Economical Extraction and Recovery of REEs and Production of Clean, Value-Added Products from Low-Rank Coal Fly Ash

DOE CONTRACT DE-FE0031490

DOE NETL Annual Project Review Meeting, April 9–11, 2019
Crosscutting, Rare-Earth Elements, Gasification Systems, and Transformative Power Generation

April 10, 2019 – SESSION C5: Transformational REE Separation
EXECUTIVE SUMMARY

Project Team

- U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL)
  - Anthony Zinn, Contracting Officer’s Technical Representative
  - Mary Anne Alvin, Rare-Earth Element Technology Manager
- Technical Team
  - University of North Dakota (UND) Energy & Environmental Research Center (EERC)
  - Pacific Northwest National Laboratory (PNNL)
- Partners
  - Basin Electric Power Cooperative
  - Southern Company Services
  - Great River Energy
  - North Dakota Industrial Commission Lignite Energy Council
The overall project goal is to demonstrate at the laboratory scale a novel, economically viable, and environmentally benign process for recovery and concentration of rare-earth elements (REEs) from low-rank coal (LRC) fly ash.

Overall technology objectives:
- Produce a domestic “green” source of REEs
- Recover other valuable minerals/elements from coal fly ash
- Remove toxic metals from the fly ash
- Convert the fly ash into a value-added product
- Generate a selective REE extraction not typical to existing approaches for REEs from coal fly ash

lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), lutetium (Lu) and transition elements: scandium (Sc) and yttrium (Y)
EXECUTIVE SUMMARY

Project Tasks

• Task 1. Management, Planning, and Reporting
  – Perform overall project planning and management, and ensure all reporting requirements are met for the project.

• Task 2. Sample Procurement and Characterization
  – Coordinate sample procurement efforts with project participants and power generation stations, and perform all standard analysis methods in accordance with the requirements of the project.

• Task 3. Laboratory-Scale Testing
  – Develop the procedures and techniques for concentrating the REEs in ash material to greater than 2 wt%.

• Task 4. Technical and Economic Analysis
  – Prepare a high-level technical and economic analysis with the goal to estimate preliminary capital and operating expenses, which will serve to direct future process development.
LRC ASH VALUE?

- Fly ash from coal combustion is particularly promising because of its enrichment in REEs (loss of diluting organic material results in ~10× concentration over coal) and also its presence in fine powder form, eliminating or reducing high-energy fine grinding typically required for REE processing.
WHAT LOW-RANK COAL (LRC) TO OFFER?

• North Dakota is host to the world’s largest lignite deposit – 350 billion tons.

• Work to date has identified coal seams in North Dakota with REE concentrations as high as anything ever measured in coal in the United States.

• The Harmon–Hanson coal seam in North Dakota has the potential to hold ~2 million tons of REEs.

• The Powder Rivr Basin (PRB) is the largest coal producing region in the United States.
WHY LRC ASH?

Group I – Unpromising
Group II – Promising
Group III – Highly Promising

1 – REE-rich coal ashes
2 – carbonatite ore deposits
3 – hydrothermal ore deposits
4 – weathered crust elution-deposited (ion-adsorbed) ore deposits

REEs IN LRC

- Rhabdophanes

- $XPO_4 \cdot nH_2O$ where $X$ stands for REE, Y, Ca, Pb, Th, U, Fe

- Significant organically associated REEs
ASH FORMATION MECHANISMS IN LRC

Coal Devolatilization Pyrolysis Char combustion vaporization Reaction/decomposition of minerals - ash formation melting coalescence fragmentation Reaction/condensation of products associated with flue gas

- Mineral grain – pyrite
- Mineral grain – kaolinite clay
- Mineral grain – crandallite – CaAlP – Host for REE

- Na S coated Ca-Fe-Al-Si particle + REE
- Na, S coated – Ca rich particle + REE
- Na, S coated – Fe rich particle
- Na, S coated – clay derived ash particle
- Ca Al – REE rich
- Al-Si rich particles
- Iron rich particle – from pyrite
- Calcium - rich + REE particle derived from organically associated elements
- Na and S rich fine particles
### TASK 2 - LRC ASH PROCUREMENT and ANALYSIS

