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

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Project Overview

- Funding
  - DOE Funds: $5,000,000
  - Cost Share: $1,333,830
- Overall Project Performance Dates
  - Phase 1: 10/1/2019 – 3/31/2021
  - Phase 2: 4/1/2021 – 12/31/2022
- Overall Project Objectives
  - 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.

Organization	Team Member
U. Kentucky	Rick Honaker
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U. Utah	Michael Free
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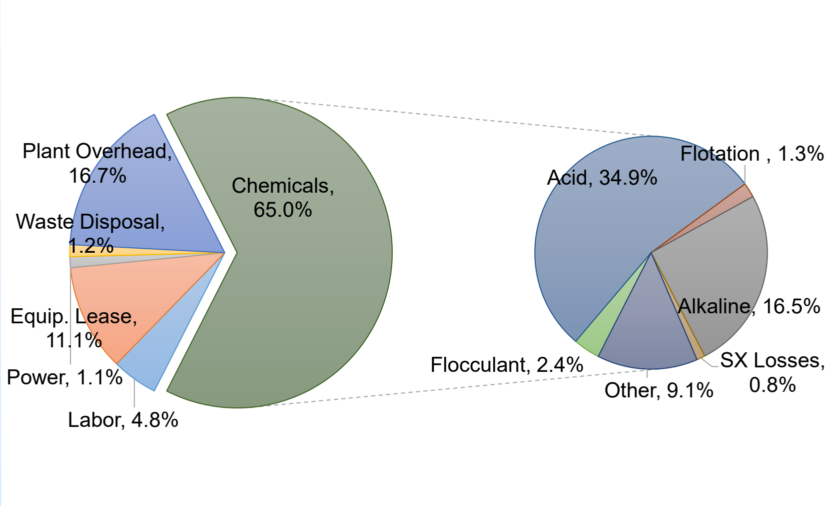
Alliance Coal	Joe White
KY River Prop	Chuck Mullins
MST	Charles Roos

Technology Background

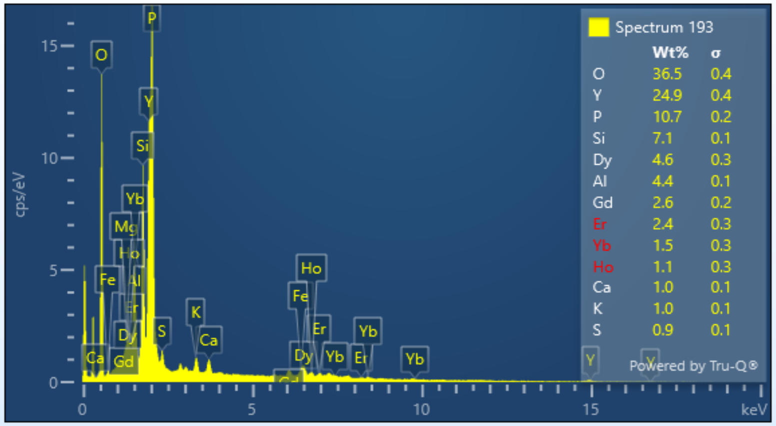
- REE mineral grain size is less than 10 microns which limits the ability to pre-concentrate.
- Requires direct hydrometallurgical processing which leads to high contamination in PLS.
- Low feed grade, poor leaching recovery, low PLS concentration, and waste disposal are other concerns of note.
- Prior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

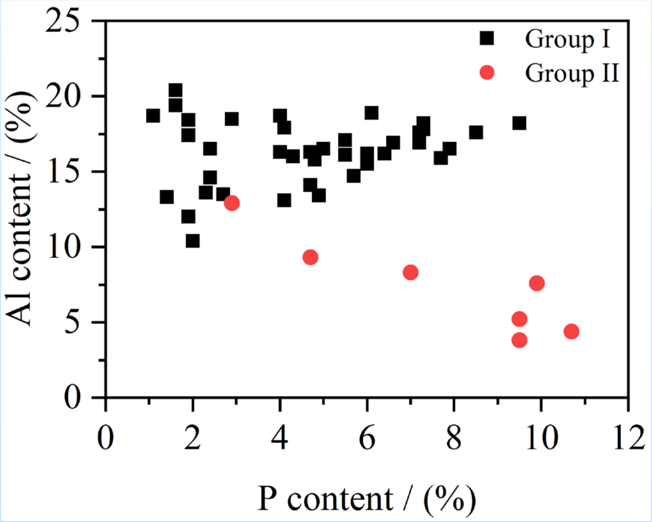


OPEX breakdown for a hypothetical coal-based REE recovery facility.

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 crandallite-group minerals.
- The REEs in zircon and xenotime were primarily heavy REEs.
- REEs in apatite were primarily light REEs.

