Pilot-Scale Testing of an Integrated Circuit for the Extraction of Rare Earth Mineral and Elements from Coal and Coal By-Products Using Advanced Separation Technologies

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DOE Project Numbers: DE-FE0027035
Period of Performance: Jan 2016 - Dec 2020
NETL Program Manager: Charles Miller

NETL Project Review Meeting
September 15-16th, 2020

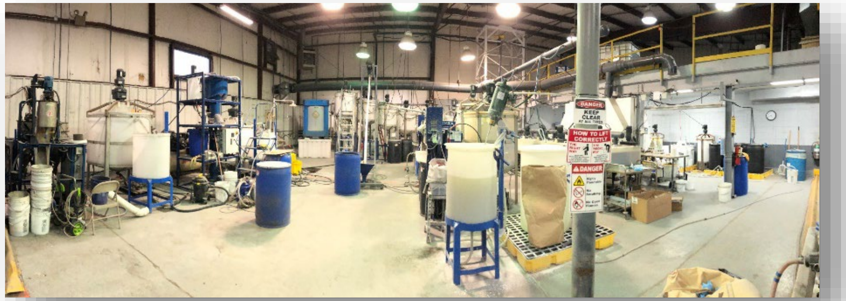
Project Objectives

- Develop, design and demonstrate a ¼-tph pilot-scale processing system for the recovery of high-value rare earth elements (REEs) from coal and coal byproducts.

Integration of physical and chemical separation processes as needed;

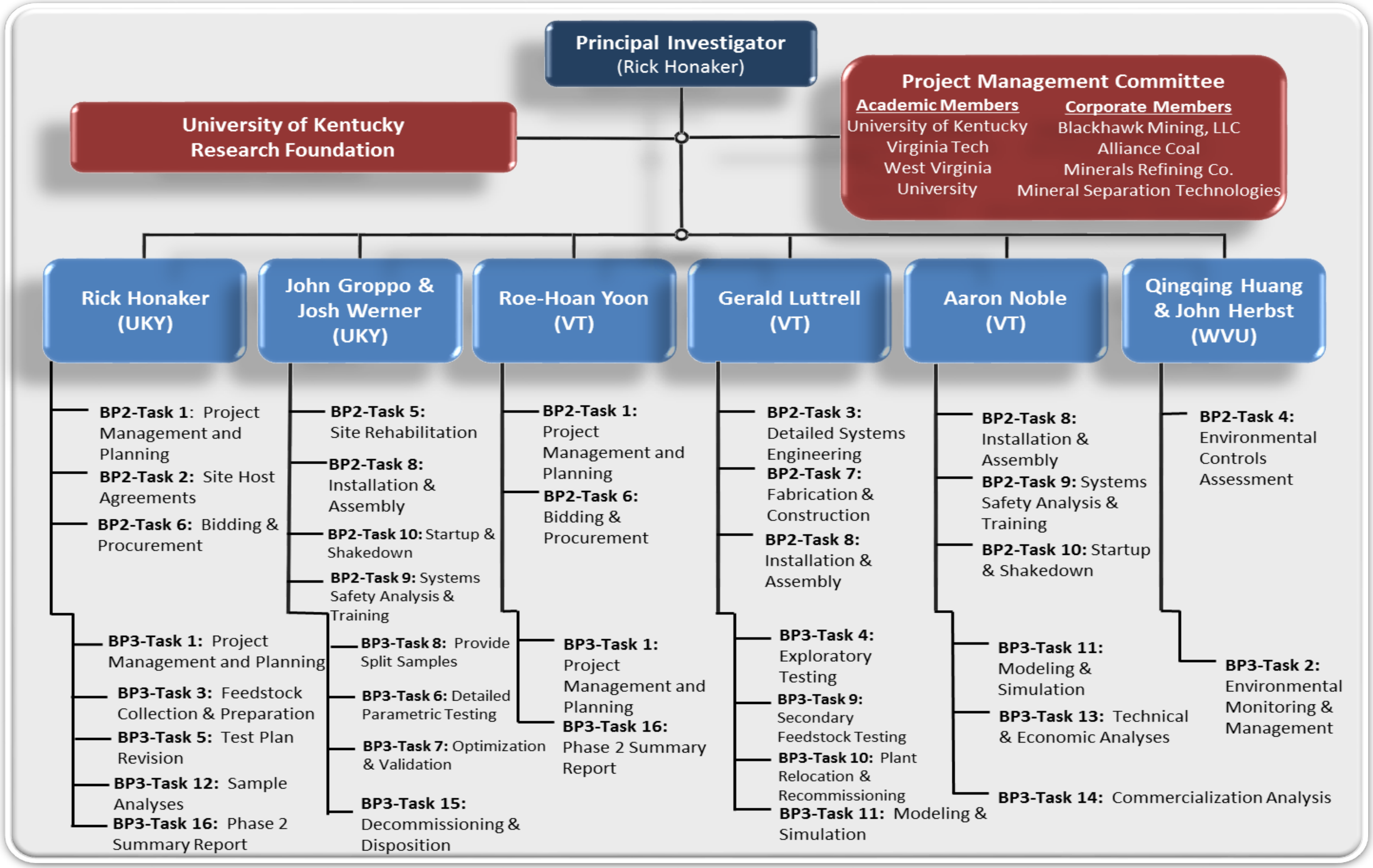
Production of concentrates with purity levels of at least 2% total REEs;

Technical and economic feasibility.



>90% Rare Earth Oxide Mix Concentrate

Project Team



*Kentucky River Properties has been added as a Corporate Member

Building Human Capital

"Human capital" – the potential of individuals – is going to be the most important long-term investment any country can make for its people's future prosperity and quality of life – *World Bank 'Human Capital Project 2019'*

Undergraduate Students

- Daniel A. Dailey, Chemical Engineering
- Vincent Mounce, Chemical Engineering
- Lucas Timmerman, Chemical Engineering
- Barbara Womack, Chemical Engineering
- Winnie Pitcock, Mining Engineering
- Lauren Pennington, Mining Engineering
- Caleb Matocha, Chemical Engineering
- Jacob Gill, Chemical Engineering
- Hannah Dykes, Chemical Engineering
- Devin Dupont, Mining Engineering
- Blanton Park Jr., Mining Engineering
- Lauren Shields, Mining Engineering
- Marysa Maier, Chemical Engineering
- Skyler Hornback, Chemical Engineering
- Gracey L. Kelley, Chemical Engineering
- Andrew Schofield, Chemical Engineering

Graduate Students

- Douglas Addo, MS
- Wencai Zhang, PhD
- Xinbo Yang, PhD
- Alind Chandra, PhD
- Tushar Gupta, PhD
- Vaibhav Srivastava, PhD
- Ahmad Nawab, PhD

- Venkat Rajagolpalan, Post Doc
- Honghu Tang, Post Doc
- Banda Raju, Post Doc
- Wencai Zhang, Post Doc
- Xinbo Yang, Post Doc & Assist. Res. Prof
- Alind Chandra, Post Doc

REE Pilot Plant Location: Providence, Kentucky

REE Pilot Plant

(https://m.youtube.com/watch?v=jR70j-MzWNE)

