Economical and Environmentally Benign Extraction of Rare Earth Elements from Coal & Coal Byproducts

DOE Contract Number  DE-FE0027155

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Omni William Penn Hotel   Pittsburgh, PA
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Outline

- Project Goals and Objectives
- Overall Approach
- Methodology
- Results
- Accomplishments
- Summary
- Status
- Future Work
## Project Goals and Objectives

### Goals
- Develop a bench-scale REE extraction process for coal fly-ash materials
- Utilize pretreatment and leaching processes along with proprietary metal sorption media to process 1-kg batches
- Deliver a REO product meeting or exceeding DOE requirements

### Objectives
- Identification/selection of coal by-product sources
- Develop leaching procedure for selected by-products
- REE sequestration and recovery
- Radioactive material separation*
- Waste water treatment for metal removal
- Scale-up of process to +2-kg coal by-product per batch
Background

• **Selection of Coal By-Product**
  - Coal *fly-ash* chosen as source material
  - Knowledge regarding the pretreatment and digestion of inorganic source materials
  - Experience with extracting REEs from phosphor powders and ore materials

• **Isolation of REEs**
  - Expertise in the separation of REEs from other metal constituents in process streams using proprietary media
  - Preliminary research on the isolation of metal constituents from ore digest liquors
Overall Approach

- Develop system utilizing pretreatment + digestion followed by U/Th removal, REE isolation, and subsequent precipitation (production) of REOs.
- Assess system performance
- Determine scaling parameters
- Evaluate economic viability

Overall Work Plan

Task 1  Project Management and Planning
Task 2  Sampling and Characterization of Feedstocks
Task 3  Feasibility Study
Task 4  Process Integration

Proposed Test System

- Develop system utilizing pretreatment + digestion followed by U/Th removal, REE isolation, and subsequent precipitation (production) of REOs.
- Assess system performance
- Determine scaling parameters
- Evaluate economic viability
Milestones

- Selection of fly ash source
- Source material characterization
- Selection of best pre-treatment method
- Selection of best digestion method
- Ability to remove U/Th from digestion liquor
- Demonstrating and overall recovery of REE from the source fly ash of >25%
- Produce an REO product that had a final REEs concentration > 2.0 wt. %.
- Verify that waste residuals from the process could meet RCRA limits and local metal discharge requirements
Methodology

TASK 1
Project Management and Planning

TASK 2
Sampling/Characterization of Feedstocks
- Source Material Identification
- Source Sampling

TASK 3
Feasibility Study
- Economic Analysis
  - Fly Ash Pretreatment
  - Wastewater Treatment
- Fly Ash Digestion
  - U/Th Removal
  - REE Sequestration
  - REE Product
  - REE Recovery and Isolation

TASK 4
Process Integration
- Process Design
  - Process Demonstration
  - Economic Analysis Review
Summary of Results

- Major project results discussed
- Separated by main process units
- Results presented represent project activities up to Go/No Go decision point

Results

- Fly Ash Materials
  - Selection
  - Characterization

- Proposed Process
  - Fly Ash Pretreatment
  - Digestion
  - U/Th Removal
  - REE Isolation and Recovery
  - REO Product
Reviewed over 700 potential sources including material locations, REE content, and availability.

Six fly ash sources selected that had documented:
- critical REE concentrations between 400-535 ppm
- outlook ratios between 1.456 to 1.535
- accessible for sampling
- available in large quantities

### Chemical Assay (ppm and %)

<table>
<thead>
<tr>
<th></th>
<th>FA-1</th>
<th>FA-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>TREE+Y</td>
<td>482</td>
<td>553</td>
</tr>
<tr>
<td>TREE</td>
<td>387</td>
<td>467</td>
</tr>
<tr>
<td>Critical REE</td>
<td>201</td>
<td>201</td>
</tr>
<tr>
<td>Excessive REE</td>
<td>161</td>
<td>212</td>
</tr>
<tr>
<td>La+Ce (% of TREE+Y)</td>
<td>44%</td>
<td>51%</td>
</tr>
<tr>
<td>Outlook Ratio</td>
<td>1.25</td>
<td>0.95</td>
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</table>

### Other Factors

<table>
<thead>
<tr>
<th></th>
<th>FA-1</th>
<th>FA-2</th>
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</thead>
<tbody>
<tr>
<td>Fly Ash Availability</td>
<td>yes</td>
<td>limited</td>
</tr>
<tr>
<td>In-place Sampling</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>Long-Term Sourcing</td>
<td>yes</td>
<td>limited</td>
</tr>
<tr>
<td>Historical Information</td>
<td>yes</td>
<td>no</td>
</tr>
</tbody>
</table>
### Chemical Assay

