New Sensing Mechanisms for REE Detection in Coal By-Products

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Project Description and Objectives

Original Project Goal:

- To determine whether peptide-based ligands (Lanthanide Binding Tags; LBT) can serve as basis for new sensing technologies for REE in coal product leachates or other solutions.

Visible luminescence emitted by lanthanides (Tb, Eu) bound to LBT

Bacteria can be genetically engineered to produce many copies of LBT on cell: see Y. Jiao presentation

Research objectives:

- Test in coal ash leachates
- Enhance luminescent signal by increasing energy transfer to bound lanthanide (antenna effect)
- Develop concentration or immobilization strategy for further signal enhancement, and or continuous monitoring applications
Project Description and Objectives

Strategic Alignment with NETL’s Rare Earth Elements Program:

→ New rapid and simple approaches for REE detection and characterization will be useful for screening coal wastes for valuable content, monitoring during industrial REE processing, and rapid evaluation of extraction or separation techniques.

→ Goal: to develop an approach suitable for field-deployable “test kits”, or for in-line real time monitoring.

• **Status at beginning of project** → We knew that Tb or Eu bound to the LBT emitted visible light when excited with UV. But we didn’t know how well this method would work with complex samples (e.g., coal ash leachates).
Project Description and Objectives

Technology Benchmarking:

• Inductively coupled plasma mass spectrometry (ICP-MS) is the most commonly used method for measuring REE in liquid samples.
  - Detection limits typically in low ppb
  - But analyses expensive, and time consuming
• X-ray fluorescence (XRF) can be used for surface or near surface REE in solids (dried liquids), but calibration for complex samples is challenging.
  - Quantitation highly dependent on sample matrix
  - Detection limits typically in ppm range.
• A rapid test kit or real time detection system with sensitivity greater than XRF could have wide ranging use.
Project Description and Objectives

Current Status of Project

- Original milestone schedule based on LBT chemistry
  - However, testing indicates that sensing based on REE complexation with LBT is ill-suited to complex chemistry of coal byproduct leachates

- Changes in project goals/objectives:
  - Approach based on lanthanide precipitation in fluoride minerals appears promising
    - New approach appears capable of detecting and distinguishing between multiple REE, at 10’s of ppb levels.
    - Can also detect heavy REE, which is challenging for portable XRF.

- Industry/input or validation – Looking for this here!
  - Aside from value recovery, industry has emphasized importance of monitoring closure of coal ash disposal sites.
    - Detection of rare earths in groundwater or leachate monitoring samples could serve as proxy for release of other hazardous metals.
Project Update

Public Outreach
• Goldschmidt, Boston, MA, August 2018
• Energy, Utility & Environment Conference, San Diego, CA, February 2019
• Contribution to an invited chapter in a special American Geophysical Union monograph on rare earth elements
  • Chapter specifically on biological beneficiation of REE; currently in review

Technical Research Summary
• Coal ash characterization
• Leachate preparation
• Geochemical equilibrium model construction and application
• Testing of LBT-based approach for sensing
• Development of alternative sensing approach
Project Update

Coal Fly Ashes Used for Leachates

- Appalachian coal ash from U. Alabama ("AL" ash)
- Wyoming Powder River Basin coal ash from U. Wyoming ("WY" ash)

<table>
<thead>
<tr>
<th>Oxides</th>
<th>AL ash (%)</th>
<th>WY ash (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>49.3 ± 0.6</td>
<td>26.8 ± 0.3</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>26.5 ± 0.3</td>
<td>14.9 ± 0.1</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>8.6 ± 0.1</td>
<td>3.9 ± 0.1</td>
</tr>
<tr>
<td>CaO</td>
<td>1.2 ± 0.0</td>
<td>26.9 ± 0.2</td>
</tr>
<tr>
<td>MgO</td>
<td>1.1 ± 0.0</td>
<td>3.3 ± 0.0</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.4 ± 0.0</td>
<td>2.0 ± 0.0</td>
</tr>
<tr>
<td>K₂O</td>
<td>2.9 ± 0.0</td>
<td>0.4 ± 0.0</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.0 ± 0.0</td>
<td>0.0 ± 0.0</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.3 ± 0.0</td>
<td>1.0 ± 0.0</td>
</tr>
<tr>
<td>MnO</td>
<td>0.0 ± 0.0</td>
<td>0.0 ± 0.0</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.2 ± 0.0</td>
<td>0.6 ± 0.0</td>
</tr>
<tr>
<td>SrO</td>
<td>0.1 ± 0.0</td>
<td>0.3 ± 0.0</td>
</tr>
<tr>
<td>BaO</td>
<td>0.1 ± 0.0</td>
<td>0.4 ± 0.0</td>
</tr>
<tr>
<td>LOI*</td>
<td>6.8 ± 0.0</td>
<td>3.5 ± 0.1</td>
</tr>
<tr>
<td>Total</td>
<td>98.5 ± 0.3</td>
<td>84.1 ± 0.5</td>
</tr>
</tbody>
</table>