Feedstocks

Fire Clay Coarse Refuse

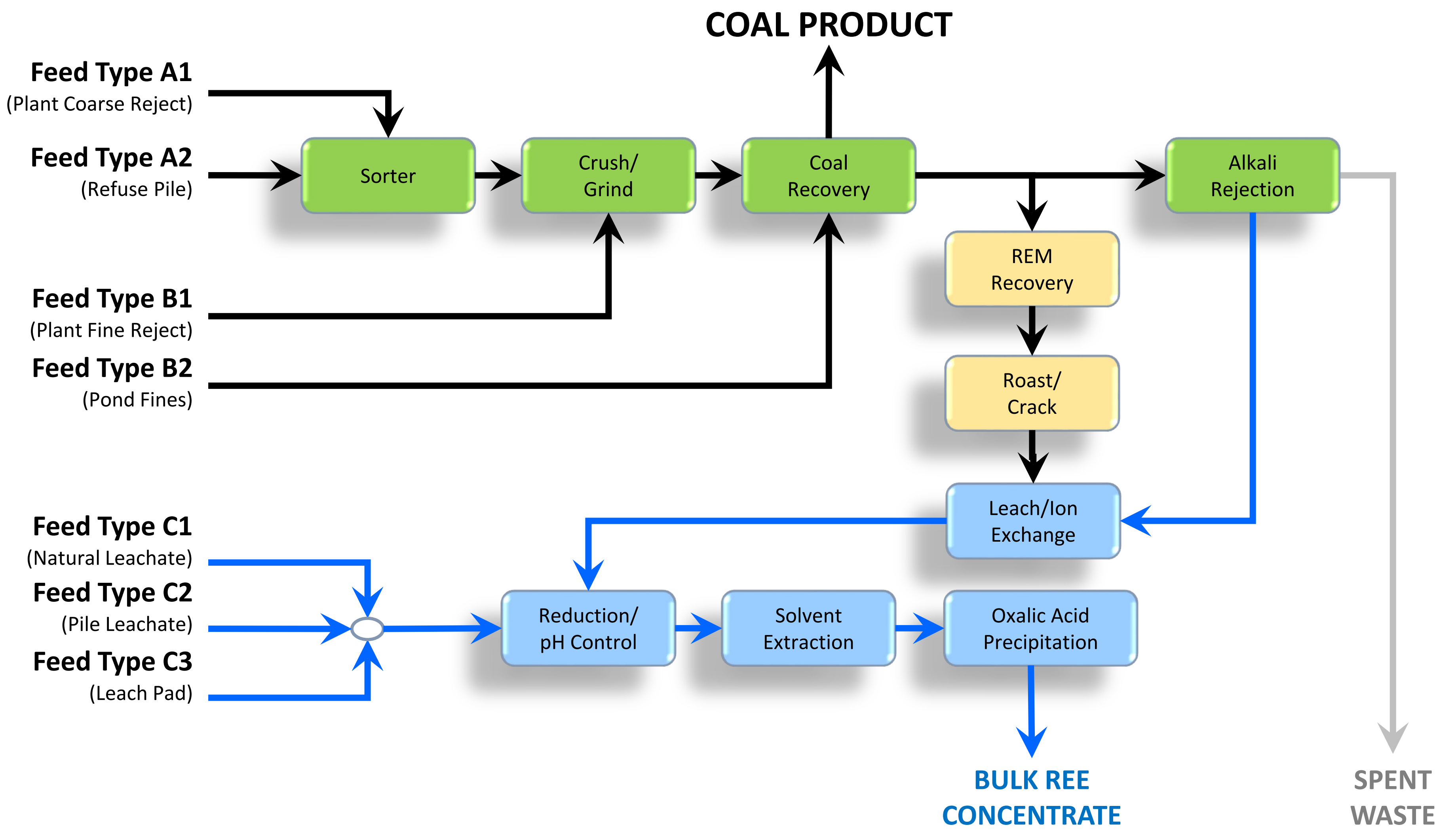
- Total REE concentration on a whole sample basis = 324 ppm.
- Coarse Refuse = 670 tph
- REE throughput = 200 kg/hr

WK No. 13 Coarse Refuse

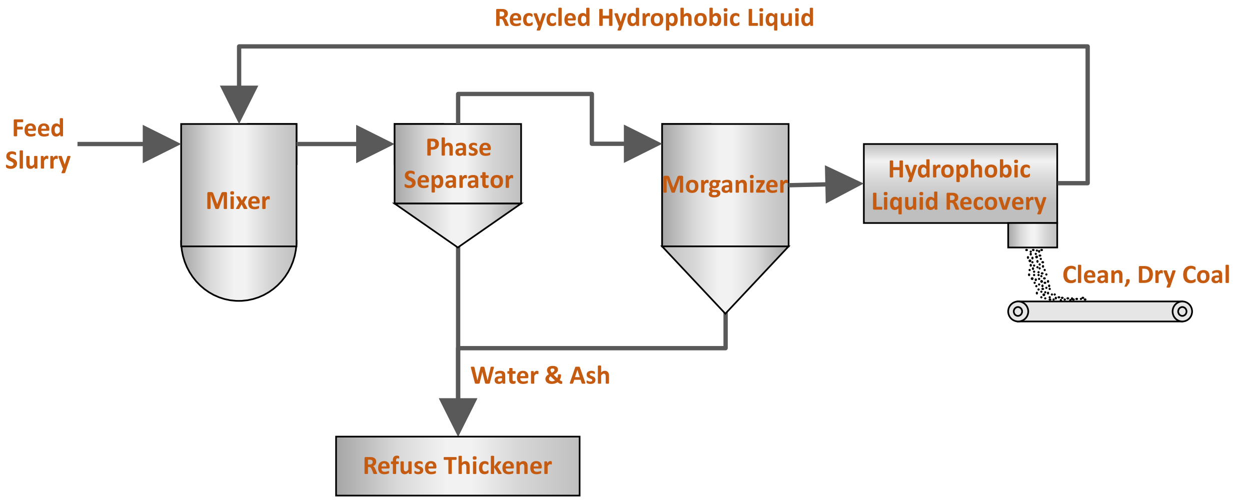
- Total REE concentration = 312 ppm.
- 17.5 million tons of coarse coal refuse currently on site
- 4600 mt of REEs, 480 tons of heavy REEs
- 10,000 tons of other CM
- Estimated total value = $1.4 billion

Category	Element	Content (ppm)	Resource (tonnes)	Market Value ($*10^6)
Light	Sc	16	273	$1,108.58
	La	47	831	$4.82
	Ce	99	1738	$10.08
	Pr	12	206	$21.39
	Nd	47	814	$56.65
	Sm	14	247	$4.74
	Eu	2	31	$1.09
Heavy	Y	3	57	$2.22
	Gd	7	131	$30.32
	Tb	1	13	$11.35
	Dy	4	77	$30.83
	Ho	2	41	$2.70
	Er	5	81	$2.59
	Tm	1	12	$20.12
	Yb	3	57	$6.60
	Lu	1	12	$10.41
Other CM	Co	18	318	$10.03
	Li	190	3324	$31.25
	Mn	227	3966	$3.97
	V	131	2298	$25.28

Initial Process Flowsheet



Mobile Hydrophobic-Hydrophilic Separation (HHS) Pilot Plant



Construction of Mobile Pilot Plant

- Installation
  - December 2018
  - Debugging and improvement
    - July, 2019
  - Optimization and testing
    - January, 2020
    - Thickener underflow
    - Screenbowl effluent
- Corvid 19 lock down
    - April 2020
  - Scale-up calculations
    - Near completion
      - Morganizer is the last unit operation to collect scale-up information
    - Industry cost share

