Feasibility of Recovering Rare Earth Elements from Thickener Underflows

by

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2019 Project Review Meeting
for Crosscutting Research for Rare Earth Elements
April 9-11, 2019
Omni William Penn Hotel, Pittsburgh, PA
Analysis of Channel Samples

Fire Clay Coal Seam

Total REE Content (ppm, dry whole sample basis)
H vs. L REE Ratio

![Graph showing the H vs. L REE Ratio with data points for different plants indicated by markers of various shapes and colors. The x-axis represents Ash Content (% dry), and the y-axis represents HREE/LREE Ratio.]
REEs are mostly associated with kaolinite

- 10.9 MM tons at 500 ppm cut-off grade
REE Grades in Kaolinite
(*Calculated, Bryan et al. 2015*)

- REE grades on clay are 5-6 times higher than whole coal.
South China
- “Weathered crust elution-deposited rare earth ore”
- 0.05-0.3% REEs
- Physisorbed by double-layer force

Low-cost extraction process
- Desorbed by ion-exchange
- Precipitated by oxalic acid and roasted to REOs.

>80% of the world’s HREEs
>35% of total Chinese REE production
IACs in US?

*Bern et al, J. Geochemical Exp. 172, 29 (2017)*

Liberty Hill, South Carolina

Stewartsville, Virginia
Upper Kittanning Coal, PA

Ion-Exchange Leaching

- Sample A
  - Top of the coal seam

- Sample B
  - Just below Sample A

595x10 µm sample in 1 M (NH₄)₂SO₄
1 hr contact time
Mineral Matter in Coal: A Rich Source of HREEs
(Serendin and Dai, 2013)

HREEs have higher adsorbabilities on clay than LHRRs.
Fine Coal Cleaning in US

>4 billion tons in impoundments
Thickener/Impoundment
Simple Approach

- **Feed**
  - Plant Fines
  - Pond Fines
  - Micronized Middlings

- **HHS**
  - Coal Recovery and Drying
  - Low-Ash Dry Coal

- **HHS and/or Flotation**
  - REMs Concentrate

- **Ion-Exchange Leaching (\& Solvent Extraction)**
  - Rare Earth Oxide

- **Product**

![Graph](image_url)

- REE Recovery
- Additional Coal Recovery

Optimistic Prices

- Fine Reject
- Middlings
- Historic Average
- Low Price Scenario

$\text{$/ton of Feed}$
HHS Pilot Plant

No binder
Leatherwood Thickener U/F

REE Recovery (%) vs REE concentration (Ash basis, ppm)

REE Recovery (%) vs REE concentration (ash basis, ppm)

d_{80} = 5.6 \mu m
## Artificial Ores

- **Chalcopyrite \( (d_{80} = 4 \, \mu m) \)**

<table>
<thead>
<tr>
<th>Feed</th>
<th>Tailings</th>
<th>Concentrate</th>
<th>Cu Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grade (%Cu)</td>
<td>Two-Liquid Flotation</td>
<td>HHS&lt;sup&gt;1&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>22.07</td>
<td>0.06</td>
<td>27.8</td>
<td>34.11</td>
</tr>
<tr>
<td>12.82</td>
<td>0.18</td>
<td>24.3</td>
<td>34.14</td>
</tr>
<tr>
<td>4.18</td>
<td>0.06</td>
<td>22.27</td>
<td>33.86</td>
</tr>
</tbody>
</table>

- **Monazite \( (d_{80} = 3 \, \mu m) \)**

<table>
<thead>
<tr>
<th>Products</th>
<th>Weight</th>
<th>REE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td>Grade</td>
</tr>
<tr>
<td>Conc.</td>
<td>3.14</td>
<td>62.57</td>
</tr>
<tr>
<td>Tail</td>
<td>96.86</td>
<td>0.15</td>
</tr>
<tr>
<td>Feed*</td>
<td>100.00</td>
<td>2.11</td>
</tr>
</tbody>
</table>

<sup>1</sup> HHS: Hydroxy-Hydroxy-Sulphate flotation
# Ion-Exchange Leaching

- **Thickener U/F**
  - **At 50°C**

<table>
<thead>
<tr>
<th>Lixiviant</th>
<th>Conc. (moles/l)</th>
<th>Feed</th>
<th>Solid Residue</th>
<th>REE Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ash (%wt)</td>
<td>REE (ppm)</td>
<td>Wt. (g)</td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>0.5</td>
<td>92.03</td>
<td>234.58</td>
<td>30.0</td>
</tr>
<tr>
<td>A</td>
<td>0.5</td>
<td>92.03</td>
<td>234.58</td>
<td>30.0</td>
</tr>
<tr>
<td>B</td>
<td>0.5</td>
<td>92.03</td>
<td>234.58</td>
<td>30.0</td>
</tr>
</tbody>
</table>

- **Artificial Ion-Exchange Clay at 25°C**

<table>
<thead>
<tr>
<th>Lixiviant</th>
<th>Conc. (moles/l)</th>
<th>Feed</th>
<th>Solid Residue</th>
<th>REE Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>REE (ppm)</td>
<td>Wt. (g)</td>
<td>REE (ppm)</td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>0.5</td>
<td>1812.5</td>
<td>15.0</td>
<td>726.8</td>
</tr>
<tr>
<td>A</td>
<td>0.5</td>
<td>1812.5</td>
<td>15.0</td>
<td>932.9</td>
</tr>
<tr>
<td>B</td>
<td>0.5</td>
<td>1812.5</td>
<td>15.0</td>
<td>1235.9</td>
</tr>
<tr>
<td>C</td>
<td>0.05</td>
<td>1812.5</td>
<td>15.0</td>
<td>643.3</td>
</tr>
</tbody>
</table>
Problem & Solution

- Colloidal phase

- Solution
XPS Spectra of La on Artificial IAC

(a) La(OH)₃

(b) La₂O₃

(c) LaCl₃

(d) La Clay
XPS Spectra of a Mineral Matter of a Middling Sample

![XPS Spectra Diagram](image_url)
LTI Project (2014)
- Audited 15 coal beneficiation plants in Central Appalachia
- Fine coal refuse produced 1,313 TPY REE.

Thus, each of the 15 plants produced 87 TPY REE.

Multiplying this number with 248, the number of operating plants, gives 21,700 TPY

Assuming 50% recovery, US beneficiation plants can produce 10,850 TPY REE.

In 2018, US consumed 9,500 tons.
Comparison with Other REE Sources

US Coal Thickener Underflow
HHS Mobile Pilot-Plant
Clay minerals in coal are rich sources of heavy REEs.

Clay minerals congregate to thickener underflows.

Heavy and critical REEs can be readily recovered at low cost and with minimal disruption.
- produce salable coal from waste streams
- ~4 billion tons of pond fines can be an additional source

XPS studies showed evidence for ion-adsorption clays in US coal byproducts
- most likely in colloidal phase
- makes IX leaching difficult
- characterization and extraction studies ongoing