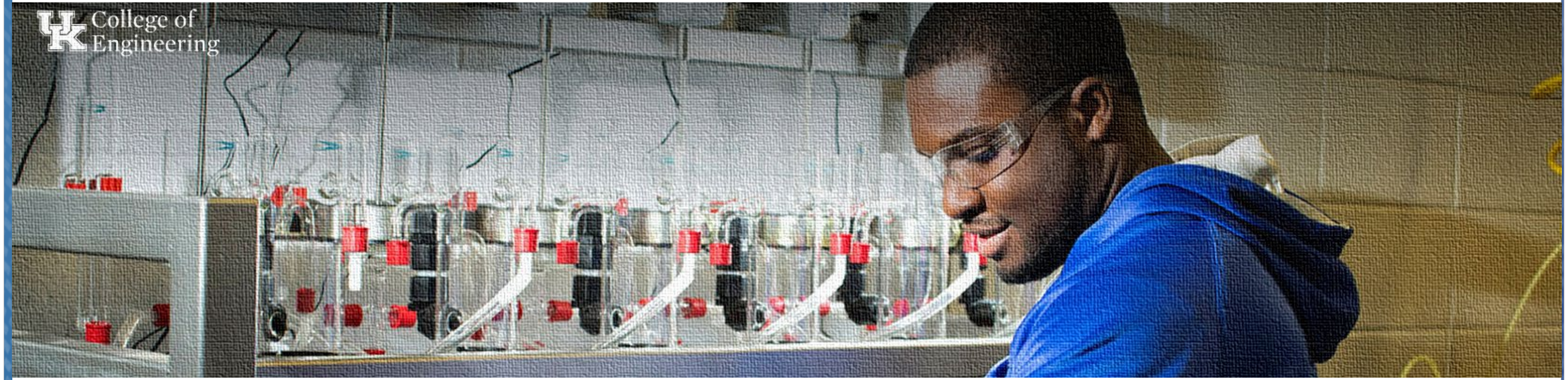

Demonstration of Scaled-Production of Rare Earth Oxides and Critical Materials from U. S. Coal-Based Sources

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Period of Performance: 10/1/2019–6/30/2022
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Project Goals & 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.
- Performance objectives:
  - >90% REO mix purity
  - 200 g/day product rate
  - Co, Li, 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.

Fire Clay Coarse Refuse

Category	Element	Content (ppm)	Resource (tonnes)	Market Value ($*10^6)
Light	Sc	17	1554	$5,441.88
	La	53	4808	$24.04
	Ce	122	10937	$54.69
	Pr	14	1296	$115.70
	Nd	51	4632	$277.93
	Sm	11	994	$16.47
	Eu	2	155	$4.66
Heavy	Y	25	2276	$76.40
	Gd	10	867	$173.32
	Tb	0	44	$33.35
	Dy	6	530	$183.59
	Ho	2	159	$9.07
	Er	5	417	$11.54
	Tm	1	83	$124.99
	Yb	3	273	$27.34
	Lu	0	2	$1.40
Other CM	Co	23	2106	$66.48
	Li	174	15625	$146.87
	Mn	278	25033	$25.03
	V	140	12557	$138.13

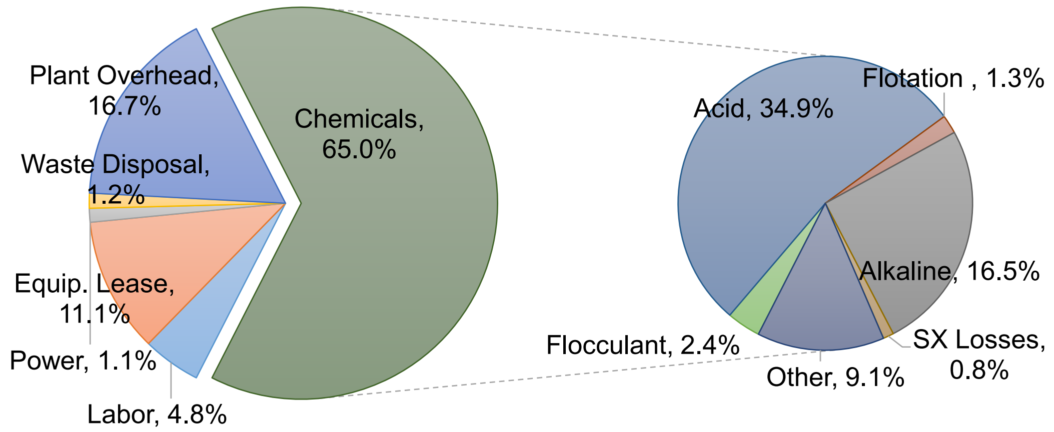
- 90 million tons in surface storage
- 29,000 metric tons of REEs
- 55,000 metric tons of other critical metals
- **$6.9 billion in total metal value**

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.

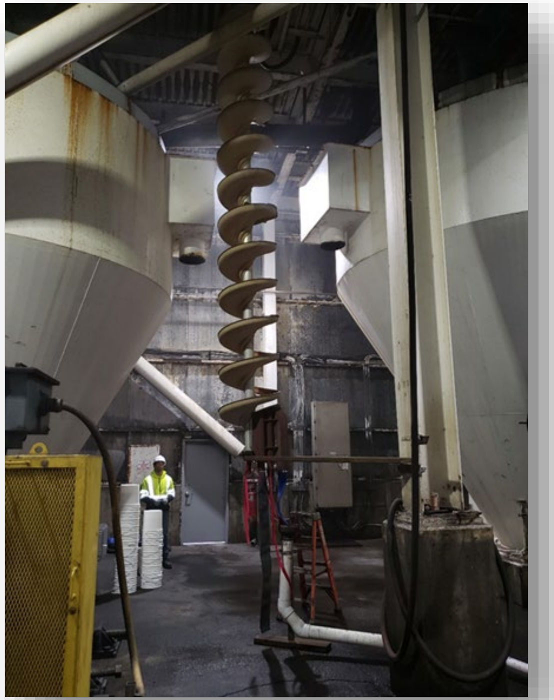
- Low feed grade, poor leaching recovery, low PLS concentration, and waste disposal are other concerns of note.



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.

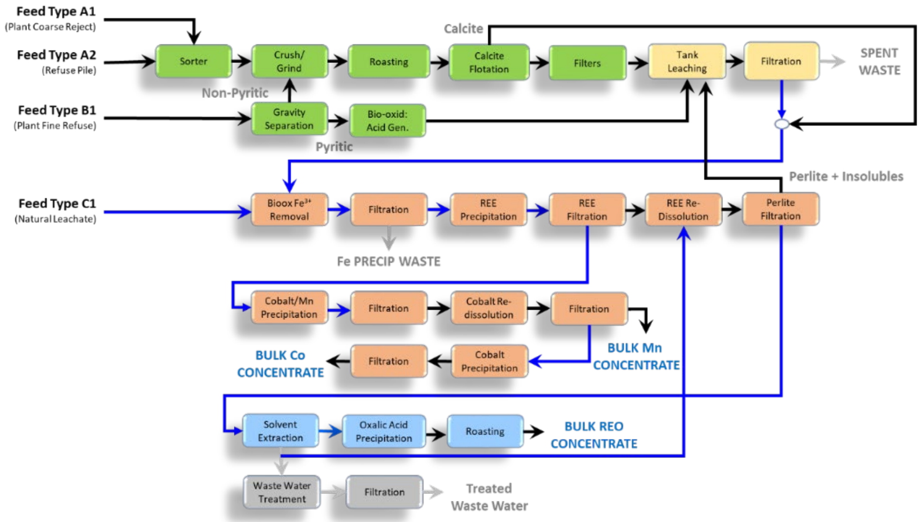


Size Fraction (mesh)	Weight (%)	Major Minerals (%)			
		Pyrite	Silica	Calcite	Kaolinite
+100	8.84	6.3	6.4	68.2	4.9
100 x 200	43.72	20.0	14.1	62.8	3.1
200 x 325	14.88	43.3	12.2	35.4	1.1
-325	32.56	30.1	44.8	21.0	3.7
Total	**100.00**	**25.5**	**23.1**	**45.6**	**3.2**

Project Justification Statement

Technical Solutions

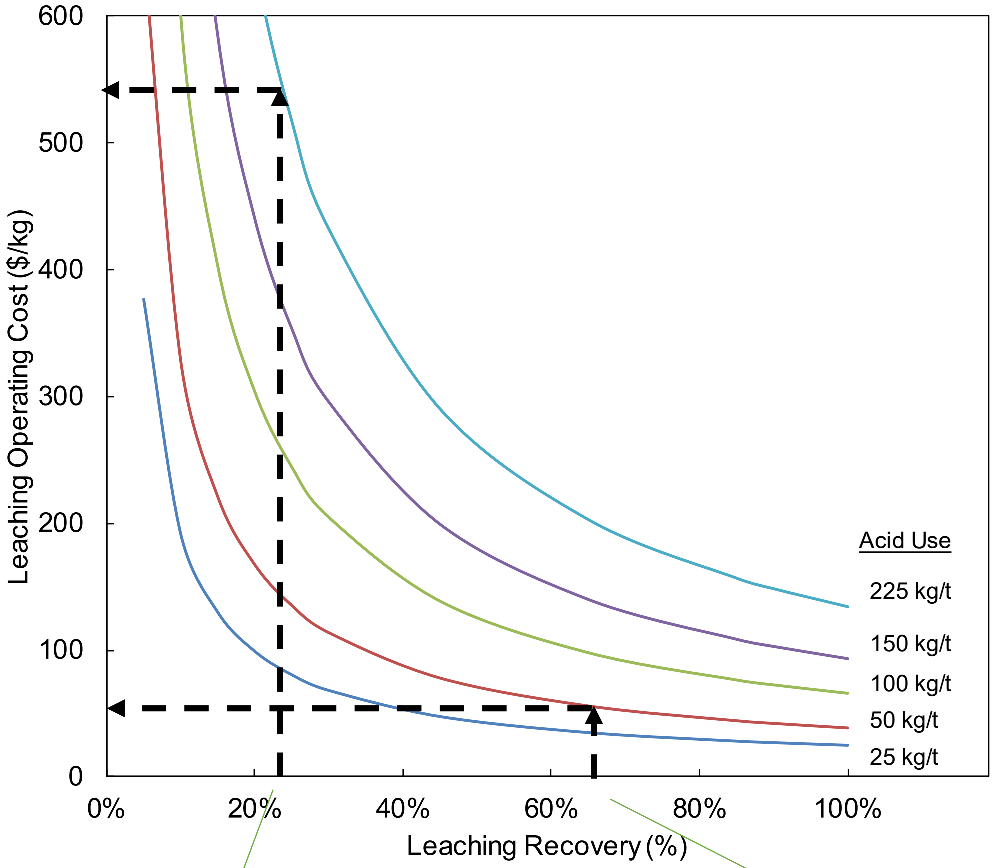
- Utilize pre-concentration sorting to maximize REE concentration entering the leaching tanks.
- Utilize roasting to improve leach recovery and reduce acid consumption.
- Utilize low cost-physical separation to isolate acid-generating and base-generating constituents
- Utilize bio-oxidation to maximize acid production.
- Integrate process components in a novel flowsheet configuration to maximize technical and economic outcomes.



Project Justification Statement

Impacts on Acid Costs

- Economic analysis performed for a 500 tph plant treating feedstock containing 400 ppm total REE.
  - Acid cost = $0.20/kg.
- Analysis shows that acid consumption values need to be less than 100 kg/t and REE recoveries must be greater than 40-50% if $100/kg of REOs produced is the goal.
- Bio-oxidation of pyrite is expected to produce acid at a cost of around $0.04/kg.
- As such, acid cost may be reduced to around $20/kg of REO concentrate and/or higher REE recoveries may be economically obtainable.



