Demonstration of Scaled-Production of Rare Earth Oxides and Critical Materials from U. S. Coal-Based Sources

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Xinbo Yang, UK
Michael Free, UU
Aaron Noble, VT
Wencai Zhang, VT

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Period of Performance: 10/1/2019–6/30/2022
NETL Program Manager: Charles Miller

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Project Organization Chart

Principal Investigator
(Rick Honaker)

University of Kentucky Research Foundation

Project Management
Plant Management
Circuit Optimization
Pyrite Recovery Circuit
Roasting/Leaching
Summary Report

Equipment Procurement
Equipment Install
Automation & Control
Roasting Design
Solvent Extraction
Summary Report

Bioreactor Testing
Bioreactor Design
Leach Recovery Optimization
Selective Precipitation

XRT Sorting
Systems Analysis
Techno-Econ Analysis
Summary Report

Selective Precipitation
Critical Materials Circuit
Roasting
Refining

Corporate Members
Alliance Coal
Kentucky River Properties
Mineral Separation Technologies

University of Kentucky
Rick Honaker

University of Kentucky
Josh Werner

University of Utah
Michael Free

Virginia Tech
Aaron Noble

Virginia Tech
Wencai Zhang
• Demonstration of scaled production of high purity rare earth oxide mix from coal refuse sources using innovative technologies that will reduce cost and improve environmental outcomes.

• Performance objectives:
  • >90% REO mix purity
  • 200 g/day product rate
  • Co, Mn and Sc products >2% purity
  • Cost reduction per kg of REO produced by 50%

• Bituminous coarse coal refuse sources will be the primary feedstock.

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<th>Element</th>
<th>Content (ppm)</th>
<th>Resource (tonnes)</th>
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<td>V</td>
<td>140</td>
<td>12557</td>
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Project Justification Statement

Economic Issues Being Addressed

• Prior analyses have shown that chemical costs (acid and base) are a major impediment to an economically viable process.

• Low feed grade, poor leaching recovery, low PLS concentration, and waste disposal are other concerns of note.

OPEX breakdown for a hypothetical coal-based REE recovery facility.
Associated Mineral Advantage

- Coal is associated with minerals that provide natural acidity and alkalinity:
  - Pyrite
  - Calcite
- Both minerals have physical properties that allow low cost recovery and concentration.

<table>
<thead>
<tr>
<th>Size Fraction (mesh)</th>
<th>Weight (%)</th>
<th>Major Minerals (%)</th>
<th>Pyrite</th>
<th>Silica</th>
<th>Calcite</th>
<th>Kaolinite</th>
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<td>200 x 325</td>
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<td>12.2</td>
<td>35.4</td>
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<td>-325</td>
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<td>25.5</td>
<td>23.1</td>
<td>45.6</td>
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</table>
• Utilize pre-concentration sorting to maximize REE concentration entering the leaching tanks.

• Utilize roasting to improve leach recovery and reduce acid consumption.

• Utilize low cost-physical separation to isolate acid-generating and base-generating constituents.

• Utilize bio-oxidation to maximize acid production.

• Integrate process components in a novel flowsheet configuration to maximize technical and economic outcomes.
# Project Schedule: Budget Period 1

(Four Month No-Cost Time Extension: BP1 end date April 2021)

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<td>J</td>
<td>F</td>
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</table>

### DOE Required Tasks

1. Project Management & Planning*
2. Financial Plan for Commercialization*
3. Techno-Economic Assessment*
4. Provide Split Samples*
5. Feasibility Study*

### Laboratory Support Tasks

6. Optimization of Physical Separations (crush, grind, sort, calcite float)
7. Optimization of Acid Generation (pyrite recovery, bioreduction)
8. Optimization of Roasting & Leaching
9. Optimization of REE Recovery (selective precip and/or SX)
10. Optimization of CM Recovery (Co/Mn/Sc Precip or SX)

