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

Project Number: DE-FE0031827

Aaron Noble, PE, PhD Virginia Tech Rick Honaker, PhD University of Kentucky

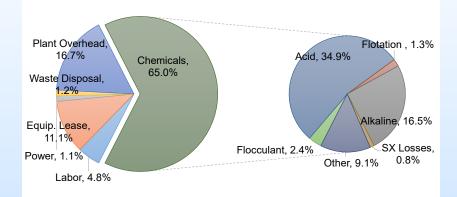
U.S. Department of Energy National Energy Technology Laboratory Resource Sustainability Project Review Meeting October 25 - 27, 2022

## **Project Overview**

| Funding   | Organization  | Team Member   |
|---|---------------|---------------|
| DOE Funds: \$5,000,000  | U. Kentucky   | Rick Honaker  |
| <ul><li>Cost Share: \$1,333,830</li></ul>   |               | Josh Werner   |
| Overall Project Performance Dates   | Virginia Tech | Aaron Noble   |
| Phase 1: 10/1/2019 – 3/31/2021  |               | Wencai Zhang  |
| <ul> <li>Phase 2: 4/1/2021 – 12/31/2022</li> </ul>  | U. Utah       | Michael Free  |
| Overall Project Objectives  |               | Xinbo Yang    |
| <ul> <li>Demonstration of scaled production of<br/>high purity rare earth oxide mix from</li> </ul> | Alliance Coal | Joe White     |
| coal refuse sources using innovative  | KY River Prop | Chuck Mullins |
| technologies that will reduce cost and  | MST           | Charles Roos  |
| improve environmental outcomes.   |               |               |

# **Technology Background**

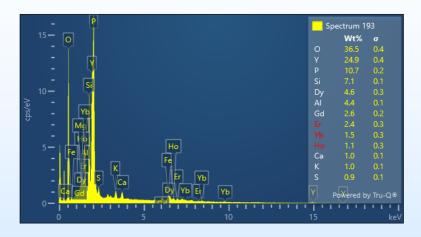
- REE mineral grain size is less than 10 microns which limits the ability to pre-concentrate.
- Requires direct hydrometallurgical processing which leads to high contamination in PLS.
- Low feed grade, poor leaching recovery, low PLS concentration, and waste disposal are other concerns of note.
- Prior analyses have shown that chemical costs (acid and base) are a major impediment to an economically viable process.

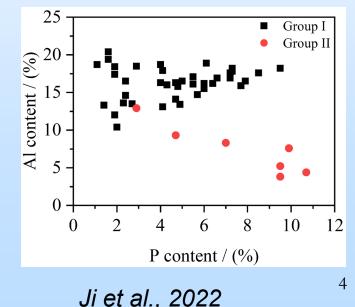


OPEX breakdown for a hypothetical coal-based REE recovery facility.

## **Mineralogical Analysis**

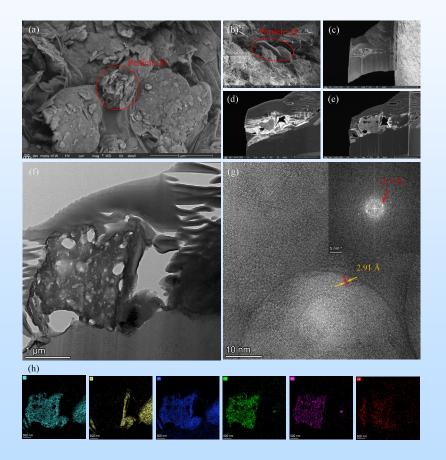
- Study was conducted on coarse refuse generated from the Baker seam.
- Most particles showed relatively high contents of Ca, Sr, and Ba, agreeing with the chemical formula of crandallitegroup minerals.
- The REEs in zircon and xenotime were primarily heavy REEs.
- REEs in apatite were primarily light REEs.

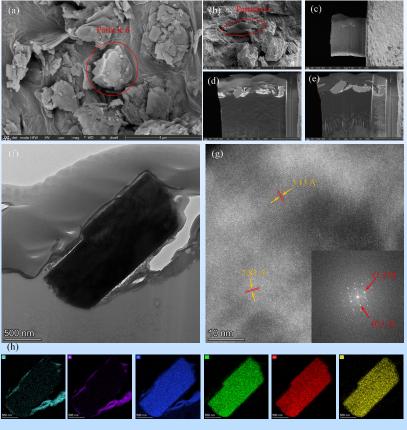




## **Mineralogical Analysis**

□ REE mineral grain size is less than 10 microns; mostly < 1 micron.





