REE-Critical Minerals (NETL FWP)
Waste Stream: Ion Exchangeable REE Extraction

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Project Current Status

NETL - RIC Separation Chemistry (Task 3)

Results compared to benchmark:

- **Reduce** in reagent consumption
- Reduction in process steps/complexity: e.g. **no pre-treatment (grinding, floatation) or reduction of solvent separations**
- Reduction in process intensity: **ambient temperature and pressure**

How have project goals changed?:

- Increased focus on maturing technologies:
  - Rapid move to larger scale experiments
  - Validation on representative feedstocks provided from industrial partners
  - Extended engagement with industry for partnership

Industry input/validation:

- Regular communication with industry partners
- Field work and test projects are underway/development with industry partners, and more are planned
Current Mines Targeting Middle Kittanning

- In 2019, 44 mines targeting the Middle Kittanning coal seam produced coal
  - 34 mines in Pennsylvania
  - 3 mines in West Virginia
  - 7 mines in Ohio

- Production at each mine ranged from 601 tons to 4,274,748 tons
  - 32 mines produced more than 10,000 tons
  - 10 mines produced more than 100,000 tons
  - 2 mines produced more than 1,000,000 tons

<table>
<thead>
<tr>
<th>Mine Name</th>
<th>State</th>
<th>Production (Tons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leer Mine</td>
<td>WV</td>
<td>4,274,748</td>
</tr>
<tr>
<td>Sentinel Mine/Leer South Mine</td>
<td>WV</td>
<td>110,6710</td>
</tr>
<tr>
<td>Mine Complex #6 Mine/Buckingham</td>
<td>OH</td>
<td>829,737</td>
</tr>
<tr>
<td>Mine No. 6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acosta Deep Mine</td>
<td>PA</td>
<td>401,848</td>
</tr>
<tr>
<td>North Fork</td>
<td>PA</td>
<td>363,971</td>
</tr>
</tbody>
</table>

Figure: Map of permitted and active coal mines targeting the Middle Kittanning coal seam. Varying data sources for mine production.
Rare Earth Elements: Understanding the resource

- Characterize underclay
- Quantification & benchtop/lab scale to inform future REE extraction techniques & optimal candidate feedstocks with salable REE concentrations
- Goal: upscale to the field/commercialization

Up to 50% of coal mined is left on the ground as waste.

Photo from https://www.flickr.com/photos/piedmont_fossil/5710646413
### REEs in Coal-Associated (Middle Kittanning) Clays

<table>
<thead>
<tr>
<th>Sample Designation</th>
<th>Coal Seam</th>
<th>General Locale</th>
<th>Total C (ppm)</th>
<th>Total S (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UC-02</td>
<td>Middle Kittanning</td>
<td>WV, 1460 ft depth</td>
<td>22,767</td>
<td>1,293</td>
</tr>
<tr>
<td>UC-12</td>
<td>Middle Kittanning</td>
<td>WV, underground mine</td>
<td>9,765</td>
<td>36,450</td>
</tr>
<tr>
<td>UC-14</td>
<td>Lower Kittanning</td>
<td>PA, surface pit mine</td>
<td>1,370</td>
<td>224</td>
</tr>
<tr>
<td>UC-15</td>
<td>Middle Kittanning</td>
<td>PA, surface pit mine</td>
<td>17,600</td>
<td>12,300</td>
</tr>
</tbody>
</table>

