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

2019 NETL Annual Crosscutting Technologies Meeting

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Project Team

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• Kai Xia, Great Northern Properties
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• Wesley Wintch, Valley City State University
Presentation Overview

- Project Background
- Summary of Phase 1
- Phase 2 Accomplishments
- Phase 2 Next Steps
- Commercialization Plans
- Questions
Project Background

**Project Title**: Investigation of REE extraction from North Dakota coal-related feed stocks (DE-FE0027006)

**3-year Phase 1/2 effort**
1. Sampling and characterization – Lignites with > 300 ppm REE
2. Laboratory-scale extraction/concentration development
3. Bench-scale extraction/concentration testing – current focus
4. TEA, market analysis and commercialization plan – next steps

**Key Findings to Date**
- REE primarily weakly associated with organics – easily leached with mild solvent from pre-combustion coal
- Process very similar to Chinese ion-exchangeable clays
  1. Leaching of REE from coal
  2. Hydrometallurgy to concentrate/purify REE in the solution
- Leaching process also a coal beneficiation process
### Coal Resources – Phase 1

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Ash Yield (wt%)</th>
<th>Total REE, ppm (dry mass basis)</th>
<th>Total REE, ppm (ash basis)</th>
<th>HREE/LREE</th>
<th>$ REE/MT Coal</th>
</tr>
</thead>
<tbody>
<tr>
<td>6A-2</td>
<td>36.3</td>
<td>642</td>
<td>1752</td>
<td>0.28</td>
<td>437</td>
</tr>
<tr>
<td>6A</td>
<td>20.1</td>
<td>564</td>
<td>2235</td>
<td>0.35</td>
<td>599</td>
</tr>
<tr>
<td>6A-1</td>
<td>75.5</td>
<td>449</td>
<td>587</td>
<td>0.28</td>
<td>307</td>
</tr>
<tr>
<td>3A</td>
<td>40.5</td>
<td>363</td>
<td>892</td>
<td>0.89</td>
<td>400</td>
</tr>
<tr>
<td>3C</td>
<td>60.9</td>
<td>322</td>
<td>525</td>
<td>0.43</td>
<td>341</td>
</tr>
<tr>
<td>6AA</td>
<td>47.0</td>
<td>212</td>
<td>449</td>
<td>2.06</td>
<td>580</td>
</tr>
<tr>
<td>7F</td>
<td>20.9</td>
<td>194</td>
<td>924</td>
<td>0.76</td>
<td>147</td>
</tr>
</tbody>
</table>

### Graphical Representation

![Graph showing the distribution of rare earth elements (REE) across different samples.](chart.png)
Unique Properties of Lignite

- Oxygen functional groups, which are uniquely prevalent in lignite, provide binding sites for inorganic cations such as REE.
- But also a challenge: acid consumers (alkali and alkaline earth metals) are also organically associated.

<table>
<thead>
<tr>
<th></th>
<th>Lignite</th>
<th>Subbituminous</th>
<th>High volatile bituminous</th>
<th>Bituminous</th>
<th>Medium volatile</th>
<th>Low volatile</th>
<th>Anthracite</th>
</tr>
</thead>
<tbody>
<tr>
<td>% C (min. matter free)</td>
<td>65-72</td>
<td>72-76</td>
<td>76-78</td>
<td>78-80</td>
<td>80-87</td>
<td>89</td>
<td>90</td>
</tr>
<tr>
<td>% H</td>
<td>4.5</td>
<td>5-4</td>
<td>5.5</td>
<td>5.5</td>
<td>5.5</td>
<td>4.5</td>
<td>3.5</td>
</tr>
<tr>
<td>% O</td>
<td>30</td>
<td>18</td>
<td>13</td>
<td>10</td>
<td>10-4</td>
<td>4-3</td>
<td>3</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>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>% O as OH</td>
<td>15-10</td>
<td>12-10</td>
<td>9</td>
<td>?</td>
<td>7-3</td>
<td>2-1</td>
<td>1-0</td>
</tr>
<tr>
<td>Aromatic C atoms % of total C</td>
<td>50</td>
<td>65</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>Avg. no. benzene rings/layer</td>
<td>1-2</td>
<td>?</td>
<td>2-3</td>
<td>5?</td>
<td>&gt;25?</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volatile matter (%)</td>
<td>40-50</td>
<td>35-50</td>
<td>35-45</td>
<td>?</td>
<td>31-40</td>
<td>31-20</td>
<td>20-10</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>
<td>1.4</td>
<td>1.8</td>
</tr>
</tbody>
</table>
Organic Associations