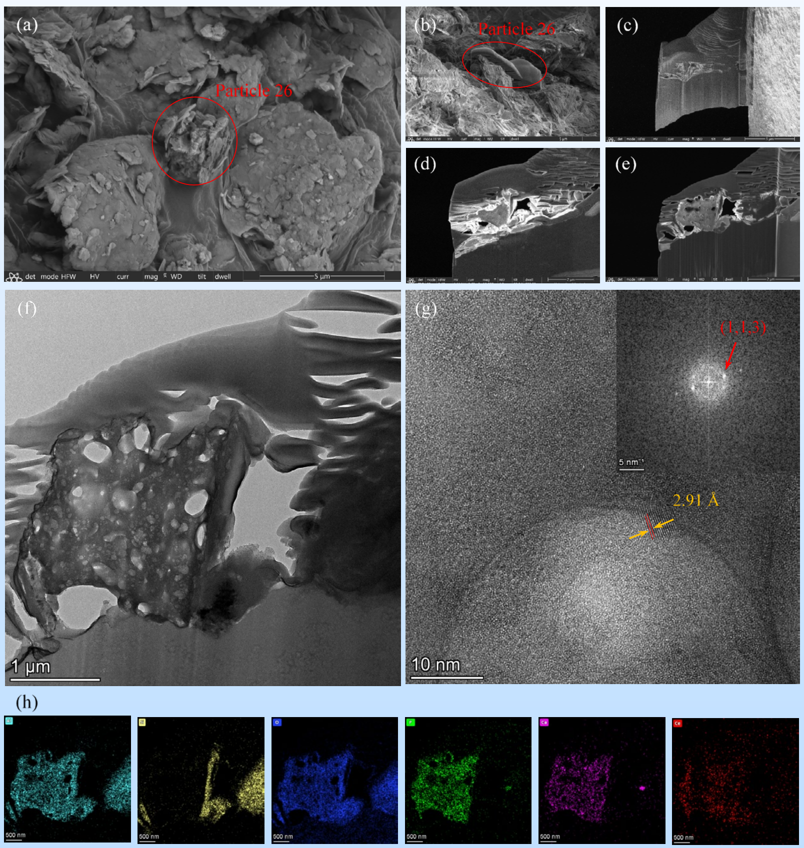


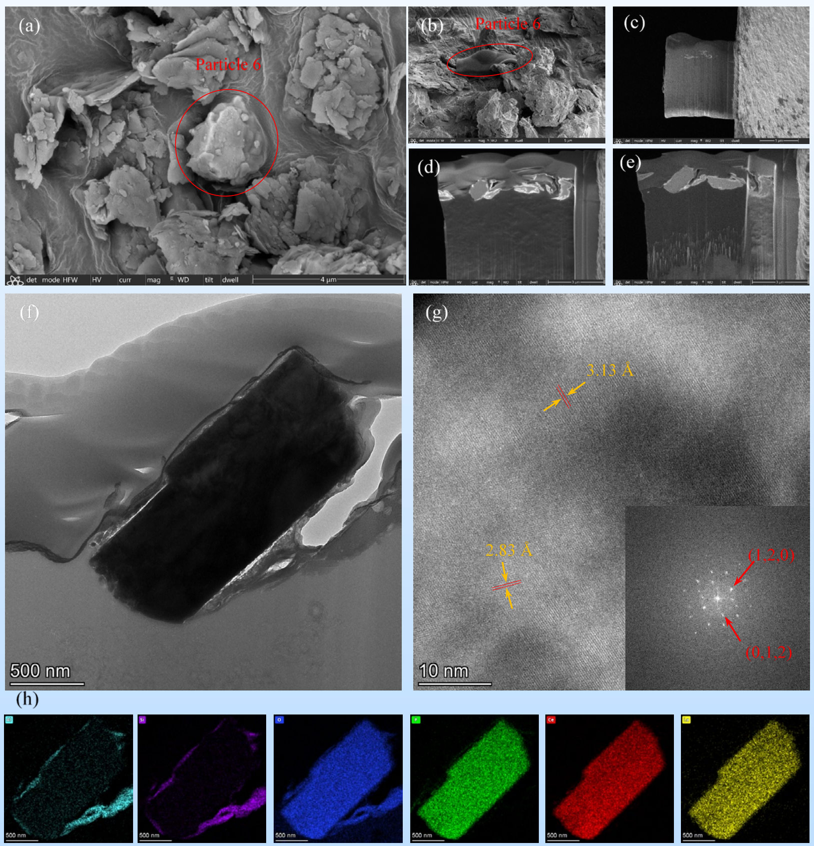


Ji et al., 2022

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 (mesh)	Weight (%)	Major Minerals (%)			
		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**