## **Technical Approach**

- 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.

| Size Fraction | Weight |        | Major Minerals (%) |         |           |  |  |  |  |  |  |  |  |
|---------------|--------|--------|--------------------|---------|-----------|--|--|--|--|--|--|--|--|
| (mesh)        | (%)    | Pyrite | Silica             | Calcite | Kaolinite |  |  |  |  |  |  |  |  |
| +100          | 8.84   | 6.3    | 6.4                | 68.2    | 4.9       |  |  |  |  |  |  |  |  |
| 100 x 200     | 43.72  | 20.0   | 14.1               | 62.8    | 3.1       |  |  |  |  |  |  |  |  |
| 200 x 325     | 14.88  | 43.3   | 12.2               | 35.4    | 1.1       |  |  |  |  |  |  |  |  |
| -325          | 32.56  | 30.1   | 44.8               | 21.0    | 3.7       |  |  |  |  |  |  |  |  |
| Total         | 100.00 | 25.5   | 23.1               | 45.6    | 3.2       |  |  |  |  |  |  |  |  |

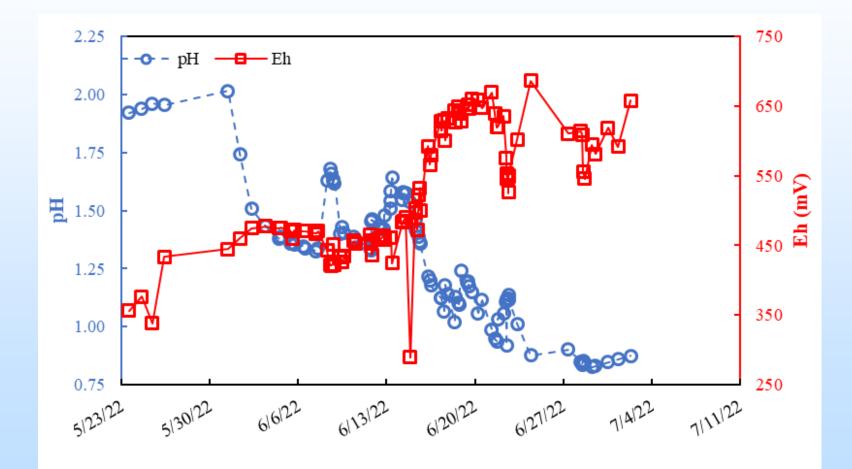


## Technical Progress Biooxidation: Sulfuric Acid Production

- Acidithiobacilus ferrooxidans was used to oxidize coal pyrite.
- Pyrite (60%+ grade) slurry was added at a 5% solids from a 3000-gal tank.
- Two 3000-gallon bioreactors.
- 300 gallons daily production of 0.5 M sulfuric acid.



### Technical Progress Biooxidation: Sulfuric Acid Production

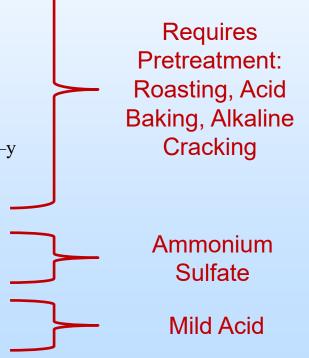


## Technical Approach Process Pretreatment Requirements

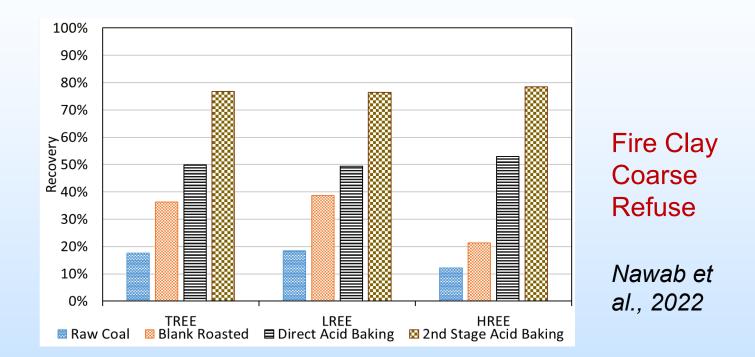
#### Mineral association

- monazite (Ce,La,Pr,Nd,Th,Y)PO<sub>4</sub>
- crandallite  $(CaAl_3(PO4)_2(OH)_5 \bullet (H_2O))$
- xenotime (YPO<sub>4</sub>)
- bastnaesite (Ce, La)CO<sub>3</sub>F
- zircon ZrSiO<sub>4</sub>, (Zr<sub>1-y</sub>, REE<sub>y</sub>)(SiO4)<sub>1-x</sub>(OH)<sub>4x-y</sub>
- apatite  $Ca_{10}(PO_4)_6(OH,F,CI)_2$
- □ Ion substitution in clay

Organic association



## Technical Progress Process Pretreatment Requirements



Calcination (roasting) at 600°C improves light REE recovery due to the decomposition of crandallite-group minerals.
 Acid baking decomposes monazite, xenotime and zircon to elevated

heavy REE recovery.

