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

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April 10th, 2019

¹ RTI International, ² Cerahelix
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.

<table>
<thead>
<tr>
<th>Team Member</th>
<th>Role</th>
</tr>
</thead>
</table>
| 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 |
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.
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

<table>
<thead>
<tr>
<th>Process Stage: Target Performance Metric:</th>
<th>Stage 1 – NF Filtration</th>
<th>Stage 2a – Target Metal Removal</th>
<th>Stage 2b – Target REE Recovery</th>
<th>Stage 3 – REE Solvent Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) &gt;95% rejection of total dissolved REE 2) &lt;30% rejection of monovalent ions</td>
<td>1) &gt;90% removal target metal(s) 2) &lt;10% removal of total REE</td>
<td>1) &gt;90% removal REE 2) &lt;10% removal of target bulk metal(s)</td>
<td>1) &gt;90% recovery of total REE 2) &lt;30% recovery other dissolved species</td>
<td></td>
</tr>
</tbody>
</table>
Framework for Project

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 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

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

- 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

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Material</th>
<th>Form Factor</th>
<th>MWCO (Da)</th>
<th>Surface Area (m^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PH</td>
<td>Ceramic</td>
<td>Tube</td>
<td>400</td>
<td>0.019</td>
</tr>
<tr>
<td>NH</td>
<td>Ceramic</td>
<td>Tube</td>
<td>800</td>
<td>0.019</td>
</tr>
<tr>
<td>UH</td>
<td>Ceramic</td>
<td>Tube</td>
<td>1200</td>
<td>0.019</td>
</tr>
</tbody>
</table>

- 7-channel 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 and Mg/Fe rejection values for the 4070 membrane at pH 4. For REE, blue = 5.46 LMHB, orange = 4.26 LMHB, gray = 3.89 LMHB. Note LMHB = L/m²/hr/bar (80% recovery).
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/m²/hr/bar. (80% recovery)
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/m²/hr/bar. (80% recovery)
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 CO₂ 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
The solid sorbent is cross-linked polyamine polymer

$$\text{Aldehyde unit} + \text{Amine unit} \xrightarrow{\text{Condensation}} \text{Imine intermediate} \xrightarrow{\text{Reduction}} \text{Solid Sorbent}$$

### 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 °C
- Insoluble in organic/aqueous media
- Stable in 50 wt% aq. NaOH and 12N HCl
- Sulfuric acid does not degrade material

### SEM Imaging
- Swells with H₂O
  - Up to 12.8 g H₂O / g Sorbent

### TEM Imaging
- Direct Mag: 200000x
Kinetics of Metal Update with Sorbent Media

Mixed Metal Kinetic Evaluation, pH 3.5, 2 g/L sorbent loading

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

30 ppm all metals
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)
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

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

Cell leveraged from DE-FE0024074
Electrochemical REE Results

Mixed Metal Removal via Electro Precipitation (1.5 V, pH = 6)

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**
Acknowledgements

- Department of Energy - National Energy Technology Laboratory project manager: Omer Bakshi
- RTI: Gyu Dong Kim, Elliot Reid, Mustapha Soukri, Eric Poitras
- Cerahelix: Tyler Kirkman
- Veolia: Kashi Banerjee
- Montrose: Jinjian Wu, Joon Min

This material is based upon work supported by the Department of Energy under Award Number DE-FE0031483.

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Thank You!

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