- Leatherwood thickener underflow
  - As received

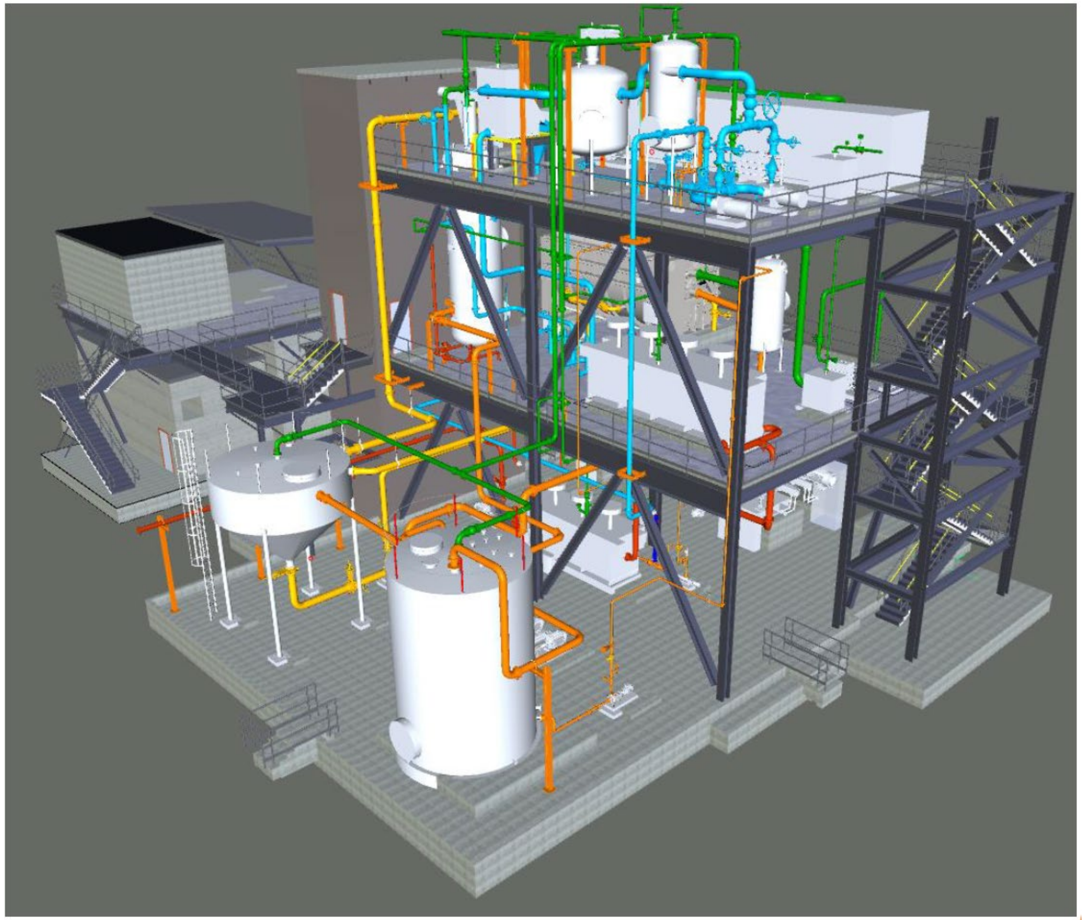
Test No	Products	Wt. (%)	Ash (%)	Moisture (%)	Organic Recovery (%)
1	Clean Coal	28.1	4.7	9.5	89.2
	Refuse	71.9	88.4	-	-
	Feed	100.0	64.9	-	-
2	Clean Coal	29.9	4.9	7.0	94.8
	Refuse	70.1	90.5	-	-
	Feed	100.0	64.9	-	-

  - Particle size effect

d_{80} (mm)	Product Ash (%)	Product Moisture (%)	Refuse Ash (%)	Mass Yield (%)	Organic Recovery (%)
0.600	8.6	1.2	69.2	44.4	75.2
0.250	6.2	1.1	76.1	48.6	83.5
0.150	5.8	1.7	82.5	52.4	90.4
0.075	7.0	2.1	85.3	54.9	93.4

Design of First Commercial HHS Plant

- 3-D Model

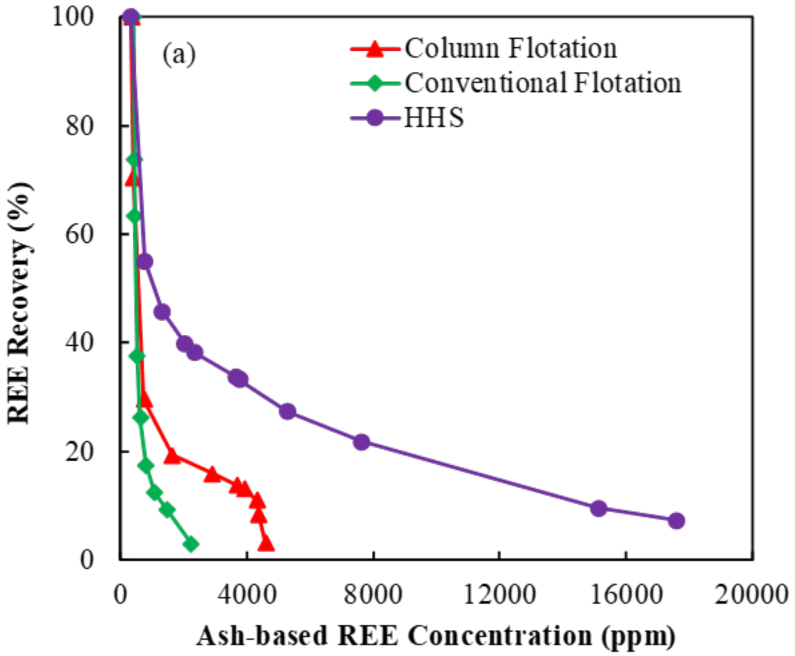


To be operational in Fall 2021

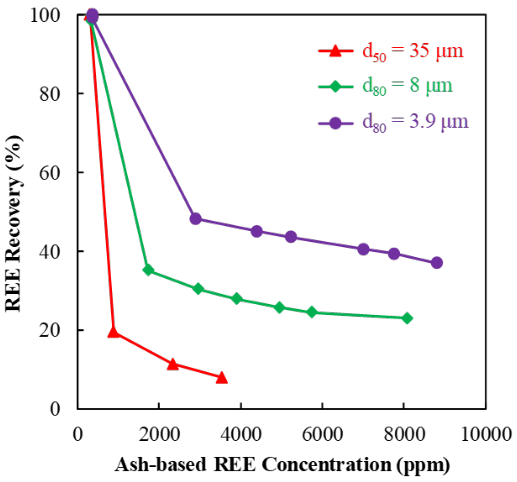
Rare Earth Minerals Recovery

Laboratory Tests Leatherwood Thickener Underflow

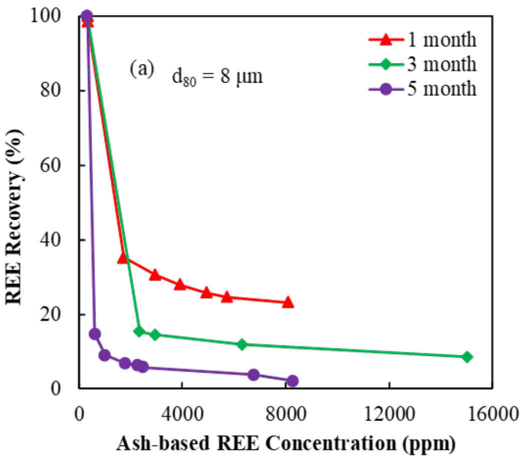
- Flotation vs. HHS



- Effect of grinding



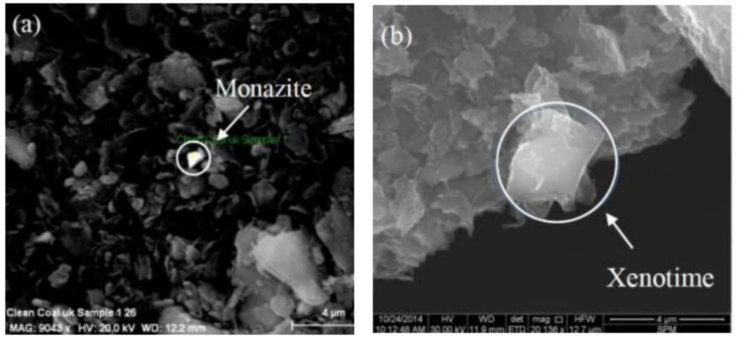
- Effect of aging



Results Obtained on an Artificial Mixture of Monazite and Silica

- Particle size
  - *d_{80} = 3 μm*
  - *Sorbitan monooleate for phase inversion*
    - *2×10^{-4} M*