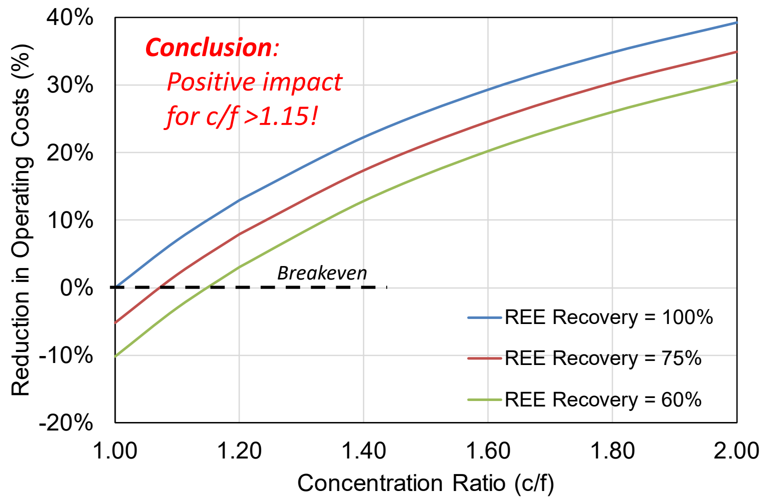
Earlier Work
- *Leach Recovery = 24%*
- *Acid Consumption = 225 kg/ton*
- *Cost per KG leached = **~$550/kg***

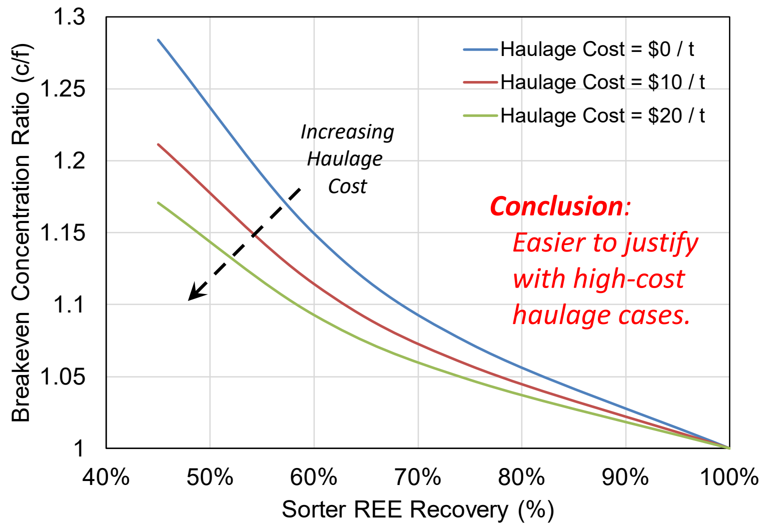
Current Target
- *Leach Recovery = 65%*
- *Acid Consumption = 50 kg/ton (eq)*
- *Cost per KG leached = **$45/kg***

Project Justification Statement

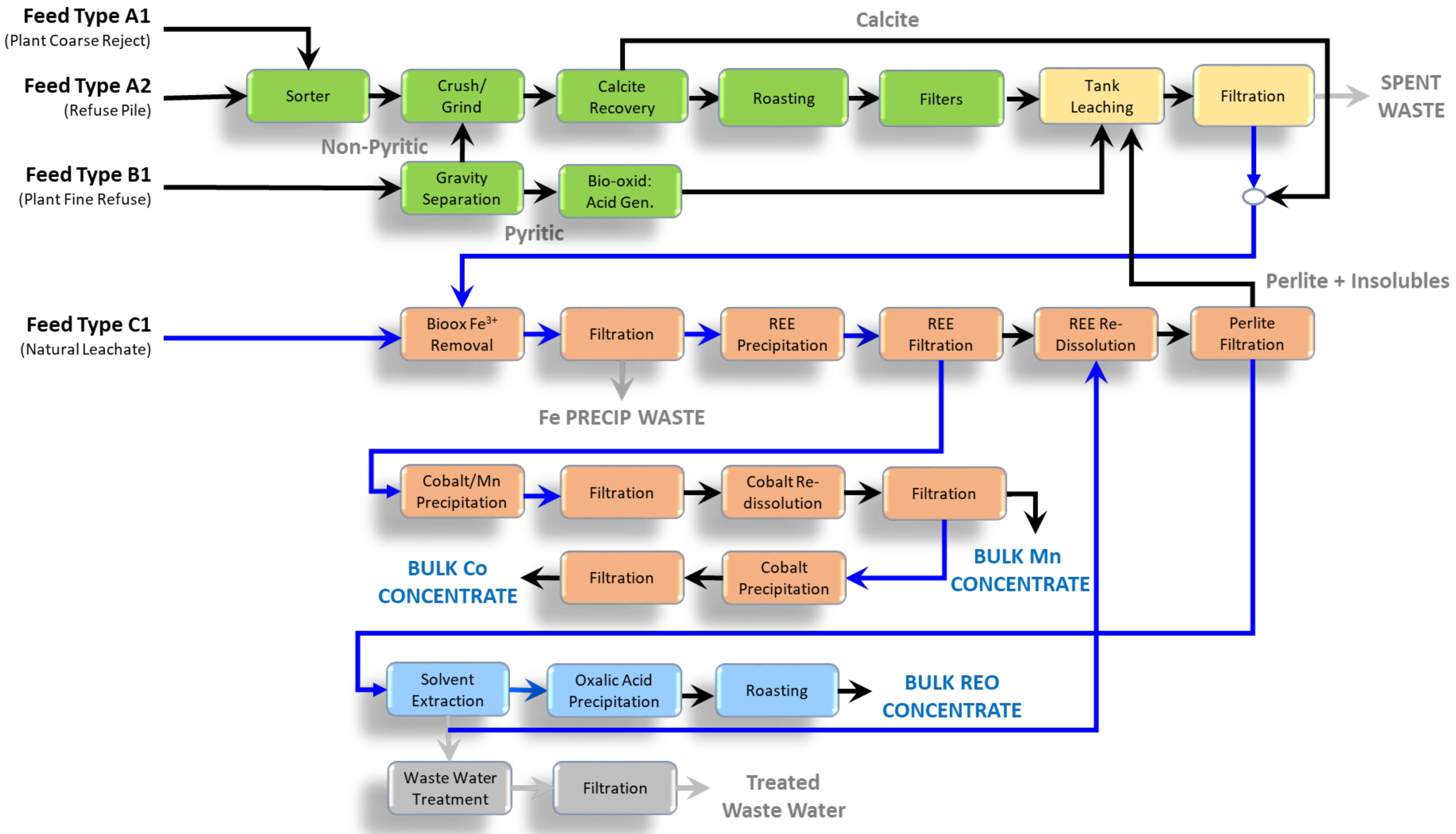
Impacts of pre-concentration

- X-ray sorting is a commercial technology used to separate materials of different density.
- In this project, x-ray sorting will be used to preconcentrate REE-enriched density fractions.
- Sorting is being upgraded with improved feeding system to improve throughput and accuracy.

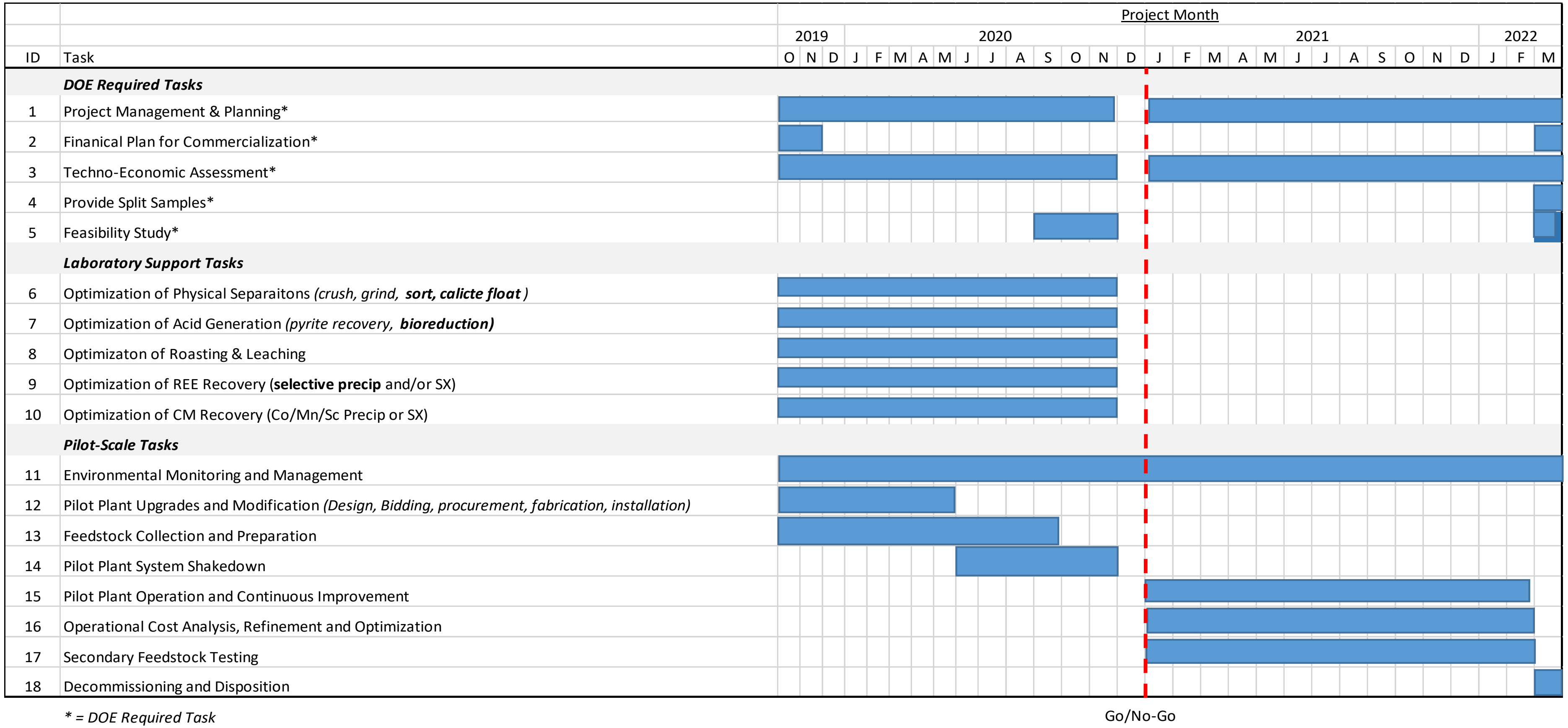




Block Flow Diagram



Project Schedule

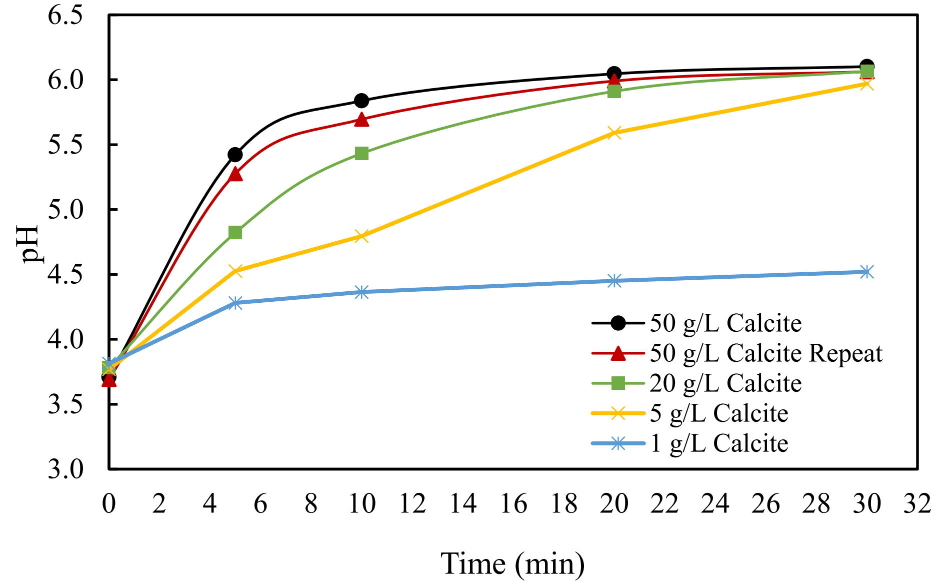


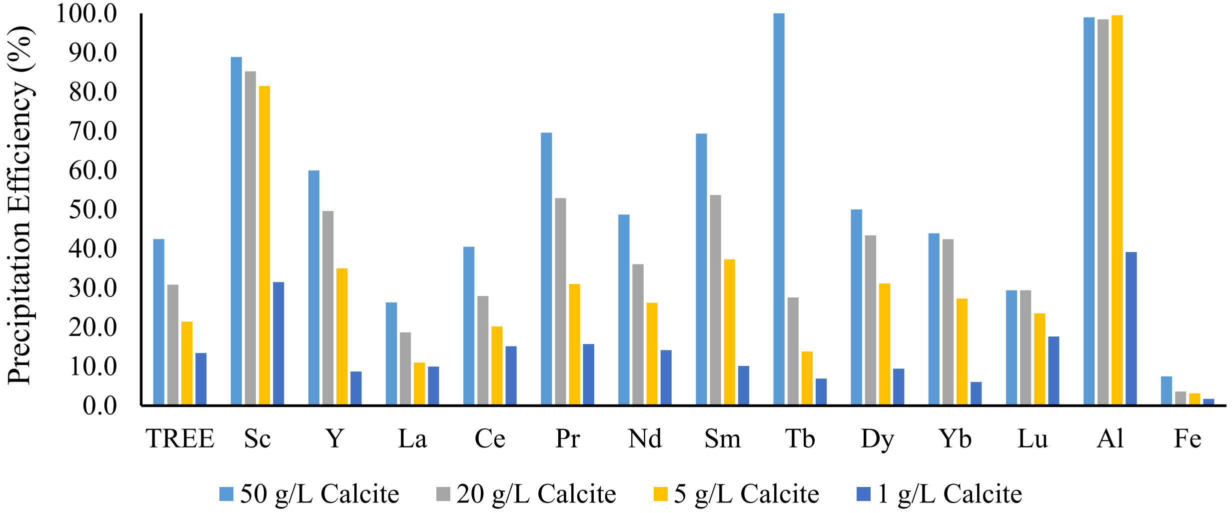
Task 6.0: Mineral Concentration

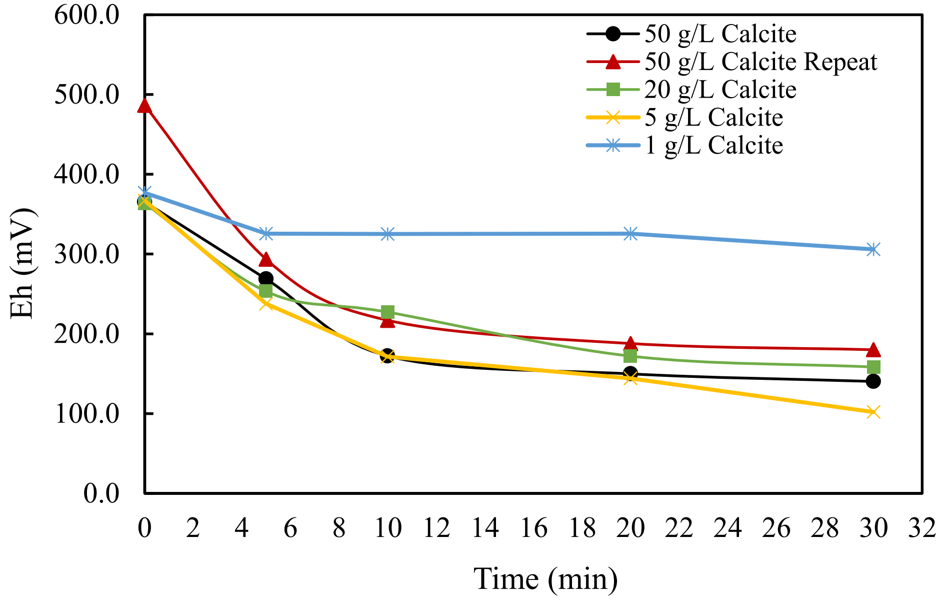
Al Precipitation using Calcite Recovered from Coal Prep Plant Waste