# Technical Approach Leaching Options

- Direct recovery from acid mine drainage
- Heap leaching of coarse refuse
- Tank leaching of coal waste

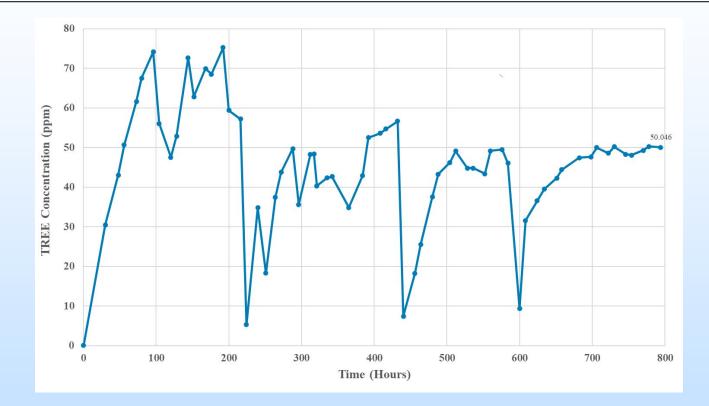


# Technical Progress Heap Leaching

- 2000 tons of Baker (West Kentucky No. 13) seam coarse coal refuse
- □ 65 x 65 ft<sup>2</sup> area with a 15-ft vertical lift
- Underlined with a clay liner and a HDPE 60 mil liner
- □ 100-yr rain event
- Sump to collect 3000 gallons of the pregnant leach solution (PLS)

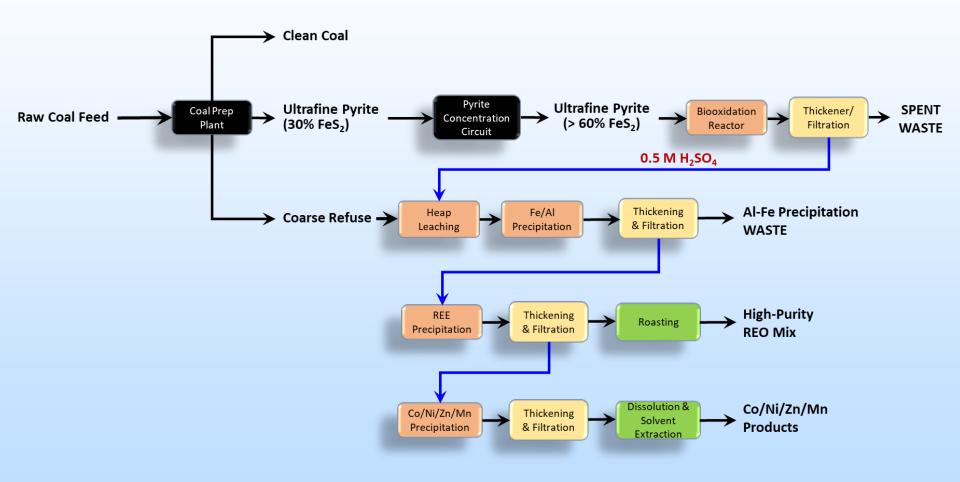


#### Technical Progress Heap Leaching: Pregnant Leach Solution

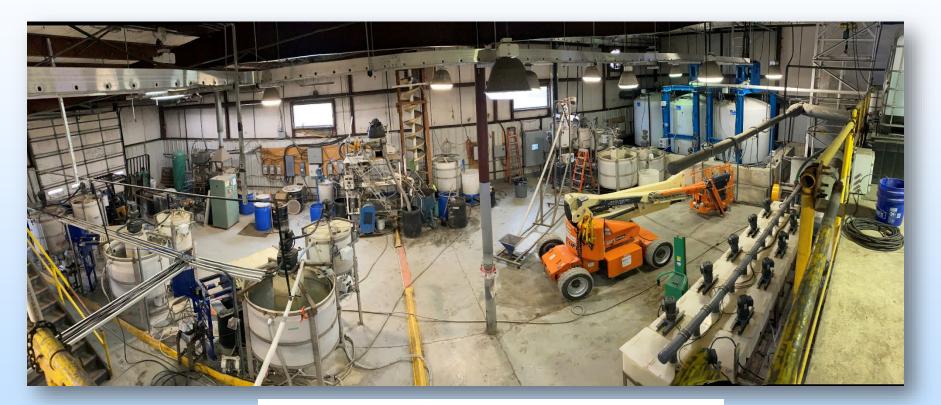


- Started at 75 ppm and leveled off at 50 ppm; spikes represent dilution from rain events.
- $\square$  > 3000 ppm of iron and aluminum if the PLS hampering economics.