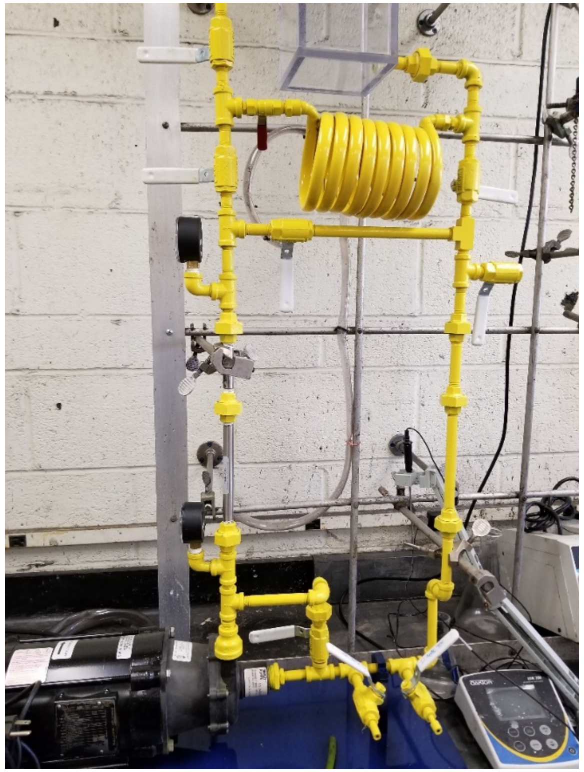
Product	Weight (%)	Grade (% TREE)	Recovery (%wt)
Concentrate	3.14	62.57	93.1
Tail	96.86	0.15	6.9
Feed	100.00	2.11	100



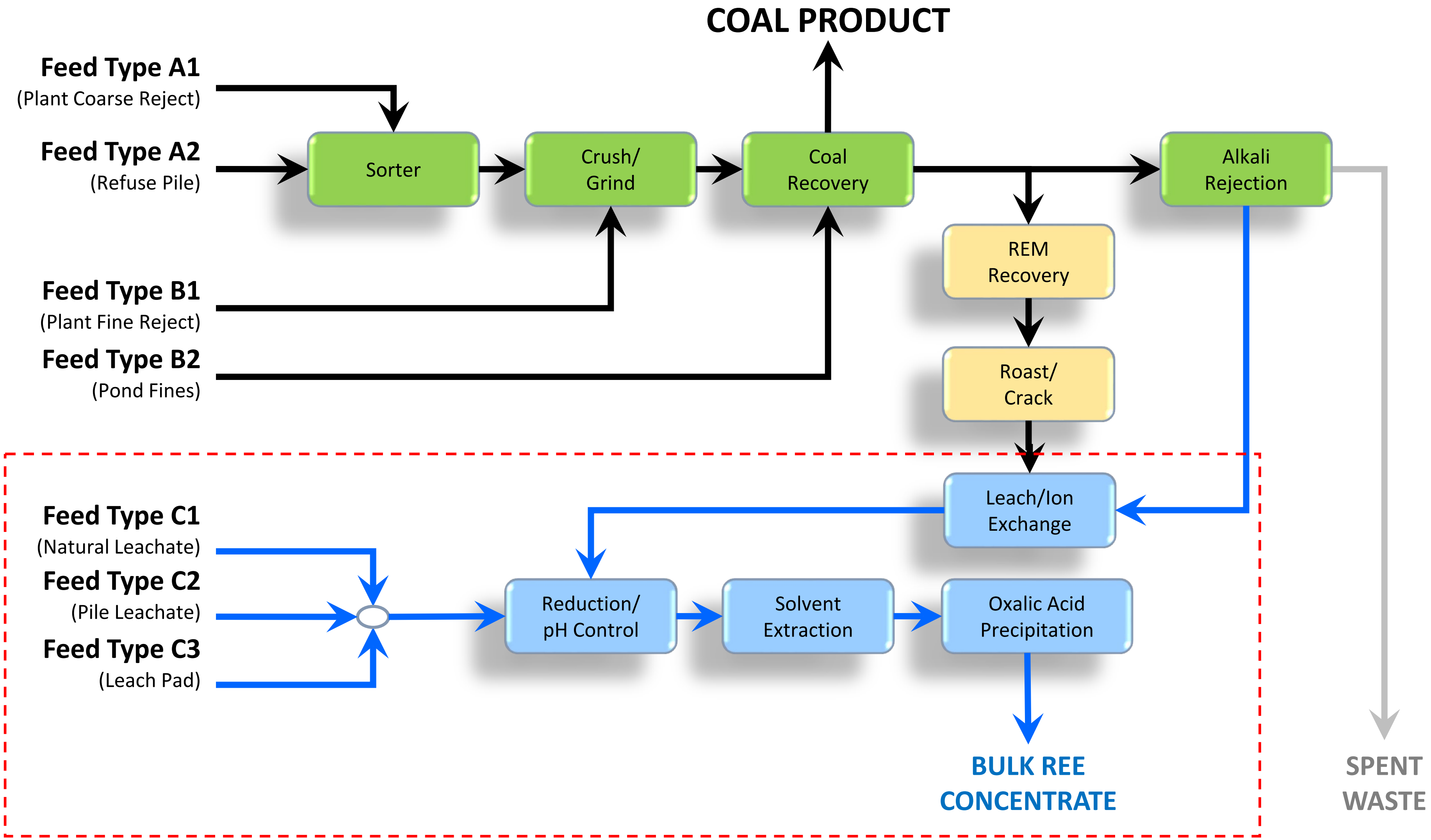
Isolated from Fireclay coal by low-temperature ashing
- 2-4 µm
- 300 ppm

Pilot-scale Tests for REM Recovery

- Pilot-scale tests
  - Decarbonization
  - REM recovery
    - Rougher
- PDU-scale tests to obtain high-grade REM concentrate
  - First test was unsuccessful
  - Decided to optimize the reagent dosages in lab tests first
    - Waiting for assays
  - Will return to PDU-scale tests



Initial Process Flowsheet



Heap Leach PLS: SX Feed

West Kentucky No. 13 Refuse Heap Leach

Elemental Analysis

Element	PPM
Sc	0.78
Y	3.90
La	0.31
Ce	2.25
Pr	0.88
Nd	1.09
Sm	0.62
Eu	0.19
Gd	2.65
Tb	0.29
Dy	0.95
Ho	< 0.003
Er	0.01
Tm	0.09
Yb	0.31
Lu	0.14
Total	**14.45**

Element	PPM
Th	<0.003
U	1.53
Fe	5453
Al	1467
Ca	459
Mg	572
Mn	77.6

SX Circuit Conditions

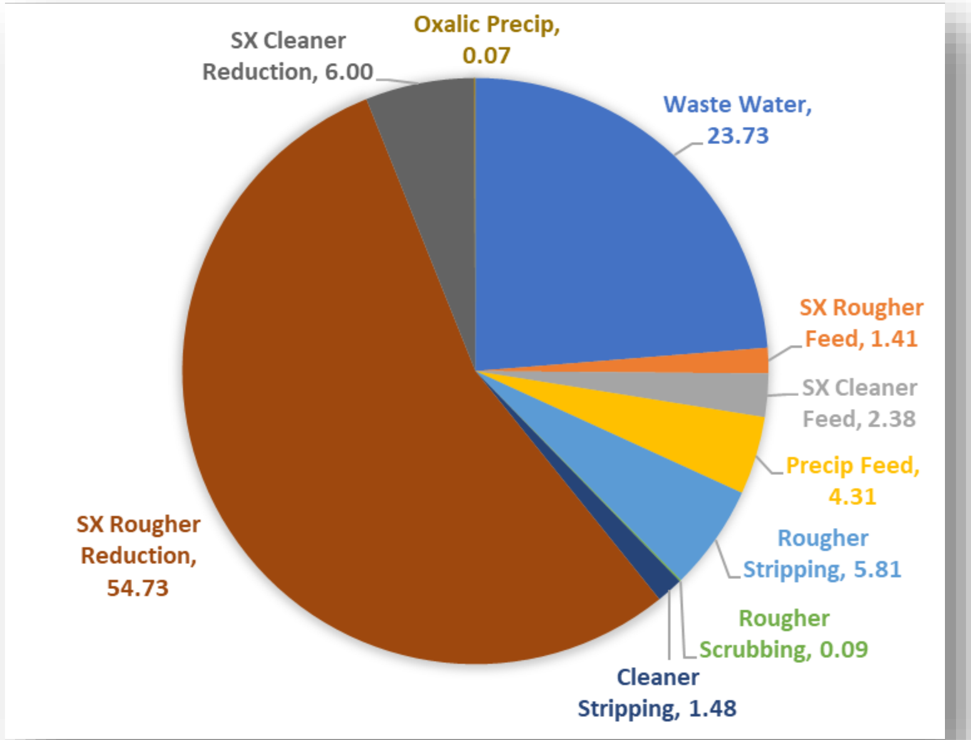
Parameter	Value
Feed Rate	0.5 gpm
Organic : Aqueous	1 : 1
Solvent	Orform
Extractant	DEHPA
Extractant Dosage	5% by volume
Phase Modifier	TBP
Modifier Dosage	10% by volume
Feed pH	2.0
Reducing Agent	Ascorbic Acid
Strip Solution	6M HCl
Scrub Solution	0.5M HCl