*LOI = Loss on Ignition (e.g., water, gases)

<table>
<thead>
<tr>
<th>REE</th>
<th>AL ash (ppm)</th>
<th>WY ash (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>94.6 ± 4.4</td>
<td>66.5 ± 1.1</td>
</tr>
<tr>
<td>Ce</td>
<td>184.8 ± 9.8</td>
<td>124.2 ± 2.1</td>
</tr>
<tr>
<td>Pr</td>
<td>22.1 ± 0.9</td>
<td>15.6 ± 0.2</td>
</tr>
<tr>
<td>Nd</td>
<td>84.7 ± 3.7</td>
<td>58.9 ± 1.0</td>
</tr>
<tr>
<td>Sm</td>
<td>18.8 ± 0.9</td>
<td>13.2 ± 0.2</td>
</tr>
<tr>
<td>Eu</td>
<td>3.8 ± 0.1</td>
<td>2.8 ± 0.2</td>
</tr>
<tr>
<td>Gd</td>
<td>16.4 ± 0.9</td>
<td>10.8 ± 0.2</td>
</tr>
<tr>
<td>Tb</td>
<td>2.6 ± 0.1</td>
<td>1.7 ± 0.1</td>
</tr>
<tr>
<td>Dy</td>
<td>16.0 ± 0.7</td>
<td>9.9 ± 0.3</td>
</tr>
<tr>
<td>Y</td>
<td>94.6 ± 4.1</td>
<td>53.6 ± 1.3</td>
</tr>
<tr>
<td>Ho</td>
<td>3.2 ± 0.2</td>
<td>1.9 ± 0.1</td>
</tr>
<tr>
<td>Er</td>
<td>9.3 ± 0.6</td>
<td>5.6 ± 0.2</td>
</tr>
<tr>
<td>Tm</td>
<td>1.4 ± 0.1</td>
<td>0.8 ± 0.0</td>
</tr>
<tr>
<td>Yb</td>
<td>8.7 ± 0.3</td>
<td>5.2 ± 0.2</td>
</tr>
<tr>
<td>Lu</td>
<td>1.2 ± 0.1</td>
<td>0.8 ± 0.0</td>
</tr>
</tbody>
</table>

Ave. Total REE 562 372
Wyoming and Alabama fly ashes have very different mineral composition—likely to affect leaching results.
Project Update

Leachate Preparation

- **Used 3 different lixiviants:** HCl, gluconic acid, acetic acid
- **Tested different acid concentrations** (0.1, 0.5, 1M), different “pulp densities” (10%, 30%), different temperature (room and 30°C).
  - All leached in batch for 24 h, with shaking.

![Left: PRB coal fly ash received from University of Wyoming](image1)

![Right: Batch leaching of fly ash in centrifuge tubes](image2)
Specific REE leaching efficiencies

Project Update

AL fly ash

Leached (%) vs ppm

AL - gluconic acid

AL - acetic acid

AL - HCl

Leached (%) vs ppm
Specific REE leaching efficiencies

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**WY fly ash**

**WY – gluconic acid**

**WY – acetic acid**

**WY - HCl**
Project Update

Total REE Leaching Results

- More REE leached from WY than from AL
- Gluconic acid more effective than acetic acid (and more effective than HCl for WY)
- REE in water leachate non-detectable (data not shown)

AA = acetic acid, GA = gluconic acid, HCl = hydrochloric acid
Project Update

Modeling Effect of Complexation

Total dissolved molality of Nd after equilibrating the AL fly ash with acetic, gluconic, and hydrochloric acid solutions as a function of pH

Calculated speciation for Nd in 0.1 m gluconic acid

Total dissolved molality of Nd after equilibrating the AL fly ash with acetic, gluconic, and hydrochloric acid solutions as a function of pH.