### Technical Progress Block Flow Diagram of Process

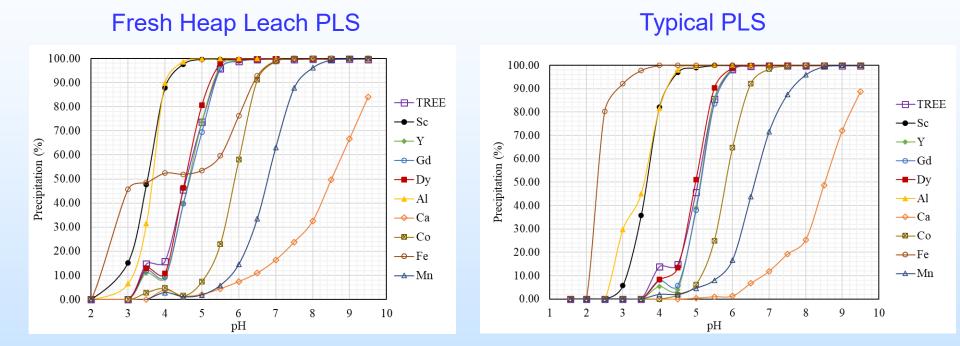


### Technical Progress Block Flow Diagram of Process



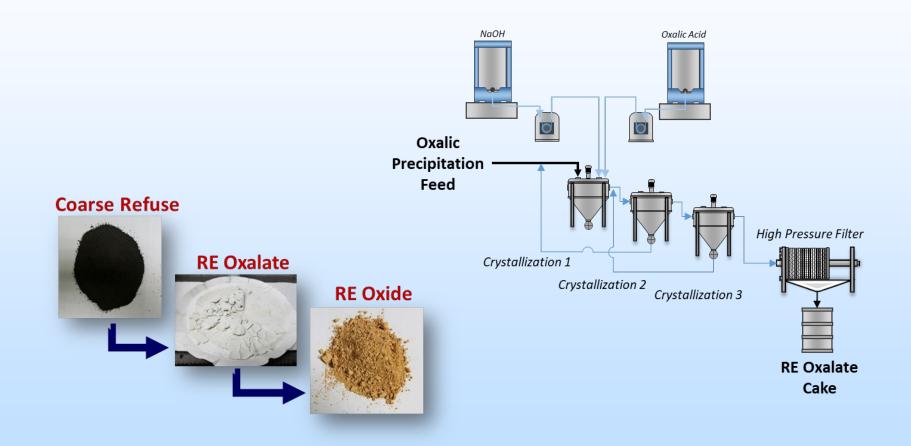
| Production Parameter                  | FOA 2003 |
|---------------------------------------|----------|
| Designed Feed Rate (kg/hr)            | 113.5    |
| Capable Daily REO Production (kg/day) | 0.44     |
| Capable Annual REO Production (kg/yr) | 110      |

#### Technical Progress Heap Leaching: Pregnant Leach Solution



- Staged precipitation can effectively remove Fe<sup>3+</sup> and Al while concentrating REEs and other critical metals.
- The natural heap PLS contains a significant amount of Fe<sup>2+</sup> which starts precipitating at pH 5.5 thereby requiring a step to oxidize ferrous to ferric potentially by biooxidixation.

#### Technical Progress High Purity REO Production



#### Technical Progress High Purity REO Production

Rare earth oxides concentrations generated through testing of various feedstocks under different circuit arrangements.

