Investigation of Rare Earth Element Extraction from North Dakota Coal-Related Feed Stocks

Energy Generation Conference
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University of North Dakota
Microbeam Technologies Inc.
Barr Engineering
Pacific Northwest National Laboratory
MLJ Consulting
Phase 2 Project Team

**Technical Team:**
- University of North Dakota – Institute for Energy Studies
- Barr Engineering
- Pacific Northwest National Laboratory
- Microbeam Technologies Inc. (MTI)
- MLJ Consulting

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- U.S. Department of Energy – National Energy Technology Laboratory
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- Great River Energy
- North American Coal Corporation
- Great Northern Properties
- Minnkota Power Cooperative
- UND/ND University System

**Advisory Support:**
- North Dakota Geological Survey
Presentation Overview

- Rare Earth Elements Background
- Phase 1 Accomplishments
- Phase 2 Goals and Objectives
What are Rare Earth Elements?

- Not actually ‘rare’, just very evenly dispersed in earth’s crust
- Very few locations with economically mineable concentrations/forms
- LREE more abundant than HREE
Why are REEs Important?

• Unique properties makes them very useful in numerous applications

• Often termed “Chemical Vitamins” → low usage, high impact

• Essential materials for many high-value and critical applications
  
  ✓ Magnets, batteries, electronics, computers, auto vehicles, renewable energy, military defense...and many many others

✓ REEs make possible $7 Trillion in value-added products globally

✓ Unique properties prevent replacement by other materials
Why Research REEs from Coal?

- Several REEs identified as ‘critical’ – mostly the less common HREE
- China dominates global market - 83% of production in 2016
- **U.S. 100% import reliant**
- Chinese production rich in the HREE; U.S. deposits deficient
- Chinese reserves dwindling (HREE-rich ion adsorbed clays)
  - Current deposit for ~100% supply of HREE gone by 2025
  - Growth market sectors are dependent on HREEs – wind turbines, HEVs and many others
- **U.S. considers national security risk**
The U.S. May Be “Producing” Over 40,000 Tons of Rare Earth Elements Annually From Coal Mining

Ekmann, 2012
Phase 1 Goal, Objectives and Scope of Work

**Overall Goal:**
- Develop high performance, economically viable, and environmentally benign concentrating technologies for U.S. coal-related feedstocks

**Objectives:**
- Identify ND coal-related materials with REE content > 300 ppm
- Develop/test methods to concentrate REE to > 2wt%
- Techno-Economic Analysis and Process Design

**Scope of Work**
- Sampling
  - Field Samples: Coal, roof, floor, partings
  - Coal Creek Station: DryFining™, fly ash, bottom ash
- Characterization
  - REE abundance
  - Forms and modes of REE occurrence
- Laboratory-scale REE Concentration Testing
- Techno-Economic Analysis
- Bench-scale Design
**ND Lignite Coal Zones & Industry Summary**

- Host to world’s largest lignite deposit at ~350 billion tons
- ~25 billion tons recoverable
- Fort Union group – Paleocene age; 55-65 million years
- State heavily invested in mining/utilization and electric generation – 71% coal electricity in 2016
- Three major coal zones: active mines in Beulah-Zap and Hagel
- ~30 Million tons/yr
- > 4,000 MWe lignite-fired total capacity
REE Abundance Hagel Coal Zone

Collected Large Sample

good consistency:

410 to 530 ppm

range in several hundred lb sample

2/2/2018
<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Ash Content (wt%)</th>
<th>Total REE, ppm</th>
<th>HREE/LREE</th>
<th>Total Critical REE, ppm</th>
<th>Total REE, ppm (ash basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6A-2</td>
<td>36.3</td>
<td><strong>642</strong></td>
<td>0.28</td>
<td>191</td>
<td>1752</td>
</tr>
<tr>
<td>6A</td>
<td>20.1</td>
<td><strong>564</strong></td>
<td>0.35</td>
<td>189</td>
<td>2235</td>
</tr>
<tr>
<td>6A-1</td>
<td>75.5</td>
<td><strong>449</strong></td>
<td>0.28</td>
<td>129</td>
<td>587</td>
</tr>
<tr>
<td>3A</td>
<td>40.5</td>
<td><strong>363</strong></td>
<td>0.89</td>
<td>151</td>
<td>892</td>
</tr>
<tr>
<td>3C</td>
<td>60.9</td>
<td><strong>322</strong></td>
<td>0.43</td>
<td>104</td>
<td>525</td>
</tr>
<tr>
<td>6AA</td>
<td>47.0</td>
<td>212</td>
<td><strong>2.06</strong></td>
<td>94</td>
<td>449</td>
</tr>
<tr>
<td>7F</td>
<td>20.9</td>
<td>194</td>
<td>0.76</td>
<td>83</td>
<td>924</td>
</tr>
<tr>
<td>15G</td>
<td>32.2</td>
<td>177</td>
<td>0.45</td>
<td>54</td>
<td>541</td>
</tr>
<tr>
<td>10</td>
<td>26.2</td>
<td>146</td>
<td>0.69</td>
<td>61</td>
<td>554</td>
</tr>
<tr>
<td>5F</td>
<td>15.9</td>
<td>105</td>
<td>0.84</td>
<td>42</td>
<td>659</td>
</tr>
<tr>
<td>7E</td>
<td>11.0</td>
<td>76</td>
<td><strong>2.19</strong></td>
<td>42</td>
<td>681</td>
</tr>
<tr>
<td>9H</td>
<td>15.7</td>
<td>76</td>
<td>1.00</td>
<td>34</td>
<td>480</td>
</tr>
<tr>
<td>5E</td>
<td>10.2</td>
<td>47</td>
<td>1.30</td>
<td>21</td>
<td>462</td>
</tr>
</tbody>
</table>