SX Circuit REO Concentrates

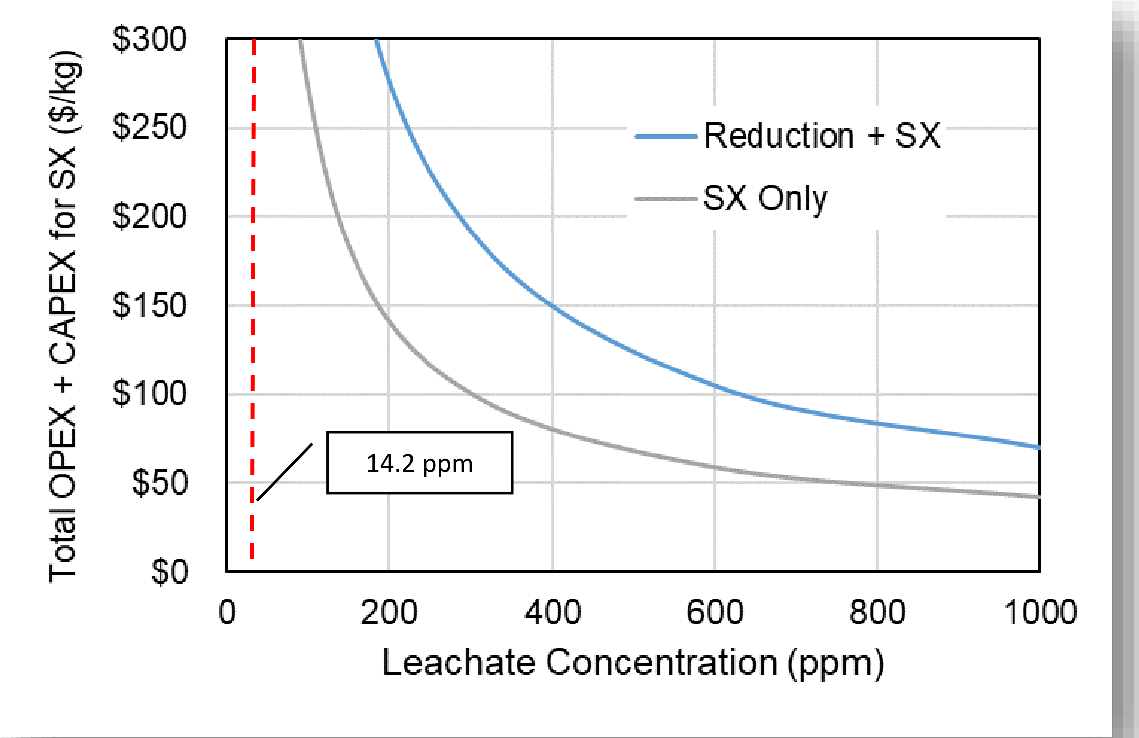
Rare Earth Element	REO Concentration (%)							
	27-Nov	28-Nov	29-Nov	3-Dec	4-Dec	5-Dec	6-Dec	7-Dec
Sc	0.02	0.01	0.02	0.03	0.03	0.03	0.02	0.02
Y	17.49	19.24	18.53	18.04	17.06	21.96	24.73	23.18
La	0.23	0.26	0.16	0.14	0.16	0.29	0.49	0.59
Ce	6.94	6.88	3.84	3.58	3.91	5.93	7.99	8.08
Pr	2.43	2.75	1.81	1.69	1.84	2.15	2.24	1.97
Nd	15.71	16.05	12.75	11.79	12.19	12.58	12.09	10.36
Sm	12.41	11.31	13.26	12.03	12.12	9.75	7.48	6.26
Eu	3.69	3.35	4.20	3.83	3.79	2.95	2.20	1.79
Gd	18.00	17.23	20.65	18.99	18.62	15.43	12.20	10.09
Tb	2.65	2.56	3.08	2.85	2.78	2.38	1.87	1.56
Dy	10.31	10.34	12.26	11.54	11.01	10.11	8.52	7.19
Ho	1.38	1.39	1.68	1.58	1.45	1.46	1.30	1.11
Er	1.65	1.83	2.41	2.27	2.02	2.23	2.06	1.81
Tm	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Yb	0.10	0.12	0.26	0.25	0.20	0.27	0.26	0.23
Lu	0.00	0.00	0.02	0.02	0.01	0.02	0.02	0.02
Total	93.02	93.32	94.93	88.63	87.20	87.55	83.48	74.27