Test Program:

- ❑ To identify the amount of calcite needed to remove Fe and Al in a subsequent step.
- ❑ To test the possibility of oxidizing all the Fe into ferric and precipitate at pH 3.
  - Oxidant assisted
- ❑ To test the possibility of separating Al and Sc
  - Sodium Phosphate (fertilizer)

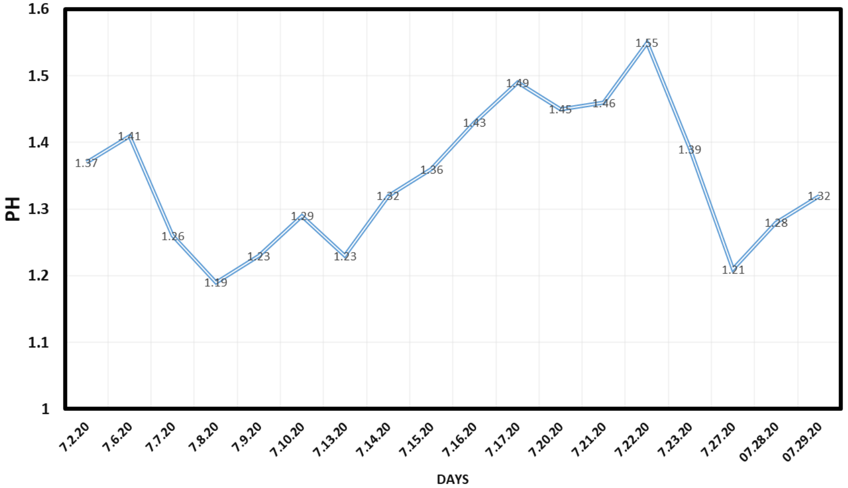






Task 7.0: Acid Generation by Biooxidation

- 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.



Bioreactor operating procedure and performance

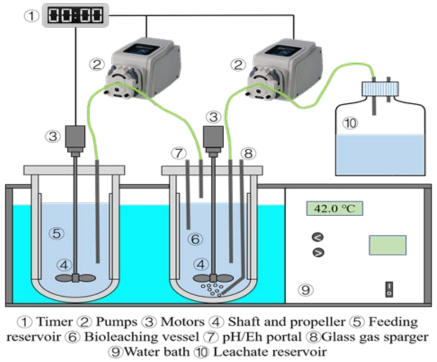


***Figure**: (a) Schematic Diagram of Bioreactor system; (b) Digital image of Bio-Reactor*

- *The bioreactor was filled with 300ml of stored bioleaching solution containing bacterial culture along with 1 L 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.*

Bioreactor restarting procedure

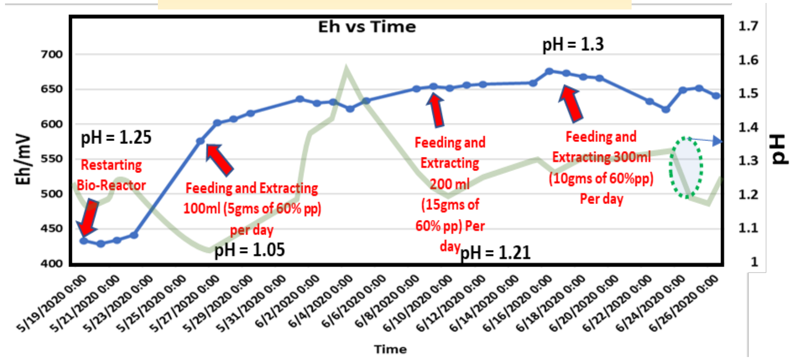
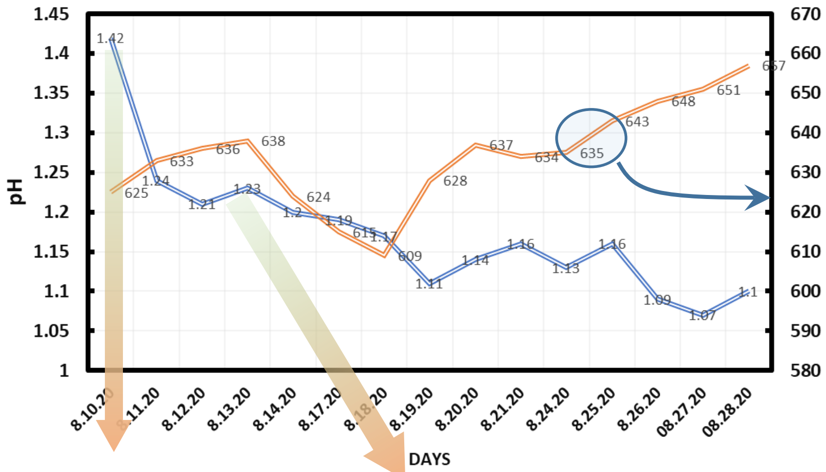


***Figure** : Eh and pH values vs. time for different amount of Feeding solution*



60% pyrite-8 g
9k medium -50 ml
DI water-50 ml
(once per day)

60% pyrite (smaller than 100 mesh)-8 g
9k medium -50 ml
DI water-50 ml
(twice per day)

The finer feed is associated with a pH decrease.

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

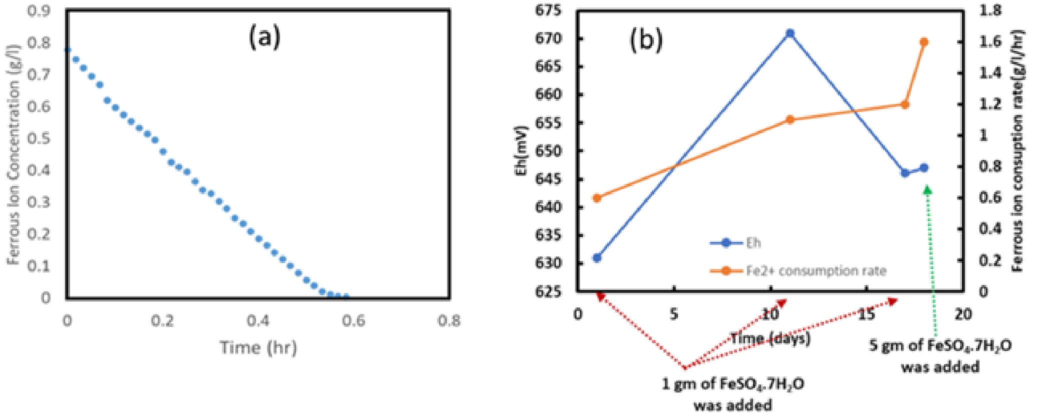
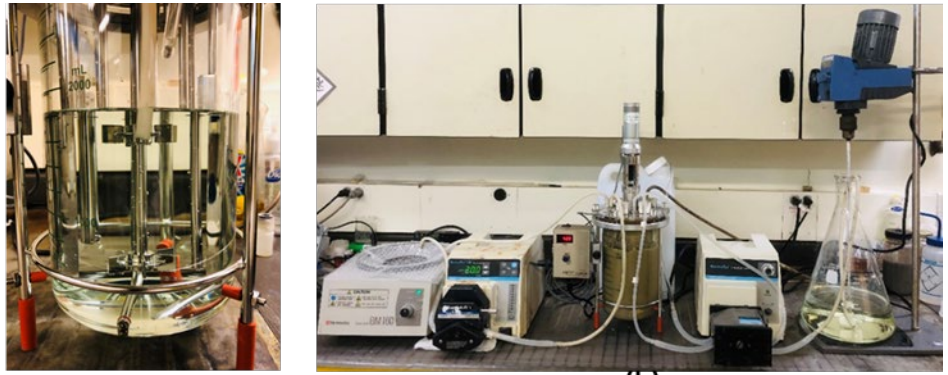


***Figure**: (a) Bio-oxidation rate assessment after addition of 5g $FeSO_4 \cdot 7H_2O$ on 06.23.2020 at Eh 647 mV; (b) overall comparison of bio-oxidation rate for different days and at different Eh values*

New 3L Bioreactor



(a) (b)

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

- *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

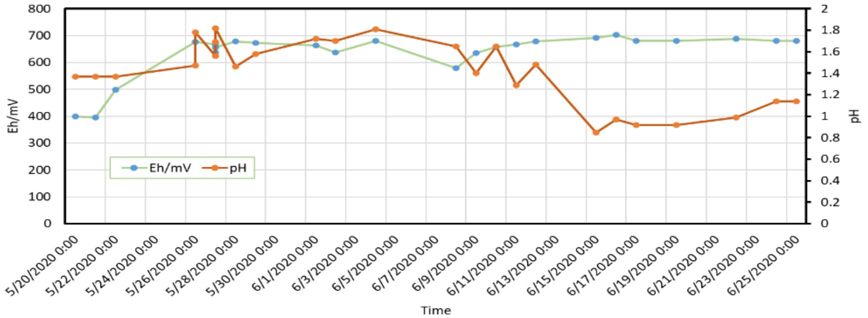
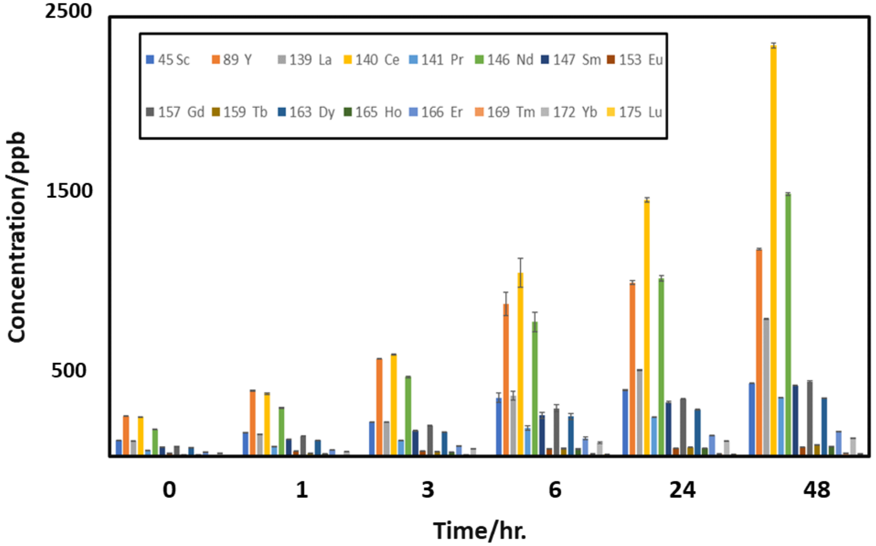


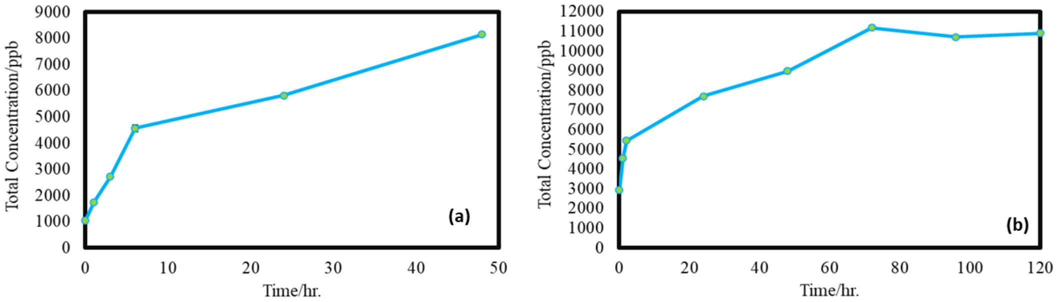
***Figure** : Eh and pH values vs. time (for new 3L bioreactor)*

Coal Waste Bioleaching

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

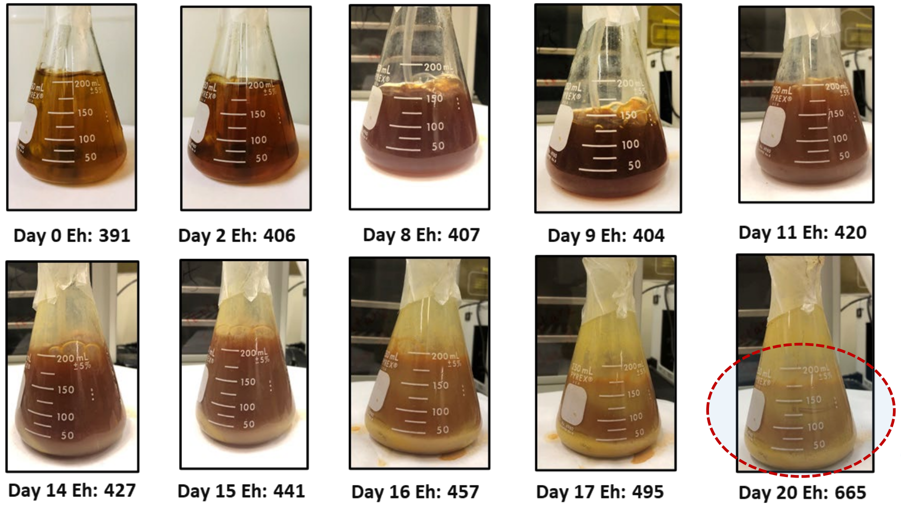


REEs concentrations in the leaching samples collected during the leaching process of Fireclay refuse.