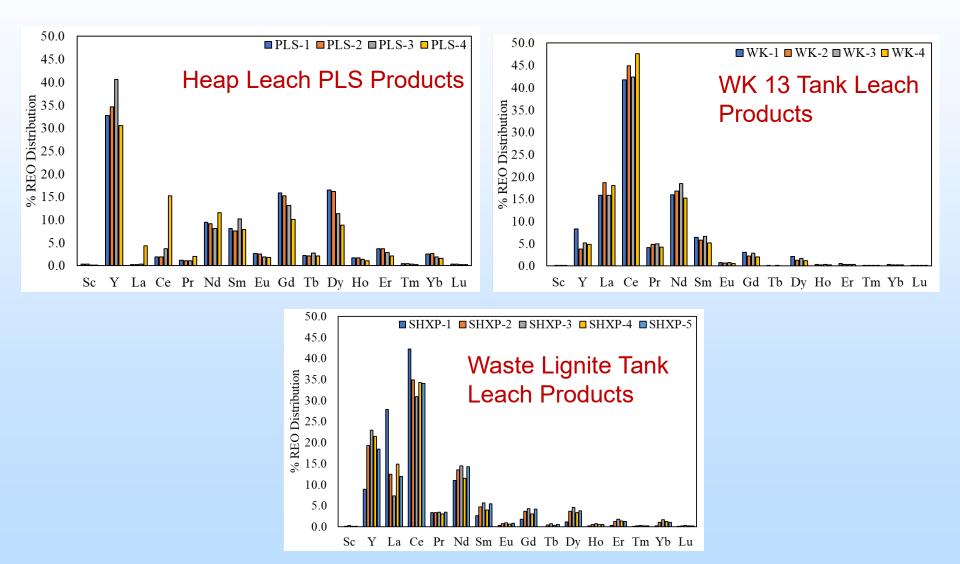
| Test Type-Number         % REO         % Heavy REO           Heap Leach PLS / Acid Mine Drainage         PLS-1         60.81         36.61           PLS-2         61.16         37.81         PLS-3         87.02         53.57           PLS-3         87.02         53.57         PLS-4         82.31         38.58           Coal Refuse-Western Kentucky No.13         WK-1         95.45         11.52         WK-2         88.19         5.37           WK-1         95.45         11.52         WK-2         88.19         5.37           WK-2         88.19         5.37         WK-3         40.90         3.27           WK-4         49.82         3.46         5.37         WK-4         49.82         3.46           SHXP-1         65.39         7.02           SHXP-2         36.19         9.60         SHXP-3         97.10         31.82           SHXP-3         97.10         31.82         SHXP-4         80.52         23.11           SHXP-5         77.71         20.01         50.51         50.51 |                  |                   |            |
|--|------------------|-------------------|------------|
| PLS-1         60.81         36.61           PLS-2         61.16         37.81           PLS-3         87.02         53.57           PLS-4         82.31         38.58           Coal Refuse-Western Kentucky No.13           WK-1         95.45         11.52           WK-2         88.19         5.37           WK-3         40.90         3.27           WK-4         49.82         3.46           Secondary Source-Shakespeare           SHXP-1         65.39         7.02           SHXP-2         36.19         9.60           SHXP-3         97.10         31.82           SHXP-4         80.52         23.11   | Test Type-Number | % REO             | %Heavy REO |
| PLS-2         61.16         37.81           PLS-3         87.02         53.57           PLS-4         82.31         38.58           Coal Refuse-Western Kentucky No.13           WK-1         95.45         11.52           WK-2         88.19         5.37           WK-3         40.90         3.27           WK-4         49.82         3.46           Secondary Source-Shakespeare           SHXP-1         65.39         7.02           SHXP-2         36.19         9.60           SHXP-3         97.10         31.82           SHXP-4         80.52         23.11   | Heap Lea         | ch PLS / Acid Min | e Drainage |
| PLS-3         87.02         53.57           PLS-4         82.31         38.58           Coal Refuse-Western Kentucky No.13           WK-1         95.45         11.52           WK-2         88.19         5.37           WK-3         40.90         3.27           WK-4         49.82         3.46           SHXP-1         65.39         7.02           SHXP-2         36.19         9.60           SHXP-3         97.10         31.82           SHXP-4         80.52         23.11  | PLS-1            | 60.81             | 36.61      |
| PLS-4         82.31         38.58           Coal Refuse-Western Kentucky No.13           WK-1         95.45         11.52           WK-2         88.19         5.37           WK-3         40.90         3.27           WK-4         49.82         3.46           Secondary Source-Shakespeare           SHXP-1         65.39         7.02           SHXP-2         36.19         9.60           SHXP-3         97.10         31.82           SHXP-4         80.52         23.11   | PLS-2            | 61.16             | 37.81      |
| Coal Refuse-Western Kentucky No.13           WK-1         95.45         11.52           WK-2         88.19         5.37           WK-3         40.90         3.27           WK-4         49.82         3.46           Secondary Source-Shakespeare           SHXP-1         65.39         7.02           SHXP-2         36.19         9.60           SHXP-3         97.10         31.82           SHXP-4         80.52         23.11   | PLS-3            | 87.02             | 53.57      |
| WK-1         95.45         11.52           WK-2         88.19         5.37           WK-3         40.90         3.27           WK-4         49.82         3.46           Secondary Source-Shakespeare           SHXP-1         65.39         7.02           SHXP-2         36.19         9.60           SHXP-3         97.10         31.82           SHXP-4         80.52         23.11  | PLS-4            | 82.31             | 38.58      |
| WK-2         88.19         5.37           WK-3         40.90         3.27           WK-4         49.82         3.46           Secondary Source-Shakespeare           SHXP-1         65.39         7.02           SHXP-2         36.19         9.60           SHXP-3         97.10         31.82           SHXP-4         80.52         23.11   | Coal Refu        | 1se-Western Kentu | cky No.13  |
| WK-3         40.90         3.27           WK-4         49.82         3.46           Secondary Source-Shakespeare         7.02           SHXP-1         65.39         7.02           SHXP-2         36.19         9.60           SHXP-3         97.10         31.82           SHXP-4         80.52         23.11  | WK-1             | 95.45             | 11.52      |
| WK-4         49.82         3.46           Secondary Source-Shakespeare         7.02           SHXP-1         65.39         7.02           SHXP-2         36.19         9.60           SHXP-3         97.10         31.82           SHXP-4         80.52         23.11  | WK-2             | 88.19             | 5.37       |
| Secondary Source-ShakespeareSHXP-165.397.02SHXP-236.199.60SHXP-397.1031.82SHXP-480.5223.11   | WK-3             | 40.90             | 3.27       |
| SHXP-1         65.39         7.02           SHXP-2         36.19         9.60           SHXP-3         97.10         31.82           SHXP-4         80.52         23.11  | WK-4             | 49.82             | 3.46       |
| SHXP-236.199.60SHXP-397.1031.82SHXP-480.5223.11  | Secon            | dary Source-Shake | speare     |
| SHXP-397.1031.82SHXP-480.5223.11   | SHXP-1           | 65.39             | 7.02       |
| SHXP-4 80.52 23.11   | SHXP-2           | 36.19             | 9.60       |
|  | SHXP-3           | 97.10             | 31.82      |
| SHXP-5 77.71 20.01   | SHXP-4           | 80.52             | 23.11      |
| 51111 5 77.71 <b>20.01</b>   | SHXP-5           | 77.71             | 20.01      |