### Pilot-Scale Tasks

11. Environmental Monitoring and Management
12. Pilot Plant Upgrades and Modification (Design, Bidding, procurement, fabrication, installation)
13. Feedstock Collection and Preparation
14. Pilot Plant System Shakedown
15. Pilot Plant Operation and Continuous Improvement
16. Operational Cost Analysis, Refinement and Optimization
17. Secondary Feedstock Testing
18. Decommissioning and Disposition

* = DOE Required Task
X = one month delay in activity
### Project Schedule: Budget Period 2
(Project end date June 30, 2022)

#### DOE Required Tasks
1. Project Management & Planning*
2. Financial Plan for Commercialization*
3. Techno-Economic Assessment*
4. Provide Split Samples*
5. Feasibility Study*

#### Laboratory Support Tasks
6. Optimization of Physical Separations (*crush, grind, sort, calcite float*)
7. Optimization of Acid Generation (*pyrite recovery, bioreduction*)
8. Optimization of Roasting & Leaching
9. Optimization of REE Recovery (*selective precip and/or SX*)
10. Optimization of CM Recovery (*Co/Mn/Sc Precip or SX*)

#### Pilot-Scale Tasks
11. Environmental Monitoring and Management
12. Pilot Plant Upgrades and Modification (*Design, Bidding, procurement, fabrication, installation*)
13. Feedstock Collection and Preparation
14. Pilot Plant System Shakedown
15. Pilot Plant Operation and Continuous Improvement
16. Operational Cost Analysis, Refinement and Optimization
17. Secondary Feedstock Testing
18. Decommissioning and Disposition

* = DOE Required Task

#### Project Month

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</table>

* = DOE Required Task
Physical Separations
Pyrite-Calcite Concentration

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<th>Size Fraction</th>
<th>Weight (%)</th>
<th>Percentage</th>
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<tr>
<td></td>
<td>Pyrite</td>
<td>Silica</td>
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<td>+100 mesh</td>
<td>8.84</td>
<td>6.3</td>
</tr>
<tr>
<td>100 mesh x 200 mesh</td>
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<tr>
<td>200 mesh x 325 mesh</td>
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<td>-325 mesh</td>
<td>32.56</td>
<td>30.1</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
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</table>
### Calcite-Pyrite Circuit Analyses

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density (g/cm³)</th>
<th>Ca (ppm)</th>
<th>Fe (ppm)</th>
<th>Si (ppm)</th>
<th>% Pyrite</th>
<th>% Calcium Carbonate</th>
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</table>
Sulfuric Acid Generation by Biooxidation

- Concentrated pyrite is used as feed to a bio-oxidation reactor.
- Bacteria is used to drive the oxidation reaction converting Fe$^{2+}$ to Fe$^{3+}$.
- Tests have indicated that 0.2M sulfuric acid can be consistently produced with a pH value around 1.0 – 1.2.
- Acid cost reduction is anticipated to be 75% or greater.
The bioreactor was filled with 300ml of stored bioleaching solution containing bacterial culture along with 1L 9K medium that was already prepared to make the total volume to 1.3L in the bioleaching reactor.

Overhead stirrer speed was set up at 680 rpm, and gas flow was set up at 0.5 l/min, which was changed to 0.2 l/min later. After that, when Eh reached to 600mV, pyrite feeding was started.

The pyrite feeding slurry was made with 5 grams of pyrite concentrate (approximately 60% pyrite) and 100ml of 9k medium and was added into the feeding vessel.

The finer feed is associated with a pH decrease.

Figure: Eh and pH values vs. time (most recent)

Figure: (a) Bio-oxidation rate assessment after addition of 5g FeSO₄·7H₂O on 06.23.2020 at Eh 647 mV; (b) overall comparison of bio-oxidation rate for different days and at different Eh values
A new 3L bioreactor was purchased from Chemglass Life Sciences (See Figure), and other accessories, such as the circulating water heating, air injection, and the automatic feeding system, that were connected to the new reactor.