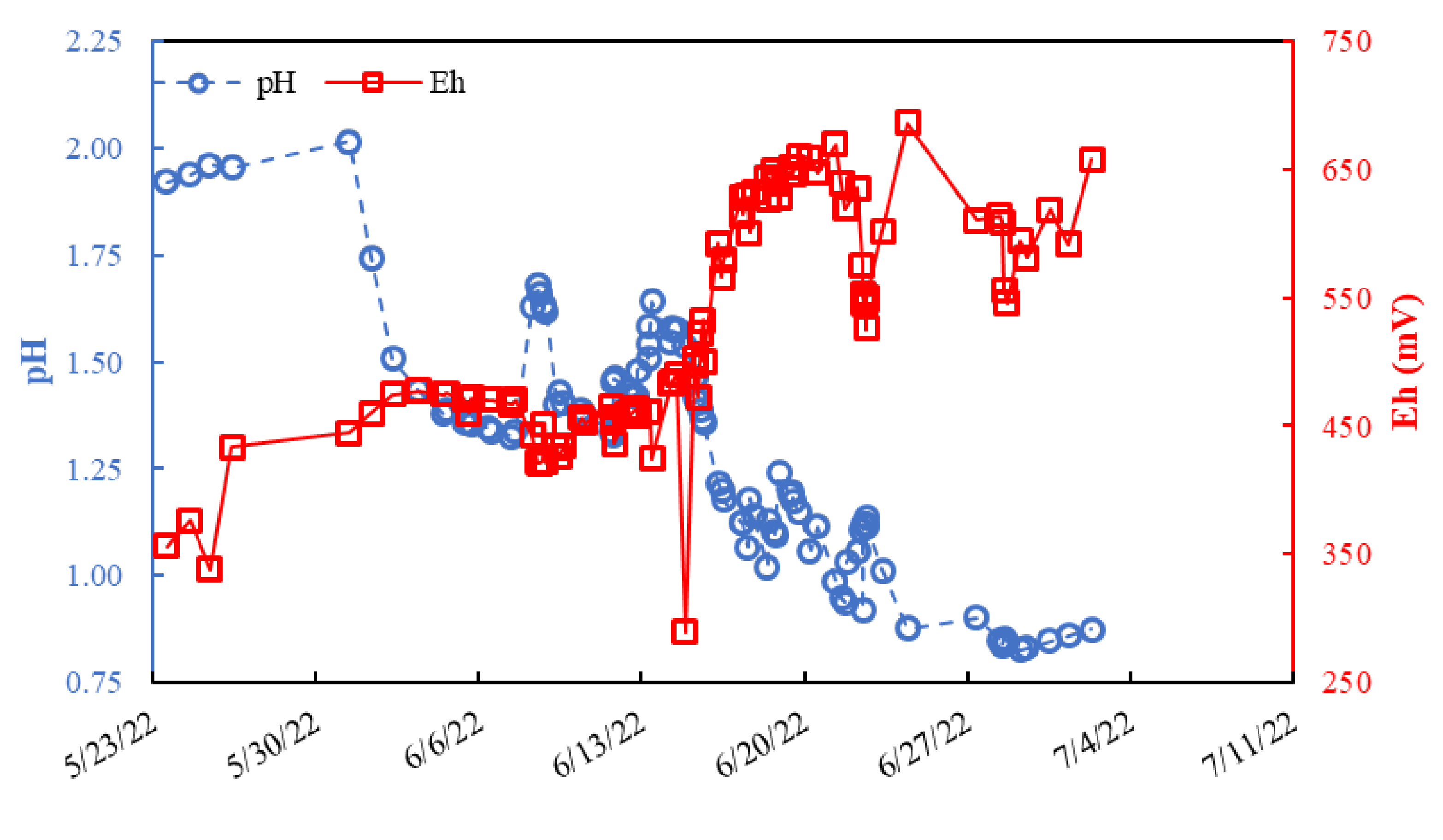
Technical Progress

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 $(Ce,La,Pr,Nd,Th,Y)PO_4$
  - crandallite $(CaAl_3(PO4)_2(OH)_5 \bullet (H_2O))$
  - xenotime (YPO_4)
  - bastnaesite $(Ce, La)CO_3F$
  - zircon $ZrSiO_4$, $(Zr_{1-y}, REE_y)(SiO4)_{1-x}(OH)_{4x-y}$
  - apatite $Ca_{10}(PO_4)_6(OH,F,Cl)_2$

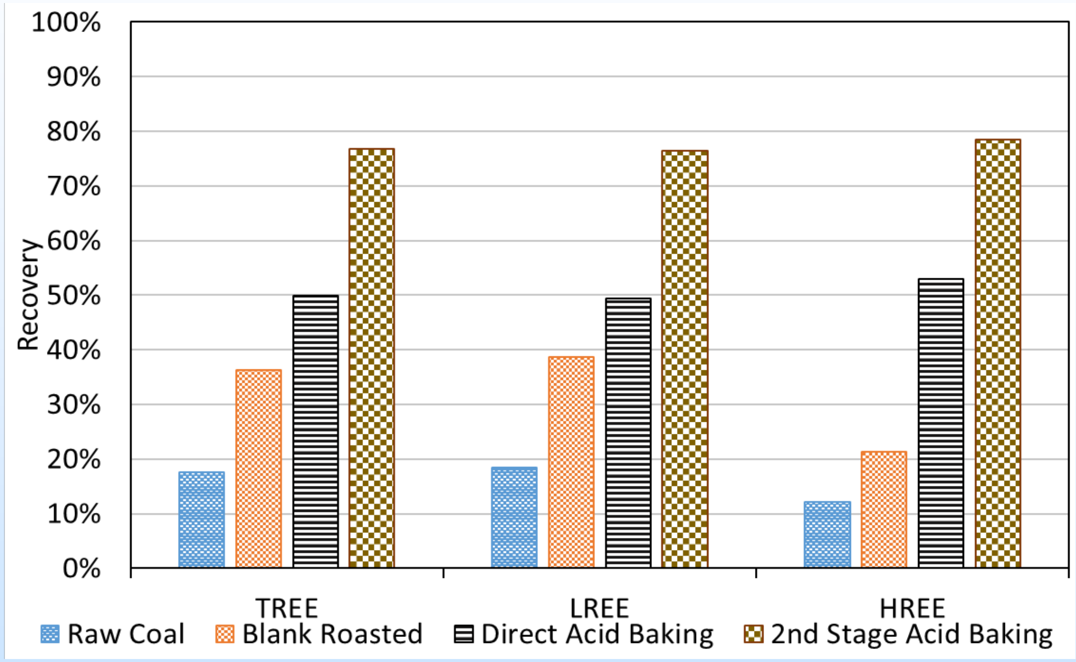
  → Requires Pretreatment: Roasting, Acid Baking, Alkaline Cracking

- Ion substitution in clay → Ammonium Sulfate

- Organic association → Mild Acid

Technical Progress

Process Pretreatment Requirements



Fire Clay Coarse Refuse

Nawab et al., 2022

- Calcination (roasting) at $600^{O}C$ 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