Heap Leach PLS from WK #13 coarse refuse

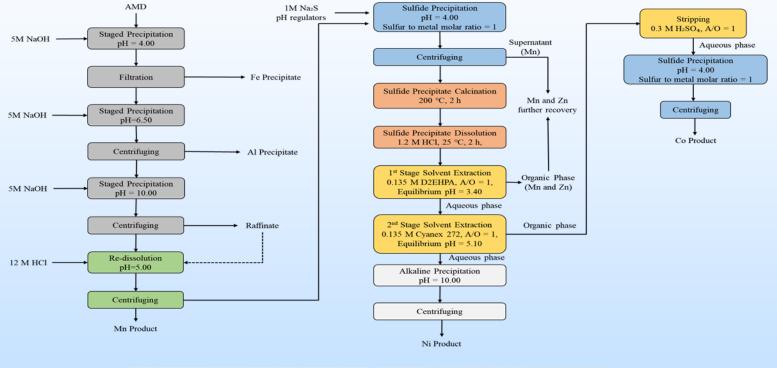
Direct Tank Leach of WK #13 coarse refuse

Lignite coal from a waste product of construction sand production

#### Technical Progress High Purity REO Production



#### Technical Progress High Purity Co/Ni/Mn Production



NiO = 96.2%



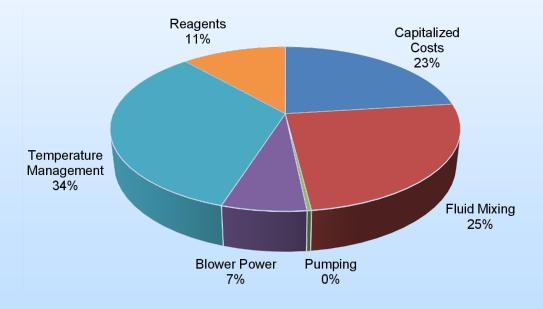


CoS = 98.0%

#### Techno-Economic Analysis Biooxidation Cost Analysis

- The biooxidation unit is a large cost component, but it shows notable cost advantages over conventional acid leaching.
- Largest cost components = mixing, temperature management, and capital (~81% of total).