- Overhead stirrer speed was set up at 680 rpm, and gas flow was set up at 0.5 l/min, which was changed to 0.2 l/min later. After that, when Eh reached to 600mV, pyrite feeding was started.
- Other restarting parameters were similar to previous one.

**Bioreactor restarting procedure**

**Figure**: (a) Digital image Bioreactor system; (b) overall setup in action

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**New 3L Bioreactor**

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**Coal Waste Bioleaching**

Two samples of coal waste (Fire Clay coarse refuse roaster feed and WK 13 coarse refuse roaster feed) were tested to evaluate their potential for heap bioleaching using bioleaching solution accumulated from other bioreactors.

REEs concentrations in the leaching samples collected during the leaching process of Fire Clay refuse.

**Figure**: Eh and pH values vs. time (for new 3L bioreactor)

**Figure**: Total REEs concentration vs. time in the (a) Fire Clay refuse leaching test and (b) WK 13 refuse leaching test.
Bio-oxidation Reactor Scaling

3-liter Biooxidation Reactor

250-gallon Biooxidation Reactor

Three 3000-gallon Biooxidation Reactors
Leaching Characteristics of Bio-oxidation Acid

- Leaching performed
- Peak recovery of TREES achievable in short leaching time.
- Prevents Al leaching thus reduce downstream chemical consumption.
- Reduction of Na and Fe indicated the formation of Na-jarosite (XRD confirmed).
- Data comparison between ICP-OES and ICP-MS.

**Leaching condition:** Bioleach Acid, S/L=1/5 (w/v), 75 °C. Solid feed: Dotiki pile minus 1.5-inch, hammer milled, roast at 600 °C 20 minutes. Solid weight gained 12% after 5 hours leaching.
Ce peak occurs at 1 hour, La peak occurs at 30 minutes.
Pr and Nd showed a slightly head down after 90 minutes of leaching.
Light REEs coprecipitation occurred with the formation of gypsum (CaSO4).
Heavy REEs not affected.
REE recovery reached peak at 30-60 minutes, whereas recovered value of REEs and critical elements increased with prolonged leaching time.
Leaching Characteristics of Bio-oxidation Acid

*Particle Size Effect*

- Lixiviant: Bioleach acid;
- S/L: 1/5 w/v;
- Temperature: 75 °C.
- Feed size: 177 microns top size
- Roasting: 600 °C for 2 hours
- Ending pH: 2.5

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- Lixiviant: Bioleach acid;
- S/L: 1/5 w/v;
- Temperature: 75 °C.
- Feed size: 2 mm top size
- Roasting: 600 °C for 20 minutes;
- Ending pH: 2.35
Leaching Characteristics of Bio-oxidation Acid

Solid-to-liquid Ratio Effect

S/L = 1/10

S/L = 2/10

S/L = 3/10

Recovery (%)

Time (min)

TREAs Leaching Recovery (%)
Leaching Characteristics of Bio-oxidation Acid

Counter Current Leaching

Counter Current (30 min per stage)

One Stage Leaching

Simulated Stage Recovery%: 15.6% 10.4% 9.8%
Optimization of Rare Earth Recovery by Pre-Leach Roasting
TGA-DSC Studies

- Leaching Recovery by Roasting Temperature
- Pronounced Effect on Light Elements
- Fe Reduction by Magnetic Material Removal

REE leaching recoveries for roasting products of 2.20 sink density fraction of WK No.13 material. (1.2 M H2SO4, 75°C for 5 hours)
Optimization of Rare Earth Recovery by Pre-Leach Roasting

LECO TGA-Fire Clay (volatiles removed at 600°C, ashed at 600°C)

Leaching at 1.2M sulfuric acid at 75°C for 1 hours at 1% solids

Leaching at 2.00x2.20

Leaching at 2.20 sink

Optimization of Rare Earth Recovery by Pre-Leach Roasting

LECO TGA-Fire Clay (volatiles removed at 600°C, ashed at 600°C)
Optimization of Rare Earth Recovery by Pre-Leach Roasting