Economic Analysis

SX Chemical Cost Distribution



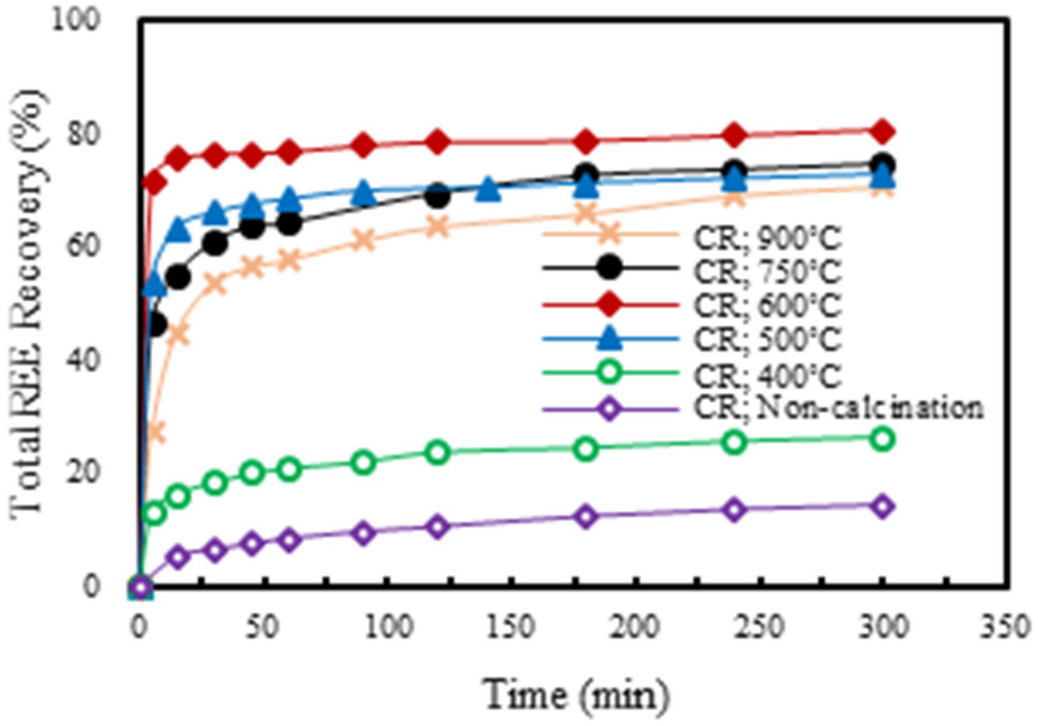
Total Cost Analysis

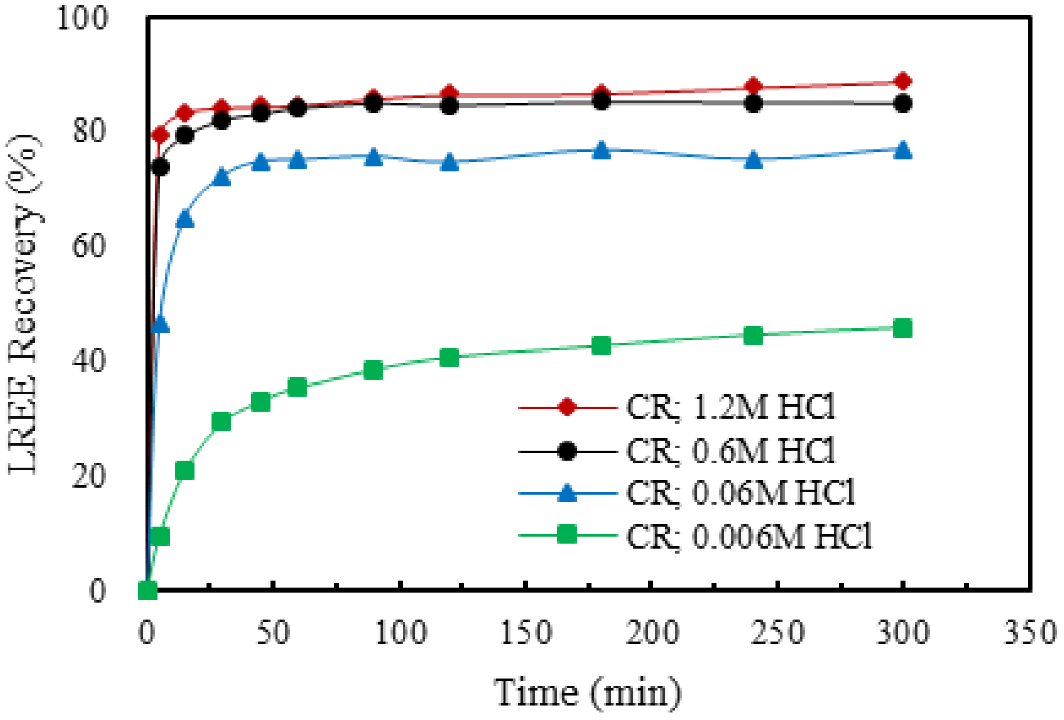


Conclusions:

- Water reduction process is uneconomical.
- Preconcentration of the REEs in the PLC to SX is required.

Pre-Leach Roasting Benefits

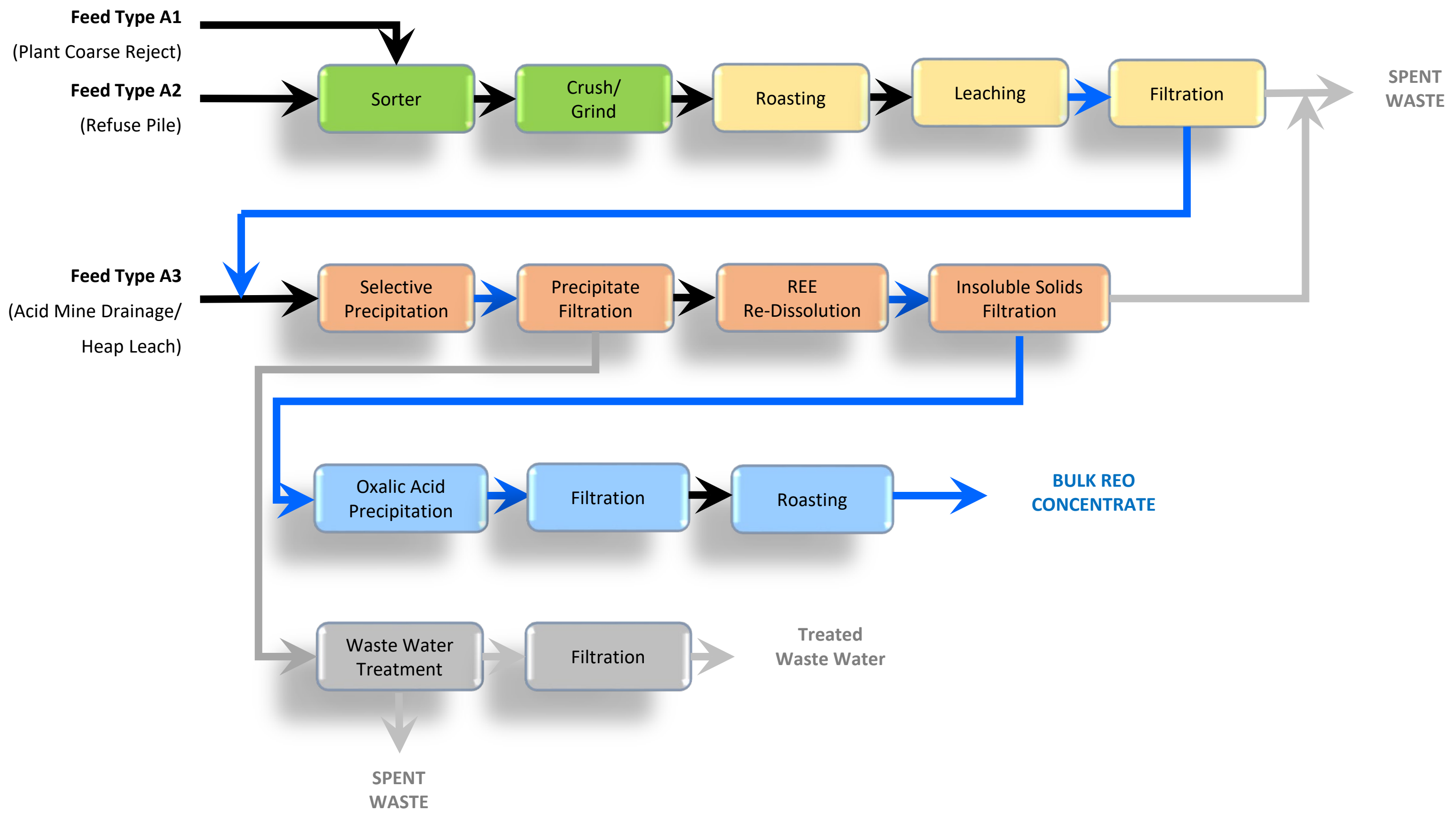




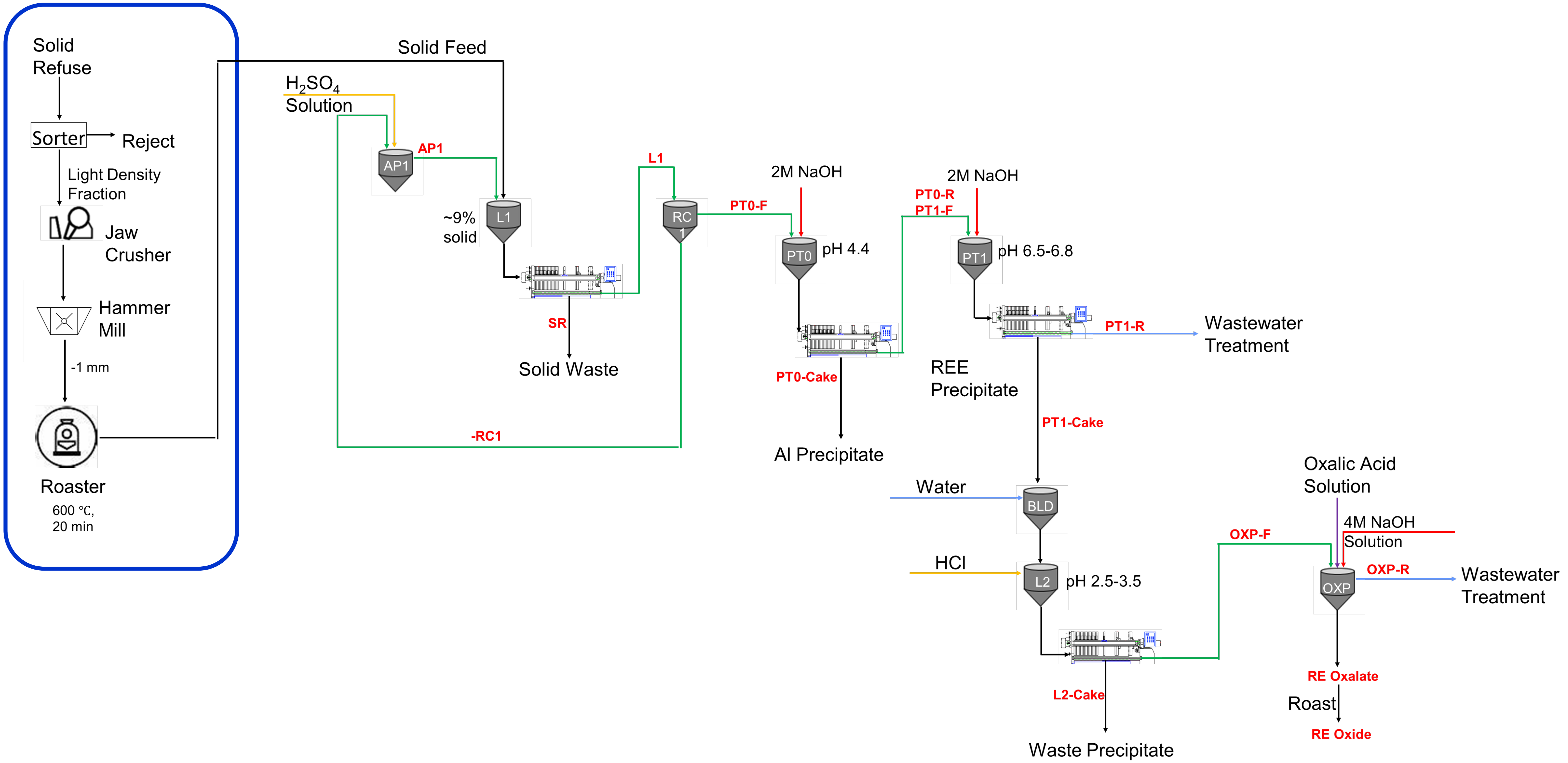
- ❑ Roasting the material at a temperature of around 600^{O}C significant enhances leach recovery values.
- ❑ Roasting provides the opportunity to significantly reduce acid consumption while achieving economic recovery values.

