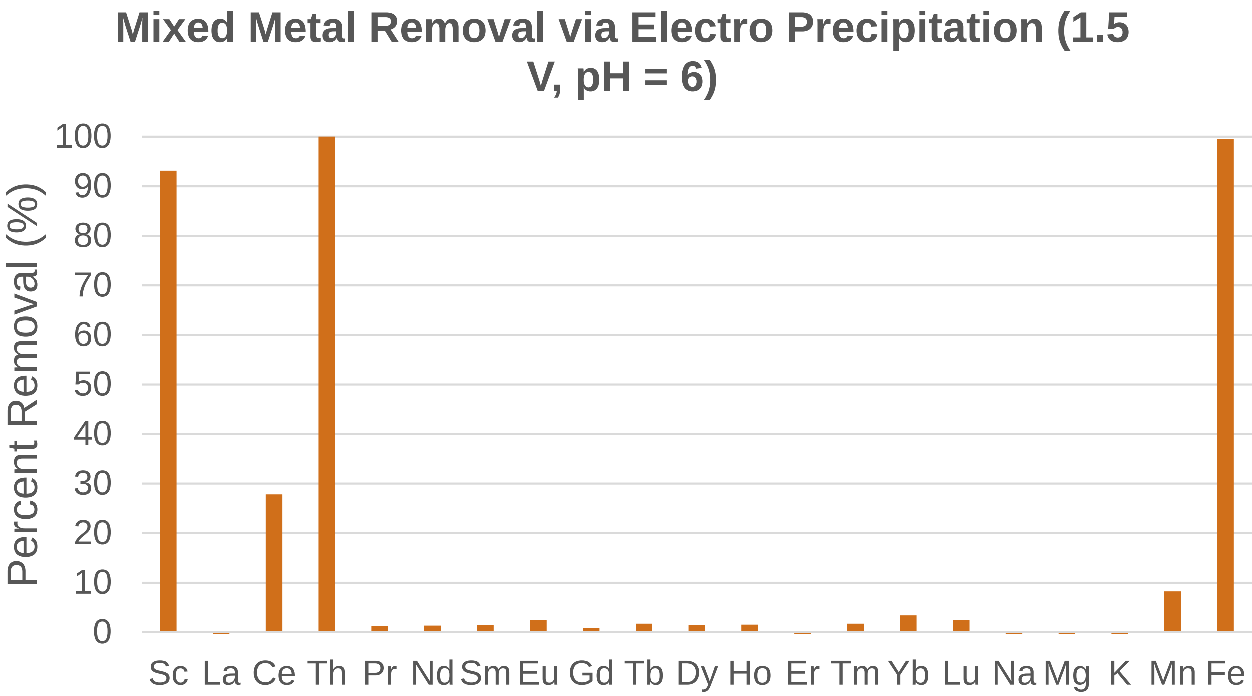


Cell leveraged from DE-FE0024074

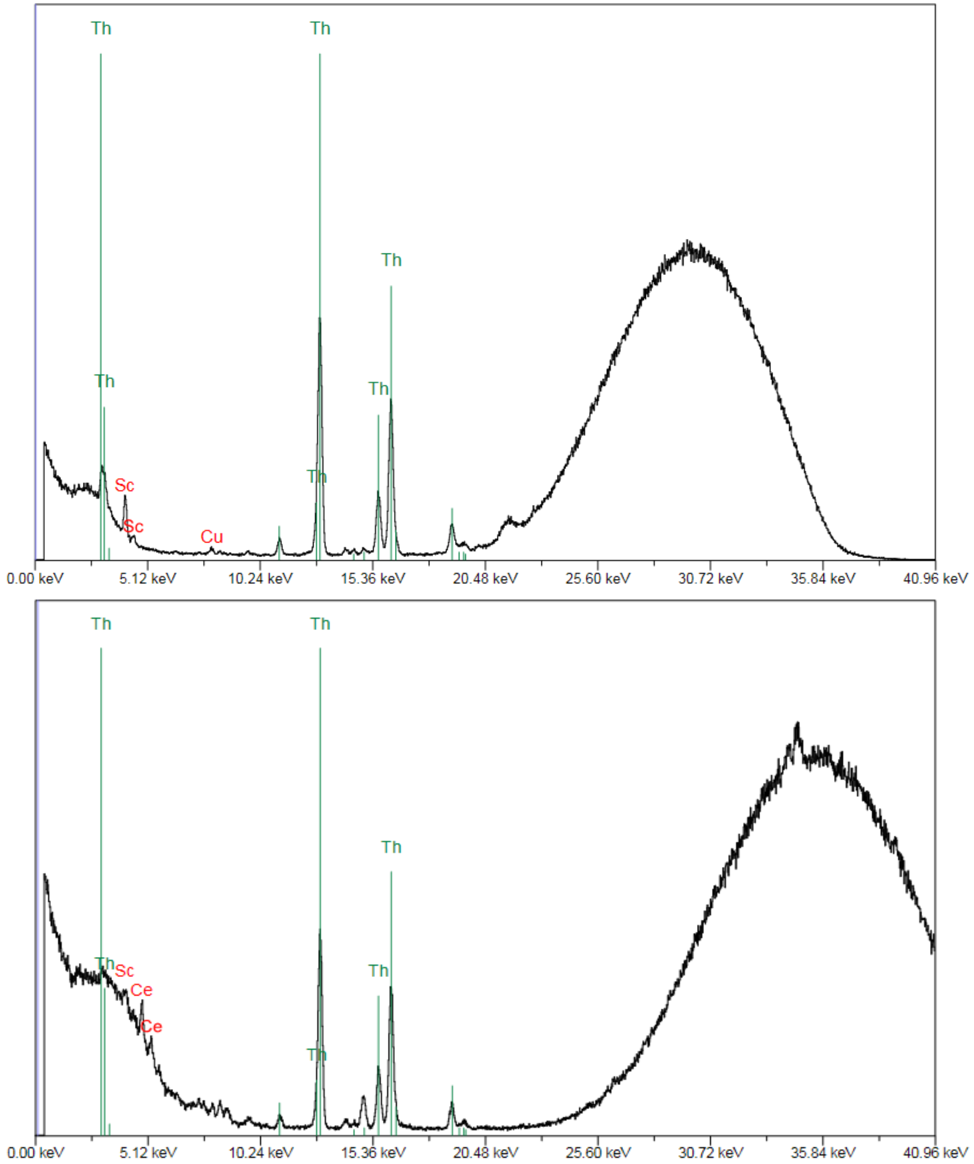


- UF membranes coated with carbon nanotubes to make electrically conductive
- Cathodically charged surface with sufficient potential to split water (^{-}OH generation)
- Low-solubility REE form hydroxide complexes and drop out of solutions
- Higher solubility metals remain in solution

Electrochemical REE Results



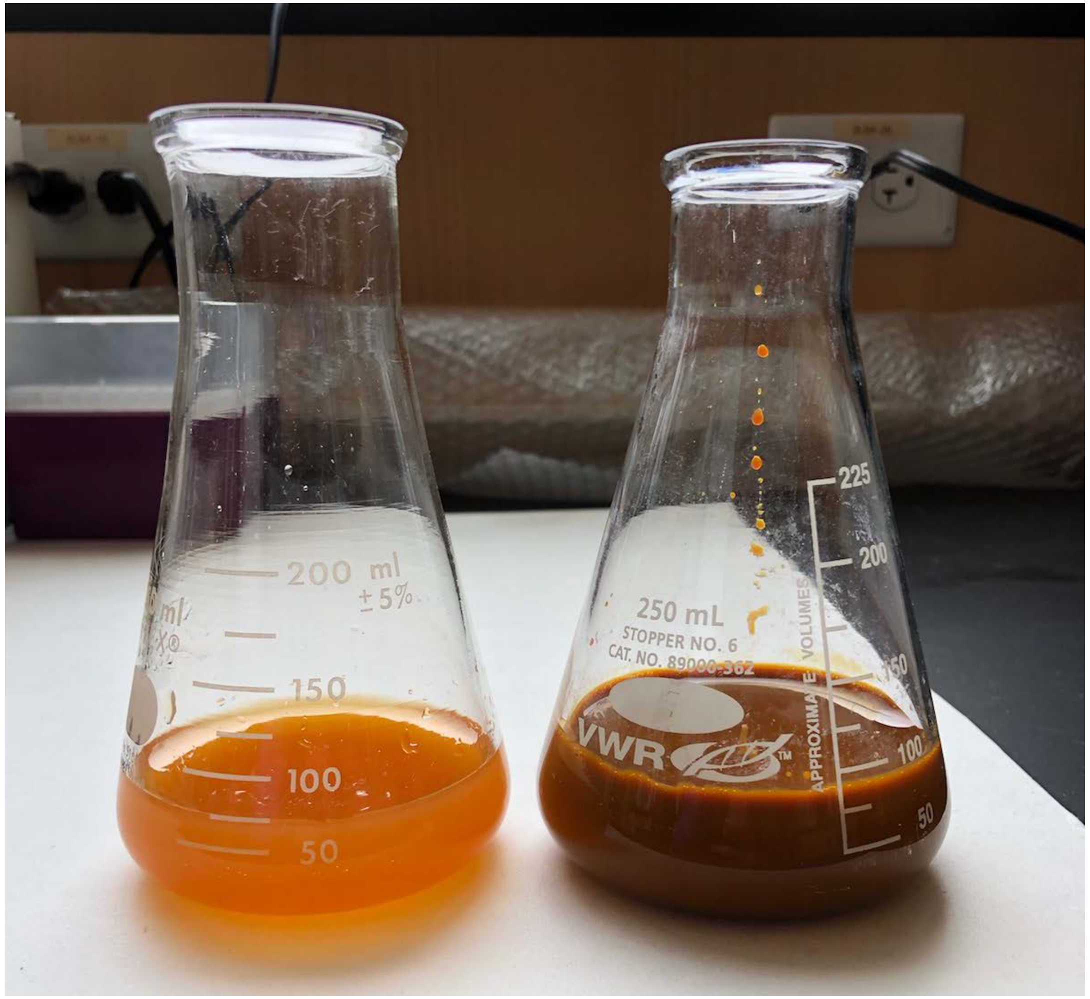
EDXRF verifies REE on surface



AMD Samples from Four Coal Mine Sites

Working with Montrose Environmental to Identify Sites for Validation Testing

- A surface coal mining site in New Mexico (NM1)
- An underground coal mining site in New Mexico (NM2)
- A coal mining site in Pennsylvania (PA2)
- A second coal mining site in Pennsylvania (PA2)



Samples from PA1 arrived on 4/4/2019

Characterization and validation testing for three REE enrichment approaches underway

Conclusions

- Project results show promise for multi-stage approach to REE recovery from AMD wastewater and solids
- Projected final MREE content from 0.10% to 12%, with potential for higher purity final products
- Currently running experiments to validate results with AMD from several coal-mine sites
- Results will inform techno-economic evaluation and feasibility of proposed process
- Investigating commercial interest for REE recovery with potential technology end users, source producers
- **Overall, the project is on track to meeting all project milestones and achieving the project objective of developing low-cost REE recovery approach from AMD**

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