![Graph showing dry whole coal/UCC ppm/ppm vs. Sc to Lu for samples 6A, 6A-2, 3A, and 6AA](image-url)
• Float-sink indicates enrichment in the low SG fractions.
• ~80% ash sample, but ~50% of REEs in the organic rich fractions.
• UND-developed sequential solvent extraction procedure indicates primarily organic association of the REEs: 85-95%.
• REE in coordination complexes much more prevalent than ion-exchangeable REE.
• Small fraction of residual – i.e. silicates/clays
### Some Chemical and Physical Properties of Coals in the Various Rank Classes (Given, 1984)

<table>
<thead>
<tr>
<th></th>
<th>Lignite</th>
<th>Subbit.</th>
<th>High-Volatile Bituminous</th>
<th>Bituminous</th>
<th>Bituminous</th>
</tr>
</thead>
<tbody>
<tr>
<td>% C, mmf</td>
<td>65–72</td>
<td>72–76</td>
<td>76–78</td>
<td>78–80</td>
<td>80–87</td>
</tr>
<tr>
<td>% H</td>
<td>4.5</td>
<td>5</td>
<td>5.5</td>
<td>5.5</td>
<td>5.5</td>
</tr>
<tr>
<td>% O</td>
<td>30</td>
<td>18</td>
<td>13</td>
<td>10</td>
<td>10–4</td>
</tr>
<tr>
<td>% O as COOH</td>
<td>13–10</td>
<td>5–2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>% as OH</td>
<td>15–10</td>
<td>12–10</td>
<td>9</td>
<td>?</td>
<td>7–3</td>
</tr>
<tr>
<td>Aromatic C atoms, % of total C</td>
<td>50</td>
<td>65</td>
<td>?</td>
<td>?</td>
<td>75</td>
</tr>
<tr>
<td>Av. no. benz. rings, layer</td>
<td>1–2</td>
<td>?</td>
<td>2–3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reflectance, % of vitrinite</td>
<td>0.2–0.3</td>
<td>0.3–0.4</td>
<td>0.5</td>
<td>0.6</td>
<td>0.6–1.0</td>
</tr>
<tr>
<td>Density, in helium</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>minimum</td>
</tr>
<tr>
<td>Total surface area</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>minimum</td>
</tr>
<tr>
<td>Plasticity and coke formation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>only</td>
</tr>
<tr>
<td>Calorific value, moist. mmf, Btu/lb</td>
<td>7000</td>
<td>10,000</td>
<td>12,00</td>
<td>13,50</td>
<td>14,500</td>
</tr>
</tbody>
</table>
Initial tests used average REE concentration Hagel coal: ~42 ppm dry coal; 580 ppm ash

Several solvent types/concentrations screened for REE extraction ability from unprocessed lignite coal.

Solvent choices based on known organic REE associations.

Extraction ~90% with Solvent A, but large impurities extraction.

Solvent B best combination of high extraction and REE-selectivity – chosen for additional testing.

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### REE Extraction/Concentration Testing – Solvent Screening Tests

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ash Content (wt%)</th>
<th>% Ash Reduction</th>
<th>Total % REE Extracted</th>
<th>Wt% REE in Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unleached Coal</td>
<td>7.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Solvent A</td>
<td>1.7</td>
<td>76.1</td>
<td>86.8</td>
<td>0.07</td>
</tr>
<tr>
<td>Solvent B</td>
<td>6.1</td>
<td>15.6</td>
<td>70.9</td>
<td>0.25</td>
</tr>
<tr>
<td>Solvent C</td>
<td>3.1</td>
<td>56.4</td>
<td>65.6</td>
<td>0.06</td>
</tr>
</tbody>
</table>
REE Extraction/Concentration Testing – Harmon-Hansen vs. Hagel Coal