<table>
<thead>
<tr>
<th>Description</th>
<th>Lanthanides</th>
<th>Lanthanides + Y</th>
<th>Lanthanides + Y +Sc</th>
<th>HREE/LREE ratio</th>
<th>Coutl</th>
</tr>
</thead>
<tbody>
<tr>
<td>ND Lignite FBC Baghouse Ash</td>
<td>110</td>
<td>144</td>
<td>156</td>
<td>0.71</td>
<td>1.37</td>
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<tr>
<td>ND Lignite FBC Air Heater Hopper Ash</td>
<td>114</td>
<td>148</td>
<td>160</td>
<td>0.70</td>
<td>1.37</td>
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<tr>
<td>ND Lignite FBC Bottom Ash</td>
<td>121</td>
<td>144</td>
<td>155</td>
<td>0.46</td>
<td>0.98</td>
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<tr>
<td>ND Lignite FBC Bottom Ash Duplicate</td>
<td>125</td>
<td>148</td>
<td>160</td>
<td>0.47</td>
<td>0.99</td>
</tr>
<tr>
<td>ND Lignite pc-Fired Fly Ash – Falkirk</td>
<td>205</td>
<td>244</td>
<td>260</td>
<td>0.47</td>
<td>1.04</td>
</tr>
<tr>
<td>ND Lignite pc-Fired Bottom Ash – Falkirk</td>
<td>192</td>
<td>238</td>
<td>257</td>
<td>0.58</td>
<td>1.16</td>
</tr>
<tr>
<td>ND Lignite pc-Fired Station Fly Ash</td>
<td>159</td>
<td>191</td>
<td>204</td>
<td>0.49</td>
<td>1.04</td>
</tr>
<tr>
<td>ND Lignite pc-Fired Station Bottom Ash</td>
<td>135</td>
<td>163</td>
<td>174</td>
<td>0.51</td>
<td>1.05</td>
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<tr>
<td>PRB pc-Fired Dry Fork Station Fly Ash</td>
<td>227</td>
<td>267</td>
<td>282</td>
<td>0.43</td>
<td>1.06</td>
</tr>
<tr>
<td>PRB pc-Fired Station Fly Ash Duplicate</td>
<td>232</td>
<td>273</td>
<td>288</td>
<td>0.43</td>
<td>1.05</td>
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<tr>
<td>PRB Blend ESP Ash from CTF Antelope</td>
<td>269</td>
<td>319</td>
<td>345</td>
<td>0.49</td>
<td>1.04</td>
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<tr>
<td>PRB Blend ESP Ash from CTF Antelope Duplicate</td>
<td>264</td>
<td>312</td>
<td>337</td>
<td>0.49</td>
<td>1.04</td>
</tr>
<tr>
<td>ND Lignite Baghouse Ash from AF-CTS</td>
<td>174</td>
<td>207</td>
<td>223</td>
<td>0.48</td>
<td>1.00</td>
</tr>
<tr>
<td>ND Lignite Baghouse Ash from AF-CTS Duplicate</td>
<td>168</td>
<td>200</td>
<td>216</td>
<td>0.48</td>
<td>1.01</td>
</tr>
<tr>
<td>PRB pc-Fired Steam Plant Class C Fly Ash – Black Thunder</td>
<td>298</td>
<td>345</td>
<td>366</td>
<td>0.41</td>
<td>0.95</td>
</tr>
<tr>
<td>PRB pc-Fired Steam Plant Fly Ash Alpha Eagle Butte</td>
<td>288</td>
<td>338</td>
<td>358</td>
<td>0.43</td>
<td>0.99</td>
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<tr>
<td>PRB pc-Fired Fly Ash – Buckskin</td>
<td>321</td>
<td>380</td>
<td>401</td>
<td>0.45</td>
<td>1.06</td>
</tr>
</tbody>
</table>
## REE ASH ANALYSIS

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Lanthanides + Y +Sc</th>
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<th>Coutl</th>
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<td>0.95</td>
</tr>
<tr>
<td>PRB pc-Fired Fly Ash – Buckskin</td>
<td>401</td>
<td>0.45</td>
<td>1.06</td>
</tr>
<tr>
<td>PRB pc-Fired Dry Fork Station Fly Ash</td>
<td>282</td>
<td>0.43</td>
<td>1.06</td>
</tr>
<tr>
<td>H Bed Lignite Coal – Ash from downfired combustor</td>
<td>1089</td>
<td>0.58</td>
<td>1.25</td>
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</tbody>
</table>

### BET Surface Analysis of Ashes Selected for REE Analysis

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Sample wt grams</th>
<th>BET Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ND Lignite pc-Fired Fly Ash – Falkirk</td>
<td>1.116</td>
<td>0.5</td>
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<tr>
<td>PRB pc-Fired Steam Plant Class C Fly Ash – Black Thunder</td>
<td>1.176</td>
<td>1</td>
</tr>
<tr>
<td>PRB pc-Fired Fly Ash – Buckskin</td>
<td>1.635</td>
<td>1.1</td>
</tr>
<tr>
<td>PRB pc-Fired Dry Fork Station Fly Ash</td>
<td>1.13</td>
<td>3.4</td>
</tr>
</tbody>
</table>
XRF ANALYSIS RESULTS