Mineral composition from semi-quantitative XRD:
- **Major (Ma) (>50%)**: Intermediate (In) (25–50%)
- **Minor (Mn) (5–25%)**: Trace (Tr) (<5%)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>UC-2</th>
<th>UC-12</th>
<th>UC-14</th>
<th>UC-15</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>NON-CLAYS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quartz</td>
<td>Mn</td>
<td>In</td>
<td>Ma</td>
<td>Mn</td>
</tr>
<tr>
<td>Pyrite</td>
<td></td>
<td>Tr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Marcasite</td>
<td></td>
<td>Tr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluorapatite</td>
<td></td>
<td>Tr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plag</td>
<td></td>
<td>Tr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbonate (calcite/siderite)</td>
<td>In</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K-spar</td>
<td>Tr</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ilmenite</td>
<td>Tr</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>CLAYS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Halloysite</td>
<td>Mn</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kaolinite</td>
<td>Mn</td>
<td>In</td>
<td>Mn</td>
<td>Mn</td>
</tr>
<tr>
<td>Smectite</td>
<td>Mn</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Muscovite</td>
<td>In</td>
<td>Mn</td>
<td>Ma</td>
<td></td>
</tr>
<tr>
<td>Illite</td>
<td>Mn</td>
<td></td>
<td>In</td>
<td></td>
</tr>
<tr>
<td><strong>Total clays</strong></td>
<td>57.3</td>
<td>65.6</td>
<td>57.7</td>
<td>72.5</td>
</tr>
</tbody>
</table>
REE in Sedimentary Deposits

Primary REE minerals

<table>
<thead>
<tr>
<th>Trace minerals in underclays</th>
<th>Secondary minerals/colloids/adsorbed components</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite (La, Ho, Dy, Lu, Yb, Er)</td>
<td>crandallite</td>
</tr>
<tr>
<td>Chalcopyrite (La, Nd)</td>
<td>apatitic minerals</td>
</tr>
<tr>
<td>Ti-oxide (Lu, Er, Nb)*</td>
<td></td>
</tr>
<tr>
<td>Zircon (Lu, Sc)*</td>
<td></td>
</tr>
<tr>
<td>Siderite</td>
<td></td>
</tr>
<tr>
<td>Galena</td>
<td></td>
</tr>
<tr>
<td>Fe-oxide (Er)</td>
<td></td>
</tr>
<tr>
<td>Monazite/ rhabdophane (La, Ce, Nd, Gd)</td>
<td></td>
</tr>
<tr>
<td>Xenotime/ churchite (Y, Sm, Eu, Gd, Dy, Er, Tm, Yb)</td>
<td></td>
</tr>
</tbody>
</table>
## REEs in Coal-Associated (Middle Kittanning) Clays

<table>
<thead>
<tr>
<th>Sample Designation</th>
<th>REY ppm</th>
<th>Sc ppm</th>
<th>Co ppm</th>
<th>Ni ppm</th>
<th>Cu ppm</th>
<th>GdN/LaN</th>
<th>YbN/LaN</th>
<th>Y*</th>
</tr>
</thead>
<tbody>
<tr>
<td>UC-02</td>
<td>276</td>
<td>18</td>
<td>20</td>
<td>24</td>
<td>20</td>
<td>1.1</td>
<td>1.2</td>
<td>1.04</td>
</tr>
<tr>
<td>UC-12</td>
<td>281</td>
<td>24</td>
<td>44</td>
<td>107</td>
<td>107</td>
<td>2.3</td>
<td>1.6</td>
<td>1.05</td>
</tr>
<tr>
<td>UC-15</td>
<td>713</td>
<td>36</td>
<td>21</td>
<td>68</td>
<td>65</td>
<td>6.2</td>
<td>2.8</td>
<td>1.17</td>
</tr>
<tr>
<td>UC-14</td>
<td>219</td>
<td>20</td>
<td>8</td>
<td>28</td>
<td>18</td>
<td>1.2</td>
<td>1.4</td>
<td>1.11</td>
</tr>
</tbody>
</table>

- Middle Kittanning clay materials from directly below the coal seam show a strong middle-REE enrichment.
- In the case of UC-15 MKT Central PA surface mine sample, middle-REE enrichment can account for a total REE content of 713 ppm.

*Samples normalized to Upper Continental Crust

MKT = Middle Kittanning
LKT = Lower Kittanning
Non-Provisional Application filed, S-150,861, September 2020.