<table>
<thead>
<tr>
<th>Mass Balance Parameter</th>
<th>Hagel B</th>
<th>Harmon-Hansen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting Ash Content (wt%)</td>
<td>7.2</td>
<td>25.6</td>
</tr>
<tr>
<td>% Ash Reduction</td>
<td>15.6</td>
<td>19.3</td>
</tr>
<tr>
<td>% REE Extracted</td>
<td>65.3</td>
<td>87.7</td>
</tr>
<tr>
<td>wt% REE in Solution</td>
<td>0.23</td>
<td>0.79</td>
</tr>
<tr>
<td>wt% Fe in Solution</td>
<td>16.0</td>
<td>68.8</td>
</tr>
<tr>
<td>wt% alkali/alkaline earth in Solution</td>
<td>69.6</td>
<td>13.6</td>
</tr>
</tbody>
</table>

- REE recovery higher with Harmon-Hansen, especially scandium
- Other high value elements also extracted: Co, Cu, Ga, Ge, Li, Ni, V, Zn, Mn
- Impurities also extracted: major components Fe, Ca, Mg, Na, K
**REE Extraction/Concentration Testing – REE Extraction Kinetics**

**Hagel B Testing**
- Plateau @ ~14 hrs
- HREE much faster
- LREE jump from 8-14hrs - possibly mineral form dissolution
- Slower scandium kinetics
- >50% HREE in 1 hr

**Harmon-Hansen Testing**
- Faster kinetics than Hagel B, especially scandium
- ~ 70% total REE extraction in 2 hr – little improvement through 14 hr
- HREE faster, but less pronounced than Hagel B
Many high value elements also fast kinetics

Many impurities significantly slower kinetics

Large improvement in REE-selectivity at short contact time

2wt% target potentially achievable with more optimization
REE Extraction/Concentration Testing – Modified Leaching Process

- Modified 2-step leaching process – Solvent D followed by Solvent B
- Achieved 2wt% REE concentration in single processing step, but only 36% REE recovery

<table>
<thead>
<tr>
<th>Product Solution</th>
<th>wt% REE</th>
<th>REE Recovery (whole coal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent D Leachate</td>
<td>2.05</td>
<td>36.0</td>
</tr>
<tr>
<td>Solvent B – 1hr Leachate</td>
<td>0.77</td>
<td>21.5</td>
</tr>
<tr>
<td>Solvent B – 4 hr Leachate</td>
<td>0.78</td>
<td>24.2</td>
</tr>
<tr>
<td>Mixture of Solvent D + 4hr</td>
<td>1.24</td>
<td>60.2</td>
</tr>
</tbody>
</table>
REE Extraction/Concentration Testing - Process Summary and Key Benefits

- REEs easily removed from the raw ND lignite coals due to weak organic bonding
- REE extraction performance summary – direct extraction from unprocessed ND lignite
  1. >2.0wt% REE concentration @ 36wt% REE recovery
  2. 1.36wt% REE concentration @ 68wt% REE recovery
  3. 0.8wt% REE concentration @ 86wt% REE recovery
- Much simpler extraction process than fly ash or mineral-bound REEs
- No physical beneficiation required – process similar to Chinese ion-adsorbed clays
  1. Solvent-based extraction of REEs from coarsely ground raw coal
  2. Hydrometallurgy techniques to concentrate REEs in the leachate
- Mild leaching process – no high temperatures or pressures; no concentrated acids/bases
- **Selective** REE extraction – only strips the organically associated REEs, leaving the mineral forms and organic matter behind – does not require digestion of entire ore/mineral
- Coal beneficiation process – reduces ash content and preserves organic content/structure; ~100% removal of ‘problem’ elements such as sodium
- Industrially proven processing methods – fast time to market and low scale-up risks
Phase 2 Plan
Phase 2 Project Objectives

The overall objective of this proposed Phase 2 project is to demonstrate at the bench scale a high performance, economically viable, and environmentally benign technology to recover rare earth elements (REE) from North Dakota (ND) lignite coal or lignite-related feed stocks.

- Based on the design of the bench-scale system developed in Phase 1, construct a bench-scale system with a REE-rich feedstock throughput of about 10 kg/hr to produce a mixed REE concentrate product of >2% by weight on a dry, elemental basis
- Obtain large samples (~2000 kg) of coal and associated sediments containing >300ppm total REE (TREE) dry whole sample basis for testing
- Conduct parametric testing of the bench-scale system in order to determine optimum conditions required to concentrate REE to >2%
- Conduct continuous testing of the bench-scale system at optimized conditions/configuration to produce a representative REE concentrate that is suitable for evaluation for further processing
- Provide splits of samples of the final product produced from the Phase 2 testing to NETL for independent analysis and verification of the quantity of REE present.
- Update the technical and economic analysis of the REE recovery process conducted in Phase 1 with the results of testing obtained in Phase 2.
- Identify opportunities for commercialization at existing mines/plants in ND and/or build the commercially feasible case for opening a new mine in an area with most favorable REE content
- Work with industry partners to develop a technology development and commercialization strategy
Phase 2 Scope of Work