Weight Percent

- Buckskin
- Black Thunder
- Falkirk
- Dry Fork
**XRD ANALYSIS RESULTS**

- Anhydrite: CaSO$_4$
- Ilvaite: CaFe$^{+2}$Fe$^{+3}$Si$_2$O$_7$O
- Perovskite: CaTiO$_3$
- Hematite: Fe$_2$O$_3$
- Periclase: MgO
- Mullite: 3Al$_2$O$_3$2SiO$_2$
- Grossular: Ca$_3$Al$_2$(SiO$_4$)$_3$
- Lime: CaO
- Magnetite: Fe$_3$O$_4$
- Calcite: CaCO$_3$
- Hannebachite: 2CaSO$_3$•(H$_2$O)
- Portlandite: Ca(OH)$_2$
COMPUTER-CONTROLLED SCANNING ELECTRON MICROSCOPY (CCSEM) ANALYSIS RESULTS
CCSEM ANALYSIS RESULTS

Particle Size 1.0 to 1.5 µm vs. Chemistry

Particle Size 1.5 to 2.0 µm vs. Chemistry
TASK 3 – LABORATORY-SCALE TESTING

• Subtask 3.2 – Fly Ash Pretreatment Testing
  – Fly ash pretreatment methods
    ♦ Thermal
    ♦ Chemical alteration
  – Examine pretreatment impacts and efficacy
2 MOLAR NITRIC ACID – 16 HOURS – 10:1 L/S RATIO

- GRE-Falkirk (124562)
- Southern Co - PRB Black Thunder (124689)
- Muscatine Power - PRB Buckskin (124731)
- Basin Electric - Dry Fork PRB (124851)
- Harmon Lignite (125221)
<table>
<thead>
<tr>
<th>Test Description</th>
<th>H+/kg Ash Ratio</th>
<th>Starting HNO₃ Molarity</th>
<th>Vol. Extract, mL</th>
<th>Mass Ash, g</th>
<th>Water Added, mL</th>
<th>Liquid/Solid Ratio</th>
<th>Extraction Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>12-11-18 test - varying H+/kg ash ratios (5, 10, 20, 30) using 3 molar HNO₃ and varying the extractant liquid to solid ratio</td>
<td>5</td>
<td>3</td>
<td>20</td>
<td>12</td>
<td>0</td>
<td>1.7</td>
<td>32%</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>3</td>
<td>20</td>
<td>6</td>
<td>0</td>
<td>3.3</td>
<td>24% 29%</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>3</td>
<td>20</td>
<td>3</td>
<td>0</td>
<td>6.7</td>
<td>44% 69%</td>
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<tr>
<td></td>
<td>30</td>
<td>3</td>
<td>20</td>
<td>2</td>
<td>0</td>
<td>10</td>
<td>55% 80%</td>
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<tr>
<td>12-12-18 test - varying H+/kg ash ratios (10, 20, 30, 50) using fixed extractant liquid to solid ratio (10:1) and varying the HNO₃ molarity (1, 2, 3, 5)</td>
<td>10</td>
<td>1</td>
<td>20</td>
<td>2</td>
<td>0</td>
<td>10</td>
<td>45% 4%</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>2</td>
<td>20</td>
<td>2</td>
<td>0</td>
<td>10</td>
<td>53% 53%</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>3</td>
<td>20</td>
<td>2</td>
<td>0</td>
<td>10</td>
<td>58% 74%</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>5</td>
<td>20</td>
<td>2</td>
<td>0</td>
<td>10</td>
<td>44% 61%</td>
</tr>
<tr>
<td>12-13-18 test - varying H+/kg ash ratios (10, 20, 30, 50) using 3 molar HNO₃ and varying the extractant liquid to solid ratio</td>
<td>10</td>
<td>3</td>
<td>20</td>
<td>6</td>
<td>0</td>
<td>3.3</td>
<td>40% 0%</td>
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<tr>
<td></td>
<td>20</td>
<td>3</td>
<td>40</td>
<td>6</td>
<td>0</td>
<td>6.7</td>
<td>53% 68%</td>
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<tr>
<td></td>
<td>30</td>
<td>3</td>
<td>60</td>
<td>6</td>
<td>0</td>
<td>10</td>
<td>58% 77%</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>3</td>
<td>100</td>
<td>6</td>
<td>0</td>
<td>16.7</td>
<td>49% 85%</td>
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<td>12-13-18 test - Fixed H+/kg ash ratios (30) using 60 mL of 3 molar HNO₃ with 6g ash, but adding varying levels of water to vary the liquid to solid ratio</td>
<td>30</td>
<td>3</td>
<td>60</td>
<td>6</td>
<td>0</td>
<td>10</td>
<td>65% 78%</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>3</td>
<td>60</td>
<td>6</td>
<td>40</td>
<td>16.7</td>
<td>66% 98%</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>3</td>
<td>60</td>
<td>6</td>
<td>60</td>
<td>20</td>
<td>56% 74%</td>
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<tr>
<td></td>
<td>30</td>
<td>3</td>
<td>60</td>
<td>6</td>
<td>120</td>
<td>30</td>
<td>56% 65%</td>
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</tbody>
</table>
FALKIRK ACID EXTRACTION ANALYSIS