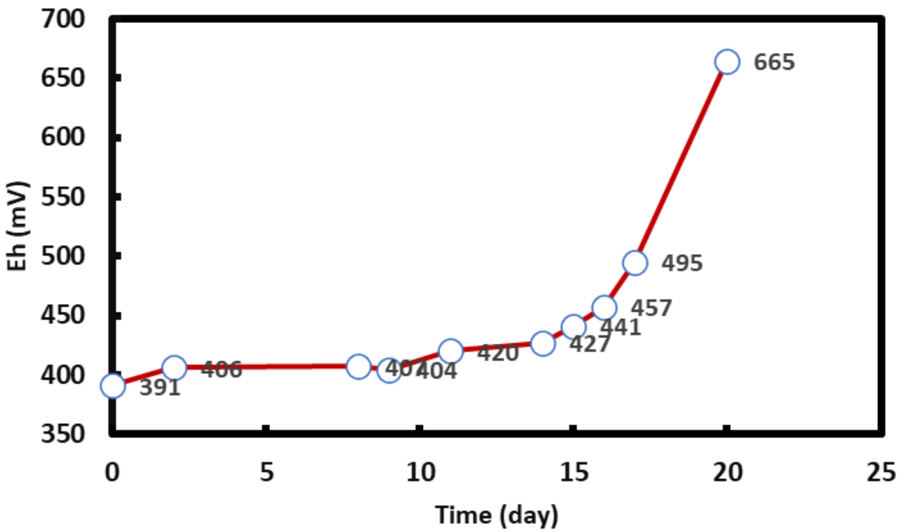


Total REEs concentration vs. time in the (a) Fireclay refuse leaching test and (b) Dotiki refuse leaching test.

Jarosite Precipitation Tests



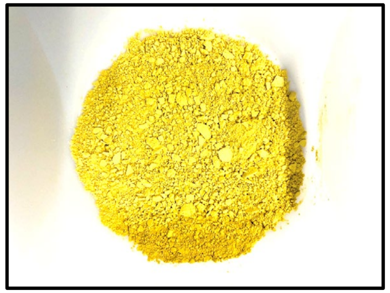
Monitoring of bioleaching solution during precipitation test



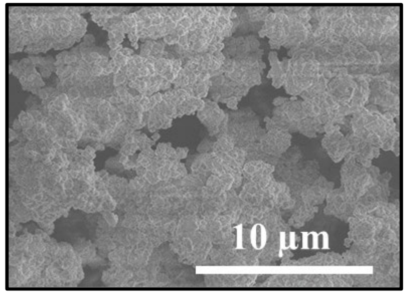
Eh vs. time behavior during Jarosite formation test
(Note that jarosite formation is likely to happen rapidly in recirculating solutions.)

Biooxidation of leaching effluent can be used to produce jarosite to avoid adding base. To evaluate jarosite formation ~ 200 ml of the filtered bioleaching solution (Fe concentration ~ 0.5 M) was collected and additional $FeSO_4 \cdot 7H_2O$ and bioleaching solution (200 ml) was added to adjust the Fe concentration to around 1.0 M. The solution was continuously stirred and air was purged into the solution. Eh variation of the solution and the precipitation was monitored during the test.

Filtered/washed /dried

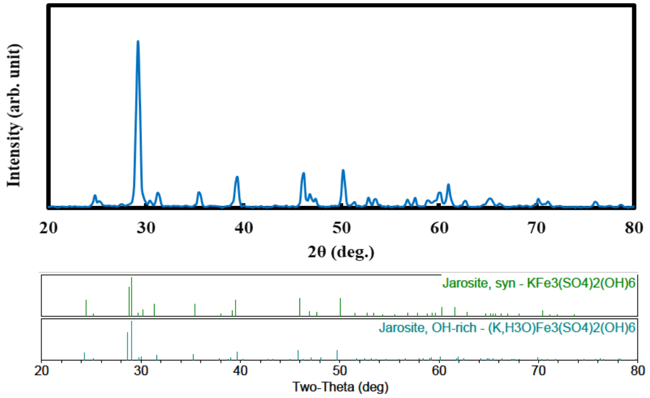


Digital image of precipitate



SEM image of precipitate

19.5% of the Fe was precipitated in the form of jarosite during the bio-oxidation process.



XRD pattern for precipitate confirms the formation of Jarosite

Task 8.0: Optimization of Roasting and Leaching
KEY FINDINGS

- Pre-heating to remove volatiles in an inert atmosphere does not increase/decrease the leachability of oxidation products (e.g. sintering).
- Leaching characteristics for heating the sample in oxidative environment are significantly higher than inert atmosphere.
- The benefits of REE recovery by roasting are due to thermal effects in an oxidative environment.
- Results show that roasting kinetics depends on feed rates, heating rates and retention time.
- Roasting products of temperatures >700°C provide lower leaching recoveries.

West Kentucky No.13 (Total REEs in ppm in 1.2 M sulfuric acid after 2 hours)

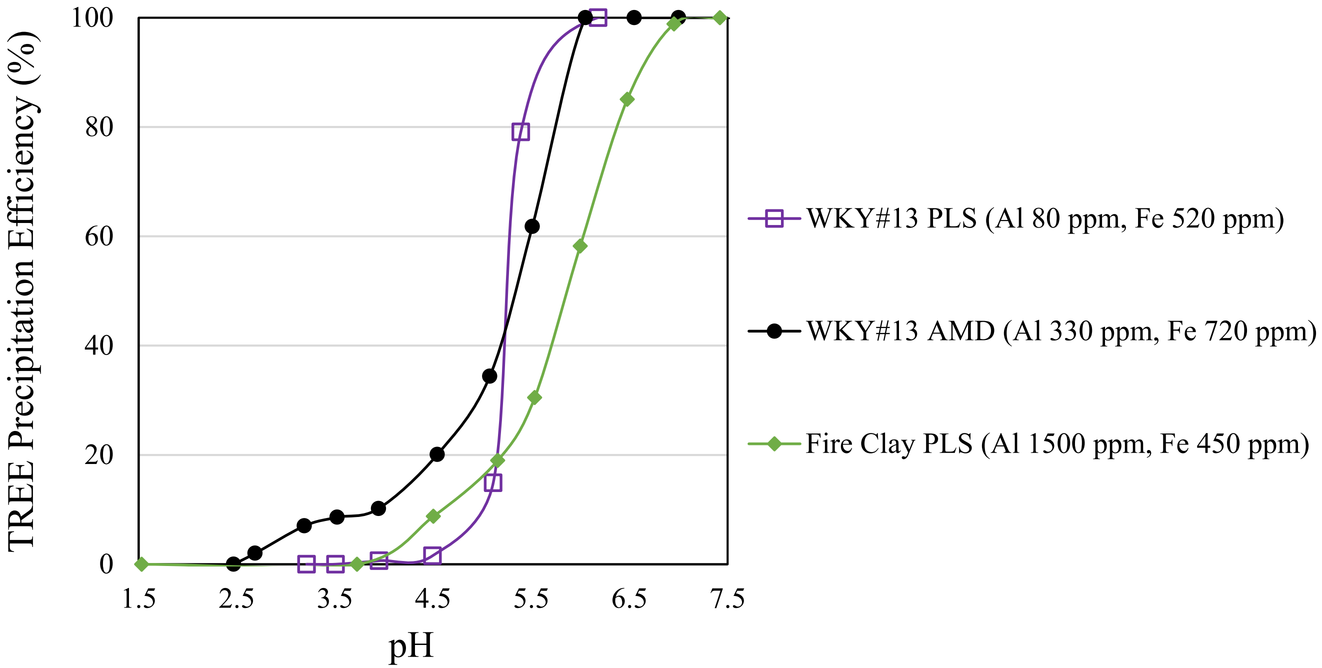
Specific Gravity	Feed	No Volatiles(600°C)	No Volatiles + Ash (600°C)	Ash (600°C)
1.80 Floats	0.22	0.54	2.27	2.43
1.80x2.00	0.46	2.67	4.43	4.30
2.00x2.20	0.53	2.50	3.62	3.51
2.20 Sink	0.39	1.38	1.45	1.88

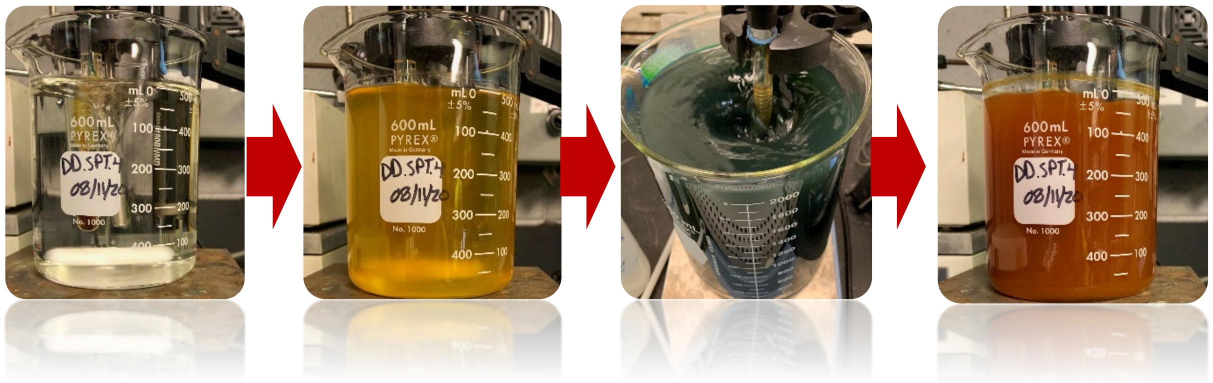
Fire Clay (Total REEs in ppm in 1.2 M sulfuric acid after 2 hours)

Specific Gravity	Feed	No Volatiles(600°C)	No Volatiles + Ash (600°C)	Ash (600°C)
1.60 Floats	0.39	0.62	4.71	4.48
1.60x1.80	0.85	0.74	2.87	2.79
1.80x2.00	1.21	1.39	3.39	3.36
2.00x2.20	1.04	1.76	3.31	3.35
2.20 Sink	0.42	1.80	1.87	1.45

Task 9.0: Rare Earth Recovery from PLS

REE Selective Precipitation





RE Precipitation Cake Produced in Pilot Plant

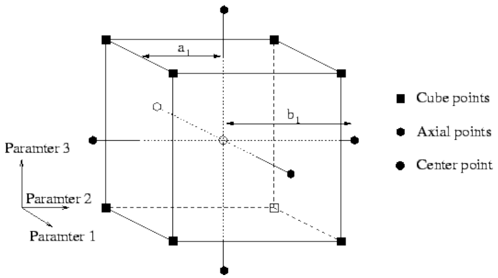
Elements	DKT-C11	DTK-C13	FC-C4	DTK-C14	DTK-AMD	DTK-C15
Sc (mg/kg)	7	27	28	22	84	19
Y (mg/kg)	161	154	151	150	1429	152
La (mg/kg)	841	557	504	903	481	905
Ce (mg/kg)	2043	1592	1317	2060	1356	1925
Pr (mg/kg)	220	181	145	207	185	205
Nd (mg/kg)	721	637	490	719	807	686
Sm(mg/kg)	145	146	111	180	285	168
Eu (mg/kg)	20	21	13	20	62	19
Gd (mg/kg)	80	74	72	66	367	74
Tb (mg/kg)	0	0	6	42	36	0
Dy (mg/kg)	35	44	49	37	347	34
Ho (mg/kg)	5	5	6	17	52	16
Er (mg/kg)	10	12	11	12	106	11
Tm (mg/kg)	2	11	2	3	21	2
Yb (mg/kg)	12	12	11	15	89	15
Lu (mg/kg)	8	8	5	11	14	11
TREE (mg/kg)	**4297**	**3472**	**2912**	**4422**	**5722**	**4243**

Task 9.0: Rare Earth Recovery from PLS
Oxalic Acid Precipitation

Oxalic acid precipitation was employed to selectively precipitate REEs from concentrated rare earth pregnant leachate solution (PLS) with presence of other contamination ions (i.e. Fe, Ca, and Al, etc.).