• Task 1 – Project management and planning
• Task 2 – Provide split samples to NETL
• Task 3 – Bench-scale system procurement/construction
• Task 4 – Sampling, characterization and large sample collection
• Task 5 – Parametric testing – batch tests
• Task 6 – Bench-scale system modification for continuous tests
• Task 7 – Continuous testing – production tests
• Task 8 – Updated TEA and commercialization plan
• Task 9 – Final report
Phase 2 Technical Project Team

• **UND’s expertise:**
  - Lignite geology/geochemistry of REEs
  - Advanced analytical techniques involving REEs in coals
  - Chemical/process engineering design and demonstration

• **MTI’s expertise:**
  - Lignite/Low-rank coal inorganic/organic geochemistry
  - Process development/lignite industry experience
  - Business planning/commercialization

• **Barr Engineering’s expertise:**
  - Mineral processing, extractive metallurgy
  - Technology and economic feasibility assessment, commercial-scale plant design
  - Market analysis experience

• **PNNL’s expertise:**
  - REE/F-block chemistry and separations
  - Hydrometallurgy and trace metals recovery technology

• **MLJ Consulting’s expertise:**
  - ND lignite industry
  - Commercialization of lignite-related technologies

• **NDGS’ expertise:**
  - Lignite geology & extensive sample database on REEs
Acknowledgements

Project Team Members
• Daniel Laudal, UND (PI)
• Steve Benson, MTI
• Dan Palo, Barr Engineering
• Shane Addleman, PNNL
• Mike Jones, MLJ Consulting
• Ned Kruger, NDGS

Project Sponsor Representatives
• Chuck Miller, NETL Project Manager
• Mike Holmes and Mike Jones, LEC/NDIC
• Dennis James, NA Coal
• Charlie Bullinger and Sandra Broekema, GRE
• Craig Bleth, Minnkota Power Cooperative
• Kai Xia, Great Northern Properties
• Rick Tonder, North Dakota University System
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Contact Information

Dan Laudal
Manager: Major Projects
Institute for Energy Studies, University of North Dakota
Daniel.Laudal@engr.und.edu
701-777-3456

Steve Benson
President
Microbeam Technologies Inc
sbenson@microbeam.com
701-213-7070
Price of REE (Golev, 2014)

### Table 4
The price dynamics for selected REO in 2007–2013 (US$/kg, FOB China).

*Source: Lynas Corporation (2013), Metal-Pages (2013).*

<table>
<thead>
<tr>
<th>Element</th>
<th>2007</th>
<th>2008</th>
<th>2009</th>
<th>2010</th>
<th>2011</th>
<th>2012</th>
<th>2013</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lanthanum oxide</td>
<td>3.4</td>
<td>8.7</td>
<td>4.9</td>
<td>22.4</td>
<td>104.1</td>
<td>25.2</td>
<td>8.0</td>
</tr>
<tr>
<td>Cerium oxide</td>
<td>3.0</td>
<td>4.6</td>
<td>3.9</td>
<td>21.6</td>
<td>102.0</td>
<td>24.7</td>
<td>8.3</td>
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<tr>
<td>Praseodymium oxide</td>
<td>29.1</td>
<td>29.5</td>
<td>18.0</td>
<td>48.0</td>
<td>197.3</td>
<td>121.0</td>
<td>92.3</td>
</tr>
<tr>
<td>Neodymium oxide</td>
<td>30.2</td>
<td>31.9</td>
<td>19.1</td>
<td>49.5</td>
<td>234.4</td>
<td>123.2</td>
<td>70.7</td>
</tr>
<tr>
<td>Samarium oxide</td>
<td>3.6</td>
<td>5.2</td>
<td>3.4</td>
<td>14.4</td>
<td>103.4</td>
<td>64.3</td>
<td>15.6</td>
</tr>
<tr>
<td>Europium oxide</td>
<td>323.9</td>
<td>481.9</td>
<td>492.9</td>
<td>559.8</td>
<td>2842.9</td>
<td>2484.8</td>
<td>1161.4</td>
</tr>
<tr>
<td>Terbium oxide</td>
<td>590.4</td>
<td>720.8</td>
<td>361.7</td>
<td>557.8</td>
<td>2334.2</td>
<td>2030.8</td>
<td>974.0</td>
</tr>
<tr>
<td>Dysprosium oxide</td>
<td>89.1</td>
<td>118.5</td>
<td>115.7</td>
<td>231.6</td>
<td>1449.8</td>
<td>1035.6</td>
<td>550.4</td>
</tr>
</tbody>
</table>