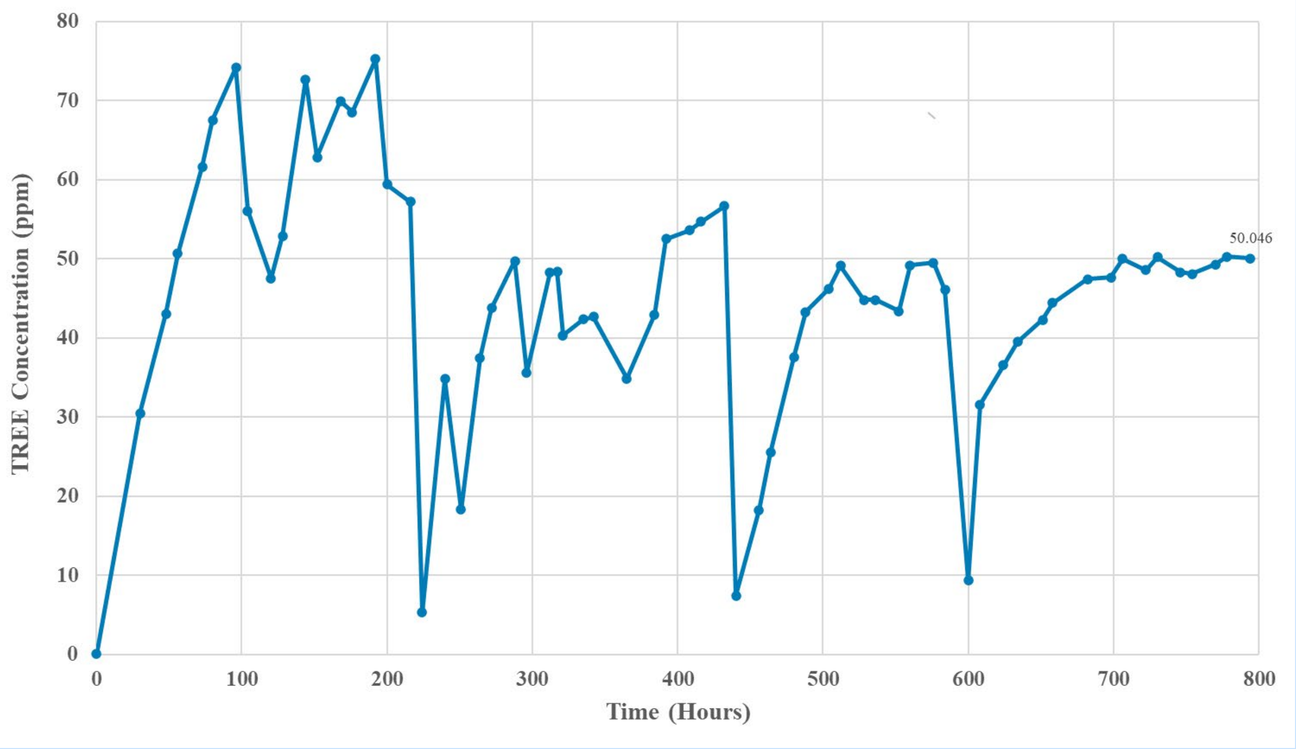
- Direct recovery from acid mine drainage
- Heap leaching of coarse refuse
- Tank leaching of coal waste

Technical Progress
Heap Leaching

- 2000 tons of Baker (West Kentucky No. 13) seam coarse coal refuse
- 65 x 65 ft^2 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

