A Pollution Prevention and Economically Viable Technology for Separation of Rare Earth Elements (REEs) from Powder River Basin Coal Ashes (DE-FE0027069)

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Main goals

• Identify and sample developable amount of coal ashes that have at least 300 ppm REEs as well as characterize the coal ashes

• Successfully develop robust processes to produce “green” solid containing at least 2.0 weight % total REE content on an elemental basis and measured on a dry basis from PRB coal ashes with high overall recovery efficiency of RREs in coal ashes and low pollutant emission

• Reduce REEs recovery energy consumption compared to current commercialized REE recovery technologies

• Decrease the overall coal ash based REEs recovery cost compared to current commercialized REE recovery technologies
Experiments
Raw Materials – Safe and inexpensive as well as widely available

• Raw materials containing REEs
  • Solids (which can contain low than 300 ppm REEs)
    • **Coal ashes – targets**
    • Overburdens or other solids containing REEs
    • Sludge from various processes
    • Ores
  • Liquids
    • Waste water from coal mining and coal-based energy industries
    • Any other produced and waste waters containing REEs

• Extracting agents
  • Wastes or low-cost materials
Extraction Operation - *Green and Short as well as Simple*

- Low or zero net addition of cations and anions to the close REEs extraction system
- Water from REEs extraction
  - Containing almost zero external species
    - Reused internally for multicycle REEs extraction
- Zero air pollutant emission
- Zero addition of anions and cations to the after-REEs-extraction coal ashes
Extraction Operation – *Green and Simple as well as Multifunctional*

- Operation steps are designed to
  - Be short
  - Be multifunctional
  - Have high selectivity for collecting desired species
  - Achieve maximum atom economy
    - Based on the integration of
      - REEs chemistry
      - Theories for separations of homogeneous and heterogeneous mixtures
      - Aqueous chemistry
      - Solid-state chemistry
      - Environmental chemistry

- Inexpensive and safe materials are used
- Generation of at least two value-added products in addition to the major desired product, REEs-containing solid.
Major Results Achieved for the Project

• **Extraction process – Green**
  • Operation steps are designed to
    • Be short
    • Be multifunctional
    • Have high selectivity for collecting desired species
    • Achieve maximum atom economy
      • Based on the integration of
        • REEs chemistry
        • Theories for separations of homogeneous and heterogeneous mixtures
        • Aqueous chemistry
        • Solid-state chemistry
        • Environmental chemistry
  • Less expensive materials are used
  • Safer materials are used
  • Generation of at least **two value-added products** in addition to the major desired product, **REEs-containing solid**.
REEs Extraction Lab
Extraction Apparatus
Grinding and C-H-N-S Analysis Equipment
BET and REEs Analysis Equipment
Results
>300 ppm REEs Containing Fly Ashes
>300 ppm REEs Containing Fly Ashes

33 M tons with REEs > 300 ppm

15 M tons with REEs > 300 ppm

100 M tons to be tested
Some Fly Ashes Collected from Power Plants
>300 ppm REEs Containing Fly Ashes

• Number of power plants contacted: 43
• Tons of fly ashes available: ~150 M tons
• Tons of fly ashes containing > 300 ppm REEs
  • Known: ~ 48 M tons in collected ~58 M tons
  • Unknown: ~ 100 M tons to be tested
### Characteristics of Several Targeted Samples

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
<th>S (%)</th>
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</thead>
<tbody>
<tr>
<td>CH</td>
<td>0.88</td>
<td>0.21</td>
<td>0.03</td>
<td>4.19</td>
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<tr>
<td>DJ</td>
<td>0.89</td>
<td>0.82</td>
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<td>FS</td>
<td>1.8</td>
<td>0.31</td>
<td>0.03</td>
<td>3.41</td>
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<tr>
<td>JE</td>
<td>0.52</td>
<td>0.01</td>
<td>0.02</td>
<td>1.28</td>
</tr>
<tr>
<td>LR</td>
<td>0.26</td>
<td>0.25</td>
<td>0.02</td>
<td>0.91</td>
</tr>
<tr>
<td>WD</td>
<td>0.56</td>
<td>0.24</td>
<td>0.04</td>
<td>3.5</td>
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</table>
### Characteristics of Several Targeted Samples

#### BET surface area

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Surface area/m²·g⁻¹</th>
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<tr>
<td>CH</td>
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<td>DJ</td>
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<td>FS</td>
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<td>JE</td>
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<td>LR</td>
<td>0.905</td>
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<td>WD</td>
<td>19.320</td>
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#### Moisture and organic carbon

