Low-Temperature Plasma Treatment for Enhanced Recovery of Highly Valued Critical Rees from Coal

PRINCIPAL INVESTIGATOR: Dr. Rick Honaker
University of Kentucky

DOE Award Number: FE0031525
Period of Performance: 11/15/2017 – 5/15/2019

NETL Program Manager: Jason Hissam

2019 Annual Project Review Meeting
Crosscutting Research, Rare Earth Elements, Gasification Systems, and Transformative Power Generation
April 9 - 11, 2019
Objectives

- A novel process is to be developed using Low-Temperature Plasma (LTP) treatment integrated with hydrometallurgical processes to recover rare earth elements (REEs)
- LTP is utilized to pre-treat the feed to liberate, release, oxidize and/or activate the REEs embedded in coal or mineral matter
- LTP technique can enhance the leaching characteristics of the REEs and a product containing \( \geq 90\% \) of total REEs (TREE) on a dry whole mass basis can be produced.
Project Team

Principal Investigator
(Rick Honaker)

University of Kentucky Research Foundation

Academic Members
University of Kentucky
Virginia Tech

Corporate Members
Alliance Coal
Blackhawk Mining

Project Management Committee

Rick Honaker (UKY)
- Task 1: Project Management Plan
- Task 2: Sampling & Characterization of Proposed Feedstocks
- Task 3: Low Temperature Treatment
- Task 4: Leaching
- Task 7: System Design

Wencai Zhang (UKY)
- Task 3: Low Temperature Treatment
- Task 4: Leaching
- Task 5: REE Concentrate Production
- Task 6: Environmental Studies

Aaron Noble (VT)
- Task 7: System Design
- Task 8: Economic & Market Analysis
- Task 9: Commercialization Assessment

Jerry Luttrell (VT)
- Task 7: System Design
- Task 9: Commercialization Assessment
Low Temperature Plasma Treatment

Electron Ionization

\[
\begin{align*}
\text{(1)} \quad e^- + O_2 &\rightarrow O_2^+ + 2e^- \rightarrow O^+ + O \\
\text{(2)} \quad e^- + O_2 &\rightarrow O_2^{2+} + 3e^- \rightarrow O^+ + O^+ \rightarrow O^{2+} + O \\
\text{(3)} \quad e^- + O_2 &\rightarrow O_2^{3+} + 4e^- \rightarrow O^{2+} + O^+ 
\end{align*}
\]

McConkey et al., 2008; Hozumi, 1977

Leaching Recovery (%) vs. Acid, Salt, and Water Leaching
Feed Characterization

- Coarse refuse samples collected from plants treating West Kentucky No.13 and Fire Clay seam sources.

- Fractions of 1.60 SG Float, 1.60-1.80 SG, 1.80-2.20 SG and 2.20 SG Sink were size reduced and analyzed for the REE concentrations.

- Fire Clay-CR composite sample had total REE concentration higher than 300ppm while the Dotiki-CR composite sample contained 250 ppm TREE.
Feed Characterization

West Kentucky No.13 Coarse Refuse

<table>
<thead>
<tr>
<th>Composition (%)</th>
<th>1.60 Floats</th>
<th>1.60-1.80</th>
<th>1.80-2.20</th>
<th>2.20 Sink</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash</td>
<td>79</td>
<td>30</td>
<td>67</td>
<td>82</td>
</tr>
<tr>
<td>Carbon Content</td>
<td>20</td>
<td>50</td>
<td>83</td>
<td>90</td>
</tr>
<tr>
<td>Moisture</td>
<td>68</td>
<td>9</td>
<td>92</td>
<td>7</td>
</tr>
</tbody>
</table>

Fire Clay Coarse Refuse

<table>
<thead>
<tr>
<th>Composition (%)</th>
<th>1.60 Floats</th>
<th>1.60-1.80</th>
<th>1.80-2.20</th>
<th>2.20 Sink</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash</td>
<td>48</td>
<td>16</td>
<td>9</td>
<td>7</td>
</tr>
<tr>
<td>Carbon Content</td>
<td>50</td>
<td>83</td>
<td>90</td>
<td>92</td>
</tr>
<tr>
<td>Moisture</td>
<td>68</td>
<td>9</td>
<td>92</td>
<td>7</td>
</tr>
</tbody>
</table>
Feed Characterization