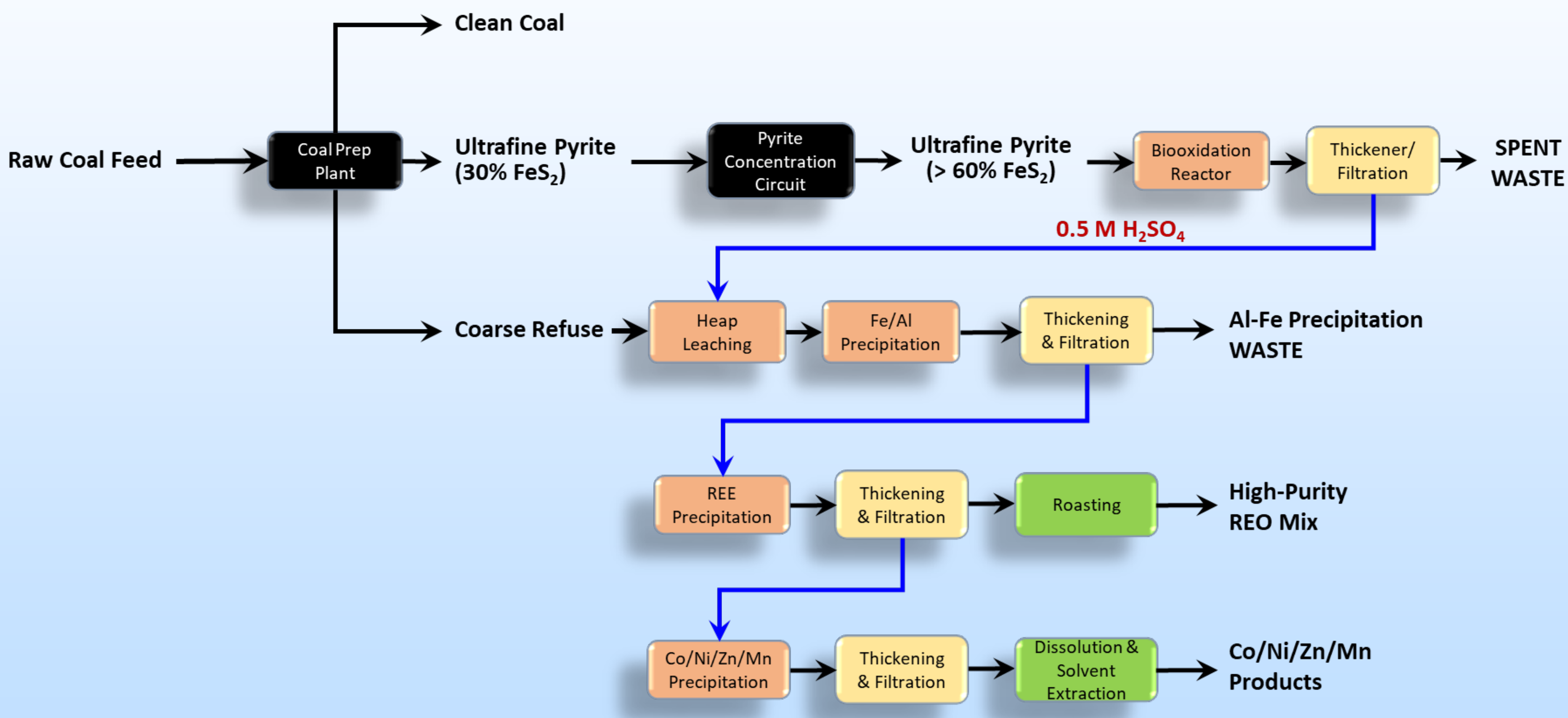
Heap Leaching: Pregnant Leach Solution



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

Technical Progress

Block Flow Diagram of Process



Technical Progress

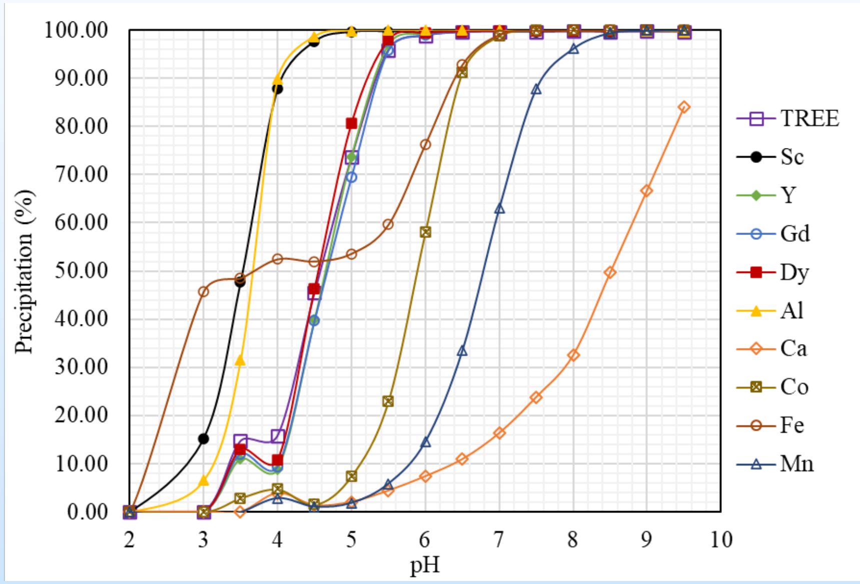
Block Flow Diagram of Process

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

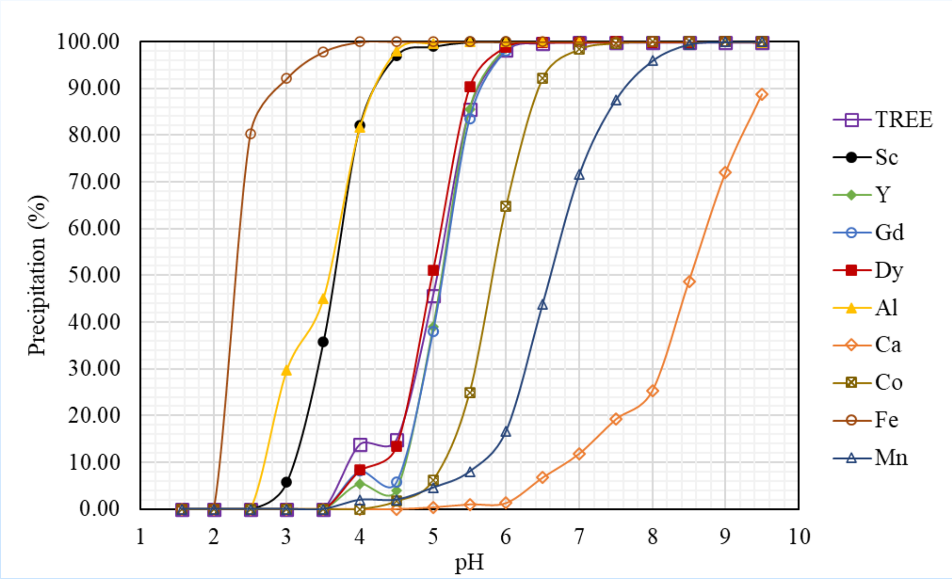
Technical Progress

Heap Leaching: Pregnant Leach Solution

Fresh Heap Leach PLS



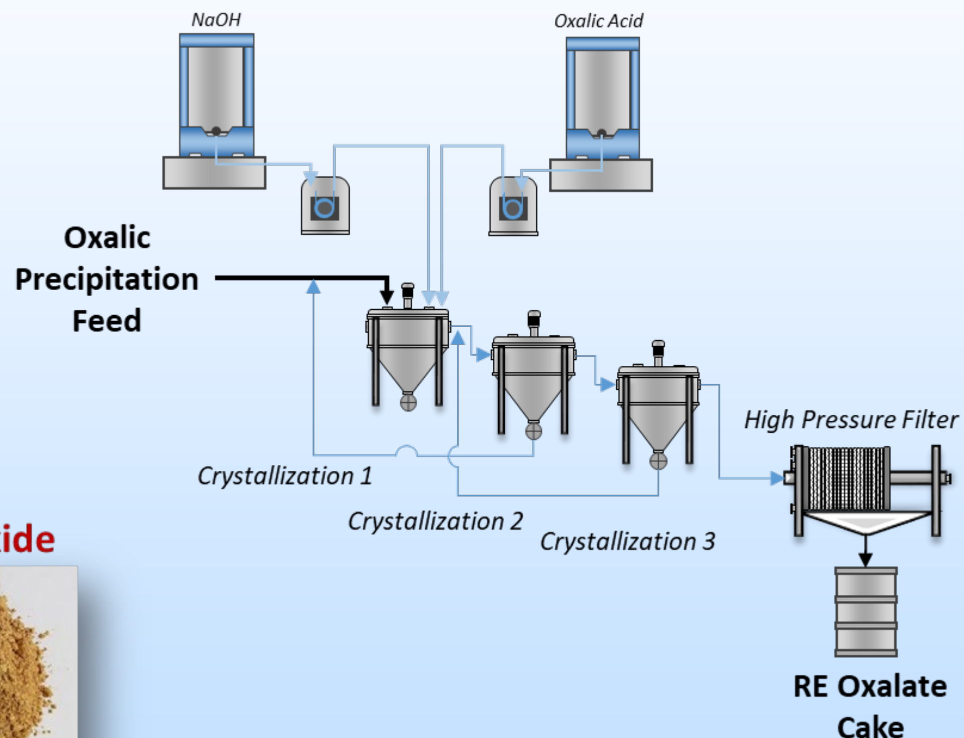
Typical PLS



- Staged precipitation can effectively remove Fe^{3+} and Al while concentrating REEs and other critical metals.
- The natural heap PLS contains a significant amount of Fe^{2+} 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-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
SHXP-5	77.71	20.01