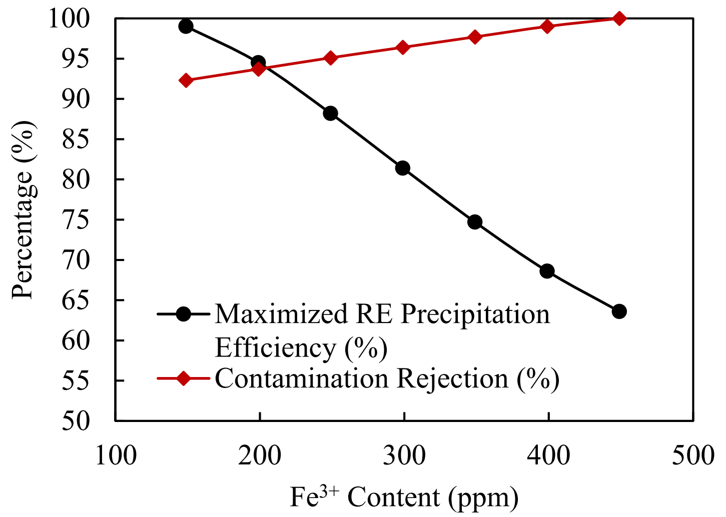
Major factors:

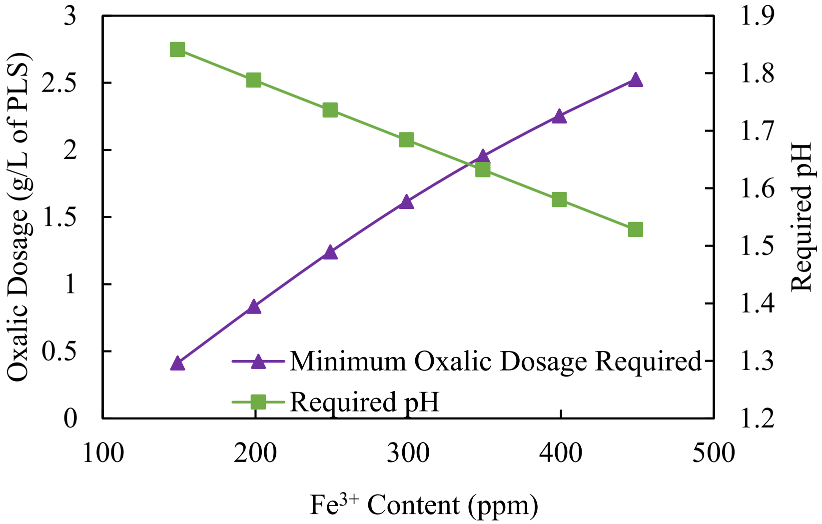
- ***Oxalic acid dosage*** - Higher dosage, higher recovery of REEs, higher contamination, and higher cost.
- ***Effect of temperature*** – Higher temperature, lower the precipitation reaction rate.
- ***Effect of Fe^{3+} Content*** – Fe^{3+} in the oxalate precipitation feed is a major consumer of oxalic acid and negative impacts product purity.
- ***Effect of pH*** - Lower the pH, higher the selectivity. Higher the pH, higher the recovery.



Central Composite Design (CCD)

Factor	Parameter	Unit	Variable Level: Low	Variable Level: High
A	Oxalic Dosage	g/L	40	120
B	Temperature	C	25	50
C	Fe Addition	ml	1	3
D	pH		1	2





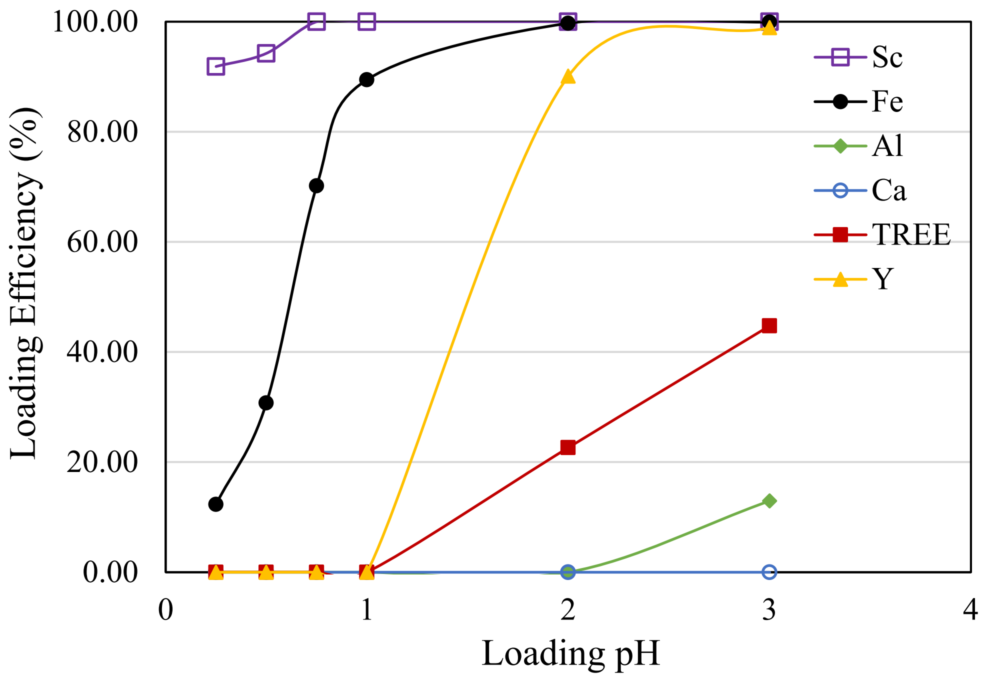
Task 9.0: Rare Earth Recovery from PLS
Scandium SX Recovery

Objective:

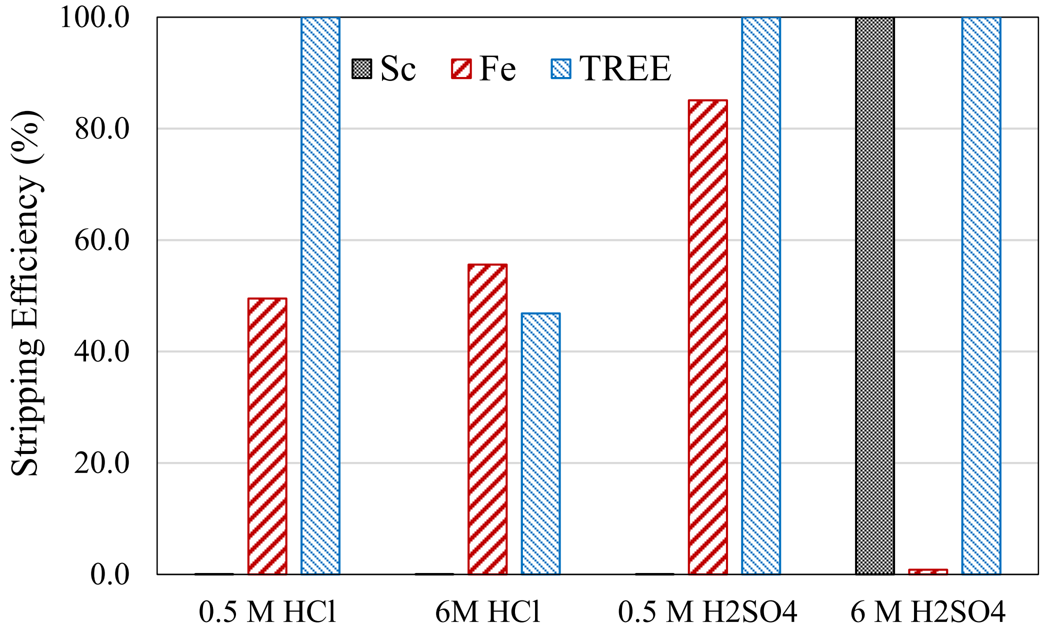
To extract Sc before Al precipitation using solvent extraction (SX).

Extractant: Cyanex 272

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



(Condition: 1% Cynex 272 in Orfom, Aqueous to organic ratio= 1:1, Contact Time = 15 min.)



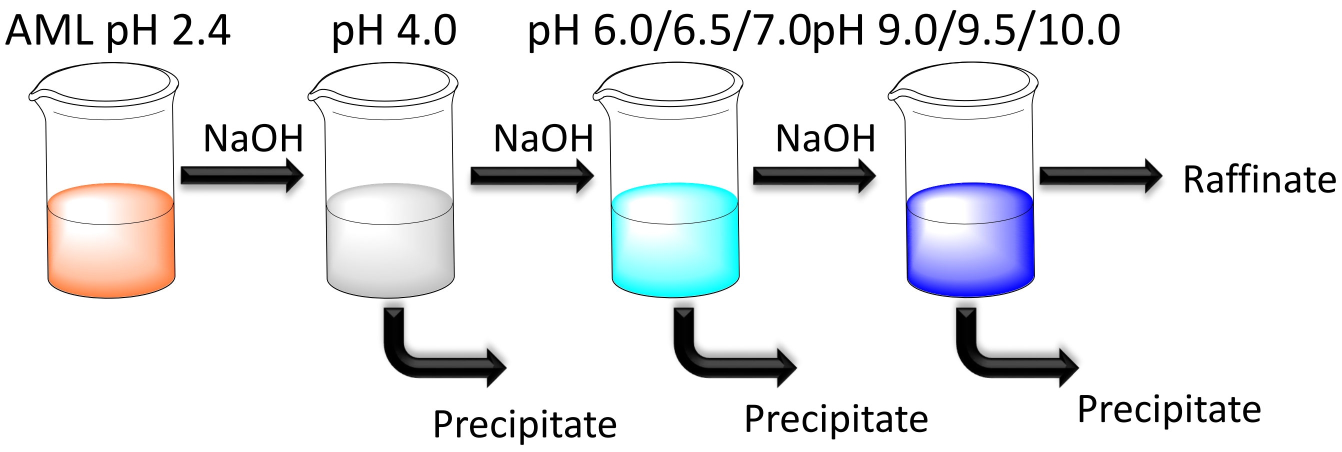
Scrubbing: *0.5M H_2SO_4 to remove Fe; Scrubbing solution reports to downstream process for RE recovery.*

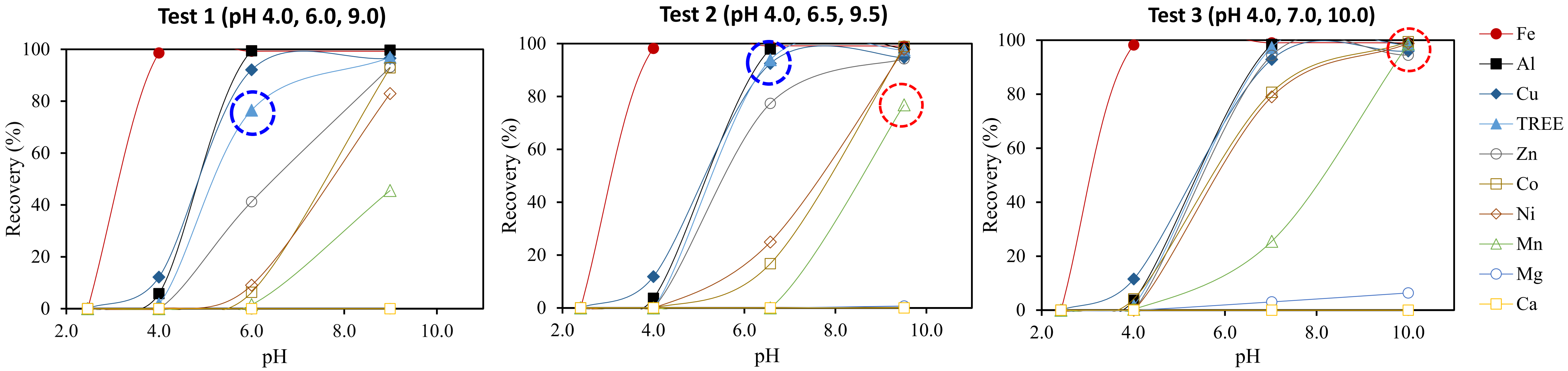
Stripping: *6M H_2SO_4 to recover Scandium.*

Task 10.0: Optimization of Critical Material Recovery

Optimization of Staged Precipitation

- Tests were performed on an acid mine leachate collected from WK No. 13
- Test 1 (pH 4.0, 6.0, 9.0); Test 2 (pH 4.0, 6.5, 9.5); and Test 3 (pH 4.0, 7.0, 10.0)
- pH 4.0-6.5 for REE recovery
- pH 6.5-10.0 for Mn recovery
- Co is associated with both the REE and Mn pre-concentrate

