Rare Earth Element Production from Coal

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Outline

✓ Background
  ▪ REE Value
  ▪ REE Forms in Coal
    ● Minerals
    ● Ion Substitution
    ● Organic Association
  ▪ REE Concentration
What are Rare Earths?

The periodic table of elements, highlighting the Rare Earth Elements (La to Lu) and Actinides (Ac to Lr).
The Significance of Rare Earths

- Numerous high technology applications:
  - Magnets
  - Batteries
  - Phosphors
  - Catalysts

- Used in end products in these sectors:
  - Health care
  - Transportation
  - Green Energy (Wind, Solar, Hybrid Vehicles)
  - Defense

- Rare Earth Chemistry in North America
  Supports:
  - $329 billion in economic output
  - Associated employment of over 618,000 people
Rare Earth Concentrations > 1000 ppm

Areas outlined in yellow were the focus of further analysis.
Outline

✓ **Background**

✓ **REE Value**
  
  ▪ REE Forms in Coal
    ● Minerals
    ● Ion Substitution
    ● Organic Association
  
  ▪ REE Concentration
However...

- “Rare Earths” is a plural concept.
- Not all the elements are created equally...
- Not all are equally desired...

<table>
<thead>
<tr>
<th></th>
<th>Oxide Price 2009 ($/kg)</th>
<th>Oxide Price 2015 ($/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lanthanum</td>
<td>30</td>
<td>2.35</td>
</tr>
<tr>
<td>Cerium</td>
<td>30</td>
<td>1.9</td>
</tr>
<tr>
<td>Praseodymium</td>
<td>38</td>
<td>59</td>
</tr>
<tr>
<td>Neodymium</td>
<td>42</td>
<td>41</td>
</tr>
<tr>
<td>Samarium</td>
<td>130</td>
<td>1.9</td>
</tr>
<tr>
<td>Europium</td>
<td>1600</td>
<td>207</td>
</tr>
<tr>
<td>Gadolinium</td>
<td>150</td>
<td>11</td>
</tr>
<tr>
<td>Terbium</td>
<td>900</td>
<td>495</td>
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<tr>
<td>Dysprosium</td>
<td>170</td>
<td>235</td>
</tr>
<tr>
<td>Holmium</td>
<td>750</td>
<td>38</td>
</tr>
<tr>
<td>Erbium</td>
<td>100</td>
<td>39</td>
</tr>
<tr>
<td>Thulium</td>
<td>1500</td>
<td>800</td>
</tr>
<tr>
<td>Ytterbium</td>
<td>325</td>
<td>24</td>
</tr>
<tr>
<td>Lutetium</td>
<td>1800</td>
<td>894</td>
</tr>
<tr>
<td>Yttrium</td>
<td>44</td>
<td>5.45</td>
</tr>
</tbody>
</table>
REEs is a “Plural” Term

Relative REE Concentration by Coal Basin

- Northern Appalachia
- Central Appalachia
- None Given
- West/Northwest
- Southern Appalachia
- Illinois Basin
- Gulf Lignite
- Mountain Pass
REEs is a “Plural” Term

Relative REE Concentration by Coal Basin

Ore deposits, like Mnt. Pass are concentrated in the “least valuable” REE’s.
Fire Clay Coal Sample

Contained Value of REEs in 1 Ton of Material

- Pessimistic Prices (2014)
- Historic Average (Before 2010)
- Optimistic Prices (2011)

<table>
<thead>
<tr>
<th>Material</th>
<th>Silver: $16</th>
<th>Copper: $27</th>
<th>Gold: $30</th>
<th>Zinc: $60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fine Reject</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Middlings</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clean Coal</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feed</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$/ton of Feed
Effect of Additional Coal Recovery

Contained Value of REEs in 1 Ton of Material

- **Fine Reject**
  - Historic Average
  - Low Price Scenario
  - Optimistic Prices

- **Middlings**
  - Historic Average
  - Low Price Scenario
  - Optimistic Prices

$/ton of Feed

REE Recovery
Additional Coal Recovery
Outline

- Background
- REE Value
- REE Forms in Coal
  - Minerals
  - Ion Substitution
  - Organic Association
- REE Concentration
REE Forms in Coal

- Mineral association
  - monazite \((\text{Ce, La, Pr, Nd, Th, Y})\text{PO}_4\)
  - xenotime \(\text{YPO}_4\)
  - bastnaesite \((\text{Ce, La})\text{CO}_3\text{F}\)
  - other

- Ion substitution in clay

- Organic association
RE mineral particles have a top size of around 10 microns and a bottom size of around 150 nm.
REE Minerals in Coal

- Ce + La + Nd = 36.7%
- High phosphorus content indicates nearly pure monazite mineral
- Confirmed by TEM.
REE Substitution

- Ionic radii decreases with increasing atomic weight.
- RE ions adsorbed in interlayer regions of clay minerals.
- RE ions are more hydrated in solution.
- Hydration Energy $>>$ Electrostatic Energy
- NaCl or $(NH_4)_2SO_4$
Outline

✓ Background
✓ REE Value
✓ REE Forms in Coal
  ● Minerals
  ● Ion Substitution
  ● Organic Association
✓ REE Concentration
REE Density Partitioning

**Fire Clay Coal**

- **REE Content (ppm)**
- **Specific Gravity**

**Eagle Coal**

- **REE Content (ppm)**
- **Specific Gravity**
REE Concentration Considerations

- **Coarse reject streams**
  - Uneconomical to crush and grind the entire material.

- **The lowest density fractions**
  - Uneconomical to crush and grind the entire material.

- **Ultrafine waste processing stream**
  - Least amount of energy required for liberation purposes.