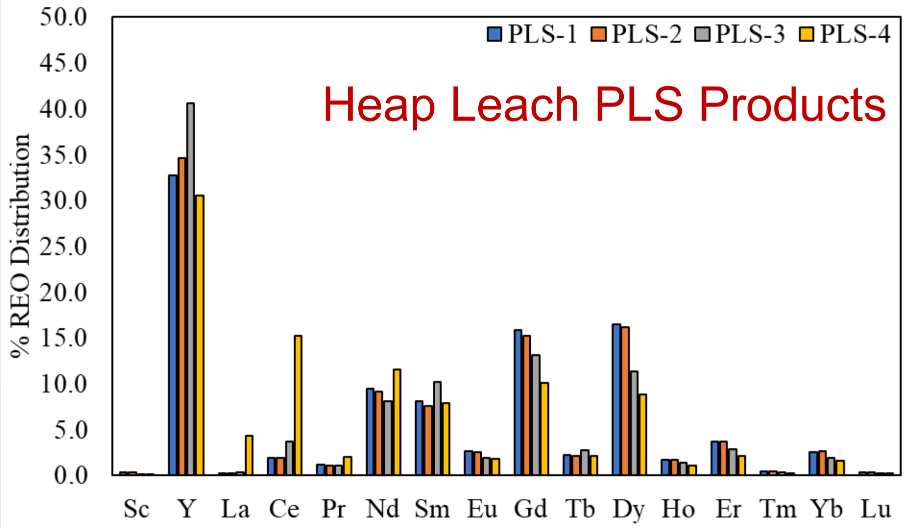
Heap Leach PLS from WK #13 coarse refuse

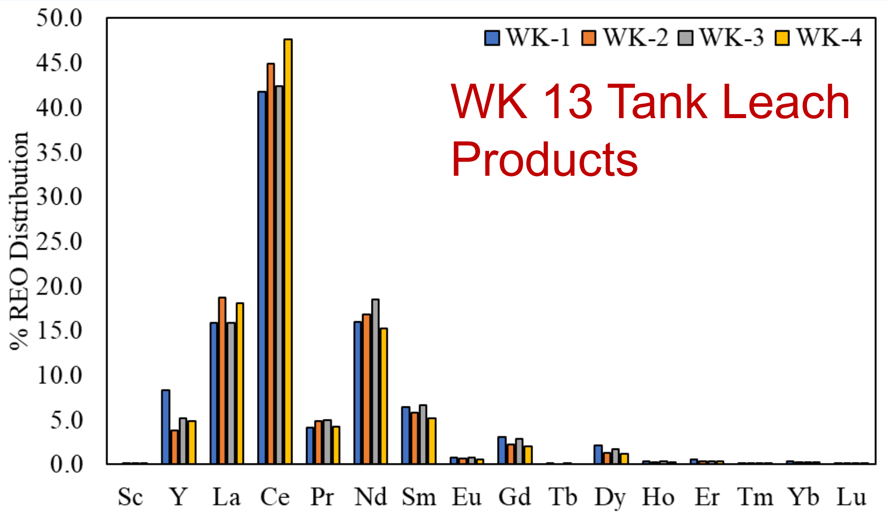
Direct Tank Leach of WK #13 coarse refuse

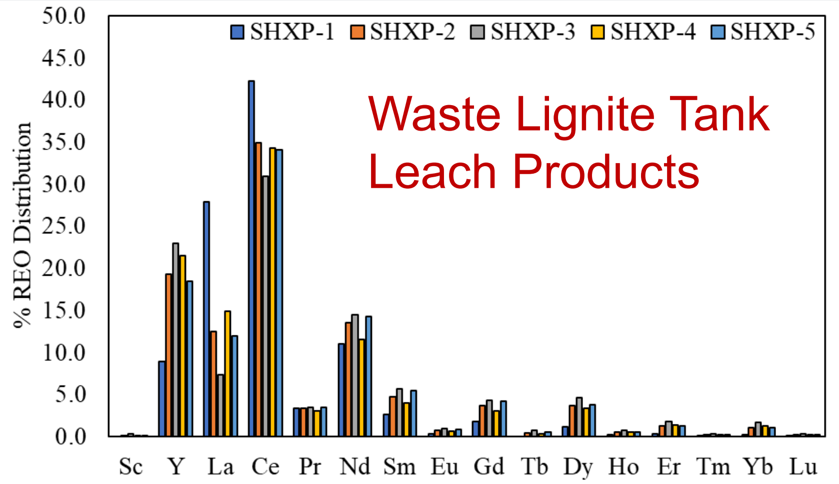
Lignite coal from a waste product of construction sand production