- **REE enriched in organic fractions of lignite**
  - opposite of high-rank coals

- Primary form as organic complexes (i.e. carboxylic acid groups)

- Cations can be easily leached (stripped) using dilute acids

![Diagram](image-url)
REE – Specific Gravity Correlations

- Concentrated in lightest SG fractions
  - Able to be concentrated with standard coal cleaning techniques
Phase 2 Accomplishments
Phase 2 Objectives and Work Scope

- **Objective**: Demonstrate technology at bench-scale (~10 kg coal/hr)
- Phase 1 Testing – batch parametric tests
  - Tune extraction chemistry/conditions to maximize REE selectivity/yield
  - Test additional unit operations to improve overall process and increase REE concentration
  - Optimize conditions and process configuration
- Phase 2 Testing – production testing (~1000 kg total feed)
- Techno-economic assessment
- Preliminary commercialization plan
Feedstock Sourcing

- New sample manually excavated in outcrop of H-Bed lignite
  - 18 55 gal drums extracted

Members of the UND and Barr team during collection of the H-Bed lignite in Slope County, ND (Nov, 2018) – approximately 7000 lbs excavated
Bench Coal Feedstock

- Eighteen 55-gal drums collected and measured to ensure REE concentration
Bench-Scale System

- Multiple tank approach for testing multiple unit operations/conditions at once

Pictured for batch parametric testing
Process Schematic

1. Crushed & Screened Lignite Coal
   - Gravity Concentration
   - High Ash Tailings
   - Low-Ash Lignite Coal

2. Concent Solvent
   - Leaching
   - Dewatering
   - Staged H2O Wash
     - Upgraded Lignite Coal
   - Stage 1 Recycle
   - Stage 2

3. Acidic H2O
   - Wastewater

4. Base Add’n
   - Fe-Rich Precip to Waste Disposal
   - Oxalic Acid
   - Base
   - REE Precip
   - Dewatering
   - REE-Ca-Oxalate
   - Roasting
   - Al-Rich Product

5. Base
   - Neutralization/Dewatering
   - Barren Solution to Disposal

6. Alkaline H2O
   - Mixed REE Oxide Product

7. University of North Dakota
   - Institute for Energy Studies
   - College of Engineering & Mines
Physical Beneficiation Results

<table>
<thead>
<tr>
<th>Coal Sample</th>
<th>Ash Content (wt%)</th>
<th>TREE (coal ppm)</th>
<th>TREE (ash ppm)</th>
<th>HREE/LREE Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>As Received</td>
<td>35.45</td>
<td>646</td>
<td>1822</td>
<td>0.28</td>
</tr>
<tr>
<td>Concentrate</td>
<td>15.09</td>
<td>657</td>
<td>4357</td>
<td>0.30</td>
</tr>
<tr>
<td>Tailings</td>
<td>70.31</td>
<td>353</td>
<td>502</td>
<td>0.26</td>
</tr>
<tr>
<td>Scav Conc</td>
<td>19.5</td>
<td>679</td>
<td>3483</td>
<td>0.30</td>
</tr>
<tr>
<td>Scav Midd</td>
<td>47.26</td>
<td>630</td>
<td>1333</td>
<td>0.28</td>
</tr>
<tr>
<td>Scav Tails</td>
<td>59.34</td>
<td>550</td>
<td>927</td>
<td>0.26</td>
</tr>
<tr>
<td>Blend</td>
<td>19.34</td>
<td>658</td>
<td>3881</td>
<td>0.30</td>
</tr>
</tbody>
</table>

- Physical concentrating factor on ash basis (versus non-REE elements) of 2.13
Leaching Equilibrium

- Similar equilibrium behavior as ion-exchange resins
  - S-Curve
Leaching Kinetics

• Rapid kinetics at each pH level
  – Likely not mineral dissolution

• Aluminum used as tracer for trivalents
  – Similar kinetics for trivalents found in other coals
Impurity Removal

- Little-to-no REE loss under pH 3 conditions
  - Effective Fe removal
- Precipitate >90% Fe on oxide basis
  - Possible Fe ore for minimization of waste streams
REE Precipitation

- Control of precipitation conditions able to generate unique depositional environment

- Low oxalate loading resulted in high REE content (>80%) with high recovery of MREE