LECO TGA-WK-13 (volatiles removed at 600°C ashed at 600°C)

Leaching at 1.2M sulfuric acid at 75°C for 1 hours at 1% solids

1.80 float

1.80 x2.00

2.20 sink

Leaching at 1.2M sulfuric acid at 75°C for 1 hours at 1% solids

1.80 float

1.80 x2.00

2.20 sink
Optimization of Rare Earth Recovery by Pre-Leach Roasting

Inert Roasting Effects at 1000°C: Fire Clay

Leaching at 1.2M sulfuric acid at 75°C for 1 hour at 1% solids
Optimization of Rare Earth Recovery by Pre-Leach Roasting Acid Baking using sulfuric acid

- The results shown in the figure compare the recoveries obtained from 1st and 2nd stage acid baking with the blank roasting using the same acid molarity in leaching.
- The blank roasting performed at 600°C yields only 35.92% REE recovery, with HREEs being approximately 22%.
- The acid baking performed at 250°C recovered approximately 33% TREEs while obtaining 35.68% in HREEs.

**Figure:**

A: Blank roasting at 600°C followed by 0.5M H₂SO₄ leaching, B: 1st stage acid baking using 1:1 acid to coal ratio and leaching with DI water, C: Two-Stage acid baking at 250°C using 1:1 acid to coal ratio and leaching with DI water (Each leaching operation was performed at 5% S/L, 75°C, and 2hrs)
Optimization of Rare Earth Recovery from PLS

Precipitation using NaOH

50 min leaching filtrate

Leachate Solution
pH: 1.708
Eh: 717.9 RmV
TRE: 14.41 ppm
Al: 1650 ppm
Ca: 747 ppm
Fe: 6723 ppm

NaOH Dose at pH 4.5: 22.49 g/L

3 hour leaching filtrate

Leachate Solution
pH: 2.091
Eh: 691.6 RmV
TRE: 12 ppm
Al: 3595 ppm
Ca: 718 ppm
Fe: 1071 ppm

NaOH Dose at pH 4.5: 15.25 g/L

5 hour leaching filtrate

Leachate Solution
pH: 2.339
Eh: 412.1 RmV
TRE: 10.69 ppm
Al: 4033 ppm
Ca: 775 ppm
Fe: 538 ppm

NaOH Dose at pH 4.5: 14.62 g/L

NaOH Dose at pH 4.5: 22.49 g/L

4M NaOH

12M NaOH

12M NaOH

Precipitation (%)

1 2 3 4 5 6 7 8 9 10 11

pH

Precipitation (%)

1 2 3 4 5 6 7 8 9 10 11

pH

Precipitation (%)

1 2 3 4 5 6 7 8 9 10 11

pH
Objective:
To extract Sc before Al precipitation using solvent extraction (SX).

Extractant: Cyanex 272
Feedstock PLS: Acid Mine Water received from West Kentucky No. 13 coal refuse pile.

Scrubbing: 0.5M H$_2$SO$_4$ to remove Fe;
Scrubbing solution reports to downstream process for RE recovery.
Stripping: 6M H$_2$SO$_4$ to recover Scandium.
Pre-concentrated Slurry Prepared from AML in the Laboratory

- Re-dissolution (pH 1.5)
  - Solid/Liquid Separation
    - Solution
    - Undissolved Precipitates (Mn)
  - Na$_2$S Precipitation (pH 3.0)
    - Solid/Liquid Separation
      - Solution
    - Cobalt Sulfide Precipitate
  - NaOH Precipitation (pH 10)
    - Mn Oxide

Optimization of Critical Material Recovery

**Cobalt Sulfide Precipitate**

<table>
<thead>
<tr>
<th>Precipitate composition (%)</th>
<th>Mn</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>16</td>
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</tbody>
</table>