#### Fly Ash Elemental Composition, wt%

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>0.0014%</td>
</tr>
<tr>
<td>Na</td>
<td>0.4712%</td>
</tr>
<tr>
<td>Mg</td>
<td>0.3950%</td>
</tr>
<tr>
<td>Al</td>
<td>10.6%</td>
</tr>
<tr>
<td>Si</td>
<td>14.5%</td>
</tr>
<tr>
<td>K</td>
<td>1.876%</td>
</tr>
<tr>
<td>Ca</td>
<td>1.795%</td>
</tr>
<tr>
<td>Ti</td>
<td>0.5998%</td>
</tr>
<tr>
<td>Fe oxide</td>
<td>9.8</td>
</tr>
<tr>
<td>Fe oxide in glass</td>
<td>10.5</td>
</tr>
<tr>
<td>Si–O</td>
<td>2.6</td>
</tr>
<tr>
<td>Si(high)–Al–K–O</td>
<td>3.2</td>
</tr>
<tr>
<td>Al–K–Fe–Si–O</td>
<td>38.4</td>
</tr>
<tr>
<td>Al–Fe(high)–K–Si–O</td>
<td>28.3</td>
</tr>
<tr>
<td>Al–Fe(high)–Ti–K–Si–O</td>
<td>2.0</td>
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<tr>
<td>Al–Ca–Fe–Si–O</td>
<td>0.2</td>
</tr>
<tr>
<td>Ba-bearing (barte)</td>
<td>0.02</td>
</tr>
<tr>
<td>Ca–Al–S–O (ettringite)</td>
<td>0.9</td>
</tr>
<tr>
<td>Ca sulfate</td>
<td>0.5</td>
</tr>
<tr>
<td>Ca-bearing</td>
<td>0.01</td>
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<tr>
<td>Miscellaneous</td>
<td>0.3</td>
</tr>
<tr>
<td>Others</td>
<td>1.2</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
</tr>
</tbody>
</table>

XRD analysis indicated 80-85% amorphous content, mineral constituents: Magnetite, Mullite, Hematite, Quartz, Portlandite

### SEM

Image of a small siliceous glass spherule with inclusions of rare earth oxides

### Particle Size Analysis

- P10 = 5.5 μm
- P50 = 13 μm
- P80 = 38 μm

TREE+Y ≈ 0.05%
Results

Process Strategy: REE Extraction from Coal Fly-Ash

Unit 1
Pretreatment

Unit 2
Digestion

Unit 3
U/Th Removal

Unit 4
REE Recovery

Unit 5
REO Production

Unit 6
Discharge
Results

Developed Process

ECONOMICAL AND ENVIRONMENTALLY BENIGN EXTRACTION OF RARE EARTH ELEMENTS FROM COAL & COAL BYPRODUCTS

2017 Project Review Meeting for Crosscutting Research, Gasification Systems, and Rare Earth Elements Research Portfolios

March 22, 2017
Physical Pretreatment
Targeted effort to develop physical process methodology followed by acid digestion to enhance REE recovery rates.

Tests included:
- Thermal shock
- Grinding
- Magnetic Separation

Base Chemical Pretreatment
Optimization of pretreatment process by utilizing various pretreatment methods followed by standard acid digestion

Tests included:
- Type of Base Solution
- Concentration of Base Solution
- Solid wt% Slurry
- Temperature
- Reaction Time

Test Apparatus
- 2L reaction kettle
- Heating mantle
- Temperature control
- High-speed mixer

Operation
- 1-kg fly ash batches
- 80-100°C
- 100-400 rpm
Results

Type of Base Solution

No Pretreatment = 15% REE Recovery

Base Solution Concentration

Solid wt% Slurry

Reaction Time
Acid Pretreatment
- Type of Solution
- Concentration of Solution
- Solid wt% Slurry
- Temperature
- Reaction Time

Test Apparatus
- 2L reaction kettle
- Heating mantle
- Temperature control
- High-speed mixer

Operation
- 1-kg fly ash batches
- 80-100°C
- 100-400 rpm mixing
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Results

Unit 2
Digestion

Acid Solution Concentration

<table>
<thead>
<tr>
<th>Acid A1 Concentration</th>
<th>Solid wt% Slurry</th>
</tr>
</thead>
<tbody>
<tr>
<td>C3</td>
<td>56%</td>
</tr>
<tr>
<td>C4</td>
<td>56%</td>
</tr>
<tr>
<td>C6</td>
<td>76%</td>
</tr>
</tbody>
</table>

Solid wt% Slurry

<table>
<thead>
<tr>
<th>Percent Weight Solids</th>
<th>Unit 2 Digestion</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>71%</td>
</tr>
<tr>
<td>S2</td>
<td>64%</td>
</tr>
<tr>
<td>S3</td>
<td>58%</td>
</tr>
</tbody>
</table>

Reaction Temperature

Reaction Time

Temperature, °C

Digestion Time, hrs

50 60 70 80 90 100 110

0 2 4 6 8 10
### Results

#### Unit 3

**U/Th Removal**

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**Overall Approach**

Unit process utilizes an adsorptive bed to bind U and Th while allowing REEs and other ions in solution to pass through for downstream processing.

**Operational Constraints**

Adsorptive bed requires influent solution to be particle free and at pH 2 to eliminate media bed clogging and to maximize U and Th sequestration.