- Secondary product with high Sc, HREE
### REE Precipitation – Low Ox Loading

- Product concentration from low oxalate loading

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td>0.26%</td>
</tr>
<tr>
<td>Y</td>
<td>10.5%</td>
</tr>
<tr>
<td>La</td>
<td>9.23%</td>
</tr>
<tr>
<td>Ce</td>
<td>29.57%</td>
</tr>
<tr>
<td>Pr</td>
<td>4.09%</td>
</tr>
<tr>
<td>Nd</td>
<td>17.76%</td>
</tr>
<tr>
<td>Sm</td>
<td>3.84%</td>
</tr>
<tr>
<td>Eu</td>
<td>0.91%</td>
</tr>
<tr>
<td>Gd</td>
<td>3.56%</td>
</tr>
<tr>
<td>Tb</td>
<td>0.52%</td>
</tr>
<tr>
<td>Dy</td>
<td>2.58%</td>
</tr>
<tr>
<td>Ho</td>
<td>0.44%</td>
</tr>
<tr>
<td>Er</td>
<td>1.02%</td>
</tr>
<tr>
<td>Tm</td>
<td>0.12%</td>
</tr>
<tr>
<td>Yb</td>
<td>0.68%</td>
</tr>
<tr>
<td>Lu</td>
<td>0.09%</td>
</tr>
</tbody>
</table>
Current Status of Project

- Finalizing parametric testing on chosen coal blend
- Initiated semi-continuous modifications to the bench unit
  - Equipment acquisition
- Initiated commercialization plan discussions
Next Steps

• Complete semi-continuous modification to system
  – Integration and shakedown

• Production testing
  – ~1000 kg of chosen coal blend from physical beneficiation
  – Produc sufficient mass of >2wt% REE concentrate suitable for further processing and detailed characterization

• Techno-economic analysis and commercialization plan development
Commercialization Plans
Additional Coal Options

- Coal in active mine in North Dakota was found to have >300ppm REE on whole coal basis
  - $C_{outl} > 2.5$ in seam, HREE/LREE > 0.8
Comparison to Harmon/Hanson

- Highest in LREE
Mining Considerations

- REE concentrated at margins of roof/floor, below partings and in thin seams
- ‘Selective’ mining likely needed to separate REE-rich coal from ROM coal – **Wirtgen Surface Miner**
- Coals near margins and/or thin seams often high ash and may be discarded during mining
- Recovery of REE via UND process can both provide value as well as reclaim and upgrade low-value coal
- Or, starting from lower-ash coal, opportunity to create high-purity carbon-based products with lower cost
• Valley City State University currently pursuing installation of activated carbon plant integrated with existing steam generation plant

• Basis of Phase 1 TEA…but really pilot or small demo-scale

• VCSU interested in being platform for pilot testing of fuel conversion technologies and REE
  ➢ ~5 MW\textsubscript{th} CHP facility: NG and Coal-fired boilers
  ➢ Advanced turbine systems, carbon-based products, coal upgrading, biomass, emissions control systems, CO\textsubscript{2} capture…etc

Integrated Facility Concept

- Potential new mine in Harmon-Hanson coal zone offers next generation opportunities
- Highest value utilization of lignite
- Multiple products
- Potential for export – 800-year supply at current mining rates
- Opportunity to deploy advanced boiler/turbine systems (small coal plant/REMS concepts)
- REE/metals, activated carbon, battery electrode materials, metallurgical coal, carbon fibers…etc
- UND is currently commercializing integrated CHP and activated carbon production system with Valley City State University – potential host site for pilot-scale demonstrations
Spiritwood CHP Station

- Update the Phase 1 TEA with a larger-scale commercial facility and based on experimental data in Phase 2
- Same overall concept as Phase 1 – integrate REE recovery with CHP and Activated Carbon
- Project co-sponsor Great River Energy has agreed to consider integrating the concept into its Spiritwood Station Plant
- Project co-sponsor Great Northern Properties interested in Coring and providing core samples of H-Bed for testing
Summary

- Discovered high REE concentrations in ND lignite
- REE weakly bound – primarily as organic complexes
- Pre-combustion extraction permits sale of upgraded coal products
  - REE concentration through selective precipitations
- Preliminary parametric testing complete
  - Finalizing operating parameters and equipment for semi-continuous testing
- Commercialization pathways
  - Multiple products for synergistic economic approach
  - VCSU/GRE Spiritwood for pilot/commercial demo opportunities
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Questions?

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