Complexation increases solubility here

NdPO₄ precipitates

All Nd dissolves

HCl

Acetic acid

Gluconic acid

Nd³⁺

NdGluc⁺²

NdH₂Gluc⁺³

NdH₃Gluc⁺⁴

NdGluc⁺⁵

NdHGluc(OH)⁺⁶

Gluc = [C₆H₁₀O₇]⁻²

Species concentration (m)

pH

0 2 4 6 8 10 12 14

0.0E+00 2.0E-03 4.0E-03 6.0E-03 8.0E-03 1.0E-02

1.0E-02 1.0E-03 1.0E-04 1.0E-05 1.0E-06 1.0E-07 1.0E-08 1.0E-09 1.0E-10 1.0E-11 1.0E-12
Project Update

Aside: Gel Formation in WY Leachates

- Gel formation can negatively effect REE recovery in processing streams
- Modelling predicts that the gelling is due to formation of amorphous silicate phases
Project Update

**REE Detection with LBT**

- Tb bound to LBT can be detected in “clean” solutions, at 10 ppb Tb.
- However, complex matrix of coal ash leachates problematic.

500 nM Tb = 79 ppb

AL leachate after adjustment to pH 6—precipitate visible

Tb present in original 1M HCl leachate at 16 ppb
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Surface Plasmon Resonance Can Help but Need Sufficient REE

TEM image of silica coated Au particles. Au particle diameter 17 ± 1 nm, Si thickness 20 nm.

Luminescence increased by adding Au@Si particles to LBT-Tb solution.

- ICP data shows most REE lost following adjustment to pH 5-6.
- Modeling indicates loss most likely due to sorption of REE to Al and or Fe hydroxides/oxides, and or silicates.

Amounts of various solids precipitating in AL leachate obtained with HCl.
**Project Update**

**Alternative Detection approach: LnF₃ Precipitation**

- **LnF₃ particles can exhibit strong luminescence.**
- **The lanthanide ions Pr³⁺, Nd³⁺, Sm³⁺, Eu³⁺, Gd³⁺, Tb³⁺, Dy³⁺, Ho³⁺, Er³⁺, Tm³⁺ can all emit luminescence.**
- **Can precipitate lanthanides by adding NH₄F to REE-containing solutions.**
  - No prior pH adjustment needed.
Project Update

Tests of LnF3 Method with Leachates

1M HCl leachates, 30% pulp density

Estim. Eu ~130 ppb
Estim. Tb ~ 20 ppb

Eu = 85 ppb
Tb = 16 ppb
Challenges and Next Steps

Technical Challenges

• Complex precipitates are formed from coal byproduct leachates—differences in lanthanide host minerals affect intensity of luminescence.
  ➢ Can still distinguish individual lanthanides, but sensitivity affected.

Next Steps

• Preparing LnF₃ and other mineral host standards and determining optimal detection conditions (excitation and emission wavelengths) and assessing quantitation of individual REE.

• Characterization of minerals formed in leachates and construction of thermodynamic model for prediction of precipitated phases in coal ash leachates.
  ➢ To determine optimal geochemical conditions for this approach.
Preparing Project for Next Steps

Market Benefits/Assessment

• Conventional methods of REE measurement are expensive and time consuming, or rapid and cheaper but less sensitive.

• The ability to rapidly assess REE content, in total and as individual REE, will be valuable for screening of potential REE resources, monitoring during REE processing, and rapid evaluation of extraction or separation technologies.

Technology-to-Market Path

• The end of result of this project will be the determination of a detection chemistry suitable for a sensing technology for rapid field site identification of promising coal-based REE resources, and or for monitoring REE during processing.

• Remaining technology challenges will include integration with a spectrometry system.

• Follow-on research would include design of a system to integrate the reaction chemistry with direct detection using a portable fiber optic spectrometer.

• Need collaborators in analytical instrumentation industry.
Concluding Remarks

• The identification of a new sensing approach that can be applied for rapid characterization of promising coal-based REE resources and or for monitoring of REE concentrations during industrial processing will advance FE’s goal of accelerating the advancement of commercially viable technologies for the extraction and recovery of REE from U.S. coal and byproduct resources.

• Next steps and current technical challenges:
  • Current technical challenge is accounting for the potential effects of complex mineral host chemistry on the sensitivity of the method for individual lanthanides.
  • Next steps include preparation and characterization of various mineral host standards, and construction of a thermodynamic model to support determination of optimal geochemical conditions for application of this sensing approach.
Project team

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- Dan Park
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