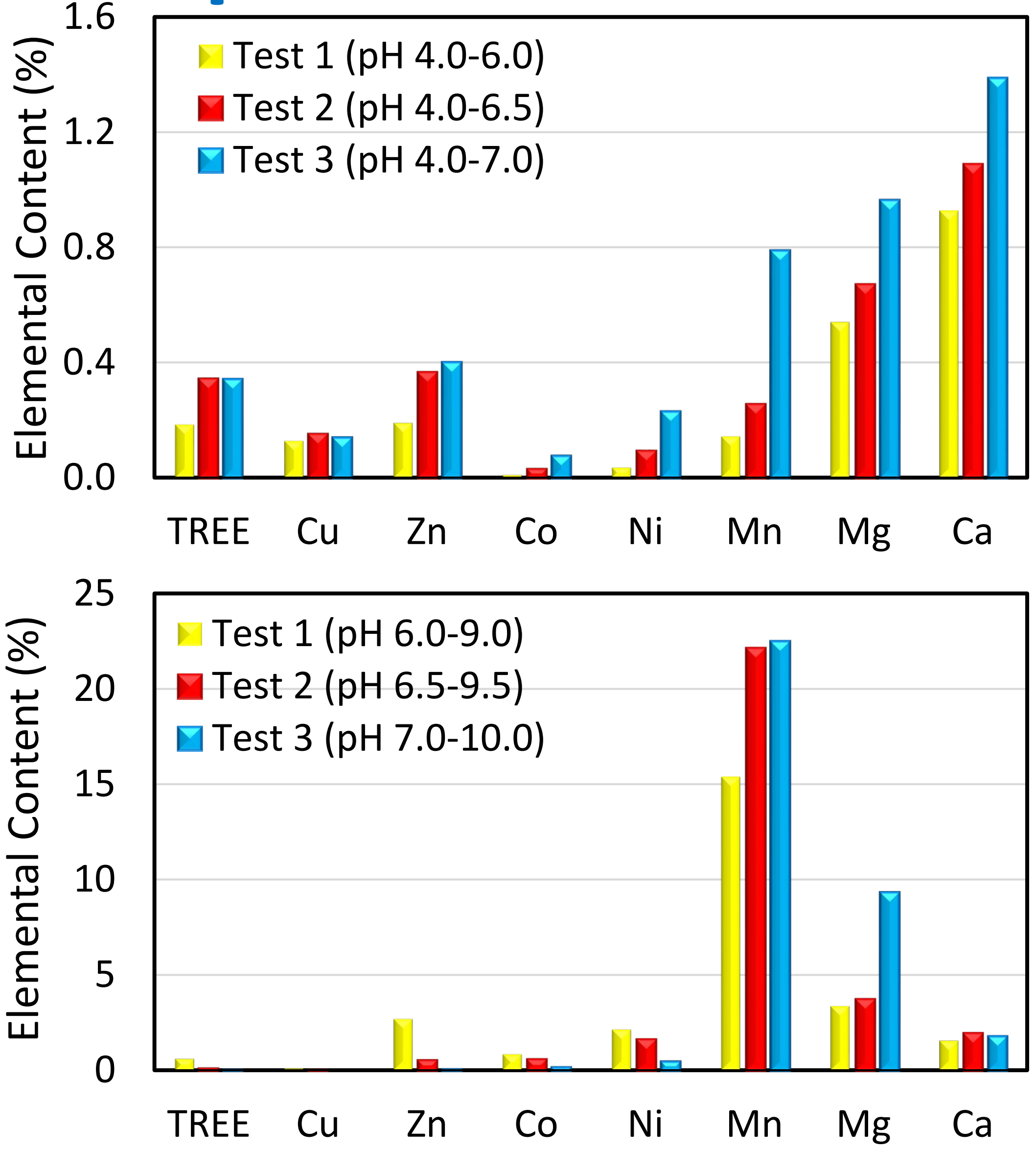




Task 10.0: Optimization of Critical Material Recovery

Pre-concentrate Composition

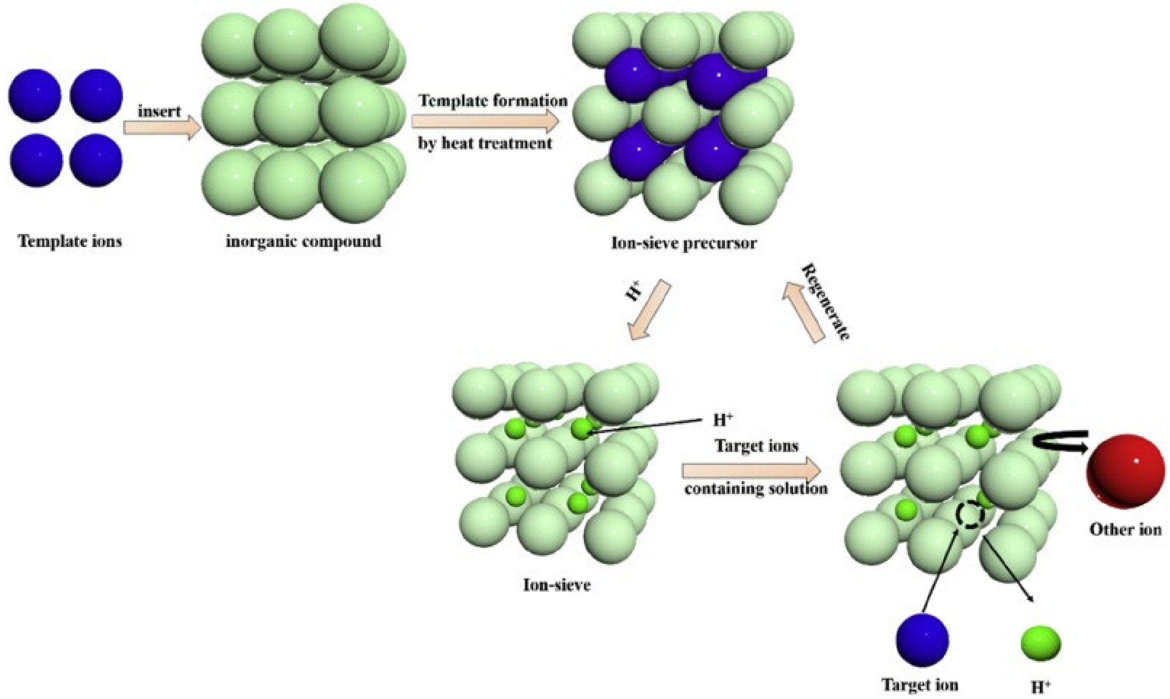
- REE pre-concentrate containing 0.3% of TREE plus 0.03% Co was obtained in the pH range of 4.0-6.5
- Mn pre-concentrate containing 22% of Mn plus 0.6% of Co was obtained in the pH range of 6.5-9.5
- Mn grade has far exceeded the target (2 wt.%)
- Co in the pre-concentrates will be separated from REEs and Mn through oxalic acid precipitation



Task 10.0: Optimization of Critical Material Recovery

Lithium Recovery

- Lithium ion-sieve was prepared for the selective recovery of lithium from solution
- Advantages: High lithium uptake capacity, and low regeneration loss of raw materials



Mix $MnCO_3$ with Li_2CO_3 or $LiOH \cdot H_2O$ (Li/Mn mole ratios =1/1)

↓

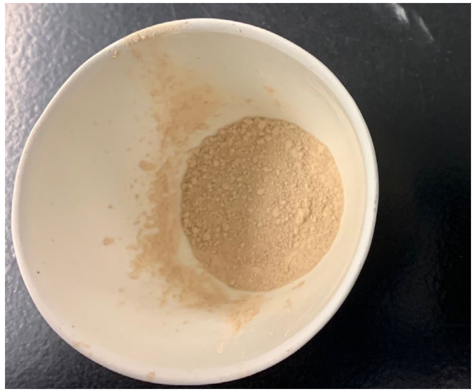
Heat at 450 °C for 8h in air

↓

Immerse 1 g lithium manganese oxide precursors in 500 mL of 0.5 M HCl solution and stir for 24 h

↓

Filter and wash with deionized water and air-dried at 70 °C



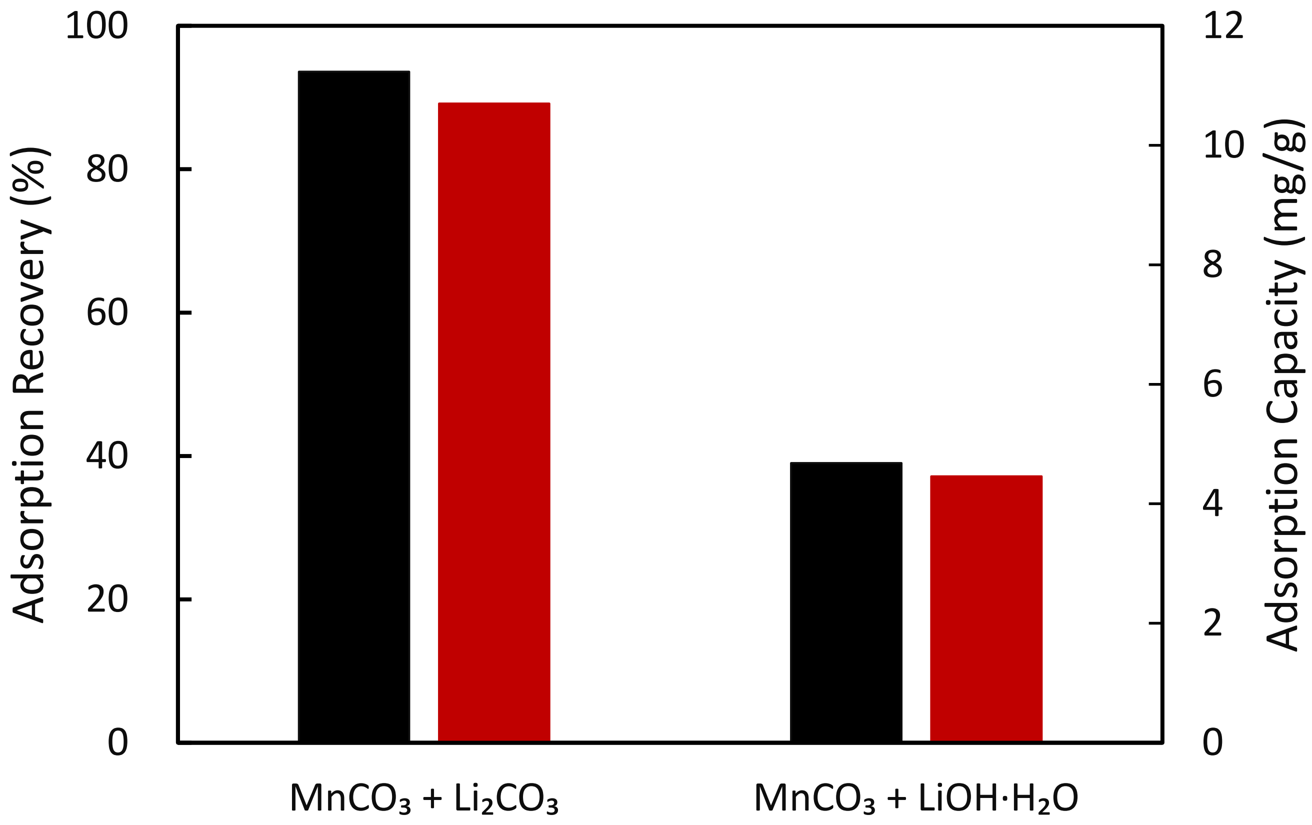
Before Calcination

After Calcination

Task 10.0: Optimization of Critical Material Recovery

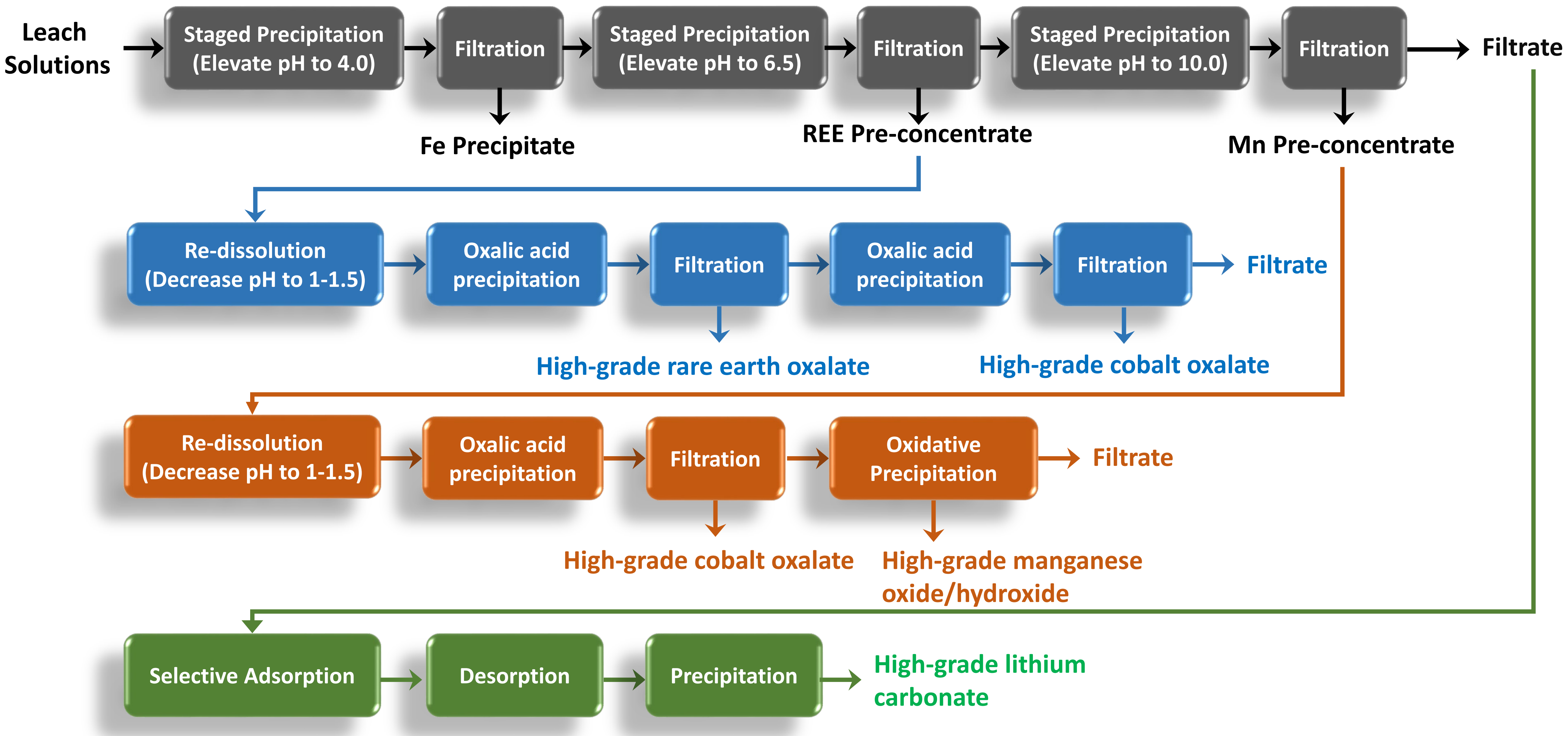
Li Recovery from Synthetic Solution

- A synthetic solution containing 10 ppm of Li was used
- The ion-sieve prepared with $MnCO_3 + Li_2CO_3$ performs better than that with $MnCO_3 + LiOH{\cdot}H_2O$
- The ion-sieve prepared with $MnCO_3 + Li_2CO_3$ providing more than 90% recovery of lithium from a synthetic solution with an uptake capacity of around 10 mg/g
- Recovery tests will be performed on the filtrate of acid mine leachate after Mn precipitation (pH 10)