<table>
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<th>Sample ID</th>
<th>Moisture (%)</th>
<th>Organic carbon (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH</td>
<td>0.41</td>
<td>1.91</td>
</tr>
<tr>
<td>DJ</td>
<td>6.54</td>
<td>4.26</td>
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<tr>
<td>FS</td>
<td>0.84</td>
<td>2.91</td>
</tr>
<tr>
<td>LR-1</td>
<td>0.37</td>
<td>0.61</td>
</tr>
<tr>
<td>LR-2</td>
<td>0.08</td>
<td>0.43</td>
</tr>
<tr>
<td>WD</td>
<td>1.23</td>
<td>3.08</td>
</tr>
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</table>
# REEs Concentrations in Several Fly Ashes

(Dry Ash Basis)

<table>
<thead>
<tr>
<th>DAB (dry ash basis)</th>
<th>CH (ppm)</th>
<th>DJ (ppm)</th>
<th>FS (ppm)</th>
<th>LR-1 (ppm)</th>
<th>LR-2 (ppm)</th>
<th>WD (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce</td>
<td>170.1</td>
<td>148.9</td>
<td>153.5</td>
<td>159.7</td>
<td>171.1</td>
<td>167.5</td>
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<tr>
<td>Dy</td>
<td>11.0</td>
<td>12.8</td>
<td>14.2</td>
<td>11.9</td>
<td>14.9</td>
<td>15.6</td>
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<tr>
<td>Er</td>
<td>7.0</td>
<td>7.4</td>
<td>8.3</td>
<td>7.4</td>
<td>9.0</td>
<td>8.9</td>
</tr>
<tr>
<td>Eu</td>
<td>3.6</td>
<td>4.7</td>
<td>5.3</td>
<td>3.8</td>
<td>5.8</td>
<td>5.4</td>
</tr>
<tr>
<td>Gd</td>
<td>14.4</td>
<td>16.5</td>
<td>22.4</td>
<td>15.2</td>
<td>22.4</td>
<td>23.6</td>
</tr>
<tr>
<td>Ho</td>
<td>2.2</td>
<td>2.5</td>
<td>2.8</td>
<td>2.4</td>
<td>2.9</td>
<td>3.0</td>
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<tr>
<td>La</td>
<td>90.7</td>
<td>79.5</td>
<td>77.6</td>
<td>86.9</td>
<td>89.0</td>
<td>87.0</td>
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<td>Lu</td>
<td>1.2</td>
<td>1.1</td>
<td>1.2</td>
<td>1.2</td>
<td>1.3</td>
<td>1.2</td>
</tr>
<tr>
<td>Nd</td>
<td>101.9</td>
<td>96.0</td>
<td>102.6</td>
<td>98.5</td>
<td>109.3</td>
<td>111.1</td>
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<tr>
<td>Pr</td>
<td>23.5</td>
<td>18.1</td>
<td>23.7</td>
<td>22.6</td>
<td>24.8</td>
<td>25.4</td>
</tr>
<tr>
<td>Sm</td>
<td>15.1</td>
<td>16.9</td>
<td>23.1</td>
<td>15.4</td>
<td>23.8</td>
<td>24.0</td>
</tr>
<tr>
<td>Tb</td>
<td>1.9</td>
<td>2.2</td>
<td>2.5</td>
<td>2.0</td>
<td>2.5</td>
<td>2.7</td>
</tr>
<tr>
<td>Tm</td>
<td>1.1</td>
<td>1.1</td>
<td>1.2</td>
<td>1.1</td>
<td>1.3</td>
<td>1.2</td>
</tr>
<tr>
<td>Y</td>
<td>61.8</td>
<td>65.5</td>
<td>72.2</td>
<td>68.6</td>
<td>76.8</td>
<td>76.4</td>
</tr>
<tr>
<td>Yb</td>
<td>6.9</td>
<td>6.8</td>
<td>7.4</td>
<td>7.1</td>
<td>8.2</td>
<td>7.8</td>
</tr>
<tr>
<td>Total REEs (ppm)</td>
<td>512.4</td>
<td>480.2</td>
<td>517.8</td>
<td>503.6</td>
<td>563.1</td>
<td>561.0</td>
</tr>
</tbody>
</table>
Piles of REEs Containing Samples from Leaching and Separation Processes for ICP-MS Analysis
Piles of REEs Containing Samples from Leaching and Separation Processes for ICP-MS Analysis
Recovery Efficiencies of REEs in Fly Ashes