REE Contents
(Dry Whole Mass Basis)

- Rare earth phosphates originating from volcanic activity contributed the higher REE content in the Fire Clay low density fractions.
- The relatively higher HREE/LREE ratio in the West Kentucky No. 13 seam is likely due to stronger organic affinity.
Feed Characterization-REE Phosphates in Fire Clay Coal

\[ R^2 = 0.8456 \]
Solely one rare earth phosphate particle was found through two batches of large area mapping, which indicated the lack of rare earth minerals in the West Kentucky No.13 coal.
Feed Characterization-XRD

**Major Minerals**

- **Q-Quartz**  
  \((\text{SiO}_2)\)

- **K-Kaolinite**  
  \((\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4)\)

- **I-Illite**  
  \((\text{K,H}_3\text{O})(\text{Al,Mg,Fe})_2(\text{Si,Al})_4\text{O}_{10}[(\text{OH})_2,(\text{H}_2\text{O})])\)

- **P-Pyrite**  
  \((\text{FeS}_2)\)

---

**West Kentucky No.13**

- S.G. < 1.60
- S.G. 1.60-1.80
- S.G. 1.80-2.20
- S.G. > 2.20

**Fire Clay**

- S.G. < 1.60
- S.G. 1.60-1.80
- S.G. 1.80-2.20
- S.G. > 2.20

---

**West Kentucky No.13**

- Major Minerals: Q-Quartz, K-Kaolinite, I-Illite, P-Pyrite

**Fire Clay**

- Major Minerals: Q-Quartz, K-Kaolinite, I-Illite, P-Pyrite

---

**Q-Quartz**

- \((\text{SiO}_2)\)

**K-Kaolinite**

- \((\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4)\)

**I-Illite**

- \((\text{K,H}_3\text{O})(\text{Al,Mg,Fe})_2(\text{Si,Al})_4\text{O}_{10}[(\text{OH})_2,(\text{H}_2\text{O})])\)

**P-Pyrite**

- \((\text{FeS}_2)\)
Low Temperature Plasma Parametric Study

- Vacuum Pump
- PE-100 RIE
- Software Controls
- Temperature Control

- Exhaust

- Sample Weight
- Particle Size
- REE Recovery
- Temp.
- Time
- RF Power
- Oxygen Flow

- Temperature Control
- Exhaust
## Two-Factorial Parametric Study

### 1.8-2.2 S.G. Fraction

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>1</td>
<td>60</td>
<td>250</td>
<td>35</td>
<td>3</td>
<td>20</td>
<td>180</td>
<td>10.09</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>60</td>
<td>100</td>
<td>35</td>
<td>1</td>
<td>20</td>
<td>75</td>
<td>10.40</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>30</td>
<td>100</td>
<td>25</td>
<td>3</td>
<td>20</td>
<td>180</td>
<td>9.92</td>
</tr>
<tr>
<td>7</td>
<td>4</td>
<td>30</td>
<td>250</td>
<td>35</td>
<td>1</td>
<td>10</td>
<td>180</td>
<td>10.35</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>60</td>
<td>100</td>
<td>25</td>
<td>1</td>
<td>10</td>
<td>180</td>
<td>10.91</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>60</td>
<td>250</td>
<td>25</td>
<td>3</td>
<td>10</td>
<td>75</td>
<td>13.56</td>
</tr>
<tr>
<td>5</td>
<td>7</td>
<td>30</td>
<td>100</td>
<td>35</td>
<td>3</td>
<td>10</td>
<td>75</td>
<td>11.86</td>
</tr>
<tr>
<td>3</td>
<td>8</td>
<td>30</td>
<td>250</td>
<td>25</td>
<td>1</td>
<td>20</td>
<td>75</td>
<td>10.67</td>
</tr>
</tbody>
</table>
# Two-Factorial Parametric Study

