Recovery of Rare Earth Elements from Coal Byproducts: Characterization and Laboratory-Scale Separation Tests

by

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Objectives

- To overcome the challenges in extracting rare earth elements (REEs) from coal byproducts:
  - Low concentration
  - Low separation efficiency

- Approach
  - Extract REEs from the kaolinite present in fine coal refuse by ion-exchange leaching.
  - Extract REEs from the monazite co-present in the refuse to increase the recovery and separation efficiency.
REEs in Coal

Seredin and Dai (2012)

\[ C_{out} = \frac{(Nd + Eu + Tb + Dy + Er)}{(Ce + Ho + Tm + Yb)} \times \frac{\sum REY}{\sum REY} \]

Ekmann and Skone (2013)
REEs are in mineral matter
- 80% from kaolinite

REEs partition to kaolinite

USGS Coal Data Base
Bryan *et al.* (2015)
A Model Based on X-Ray Absorption Studies

Boris et al. (Nature, 2020)

• Basal surfaces: permanent surface charge (outer-sphere complexes)
• Edge surfaces: pH-dependent surface charge (inner-sphere complexes)
Laser-Ablation ICP-MS Analysis of a Single Kaolinite Particle

Before and After Ammonium Sulfate Treatment (Mukai et al., Nature, 2020)

<table>
<thead>
<tr>
<th>Kaolinitic particle01</th>
<th>Before treatment</th>
<th>After treatment</th>
<th>Desorption ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y (ppm)</td>
<td>74.3</td>
<td>23.6</td>
<td>68.2</td>
</tr>
<tr>
<td>La (ppm)</td>
<td>61.4</td>
<td>16.2</td>
<td>73.6</td>
</tr>
<tr>
<td>Ce (ppm)</td>
<td>629</td>
<td>324</td>
<td>48.5</td>
</tr>
<tr>
<td>Pr (ppm)</td>
<td>24.1</td>
<td>7.30</td>
<td>69.8</td>
</tr>
<tr>
<td>Nd (ppm)</td>
<td>97.1</td>
<td>32.4</td>
<td>66.6</td>
</tr>
<tr>
<td>Sm (ppm)</td>
<td>28.2</td>
<td>9.15</td>
<td>67.6</td>
</tr>
<tr>
<td>Eu (ppm)</td>
<td>5.41</td>
<td>2.00</td>
<td>63.1</td>
</tr>
<tr>
<td>Gd (ppm)</td>
<td>26.3</td>
<td>8.08</td>
<td>69.2</td>
</tr>
<tr>
<td>Tb (ppm)</td>
<td>4.04</td>
<td>1.45</td>
<td>64.2</td>
</tr>
<tr>
<td>Dy (ppm)</td>
<td>23.1</td>
<td>10.2</td>
<td>55.6</td>
</tr>
<tr>
<td>Ho (ppm)</td>
<td>4.04</td>
<td>1.64</td>
<td>59.5</td>
</tr>
<tr>
<td>Er (ppm)</td>
<td>11.7</td>
<td>4.88</td>
<td>58.4</td>
</tr>
<tr>
<td>Tm (ppm)</td>
<td>1.72</td>
<td>0.74</td>
<td>56.9</td>
</tr>
<tr>
<td>Yb (ppm)</td>
<td>12.4</td>
<td>5.73</td>
<td>53.9</td>
</tr>
<tr>
<td>Lu (ppm)</td>
<td>1.68</td>
<td>0.93</td>
<td>45.0</td>
</tr>
<tr>
<td>LREE (ppm)</td>
<td>845</td>
<td>391</td>
<td>53.7</td>
</tr>
<tr>
<td>LREEa (ppm)</td>
<td>216</td>
<td>67.1</td>
<td>69.0</td>
</tr>
<tr>
<td>HREE (ppm)</td>
<td>85.0</td>
<td>33.7</td>
<td>60.4</td>
</tr>
<tr>
<td>REE (ppm)</td>
<td>985</td>
<td>448</td>
<td>54.5</td>
</tr>
<tr>
<td>REEa (ppm)</td>
<td>301</td>
<td>101</td>
<td>66.6</td>
</tr>
<tr>
<td>REY (ppm)</td>
<td>1059</td>
<td>472</td>
<td>55.4</td>
</tr>
</tbody>
</table>

Chinese IAC industry practice
- 40-70% recovery
- 2,000-4,000 REE ores

(Schultze et al., 2017)
Formation and Passivation of Ion-adsorption Clays

- **Weathering of granite**
  - **Feldspar (>65%)**
    - *by meteoric water*
    
    \[
    2\text{KAlSi}_3\text{O}_8 + 2\text{CO}_2 + \text{H}_2\text{O} \rightarrow \\
    \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 4\text{K}^+ + 4\text{HCO}_3^- + 4\text{SiO}_2
    \]
  
  - **REE-bearing accessory minerals**
    - *Liberate Ln$^{3+}$ ions into solution*
    - *Adsorb onto kaolinite surface*
    - *Can be passivated by phosphorous*

Li et al., 2017)

Bryan et al., 2015)
IACs in the U.S.
Foley and Ayuso (2015)

- Stewartsville

- Heling, China
Effect of Phosphor on Ion-Exchange Leaching

- Sanematsu et al. (2015)
- Bern et al. (2017)

PER: ion-exchangeable rare earths

Phosphate minerals scavenge Ln\(^{3+}\) ions from solution during IAC formation.
P content and/or P/TREE ratio may be used to identify promising feedstocks.
- Eastern coals, P/TREE = 1 to 4
- Western coals, P/TREE > 10

Some Appalachian coal seams have nearly negligible P content.