- High REEs recovery efficiencies are achievable with the new method which is
  - Environmentally friendly
  - Highly selective
  - Inexpensive
Recovery Efficiencies of REEs in Coal Overburden

- Coal overburden in Wyodak contains ~ 150 ppm REEs
- The new REEs extraction method works well for overburden
  - 83-93% REEs extraction efficiencies were achieved
  - The conditions for extracting the REEs from overburden are milder than those with fly ashes
  - It is anticipated that the concentrations of REEs in REEs-containing products are higher
**REEs Separation**

- High separation efficiency for the two approaches

<table>
<thead>
<tr>
<th>Conditions</th>
<th>% REEs in product (REEs-containing solids)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.1</td>
</tr>
<tr>
<td>2</td>
<td>3.5</td>
</tr>
<tr>
<td>3</td>
<td>2.7</td>
</tr>
<tr>
<td>4</td>
<td>3.7</td>
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<tr>
<td>5</td>
<td>6.0</td>
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<tr>
<td>6</td>
<td>7.6</td>
</tr>
<tr>
<td>7</td>
<td>8.2</td>
</tr>
<tr>
<td>8</td>
<td>10.8</td>
</tr>
</tbody>
</table>

- Graphs showing separation efficiency for different conditions.
By-products

• The process generates highly valuable by-products along with REEs oxides
  • Al/Fe (coagulants)
  • Sc ($4,200,000/ton)

• The green nature of the recovery method makes ashes re-usable after REEs recovery
Photos of the Products Containing Different % of REEs (elements based)
SEM-EDS Images of REEs-Containing Solid
SEM-EDS Images of REEs-containing Solid

• A- The morphology image indicate the presences of various undesired material in the REEs-containing solid or product
• B- Dispersion image clearly show the existence of the four major REEs in the product
• C- The semi-quantitative analyses of REEs in the REEs-containing solid with SEM-EDS
  • Major REEs in the solid are Ce, La, Nd and Y
  • Major inorganic impurities are Ca, Fe, Mg, Al and Si
  • The concentrations in the table are close to with those detected with ICP-MS
Environmental Impact

- Conventional method
  - Heavy metals/radioactive/water/gas emission
  - Waste gas (9,600-60,000 m³/ton REEs)
    - Flue gas concentrate
    - HF
    - SO₂
    - H₂SO₄
  - Acid water (200 m³/ton REEs)
  - Radioactive waste (1.4 tons/ton REEs)

- New method
  - No heavy metals/radioactive waste discharge
  - No air pollution
  - Water reuse
  - Ash reuse

Navarro and Zhao, 2014

Haque et al., 2014
Cost-Effectiveness

• > 50% energy consumption reduction – why?
  • Equipment – Simple
  • Operation – Safe and easy
  • Process – Short
  • Extraction condition - Mild

• > 30% cost reduction – Why?
  • Materials – Inexpensive
    • Waste materials from other industries can be used for recovering REEs
  • Capital investment – Low
  • Labor requirement – Low
  • Emission and discharge control or secondary pollution prevention – Almost zero

<table>
<thead>
<tr>
<th>REOs</th>
<th>Primary Energy (MJ/kg)</th>
<th>GHG (kg CO₂-e/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>177</td>
<td>9.3</td>
</tr>
<tr>
<td>Ce</td>
<td>157</td>
<td>8.3</td>
</tr>
<tr>
<td>Pr</td>
<td>798</td>
<td>41.4</td>
</tr>
<tr>
<td>Nd</td>
<td>743</td>
<td>38.5</td>
</tr>
<tr>
<td>Sm, Eu, Gd (mixed oxide)</td>
<td>1,074</td>
<td>55.6</td>
</tr>
</tbody>
</table>
Conclusions

• All the goals set for the project are achieved, especially
  • The actual REEs concentrations (the highest one to date: 10%) in products >> the set goal (2%); and >10% or >> 10% is achievable.
  • The tons of qualified coal ashes we found >> the set goal (10 M tons)
• A new pathway for producing critical materials – REEs is opened by integrating the knowledge from multi fields
  • With various desired characteristics
  • Without the limitation of location and time
• The new pathway makes impossible possible in REEs production field - huge amounts of conventionally considered unrecoverable REEs can be recovered with the transformational technology
• The new pathway could inspire the significant advancement of new theories in chemistry and technologies in mineral processing industries