#### Total cost = \$0.05 / kg H<sub>2</sub>SO<sub>4</sub> equivalent



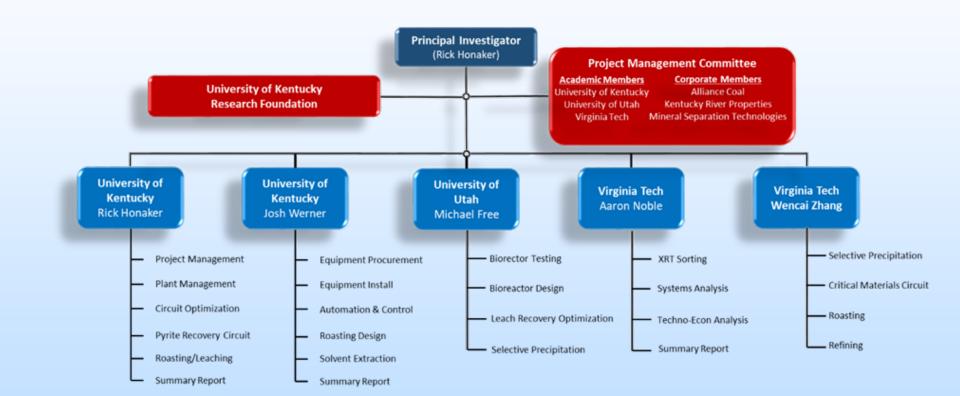
## Summary

- REE mineralization in high rank coals presents an economic challenge.
- Bioreactors have been tested at large scale and successfully produced 0.5 M sulfuric acid solutions having 0.75 pH from coal pyrite.
- REEs and CMs effectively recovered from various coal-based sources at an expanded scale.
- □ REO purity levels higher than 90% REO mix achieved.
- Co and Ni greater than 98% have been produced as well as a MnOH product.
- Heap leaching presents economic challenges due PLS contaminants and geotechnical issues.

### Questions

Rick Honaker rick.honaker@uky.edu

## **Organization Chart**



## Gantt Chart (Phase 1)

|    |   |         | Project Month |     |    |     |   |   |    |     |   |     |    |              |
|----|---|---------|---------------|-----|----|-----|---|---|----|-----|---|-----|----|--------------|
| ID | Task  |         | 019           |     |    |     |   |   | 20 |     |   |     | 20 |              |
|    |   | 0       | ND            | ) ] | FN | 1 A | Μ | J | J  | A S | 0 | N D | JF | M            |
|    | DOE Required Tasks  |         |               | 1 1 | 2/ |     |   |   |    |     | - |     |    | _            |
| 1  | Project Management & Planning*  |         | Ŷ             | Ϋ́  | 4  |     |   |   |    |     |   |     |    |              |
| 2  | Finanical Plan for Commercialization*   |         |               |     | 4  |     |   |   |    |     |   |     |    |              |
| 3  | Techno-Economic Assessment*   |         |               |     |    |     |   |   |    |     |   |     |    |              |
| 4  | Provide Split Samples*  |         |               |     |    |     |   |   |    |     |   |     |    |              |
| 5  | Feasibility Study*  |         |               |     |    |     |   |   |    |     |   |     |    | V            |
|    | Laboratory Support Tasks  | <b></b> |               |     |    | -   | - |   |    |     |   |     |    |              |
| 6  | Optimization of Physical Separaitons (crush, grind, sort, calicte float)  |         |               |     | )  | x   | х |   |    |     |   |     |    |              |
| 7  | Optimization of Acid Generation (pyrite recovery, bioreduction )  |         |               |     | )  | x   | х |   |    |     |   |     |    | 5            |
| 8  | Optimizaton of Roasting & Leaching  |         |               |     | )  | x   | х |   |    |     |   |     |    | 6            |
| 9  | Optimization of REE Recovery (selective precip and/or SX)   |         |               |     | )  | x   | х |   |    |     |   |     |    | $\mathbb{V}$ |
| 10 | Optimization of CM Recovery (Co/Mn/Sc Precip or SX)   |         |               |     | )  | x   | х |   |    |     |   |     |    | 8            |
|    | Pilot-Scale Tasks   | _       |               |     |    |     |   | _ |    |     |   |     |    |              |
| 11 | Environmental Monitoring and Management   |         |               |     |    |     |   |   |    |     |   |     |    |              |
| 12 | Pilot Plant Upgrades and Modification (Design, Bidding, procurement, fabrication, installation)                     |         |               |     |    |     |   |   |    |     |   |     |    |              |
| 13 | Feedstock Collection and Preparation  |         |               |     |    |     |   |   |    |     |   |     |    | Ψ.           |
| 14 | Pilot Plant System Shakedown  |         |               |     |    |     |   |   |    |     |   |     |    | 1            |
| 15 | Pilot Plant Operation and Continuous Improvement  |         |               |     |    |     |   |   |    |     |   |     |    | Ą            |
| 16 | Operational Cost Analysis, Refinement and Optimization  |         |               |     |    |     |   |   |    |     |   |     |    |              |
| 17 | Secondary Feedstock Testing   |         |               |     |    |     |   |   |    |     |   |     |    |              |
| 18 | Decommissioning and Disposition   |         |               |     |    |     |   |   |    |     |   |     |    |              |
|    | * = DOE Required Task $X$ = one month delay in activity due to COVID issues<br>$\frac{1}{2}$ = milestone completion |         |               |     |    |     |   |   |    |     |   |     |    |              |