West Kentucky No.13 1.8-2.2 S.G. Fraction

<table>
<thead>
<tr>
<th>Std. Run</th>
<th>Factor 1</th>
<th>Factor 2</th>
<th>Factor 3</th>
<th>Factor 4</th>
<th>Factor 5</th>
<th>Factor 6</th>
<th>REE Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A:Temp</td>
<td>B:RF</td>
<td>C:Oxygen</td>
<td>D:Time</td>
<td>E:Weight</td>
<td>F:Size</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Celsius</td>
<td>Watts</td>
<td>CC/min</td>
<td>Hours</td>
<td>Grams</td>
<td>Microns</td>
<td>%</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>60</td>
<td>250</td>
<td>35</td>
<td>3</td>
<td>20</td>
<td>180</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>60</td>
<td>100</td>
<td>35</td>
<td>1</td>
<td>20</td>
<td>75</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>30</td>
<td>100</td>
<td>25</td>
<td>3</td>
<td>20</td>
<td>180</td>
</tr>
<tr>
<td>7</td>
<td>4</td>
<td>30</td>
<td>250</td>
<td>35</td>
<td>1</td>
<td>10</td>
<td>180</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>60</td>
<td>100</td>
<td>25</td>
<td>1</td>
<td>10</td>
<td>180</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>60</td>
<td>250</td>
<td>25</td>
<td>3</td>
<td>10</td>
<td>75</td>
</tr>
<tr>
<td>5</td>
<td>7</td>
<td>30</td>
<td>100</td>
<td>35</td>
<td>3</td>
<td>10</td>
<td>75</td>
</tr>
<tr>
<td>3</td>
<td>8</td>
<td>30</td>
<td>250</td>
<td>25</td>
<td>1</td>
<td>20</td>
<td>75</td>
</tr>
</tbody>
</table>

Fire Clay 1.8-2.2 S.G. Fraction

<table>
<thead>
<tr>
<th>Std. Run</th>
<th>Factor 1</th>
<th>Factor 2</th>
<th>Factor 3</th>
<th>Factor 4</th>
<th>Factor 5</th>
<th>Factor 6</th>
<th>REE Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A:Temp</td>
<td>B:RF</td>
<td>C:Oxygen</td>
<td>D:Time</td>
<td>E:Weight</td>
<td>F:Size</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Celsius</td>
<td>Watts</td>
<td>CC/min</td>
<td>Hours</td>
<td>Grams</td>
<td>Microns</td>
<td>%</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>60</td>
<td>250</td>
<td>35</td>
<td>3</td>
<td>20</td>
<td>180</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>60</td>
<td>100</td>
<td>35</td>
<td>1</td>
<td>20</td>
<td>75</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>30</td>
<td>100</td>
<td>25</td>
<td>3</td>
<td>20</td>
<td>180</td>
</tr>
<tr>
<td>7</td>
<td>4</td>
<td>30</td>
<td>250</td>
<td>35</td>
<td>1</td>
<td>10</td>
<td>180</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>60</td>
<td>100</td>
<td>25</td>
<td>1</td>
<td>10</td>
<td>180</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>60</td>
<td>250</td>
<td>25</td>
<td>3</td>
<td>10</td>
<td>75</td>
</tr>
<tr>
<td>5</td>
<td>7</td>
<td>30</td>
<td>100</td>
<td>35</td>
<td>3</td>
<td>10</td>
<td>75</td>
</tr>
<tr>
<td>3</td>
<td>8</td>
<td>30</td>
<td>250</td>
<td>25</td>
<td>1</td>
<td>20</td>
<td>75</td>
</tr>
</tbody>
</table>
## Two-Factorial Parametric Study