Coal waste & underclay as a feedstock

- **Mild organic acid**: less hazardous chemicals than conventional approaches
- Targets accessible ion-exchangeable REE species & mineral surfaces at ambient pressure/temperature
- **Up to 30% of REE** without extracting other gangue materials, reducing chemical costs and downstream processing requirements

Multiple Potential Applications:
- *Ex situ heap leach recovery & plant processing* from coal mining waste and co-mined materials
- *In situ recovery* from undisturbed sedimentary rock layers, open pits, or underground mines
• Determine efficacy of citrate solutions in extracting sorbed lanthanides on clay surfaces, using a synthetically prepared La-sorbed clay
• Isolate the effect of ligand-promoted extraction from ion exchange
• Isolate effect of citrate speciation (with NaOH buffer)
• Compare efficacy of citrate solutions to (NH₄)₂SO₄ and Na₂SO₄
Waste Coal heap leaching applications

Upscaled (~10kg) column experiments

- Packed columns with Middle Kittanning (UC-12) underclay with a 0.1 M citric acid/sodium citrate solution buffered at pH 5 (1:1.2 leach ratio)
- ~4% TREY
- Similar extractions levels obtained using ammonium sulfate solution
- 30-35% Co; 20% Ni; 10-13% Cu extracted in both the citrate and ammonium sulfate
- Sharp drop in pH $\rightarrow$ pyrite oxidation or other Fe sulfide phase.

![Graph showing extraction levels of various elements](image)
0.1M sodium citrate solution (pH 5) will be continually mixed with pulverized underclay for up to 48 hours

10 kg underclay – 100 L solution (1:10)

3% TREY

~ 8% Gd and Tb <2% La, Ce, Pr, and Nd

24% Co; 14% Ni; 15% Cu; 18% Zn

Low recovery, but may need longer residence time or different water amount

- Experiment being repeated for longer duration (May 2021)
In-situ applications: underclay-coal partings

Flow-through & rocking autoclave experiments

- Simulated downhole testing ranging from 20 min to 30 days; limited extraction <2.5%
- 2-7 days for maximum REY extraction (lithology dependent)
- Citrate solutions show tendency towards heavy REE recovery relative to light REE
- Recycling solution will play a role to improve recovery
Waste Coal optimization

Organic acid by pH

- Scoping tests were conducted on a Middle Kittanning underclay sample (West Virginia) to isolate a mechanism of REE (and other critical metal) extraction
- Maximum REE extraction of ~30% at pH 2
Extraction liquids were relatively more enriched in MREE/HREEs

- 70-80% extraction for Gd and Tb at pH ~2
- Co-extraction of ~70% Co, ~40% Ni, ~25% Cu
Waste Coal optimization

Conventional mineral acid recovery

- Optimal solution composition (i.e., REE and critical metal extraction against gangue element). Mildly acidic solutions (pH 2-3) were found to have comparable performance in REE compared to concentrated acids (Middle Kittanning).

- \( \text{H}_2\text{SO}_4 \) or HCl extracted **32% and 37%** of the REEs

- 100%* Co, ~65% Ni, ~50% Cu

- Nearly 4-5x amount of Al and Fe in concentrated acids compared to mildly acidic solutions
Citrate recycling: Sorbent

Synergistic effort BIAS Sorbent to Enable Solution Recycling

- REE concentrates of 3.6 wt% (~70% REE) from 300 ml and <1.4 wt% (<30% REE) from 1 L citrate-underclay PLS feedstock from BIAS 181D packed beds
  - Citrate concentration issue (ion-exchange/sorbent pairing)

- Successful coupling of these technologies will allow acid recycling, dramatically reducing operating costs

- 30 g of 181D per L of leachate may be required (10x more)

- Additional testing required
EY20 Field work (PA, WV)

- Fairmont repository / waste rock facility.
  - Isabella refuse site – Fayette County, PA
  - 9 samples collected from repository and gob piles
  - Selected based on trace metal content and Y (pXRF)