Modified Flowsheet

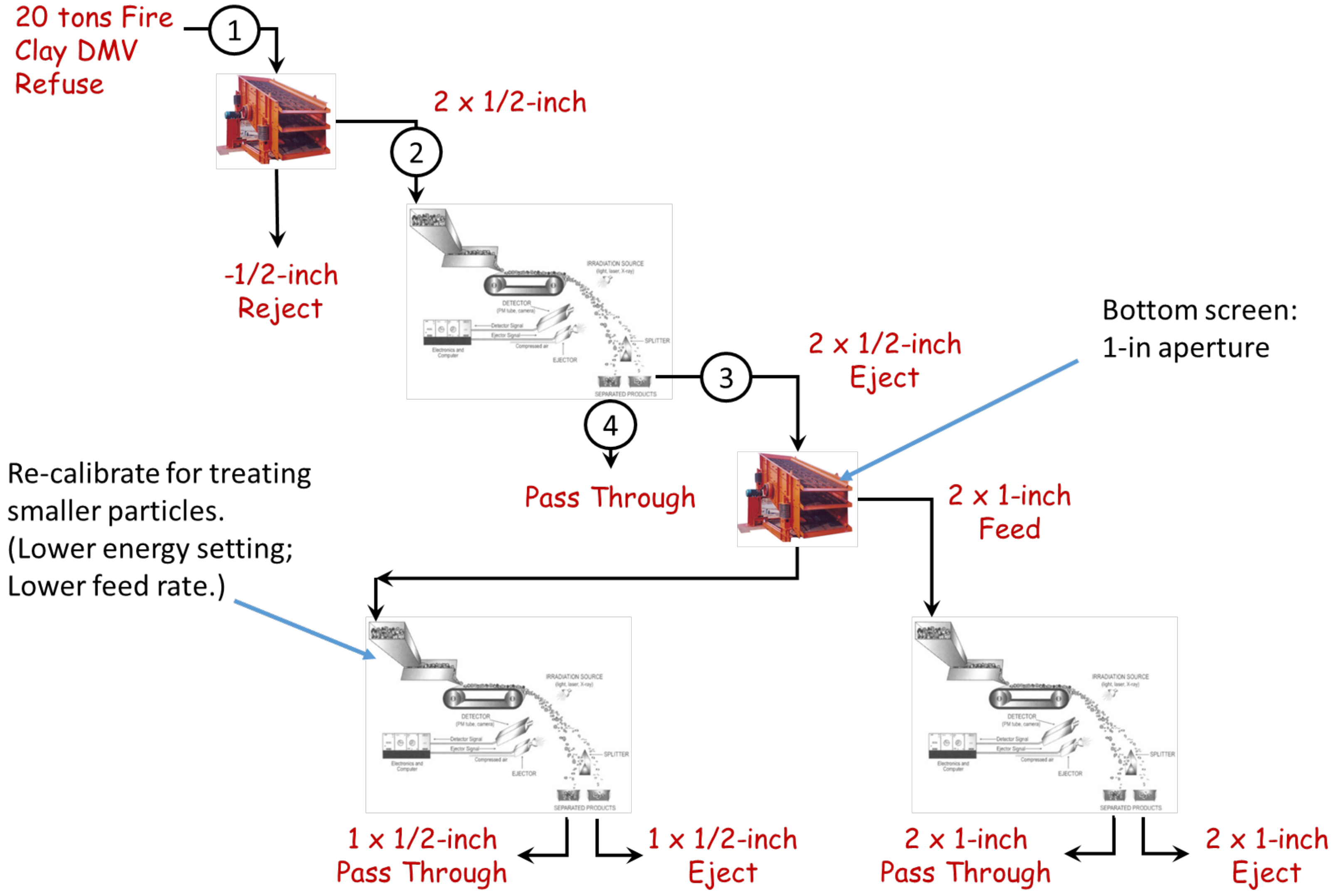
- Incorporates a pre-leach roasting step
- Utilizes precipitation steps to remove impurities
- Selectively precipitates the REEs
- Removes solvent extraction from the process circuit