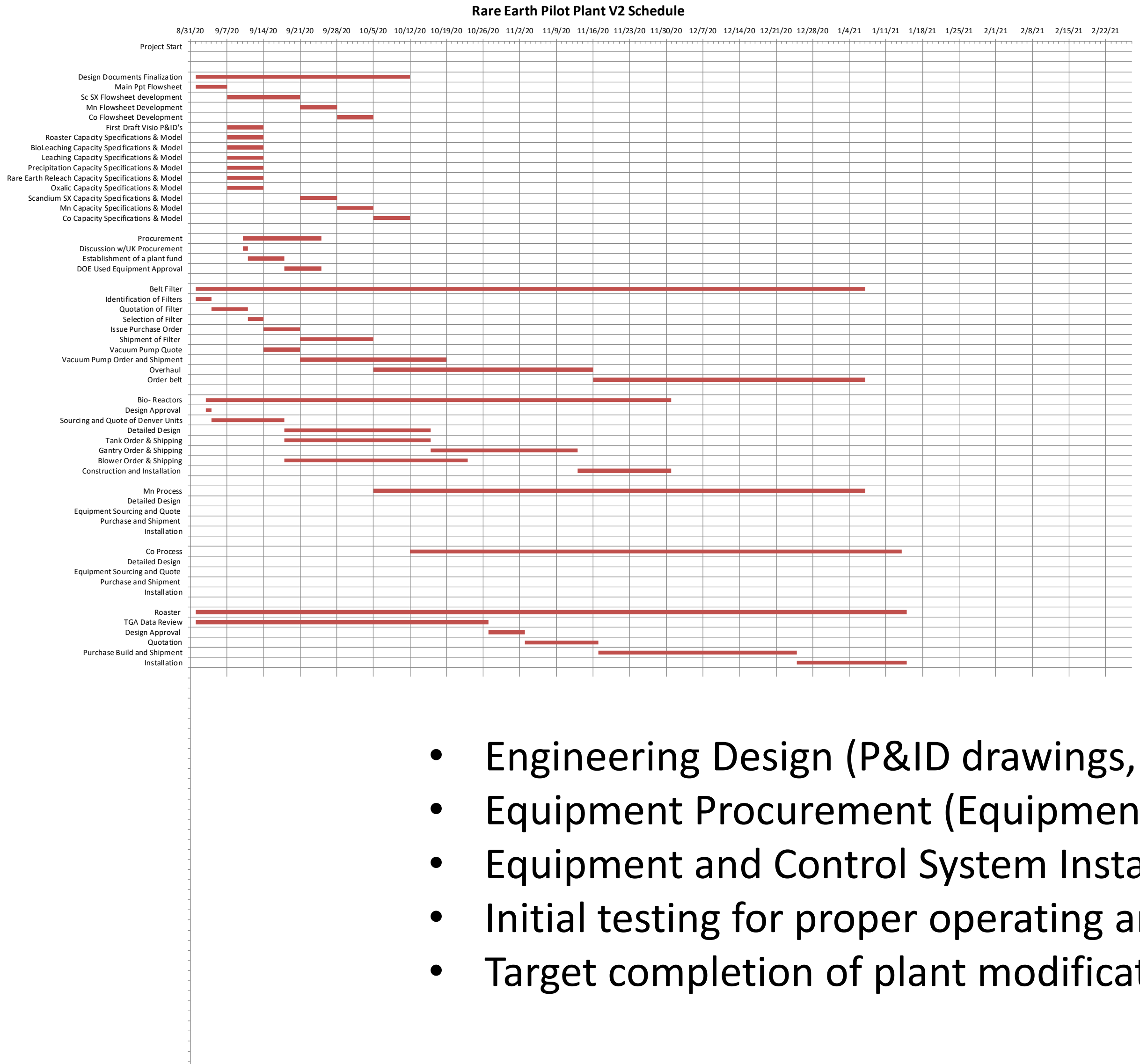
Task 10.0: Optimization of Critical Material Recovery

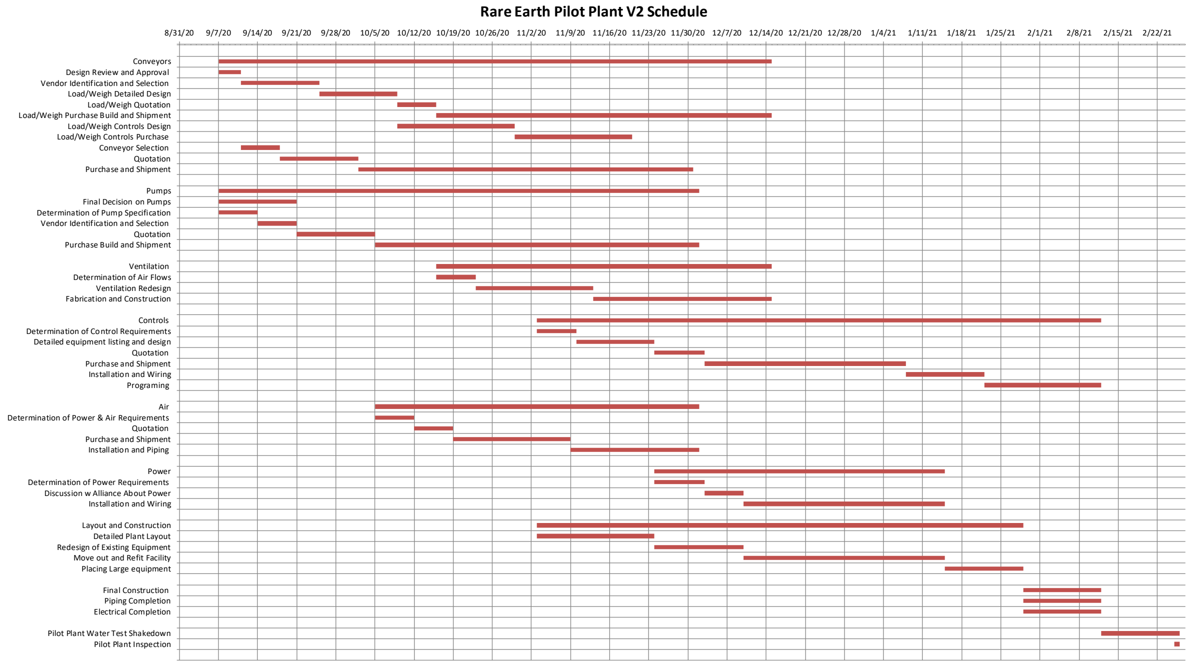
Next Steps



Task 12.0: Plant Modifications

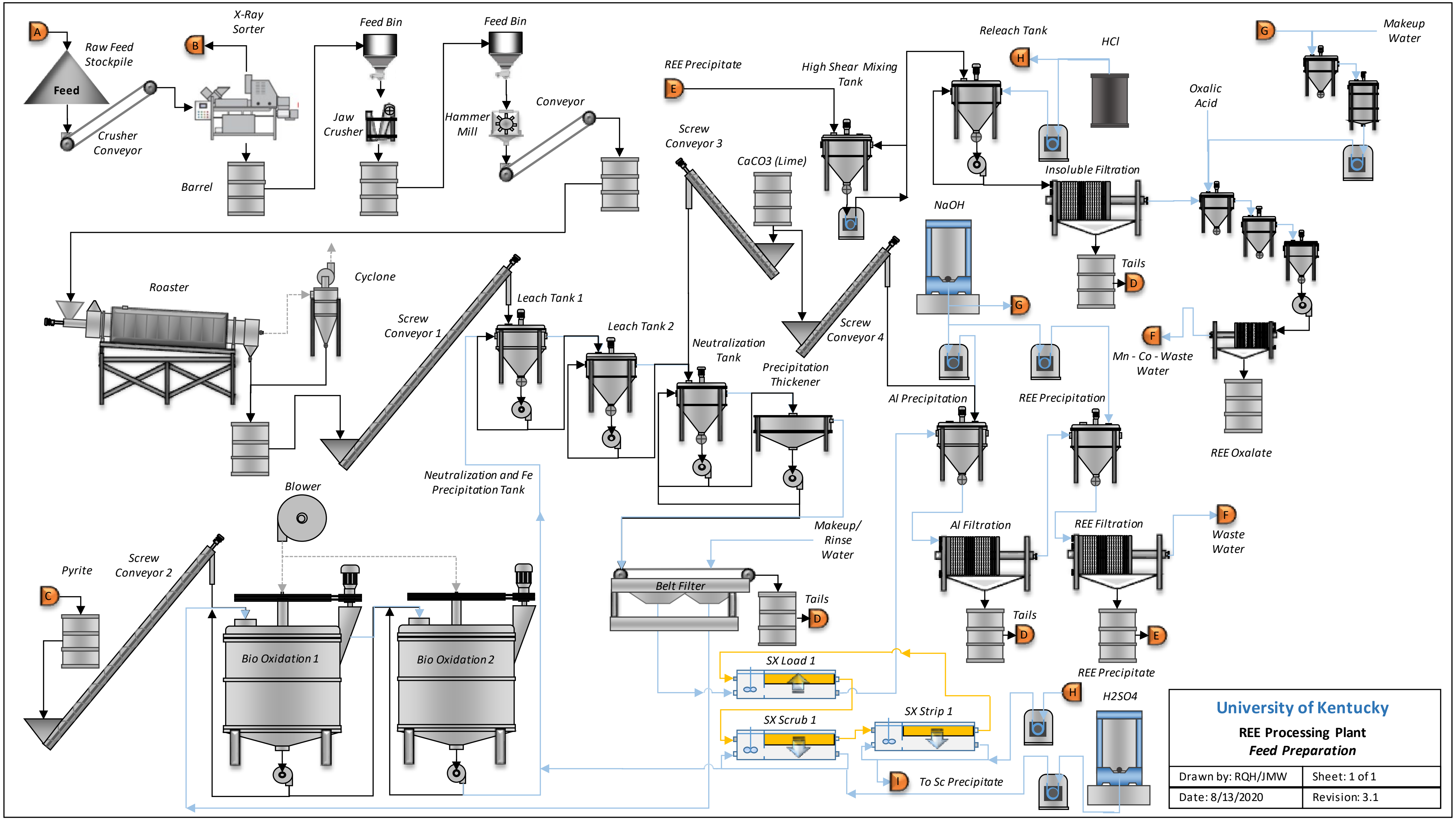
Pilot Plant Modification Schedule





- Engineering Design (P&ID drawings, flowsheet development, layout drawings, etc.)
- Equipment Procurement (Equipment selection, ordering and delivery)
- Equipment and Control System Installation
- Initial testing for proper operating and safety issues
- Target completion of plant modifications: ***February 28, 2021***