- Mine wall underclay sampled (Middle and Lower Kittanning) from PA surface mine

- Goal: clarify vertical heterogeneity
  AHA/approval was granted; mine access request pending
  Evaluating alternative feedstock sources.
Cash Flow Summary (Ex-situ Heap Leaching)

- Variable operating expenses are lower than the maximum basket price scenario at 35% extraction efficiency with a total expected net revenue of $66 M/year
- Facility throughput assumes Appalachian waste reserves extracted over 25-year period
- Maximum Basket Price Assumption: $1,100/kg of REE

<table>
<thead>
<tr>
<th>Parameter</th>
<th>5% Recovery</th>
<th>12% Recovery</th>
<th>35% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Variable Operating Expenses – Recycling Scenario, 10% L:S</td>
<td>$5,000/kg</td>
<td>$2100/kg</td>
<td>$770/kg</td>
</tr>
<tr>
<td>Fixed Costs</td>
<td>$190/kg</td>
<td>$79/kg</td>
<td>$27/kg</td>
</tr>
<tr>
<td>REE net revenue</td>
<td>-$4,100/kg</td>
<td>-$1,100/kg</td>
<td>$300/kg</td>
</tr>
<tr>
<td>REE production</td>
<td>33 Ton/yr</td>
<td>78 Ton/yr</td>
<td>230 Ton/yr</td>
</tr>
</tbody>
</table>
Modeling pH Dependency of Recovery

Based on experimental Citrate and Sodium Citrate solutions

• Wastewater disposal/chemical costs increase with lower pH

• REE extraction efficiency outpaces operational costs with increasing acid consumption.
  ◦ Basket prices are relatively constant.

• Economics will depend on further optimization

![Graph showing pH dependency of recovery costs](image-url)
Next Steps
Coal waste & underclay

Use TEA screening results to target improvements to extraction plans to reduce operational costs

- Maximizing extraction yields
  - Optimize heap depth, crush size (hydraulic conductivity)
  - Optimize residence time of solution, optimize the level of saturation
- Isolate chemical controls on extraction and identify REE phase extraction selectivity to develop feedstock criteria of future targets
  - i.e. water soluble, ion absorbed/exchangeable, Mn/Fe oxides, sulfides, and residual.
- Demonstrate REE separation from pregnant leachate via mineralization/precipitation and conversion to REE-oxides or chloride precipitates.
- Evaluate Critical Metal co-extraction (Cu, Co, Ni, etc.)
- Demonstrate feasibility of ex-situ extraction at next largest scale
Collaboration & Future Field Work

Coal waste & underclay

Industry partnerships are crucial for scale up demonstrations of underclay targets.

- Waste coal processing/characterization of the Fairmont Repository and GOB piles
- Identify target mines with characteristics that align with necessary feedstock parameters for potential field site.

**PHASE I:**
- Develop industrial CRADA
- Constrain real world heap leach heterogeneity etc.
  - (e.g. core drilling or LIDAR)
  - Constrain heap leach parameters on benchtop
- Preliminary site coordination and planning for operations (material supply/waste disposal)
- Go/no go: access/permitting to proceed with PHASE II

**PHASE II:**
- Develop field test to demonstrate that NETL developed technology can work in the field and be scalable.
  - EY22 Execute preliminary testing to deploy extraction methods beyond the lab scale
  - Determine field test scale, optimize controls for environmental conditions
  - Contingent upon achieving benchmarks for extractability and industrial partnership
Acknowledgements

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Sources of Mine Production Data

Coal Data Browser - List of mines for all coal, total, Appalachia Northern, all mine statuses [WWW Document], n.d. URL https://www.eia.gov/coal/data/browser/#/topic/38?agg=0.2,1&rank=g&geo=00000000000001&mntp=g&freq=A&start=2001&end=2019&ctype=map&ltype=pin&rtype=b&pin=&rse=0&maptype=0&datecode=2019