Falkirk 3m HNO₃ Extraction Efficiency, %

Extraction Efficiency, %

<table>
<thead>
<tr>
<th></th>
<th>Baseline</th>
<th>900°C/1 HR</th>
<th>900°C/4 HR</th>
<th>1050°C/1 HR</th>
<th>1050°C/4 HR</th>
</tr>
</thead>
<tbody>
<tr>
<td>5m HNO₃</td>
<td>28%</td>
<td>26%</td>
<td>17%</td>
<td>18%</td>
<td></td>
</tr>
</tbody>
</table>

Falkirk 1M HCl Extraction Efficiency, %

Extraction Efficiency, %

<table>
<thead>
<tr>
<th></th>
<th>Baseline</th>
<th>900°C/1 HR</th>
<th>900°C/4 HR</th>
<th>1050°C/1 HR</th>
<th>1050°C/4 HR</th>
</tr>
</thead>
<tbody>
<tr>
<td>1M HCl</td>
<td>46%</td>
<td>27%</td>
<td>26%</td>
<td>17%</td>
<td>18%</td>
</tr>
</tbody>
</table>

Falkirk 2M HCl Extraction Efficiency, %

Extraction Efficiency, %

<table>
<thead>
<tr>
<th></th>
<th>Baseline</th>
<th>900°C/1 HR</th>
<th>900°C/4 HR</th>
<th>1050°C/1 HR</th>
<th>1050°C/4 HR</th>
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</thead>
<tbody>
<tr>
<td>2M HCl</td>
<td>59%</td>
<td>29%</td>
<td>27%</td>
<td>18%</td>
<td>18%</td>
</tr>
</tbody>
</table>
DRY FORK ACID EXTRACTION ANALYSIS

**Dry Fork 3 M HNO₃ Extraction Efficiency, %**

- Baseline: 91%
- 900°C/1 HR: 86%
- 900°C/4 HR: 87%
- 1050°C/1 HR: 54%
- 1050°C/4 HR: 47%

**Dry Fork 1 M HCl Extraction Efficiency, %**

- Baseline: 5%
- 900°C/1 Hr: 24%
- 900°C/4 Hr: 29%
- 1050°C/1 Hr: 14%
- 1050°C/4 Hr: 16%

**Dry Fork 2 M HCl Extraction Efficiency, %**

- Baseline: 80%
- 900°C/1 Hr: 79%
- 900°C/4 Hr: 78%
- 1050°C/1 Hr: 49%
- 1050°C/4 Hr: 43%
ACID EXTRACTION ANALYSIS WATER WASH

124562-Falkirk Ash Extraction Efficiency, %

- WW-3M HNO3-10:1: 65%
- UW-3M HNO3-10:1: 58%
- WW-2M HCl-10:1: 65%
- UW-2M HCl-10:1: 59%

124851-Dry Fork Ash Extraction Efficiency, %

- WW-3M HNO3-10:1: 92%
- UW-3M HNO3-10:1: 85%
- WW-2M HCl-10:1: 77%
- UW-2M HCl-10:1: 80%

125221-Harmon Combustor Ash Extraction Efficiency, %

- WW-3M HNO3-10:1: 69%
- WW-2M HCl-10:1: 68%
- 3M HCl-10:1: 66%
- 3M HCl-15:1: 65%
MILD SOLVENT LEACHING ANALYSIS

![Graph showing extraction percentages for Buckskin, Black Thunder, Falkirk, and Dry Fork. The graph compares Total REE Extracted and Total REE + Y + Sc Extracted.]
TASK 3 – LABORATORY-SCALE TESTING

• Solvent extraction testing
  – Goal to identify the most effective conditions (the combination of organic ligands, cosolvents and proportions, contact time) required to achieve the highest level of REE extraction.
  – Organic ligands commonly employed with the solvent extraction system.
  – Novel low-cost ligands currently being developed.

![Chemical structures of TBP, HDEHP, and CYANEX 272](image)
REE EXTRACTION SOLUTIONS

Substitutions for La and Ce:
REE, Y, Ca, Pb, Th, U, Fe
HIGH-PRESSURE EXTRACTION SETUP
CURRENT SETUP FOR PRESSURIZED EXTRACTION