**Mn Oxide**

<table>
<thead>
<tr>
<th>Precipitate composition (%)</th>
<th>Mn</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
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<tbody>
<tr>
<td></td>
<td>25</td>
<td></td>
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</table>
CoS Precipitate Re-dissolution

Roasting at appropriate temperature increased the dissolution of cobalt sulfide.
Precipitate Produced at REE Pilot Plant

Re-dissolution (pH 1.5)

Solid/Liquid Separation

Undissolved Precipitate

Na₂S Precipitation (pH 3.0)

Solid/Liquid Separation

Sulfide Precipitate

Re-dissolution (1.2 M HCl)

Extraction I

(0.135 M DEHPA, equilibrium pH 2.98)

Organic Phase

Stripping I

(0.3 M H₂SO₄)

Aqueous Phase

Extraction II

(0.135 M DEHPA, equilibrium pH 3.93)

Organic Phase

Stripping I

(0.3 M H₂SO₄)

Aqueous Phase

Precipitation (NaOH)

Cobalt Product

Elemental Composition of the Extraction I

Feed Solution

Elemental Composition of the Cobalt Product

Metal Oxide Content in the Cobalt Product
Process Flow Sheet (Co/Mn Flowsheet)
Completed REE/CM Pilot Plant

<table>
<thead>
<tr>
<th>Production Parameter</th>
<th>FOA 2003</th>
</tr>
</thead>
<tbody>
<tr>
<td>Designed Feed Rate (kg/hr)</td>
<td>113.5</td>
</tr>
<tr>
<td>Capable Daily REO Production (kg/day)</td>
<td>0.44</td>
</tr>
<tr>
<td>Capable Annual REO Production (kg/yr)</td>
<td>110</td>
</tr>
</tbody>
</table>
Both PLC Control Panels are wired and labeled. (Shown 1 of 2 PLC Control Panels).

PLC and power boxes installed on all associated equipment.

Complete PLC and power box shown.
Feasibility study analyzed the commercial production of REEs and CM from coarse refusing (500 tph feed) utilizing technology components from the project:

- Roasting
- Biooxidation
- Selective Precipitation
- Dedicated Scandium Recovery
- Dedicated Co and Mn Recovery

Output production is estimated at around 300 Mt annually of total rare earth oxide, 18 Mt Sc, 32 Mt Co and 405 Mt Mn.
Process Economics
Biooxidation Cost Analysis

• The biooxidation unit is a large cost component, but it shows notable cost advantages over raw acid leaching.

• Total acid production cost = $0.05 /kg, a reduction of approximately 75% vs. bulk sulfuric acid.

• Largest cost components = mixing, temperature management, capitalization costs (~81% of total).

Total cost = $0.05 / kg H₂SO₄ equivalent
Process Economics
Feasibility Study

• Key Findings:
  1. Plant capital cost = $137 million. Biooxidation circuit = ~1/3 of total capital expenditure.
  2. Achieved project objective of 50% operating cost reduction versus existing pilot plant. Contributing factors = biooxidation, use of coal calcite, and use of Al wash.
  3. Highest single line item cost = neutralization base.
  4. Under the baseline conditions evaluated, the project was found economically viable; however, this viability is very sensitive to the scandium price.
  5. The overall system recovery is very low, and even modest improvements to recovery could greatly increase the economic robustness of the process.
Summary

- Biooxidation using concentrated ultrafine coal pyrite can produce a 0.2 M H₂SO₄ solution at 25% of the cost of commercial acid.
- Biooxidation acid can be used to effectively leach REEs and CMs from coarse coal refuse.
- Magnetic iron oxide can be produced by roasting at 400°C.
- Acid baking after roasting provides leach recoveries of HREEs and LREEs greater than 80%.
- Sc and Co/Ni/Zn/Mn circuits have been developed providing well over 2% product grades.