Further investigations will be useful.
Ion-exchange Leaching of La$^{3+}$ from Kaolinite
In the Absence of Phosphate

95% of La$^{3+}$ ions have been removed.
Ion-exchange Leaching of La$^{3+}$ from Kaolinite
In the Presence of Phosphate

18% of La$^{3+}$ ions have been removed.
Passivation of an IAC Sample from South China by Phosphate

![Graph showing recovery percentage for various elements (TREE, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th, U) under different conditions: IACs+P+AS pH4 and IACs+AS pH4. Recovery percentages vary across elements, with some showing higher recovery under specific conditions.]
Ion-exchange Leaching of Upper Kittanning Coal, PA
Rozelle et al. (2016)

- 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
Rare Earth Minerals in Appalachian Coal

HHS Product
REE Recovery from Fine Coal Refuse: New Approach

Fine Coal Refuse

HHS PROCESS for Carbon

Low-Ash Dry Coal

Mineral Matter

HHS PROCESS for REMs

ION-EXCHANGE LEACHING (I) for Clay

Reject

IAC

REM

Monazite Conc. from Beach Sands

ION-EXCHANGE LEACHING (II) for REMs

REEs in Solution

Mixed Rare Earth

Oxalic Acid/Heat

Reject
Hydrophobic-Hydrophilic Separation (HHS) Process


- No lower particle size limit
- No entrainment
- Dry products

- Construction in progress for coal recovery
Monazite Recovery by HHS

- Preliminary test results
  - *Oil washing*

<table>
<thead>
<tr>
<th>Test</th>
<th>Particle Size</th>
<th>Conc Grade, % (Total)</th>
<th>Overall Recovery, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>HHS 4</td>
<td>5.0</td>
<td>0.55%</td>
<td>6.6%</td>
</tr>
<tr>
<td>HHS 8</td>
<td>3.0</td>
<td>0.29%</td>
<td>1%</td>
</tr>
</tbody>
</table>

  - *Water washing*

<table>
<thead>
<tr>
<th>Test</th>
<th>Particle Size</th>
<th>Conc Grade, % (Total)</th>
<th>Conc Grade, % (Dry Ash Basis)</th>
<th>Overall Recovery, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>HHS 4</td>
<td>2.2</td>
<td>6.34%</td>
<td>56.14%</td>
<td>14.2%</td>
</tr>
<tr>
<td>HHS 8</td>
<td>3.0</td>
<td>3.73%</td>
<td>-</td>
<td>4.54%</td>
</tr>
</tbody>
</table>

- Rozelle *et al.* (2019)
  - *DOE report*
Ion-Exchange Leaching of Monazite

- Solubility diagram

- Leaching experiment
  - 50% NaOH, 80°C, 24 hrs, ion-exchange leaching at pH 4

- Model
  - Dissolution of Ln(OH)₄⁺ by H⁺ ions
  - Adsorption of SO₄²⁻ ions via electrostatic force
  - Displacement of Ln⁺⁺ by NH₄⁺ ions

Ion-Exchange Leaching of Monazite
Ion-Exchange vs. Acid Leaching

Kinetics

Ion-Exchange Leaching

Acid Leaching
8. Clay deposit in Stewartsville, VA
10. (yellow) Atlantic coastal plain, monazite from beach sands
Ion-exchange Leaching of IAC
(Chelating Agents to Solubilize at Neutral pH)

$[\text{La}^{3+}]_{\text{TOT}} = 10.00 \, \mu \text{M}$

$[\text{PO}_4^{3-}]_{\text{TOT}} = 10.00 \, \mu \text{M}$

Dissolution of La($\text{PO}_4$)$_3$(s), e.g., monazite and apatite, is thermodynamically possible at neutral pH.

Ethylenediaminetetra(methyleneephosphonic acid) (EDTPO)

$t = 25^\circ \text{C}$
A small amount of NaOH is need due to the co-presence of monazite and passivated IACs in our sample.
Effect of Chelating Agents

- In presence of small amount of LaPO₄(s)
  - 10 µM La³⁺
  - 10 µM PO₄³⁻

- In presence of large amount of LaPO₄(s)
  - 10 µM La³⁺
  - 0.1 mM PO₄³⁻

Remove monazite prior to ion-exchange leaching of passivated IACs!
Summary

- Fine coal refuse has two REE-bearing minerals.
  - Rare earth minerals (monazite)
    - Residual accessory minerals
  - Ion-adsorption clays (kaolinite/halloysite)
    - Passivated by phosphate ions from solution

- Developed an ion-exchange leaching process for monazite.
  - Requires mild operating conditions

- HHS process may be used to increase the contained values and thereby overcome the problems associated with:
  - low REE+Y grades in coal byproducts
  - passivating effects of phosphates
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