### West Kentucky No.13 1.4 SG Float

<table>
<thead>
<tr>
<th>Std</th>
<th>Run</th>
<th>A: TEMP</th>
<th>B: RF POWER</th>
<th>C: OXYGEN</th>
<th>D: TIME</th>
<th>E: WEIGHT</th>
<th>F: SIZE</th>
<th>Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CELCIUS</td>
<td>WATTS</td>
<td>CC/MIN</td>
<td>HOURS</td>
<td>GRAMS</td>
<td>MICRONS</td>
<td>%</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>60</td>
<td>450</td>
<td>40</td>
<td>5</td>
<td>30</td>
<td>180</td>
<td>24.8</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>60</td>
<td>100</td>
<td>40</td>
<td>1</td>
<td>30</td>
<td>75</td>
<td>24.6</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>30</td>
<td>100</td>
<td>25</td>
<td>5</td>
<td>30</td>
<td>180</td>
<td>20.6</td>
</tr>
<tr>
<td>7</td>
<td>4</td>
<td>30</td>
<td>450</td>
<td>40</td>
<td>1</td>
<td>10</td>
<td>180</td>
<td>20.7</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>60</td>
<td>100</td>
<td>25</td>
<td>1</td>
<td>10</td>
<td>180</td>
<td>14.2</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>60</td>
<td>450</td>
<td>25</td>
<td>5</td>
<td>10</td>
<td>75</td>
<td>30.2</td>
</tr>
<tr>
<td>5</td>
<td>7</td>
<td>30</td>
<td>100</td>
<td>40</td>
<td>5</td>
<td>10</td>
<td>75</td>
<td>27.3</td>
</tr>
<tr>
<td>3</td>
<td>8</td>
<td>30</td>
<td>450</td>
<td>25</td>
<td>1</td>
<td>30</td>
<td>75</td>
<td>20.3</td>
</tr>
</tbody>
</table>
The variables shaded orange are positively associated with the response variable while the ones shaded blue are negatively associated with REE recovery.
Time Based Plasma Treatment

- Bottom layers of the sample limits exposure to the oxygen plasma.
- LTP treatment with periodic mixing provides better leaching kinetics due to a more thorough treatment of the sample.
LTP treatment liberated some REEs especially HREEs which can be readily extracted.

HREEs can be recovered by benign methods such as by using 0.1 M ammonium sulfate solution at a pH of 6.
The LTP pretreatment of West Kentucky No.13 material improved the total REE recovery for lower density fractions.

LTP pretreatment exhibits selectivity for HREEs for the high ash fractions of West Kentucky No.13 sample.
Poor leachability with ammonium salts for Fire Clay density fractions.

However, the trend for HREE leaching characteristics is similar to that for West Kentucky No.13 material.

Some HREEs appear to be associated in an the organic matter in coal.
No significant change in REE recovery was observed despite 16 hours of LTP treatment.

The association of REEs in the Fire Clay material is different to the West Kentucky No.13 material.

The small increase in the ash content of the LTP material shows very limited effect of plasma oxidation on the Fire Clay sample.
Modes of Occurrence of REEs in Coal
(Sequential Extraction)

Samples

Reactants
- MgCl₂ (1M, 40ml)
- CH₃COONa (1M, 40ml)
- 0.04M NH₂OH·HCl in 25% Acetic Acid (100ml)
- 2M HNO₃
- Aqua Regia plus HF

Conditions
1 hour; 25°C
5 hours; 25°C
5 hours; 95°C
18 hour, 25°C
Complete Digestion

Occurrence
- Ion-exchangeable
- Carbonate
- Metal Oxide
- Acid Soluble
- Insoluble/Silicate

Chou et al., 2009; Finkelman et al., 2018; Pan et al., 2009
Modes of Occurrence of REEs in Calcined Coals

1.4 SG Float/600°C 2 hours

REE Recovery (%)

- Ion-exchangeable
- Carbonates
- Metal Oxides
- Acid Soluble
- Insoluble

HREE/LREE

- Ion-exchangeable
- Carbonates
- Metal Oxides
- Acid Soluble
- Insoluble

Fire Clay  West Kentucky No.13  Illinois No.6
Modes of Occurrence of REEs in Calcined Coals

West Kentucky No.13
1.4 SG Float/600°C 2 hours

Fire Clay
1.4 SG Float/600°C 2 hours
Low vs High Temperature Oxidation

- SEM-EDX studies of West Kentucky No.13 LTP treated material show the presence of particles with increased porosity, surface area and pore volume.
Industrial Plasma Oxidation Systems