Technical Progress

High Purity REO Production

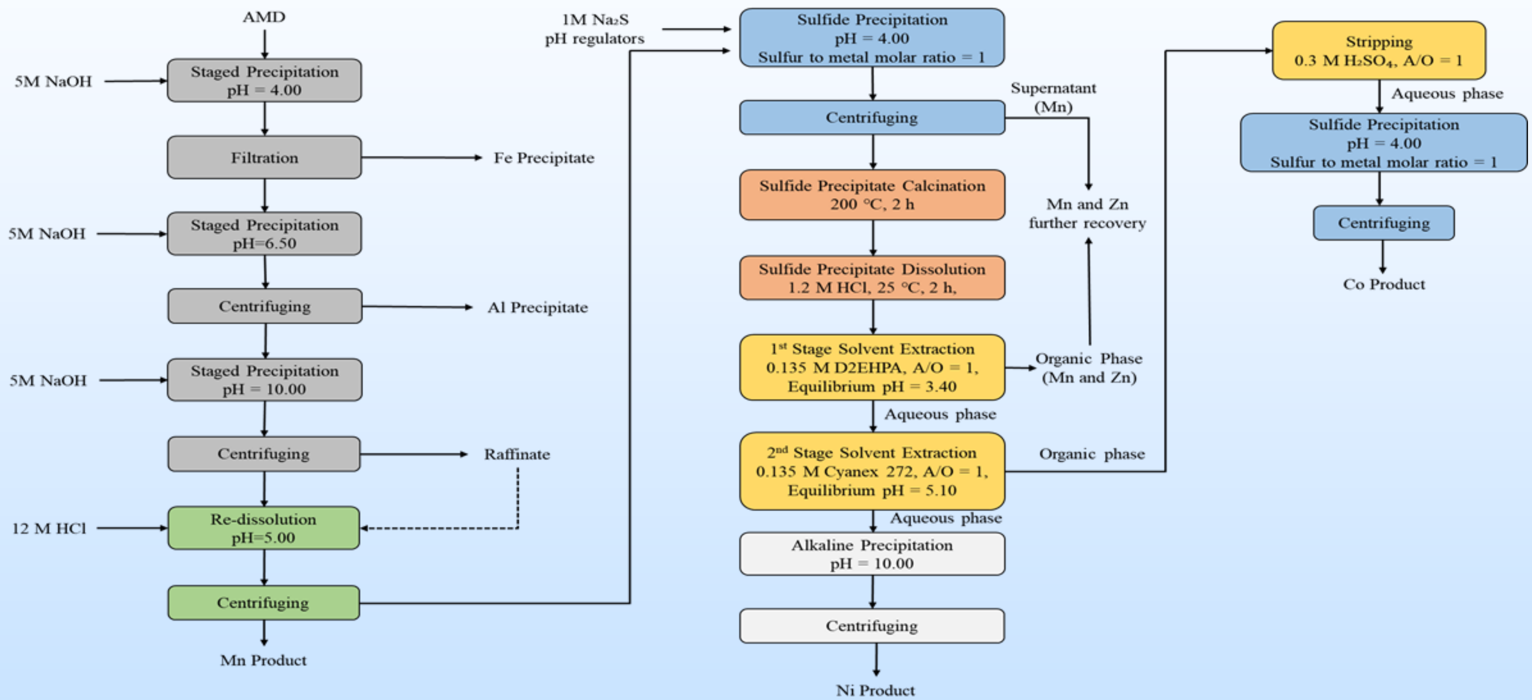




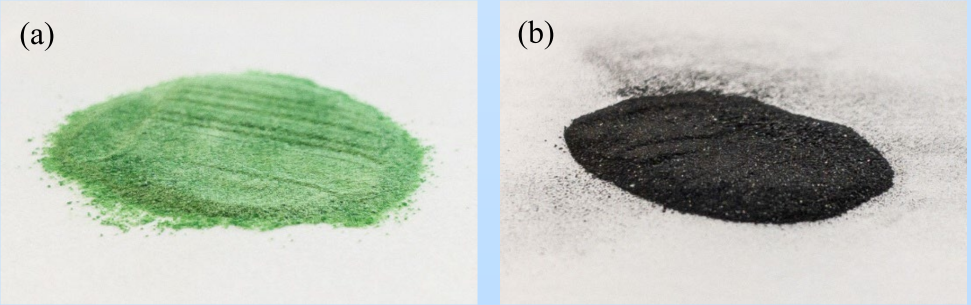


Technical Progress

High Purity Co/Ni/Mn Production



NiO = 96.2%



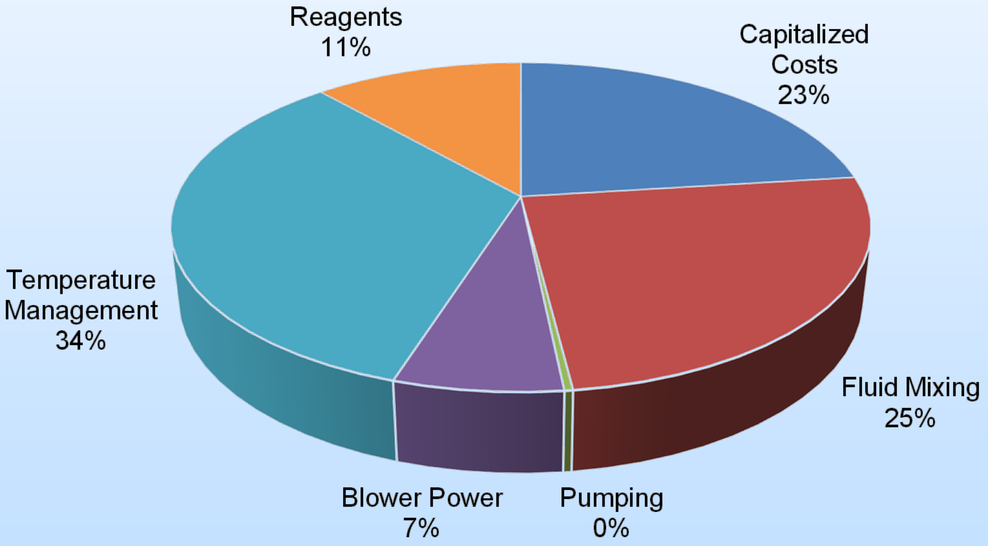
CoS = 98.0%

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_2SO_4 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