## Gantt Chart (Phase 2)

|    |  |   |  |   | Project Month<br>21 2022 |     |   |   |   |   |   |   |    |   |     |   |    |     |     |     |          |
|----|--|---|--|---|--------------------------|-----|---|---|---|---|---|---|----|---|-----|---|----|-----|-----|-----|----------|
| ID | Task   |   |  |   |                          | 202 | _ | 0 |   | - |   | - |    |   |     |   | _  |     |     |     | <b>D</b> |
|    | DOS De surfre d'Encle  | A |  | J | J                        | A   | 5 | 0 | N | D | J | - | MA | 4 | IVI | J | JA | 4 2 | s c | N N |          |
| 1  | DOE Required Tasks   |   |  |   |                          |     |   |   |   |   |   |   |    |   |     |   |    |     |     |     |          |
| 1  | Project Management & Planning*   |   |  |   |                          |     |   |   |   |   |   |   |    |   |     |   |    |     |     | ╞   | -        |
| 2  | Finanical Plan for Commercialization*                                    |   |  |   |                          |     |   | _ |   |   |   |   |    |   |     |   |    |     |     | 1   | 16/      |
| 3  | Techno-Economic Assessment*  | _ |  |   |                          |     |   |   |   |   |   |   |    |   |     |   |    | _   | 17/ |     |          |
| 4  | Provide Split Samples*   |   |  |   |                          |     |   |   |   |   |   |   |    |   |     |   |    |     | Ý   | Ļ   |          |
| 5  | Feasibility Study*   |   |  |   |                          |     |   |   |   |   |   |   |    |   |     |   |    |     |     | 1   |          |
|    | Laboratory Support Tasks   |   |  |   |                          |     |   |   |   |   |   |   |    |   |     |   |    |     |     | İ.  |          |
| 6  | Optimization of Physical Separaitons (crush, grind, sort, calicte float) |   |  |   |                          |     |   |   |   |   |   |   |    |   |     |   |    |     |     |     |          |
| 7  | Optimization of Acid Generation (pyrite recovery, bioreduction)          |   |  |   |                          |     |   |   |   |   |   |   |    |   |     |   |    |     |     | i.  |          |
| 8  | Optimizaton of Roasting & Leaching                                       |   |  |   |                          |     |   |   |   |   |   |   |    |   |     |   |    |     |     | 1   |          |
| 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                                    |   |  |   |                          |     |   |   |   |   |   |   |    |   |     |   |    |     |     |     |          |
| 13 | Feedstock Collection and Preparation                                     |   |  |   |                          |     |   |   |   |   |   |   |    |   |     |   |    |     |     | i.  |          |
| 14 | Pilot Plant System Shakedown   |   |  |   |                          |     |   |   |   |   |   |   |    |   |     |   |    |     |     |     |          |
| 15 | Pilot Plant Operation and Continuous Improvement                         |   |  |   |                          |     |   |   |   |   |   |   |    |   |     |   | 14 |     |     | i.  |          |
| 16 | Operational Cost Analysis, Refinement and Optimization                   |   |  |   |                          |     |   |   |   |   |   |   |    |   |     |   |    |     |     | !   |          |
| 17 | Secondary Feedstock Testing  |   |  |   |                          |     |   |   |   |   |   |   |    |   |     |   | 15 |     |     |     |          |
| 18 | Decommissioning and Disposition  |   |  |   |                          |     |   |   |   |   |   |   |    |   |     |   |    |     |     |     |          |
|    | * = DOE Required Task  |   |  |   |                          |     |   |   |   |   |   |   |    |   |     |   |    |     |     |     |          |
| 7  | $\frac{1}{1}$ = milestone completion                                     |   |  |   |                          |     |   |   |   |   |   |   |    |   |     |   |    |     |     | i I |          |