**Evaluation**

Tests included:

1. Determining Operation pH Range for U/Th Sequestration (selective precipitation)
2. Evaluation and Selection of Adsorptive Media
3. Adsorptive Column Performance

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**Test Apparatus**

- 1 cm Ø x 50 cm column
- Adjustable bed height
- Diffusers (both ends)
- Infl./Eff. pH measurement
- Precision metering pump

**Operation**

- 1g to 20g media
- 0.01 to 5 ml/min
- 0.01 to 3M Acid

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**ECONOMICAL AND ENVIRONMENTALLY BENIGN EXTRACTION OF RARE EARTH ELEMENTS FROM COAL & COAL BYPRODUCTS**

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March 22, 2017
Results

Unit 3
U/Th Removal

pH of Influent Solution

Column Retention Time

U Operational Isotherm

Th Operational Isotherm

ECONOMICAL AND ENVIRONMENTALLY BENIGN EXTRACTION OF RARE EARTH ELEMENTS FROM COAL & COAL BYPRODUCTS

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March 22, 2017
Overall Approach
Unit process utilizes an adsorptive bed to bind REEs and other ions with subsequent acid “stripping” to produce concentrated REE solution with decreased amounts of ancillary metals.

Operational Constraints
Adsorptive bed requires influent solution to be particle free and at pH 4 to eliminate media bed clogging and to maximize REE sequestration and isolation.

Evaluation
 Tests included:
1. Flow Rate
2. “Push”/Strip Volume and Concentration
3. Feed Volume
4. Media Size
5. Aspect Ratio

Test Apparatus
- 1 cm Ø x 50 cm column
- Adjustable bed height
- Diffusers (both ends)
- Inf./Eff. pH measurement
- Precision metering pump

Operation
- 1g to 20g media
- 0.01 to 5 ml/min
- 0.01 to 3M Acid
Can remove upwards of 60% of Al and Fe from process solution while only losing 5% REEs
- Translates into 2.5x increase in TREE wt%
- Removal of 15 to 20% of unwanted cations
Experimental Procedure
- Hydroxide precipitation at pH 10
- Filtering of solids and drying at 50°C
- Oxidizing at 550°C
- Re-dissolution of metal oxides
- Elemental analysis by ICP

Results
- Wt% of REOs in final product increased by over 65x compared to original fly-ash material

![Graphs showing REO and TREE and U/Th wt% results](image-url)
Summary

**Operational Parameters**

**Pretreatment**
- Base, 0.4-0.6 g/g-fly ash, 100°C, 4 hrs, 10-30wt% solids

**Digestion**
- Acid, 0.4-1 g/g-fly ash, 80°C, 4 hrs, 10-30wt% solids
- REE Concentration of 30,000 ppm TREE+Y

**U/Th Removal**
- Tusaar Media AM4, chromatography, 2,200 ppb U and 1,350 ppb Th solutions, 4-8 minutes EBCT, pH 2

**REE Isolation/Recovery**
- Tusaar Media AM5, load/strip, 4-20 minutes EBCT, pH 4, REE concentration as high as 100,000 ppb

**REE Recovery and REO Production**
- REE recovery is proportional to concentration
- REE recoveries between 40-70%
- 3.2% REO wt% in final product
- $13-20/ton fly ash

**Process Design**
- Overall PID complete
- Incorporates 6 unit process
- Recycling of process streams
- Production of zeolite material

**Zeolite Production (Value-Added Product)**
- Na-P1 zeolite successfully produced
- Used 80-100% of Al isolated within chromatography unit process
- 0.1kg zeolite/kg fly ash
Accomplishments

PRIMARY

• The developed treatment system achieved a **60% REE recovery** rate
• A final product was produced with more than **2.5wt% REOs**
• U/Th ratio in final product is lower than ratio in source fly ash
• System is **robust and reliable** for scale-up operations
• Waste and residuals treatment system **met RCRA discharge** requirements

SECONDARY

• Production of a zeolite (NaP1) was successfully demonstrated
• Residuals streams can be repurposed with minimization of waste disposal
• Optimization of the system may further increase the economic viability
• Developed process strategies providing scientific foundation for technology advancement
## Project Status

<table>
<thead>
<tr>
<th>Timeline</th>
<th>Current Status</th>
<th>Next Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feasibility Study</td>
<td>Economic Analysis review sub-tasks</td>
</tr>
<tr>
<td></td>
<td>Process meets/exceeds performance criteria</td>
<td>Process instrumentation and design (P&amp;ID)</td>
</tr>
<tr>
<td></td>
<td>Overall treatment system (process) design</td>
<td>Scaled-up system bill of materials (BOM)</td>
</tr>
<tr>
<td>Process Development</td>
<td>Results are encouraging</td>
<td>Scale system up to -kg batches in laboratory</td>
</tr>
<tr>
<td></td>
<td>Lab-scale experiments limited to 1kg batches</td>
<td>Validate REO production rates over multiple runs</td>
</tr>
<tr>
<td>Validation and Scale-Up</td>
<td></td>
<td>Determine scale-up factors</td>
</tr>
</tbody>
</table>
Future Work

Optimize REO Production

Zeolite Production?

Financial Analysis

Process Scale-Up
Thank You

Questions