- Plasma Oxidation is a proven technology for the manufacture of carbon fibers.
- Multi-year DOE-funded R&D technology demonstration already completed.
  - Joint effort between RMX Technologies (RMX) and Oak Ridge National Laboratory (ORNL).
  - 2004 – first benchtop unit
  - 2014 – first 1 MT prototype
- Claimed benefits:
  - Lower energy (75% less)
  - Increased kinetics (300% faster)
  - Smaller footprint (67% lower)
  - Less costly (20% reduction)
  - Better fiber (30% stronger)
- Pushed by EPA for automotive manufacturing.
Industrial Plasma Oxidation Systems
Industrial Plasma Oxidation Systems
Industrial Plasma Oxidation Systems

Ref: American Jobs Project, 2017

Carbon Fiber: How It’s Made and Future Uses

The Precursor: A Costly First Step
The precursor is exposed to extreme heat in an inert gas to activate the carbonization process, turning the entire thread crystalline into a single columnar filament. High-carbon filaments typically 95 percent carbon are converted into fabric bundles made of several thousand filaments and used for commercial use on 5- to 25-pound spools.

Carbon Fiber Thread Is Woven
The bundles of carbon fiber are woven into fabric sheets of varying thickness and weaving patterns. Sometimes fabrics are blended with other high-strength synthetic fibers. Fabric is sold on rolls to component makers.

Epoxy Resin Added for Compressive Strengths
Manufacturers add plastic resin to the fabric. This type of resin addition is called propelling. If done before it is ready to mold, some fabrics can be compressed with resin and directly set in the form molds.

Composite Is Vacuum Sealed and Trimmed
The coated fabric is set in the mold, then vacuum sealed before curing at high temperatures. Once the curing is complete, the product is removed from the mold and then trimmed and drilled as needed.

End Uses and Applications
- TRANSPORTATION
  - CFRPs can reduce vehicle weight.
- ENERGY
  - Wind turbine blades made of CFRPs can.
- MEDICAL
  - CFRP prosthetics are innovative.

Cumulative Carbon Fiber Demand by Market Sector


Carbon fiber demand will increase most in the industrial sector.

CFRPs begin as a rayon or spun polyacrylonitrile strand known as a precursor. A long filament of some basic material that has a high carbon content. The most common is polyacrylonitrile (PAN) which makes up 89 percent of source material for carbon fibers and is cost-prohibitive.
Industrial Plasma Oxidation Systems

- Carbon fibers typically manufactured from polyacrylonitrile (PAN) in a 3-step process.
  - oxidation/stabilization
  - carbonization
  - surface treatment/sizing
- Source of petroleum tar/pitch usually preferred over coal-based feedstocks.
- Contacted 4M regarding use of “coal-based feedstocks” but without reference to potential co-production of REEs.
- Representatives attended DOE stakeholders meeting/Workshop in Pittsburgh – “Improving the Competitiveness of US Coal”
Industrial Plasma Oxidation Systems

• Currently, 10 companies (10 US, 4 international) produce laboratory and production-scale plasma oxidation units.

• Technical details for these units vary within the following ranges:
  • RF Power: 50W to 10,000W
  • RF Frequency: 20 kHz to 2.45 Ghz
  • Gas Flow: 0 to 5,000 sccm
  • Chamber Volume: 1 to 8,000 L

• Scaling data shows that RF power scales exponentially (exponent = 0.4155) with chamber capacity.

• This data will be used for scaling studies and preliminary techno-economic analysis.

\[ y = 120.58x^{0.4155} \]
\[ R^2 = 0.753 \]
Summary & Conclusions

- Low-temperature plasma treats the coal on the surface of the specimen.

- Change in the deeper layers of the samples was not achieved even with prolongation of treatment time.

- The pretreatment facilitates higher REE recovery values under mild leaching conditions for West Kentucky No. 13 coal.

- Partial ashing of the feed material is sufficient to enhance REE recovery while keeping mineralogical composition unchanged.

- A significant portion of the HREEs in West KY 13 coal are bound in the organic matrix and recoverable in a salt solution.

- Association characteristics of REEs with the coal samples differ and thus leaching behaviors of REEs are distinct.

- Further studies pertaining to sequential REE leaching and effect of LTP on Solvent Extraction are undergoing.
Final products containing more than 90% of REO will be generated using selective precipitation and/or solvent precipitation methods.