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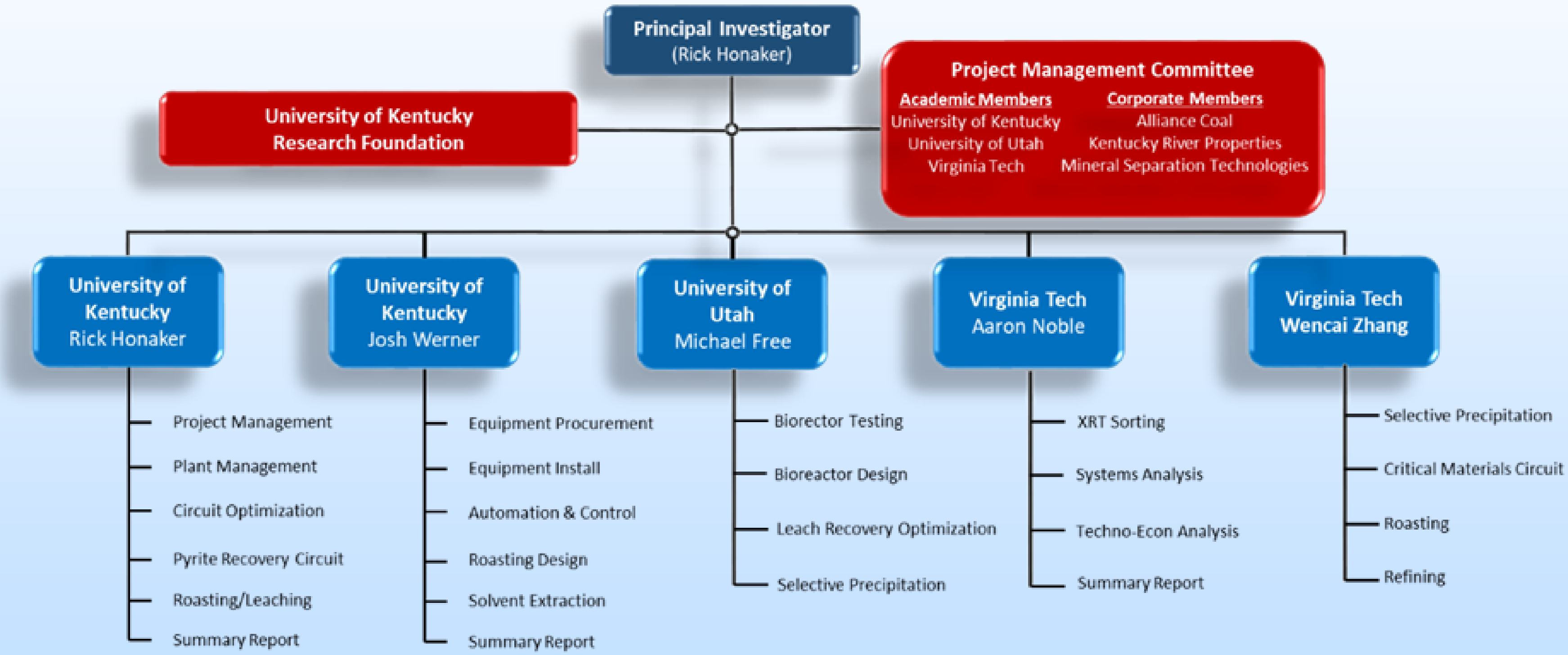
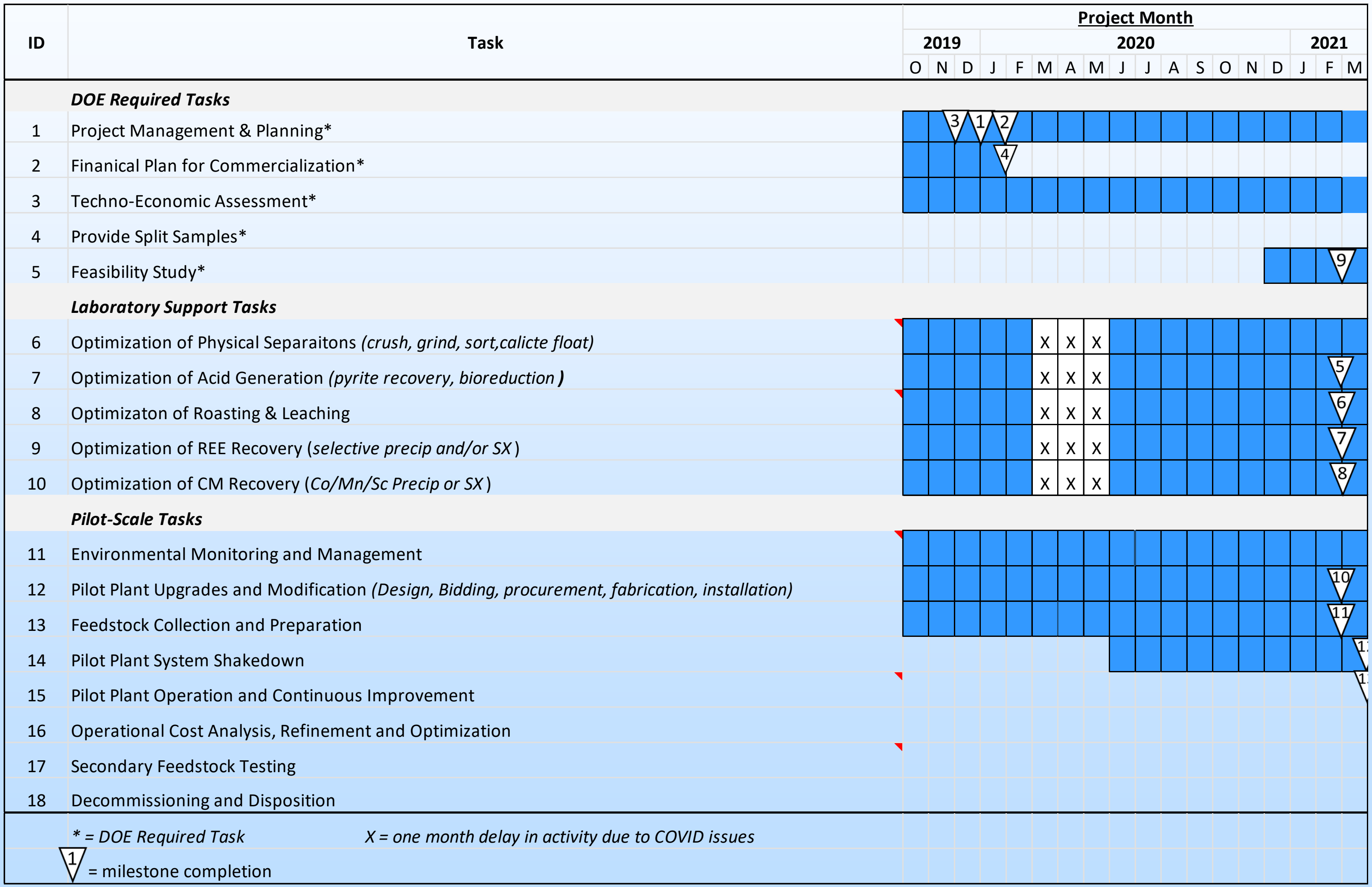
Organization Chart



Gantt Chart (Phase 1)



Gantt Chart (Phase 2)