- **The 1.60 x 2.00 SG fraction**
  - Typically rejected to meet coal quality specs
  - Typically ~ 5% to 10% of total plant feed.
  - Crushing and grinding liberates both coal and RE minerals.
  - Heavy REE concentrations are significant.
Feed Stocks Evaluated

- **Coal Sources**
  - Fire Clay
  - West Kentucky No. 13
  - Lower Kittanning

- **Process Streams**
  - Thickener Underflow
  - Middlings
  - Coarse Reject
Hydrophobic Hydrophilic Separation (HHS)

- **Step I**
  - Hydrophobic particles are transferred to a hydrophobic liquid
    - Spontaneous process

- **Step II**
  - Hydrophobic particles are separated from hydrophobic liquid
    - Solid/liquid separation
    - Vaporization/condensation
  - Spent hydrophobic liquid is recycled

\[ \Delta G_t < 0 \quad \Delta G_e > 0 \]
### HHS REE Concentration

**Feed**
- REE = 346 ppm

**HHS Rougher**
- Rougher Tails
  - REE = 229 ppm

**HHS Cleaner**
- Cleaner Conc
  - REE = 9,539 ppm

**Cleaner Tails**
- REE = 542 ppm

**REE Assays (ppm)**

<table>
<thead>
<tr>
<th>Process Stream</th>
<th>Ash (%)</th>
<th>REE Assays (ppm)</th>
<th>Mass Yield (%)</th>
<th>REE Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ash</td>
<td>Whole Mass</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Basis</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cleaner Concentrate</td>
<td>48.7</td>
<td>9539</td>
<td>4644</td>
<td>1.8</td>
</tr>
<tr>
<td>Cleaner Tails</td>
<td>90.0</td>
<td>542</td>
<td>487</td>
<td>8.3</td>
</tr>
<tr>
<td>Rougher Tails</td>
<td>91.4</td>
<td>229</td>
<td>210</td>
<td>89.8</td>
</tr>
<tr>
<td>Feed</td>
<td>90.5</td>
<td>346</td>
<td>313</td>
<td>100.0</td>
</tr>
</tbody>
</table>
**Objective:**
To determine ion-exchangeable REE in coal refuse.

**Conditions:**
Leaching Solution: 1% Nitric Acid (pH =1.0)
Temperature: 80 °C
Solid Concentration: 1%~5%
Analytical Method: ICP-OES

**Variable:**
Leaching Time
### Fire Clay Middlings

<table>
<thead>
<tr>
<th>P80 (microns)</th>
<th>Total REE Recovery (%)</th>
<th>LREE Recovery (%)</th>
<th>HREE Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.7</td>
<td>83.7</td>
<td>86.9</td>
<td>64.8</td>
</tr>
<tr>
<td>7.3</td>
<td>84.3</td>
<td>87.7</td>
<td>65.0</td>
</tr>
<tr>
<td>6.5</td>
<td>83.6</td>
<td>87.1</td>
<td>63.2</td>
</tr>
<tr>
<td>5.0</td>
<td>82.3</td>
<td>85.9</td>
<td>62.1</td>
</tr>
<tr>
<td>0.9</td>
<td>82.0</td>
<td>86.2</td>
<td>59.2</td>
</tr>
</tbody>
</table>
Recent REE Concentration Results

Concentration Ratio = 98
## Recent REE Concentration Results

### Light Rare Earth Element Content (ppm)

<table>
<thead>
<tr>
<th>Stream</th>
<th>Sc</th>
<th>Sm</th>
<th>La</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td>21</td>
<td>12</td>
<td>60</td>
<td>135</td>
<td>19</td>
<td>53</td>
</tr>
<tr>
<td>Product</td>
<td>34</td>
<td>2063</td>
<td>3834</td>
<td>16228</td>
<td>1723</td>
<td>7446</td>
</tr>
<tr>
<td>Ratio</td>
<td>2</td>
<td>179</td>
<td>64</td>
<td>121</td>
<td>89</td>
<td>140</td>
</tr>
</tbody>
</table>

### Heavy Rare Earth Element Content (ppm)

<table>
<thead>
<tr>
<th>Stream</th>
<th>Y</th>
<th>Eu</th>
<th>Gd</th>
<th>Tb</th>
<th>Dy</th>
<th>Ho</th>
<th>Er</th>
<th>Tm</th>
<th>Yb</th>
<th>Lu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td>32</td>
<td>2</td>
<td>10</td>
<td>1</td>
<td>6</td>
<td>2</td>
<td>6</td>
<td>1</td>
<td>4</td>
<td>NA</td>
</tr>
<tr>
<td>Product</td>
<td>1200</td>
<td>173</td>
<td>1283</td>
<td>3</td>
<td>935</td>
<td>112</td>
<td>269</td>
<td>114</td>
<td>7</td>
<td>20</td>
</tr>
<tr>
<td>Ratio</td>
<td>37</td>
<td>99</td>
<td>127</td>
<td>4</td>
<td>161</td>
<td>74</td>
<td>48</td>
<td>94</td>
<td>2</td>
<td>NA</td>
</tr>
</tbody>
</table>
Summary

- REEs exist in mineral and ion exchange form in high rank coals with compositions of each varying significantly.
- RE minerals of monazite, xenotime and bastnasite have been identified with grain sizes from a couple hundred nanometers to ten microns.
- Thickener underflow and middlings material offers an excellent opportunity for coal and REE recovery.
- HHS process has successfully concentrated REE minerals from 346 ppm to 9,539 ppm.
- Solvent extraction produced a REE oxide concentrate containing 35,443 ppm.