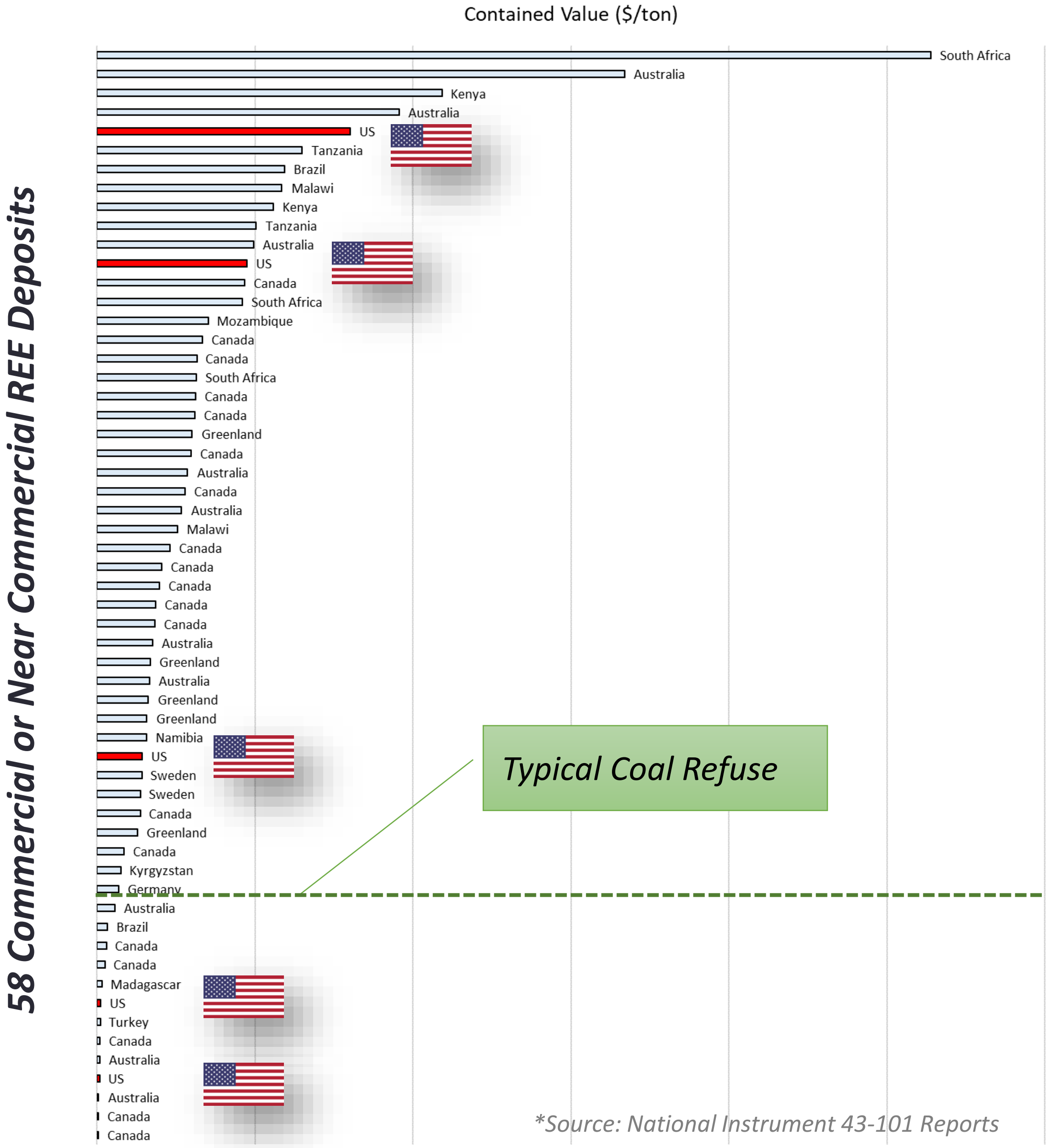
Process Flow Sheet



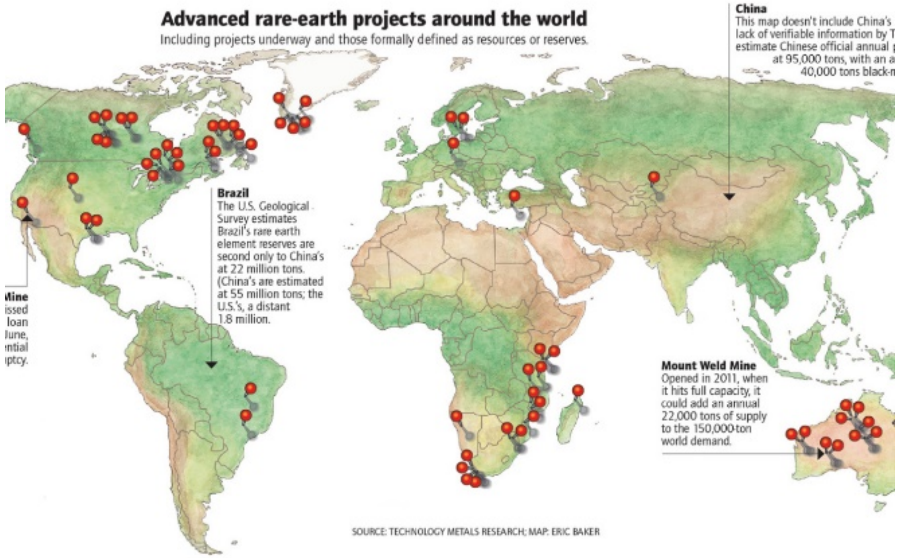
University of Kentucky	
REE Processing Plant *Feed Preparation*	
Drawn by: RQH/JMW	Sheet: 1 of 1
Date: 8/13/2020	Revision: 3.1

Task 2: Pathways to Commercialization

Market Factors



*Source: National Instrument 43-101 Reports

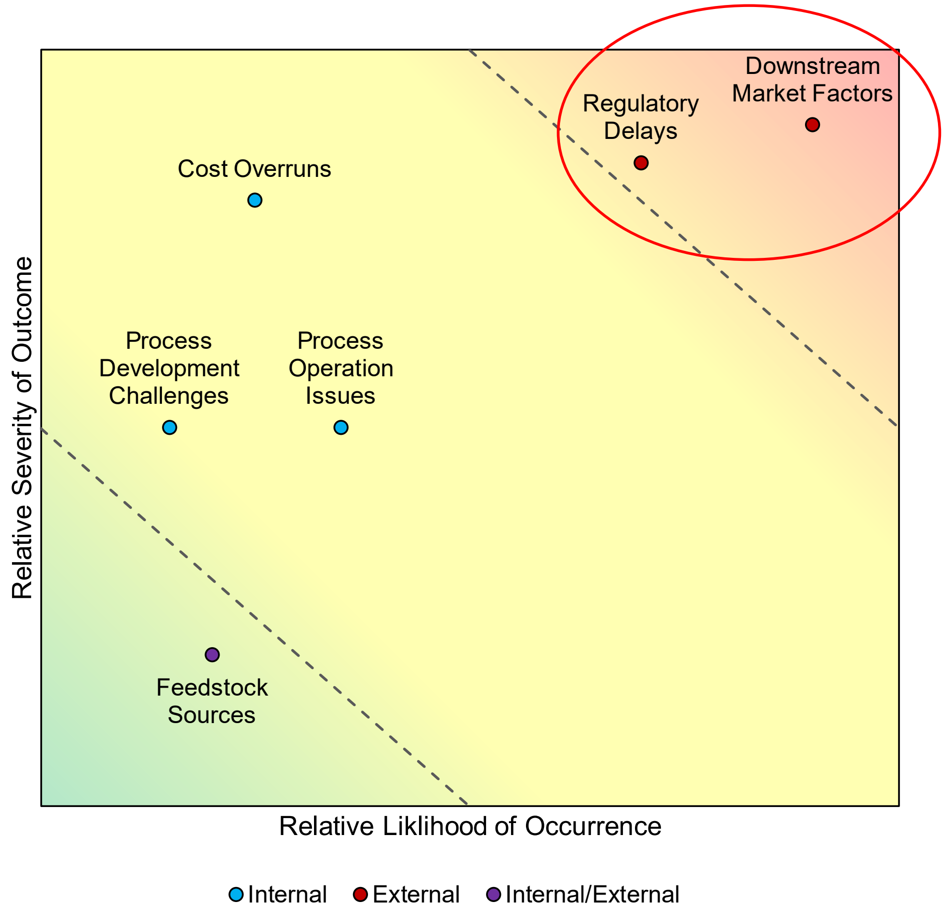


- Other considerations:
  - No mining costs
  - Synergistic production of other critical byproducts
  - Existing work force
  - Rebuilding academic knowledgebase needed for technical training
- Coal refuse can be competitive with other viable REE sources, key is delivering a competitive OPEX

Pathways to Commercialization
Technology Scale Up

Rapid TRL advancement is anticipated with current flowsheet.

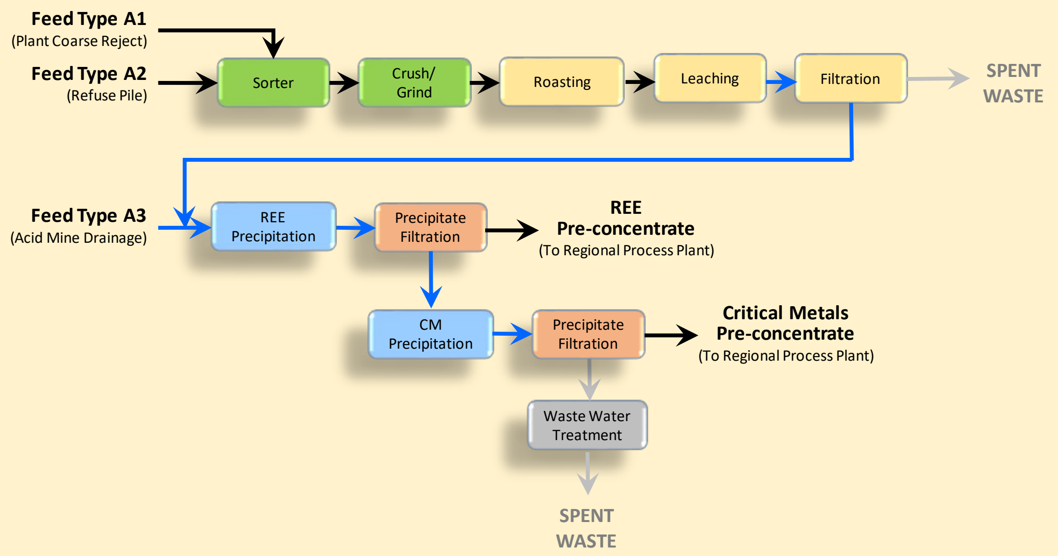
- Being implemented into existing pilot facility.
- Capacity target = 200 g/day or ~30 kg total during project period.
- Unit operations are mature technologies where scaling relationships are well known.
- Commercialization assessment shows major risks are external to the process development.



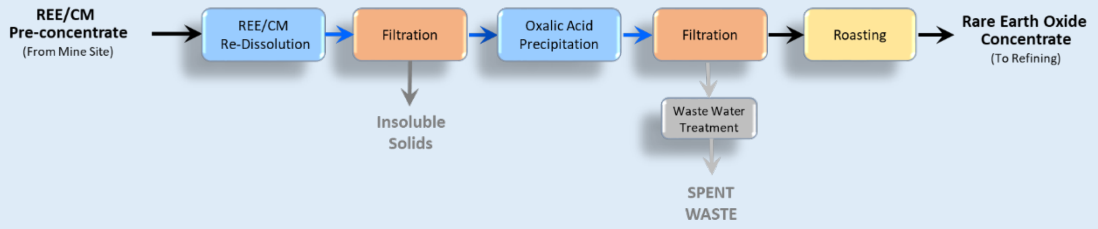
Commercialization risk assessment conducted for project commercialization assessment.

Pathways to Commercialization
Implementation Strategy

On-Site Operations



Regional Processing Facility

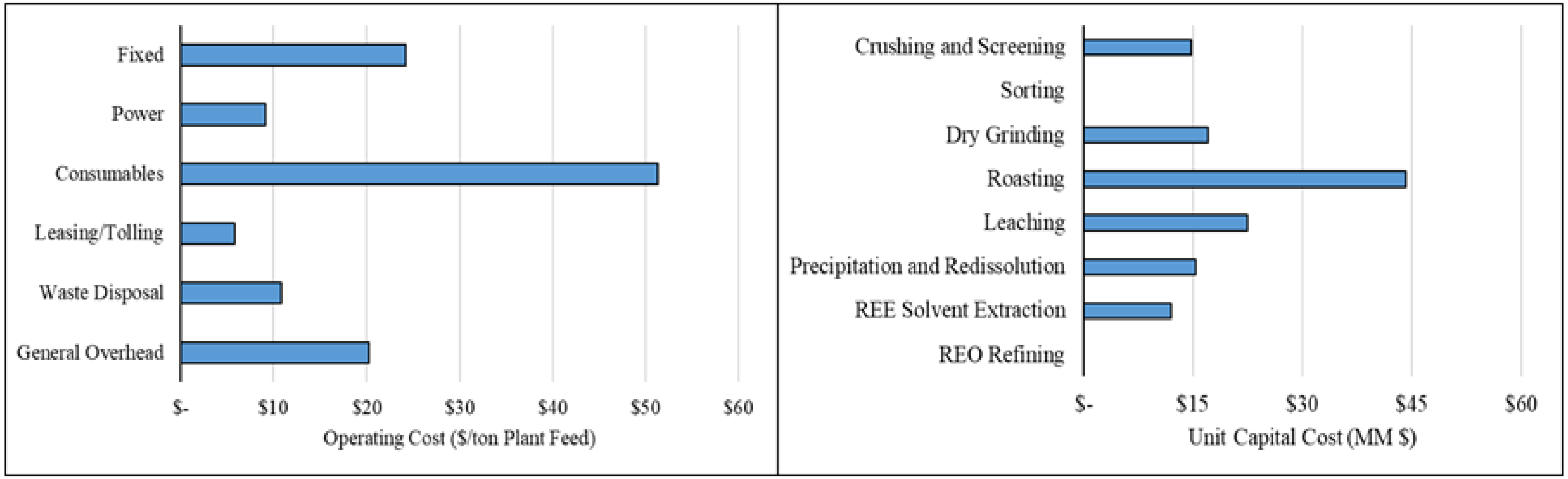


Pathways to Commercialization

Preliminary TEA

- Assumptions
  - Plant Feed = 648 tph @324 ppm REE
  - Product = MREO at >95% purity.
  - Leasing/toll arrangements for sorting & refining

Parameter	Value
Total CAPEX	$126 million
Total OPEX	$122 / kg
Total Annual REE Production	825 t/yr
REE Revenue	$178 / kg
Gross Profit	$56 / kg
Payback	5.5 operating years
Internal Rate of Return	27%



Next Steps

- Complete the design of the process flowsheet based on processing 250 lbs/hr of feed and producing high purity products of REEs, Sc, Co, Mn and possibly Li.
- Conduct TEA and feasibility studies.
- Select, procure and install equipment and control system.
- Perform water testing and safety analysis by February 2021.
- Initiate pilot plant testing in April 2021.