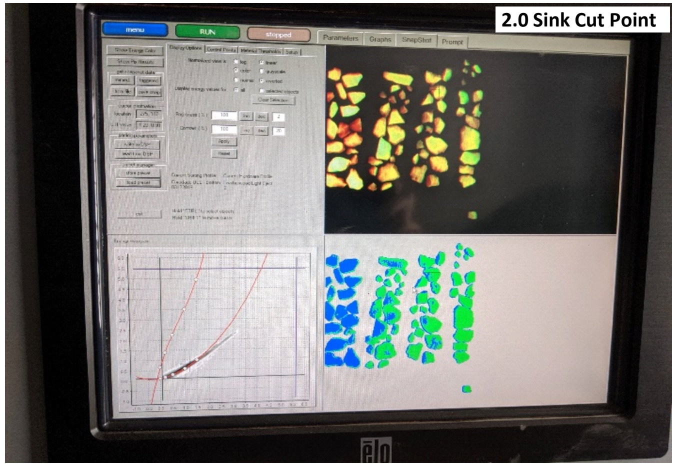


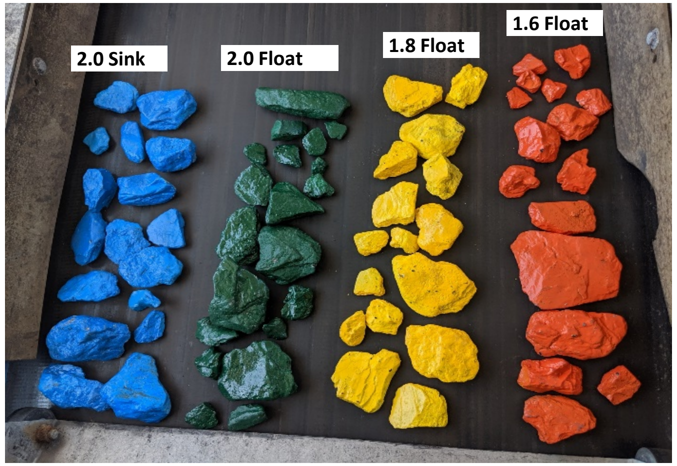
Pilot Plant Flowsheet



X-ray Sorter Optimization







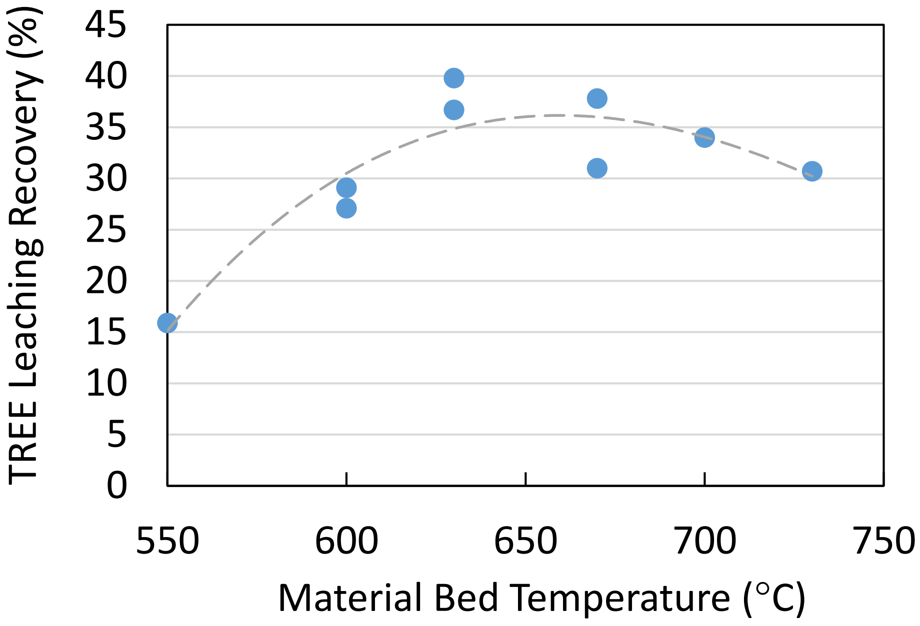
Roasting Pretreatment Optimization

Feed:

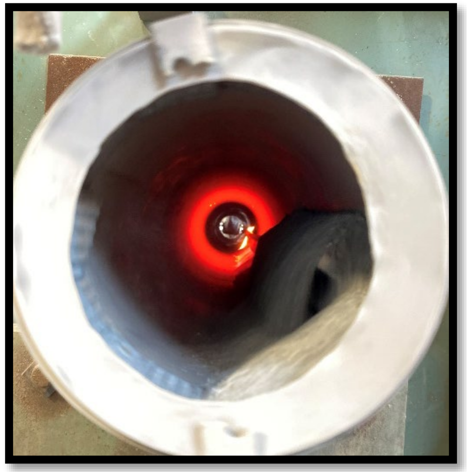
- West Kentucky No. 13 and Fire Clay coarse refuse
- X-Ray sorter: 2.0 sg float fraction
- Crush to -1 mm size

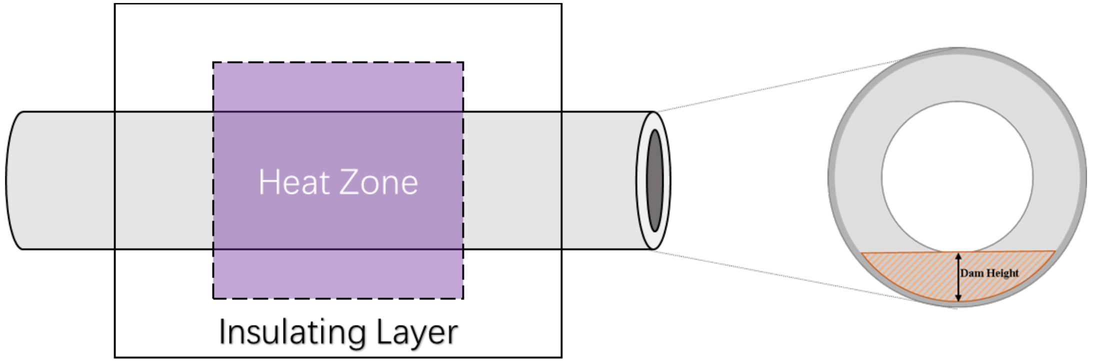
Critical:

- Retention time
- Inner tube bed temperature



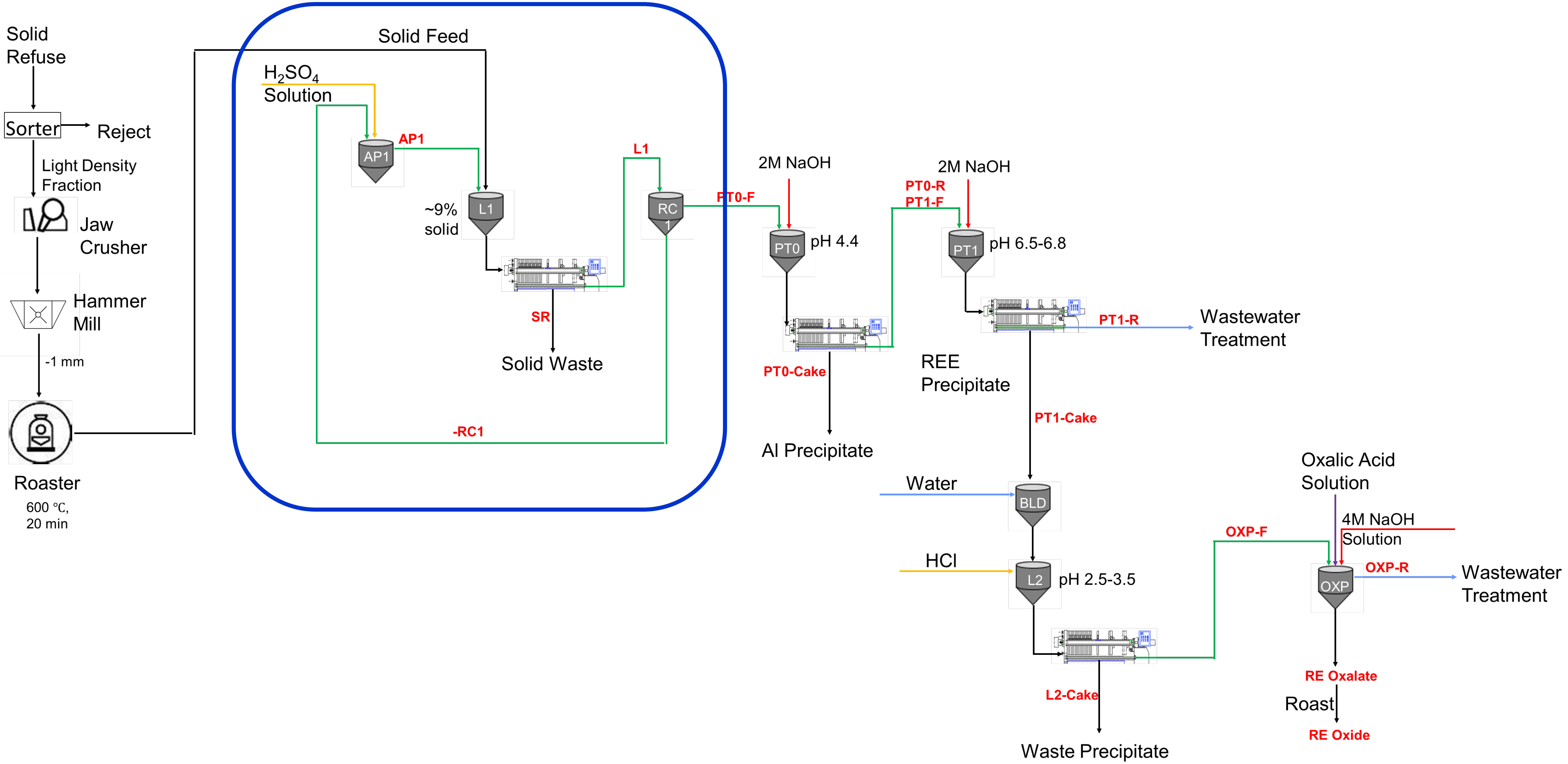
Leaching recovery improvement. (WKY13)
(1M H_2SO_4, S/L=1/5, room temperature, retention =15 min)



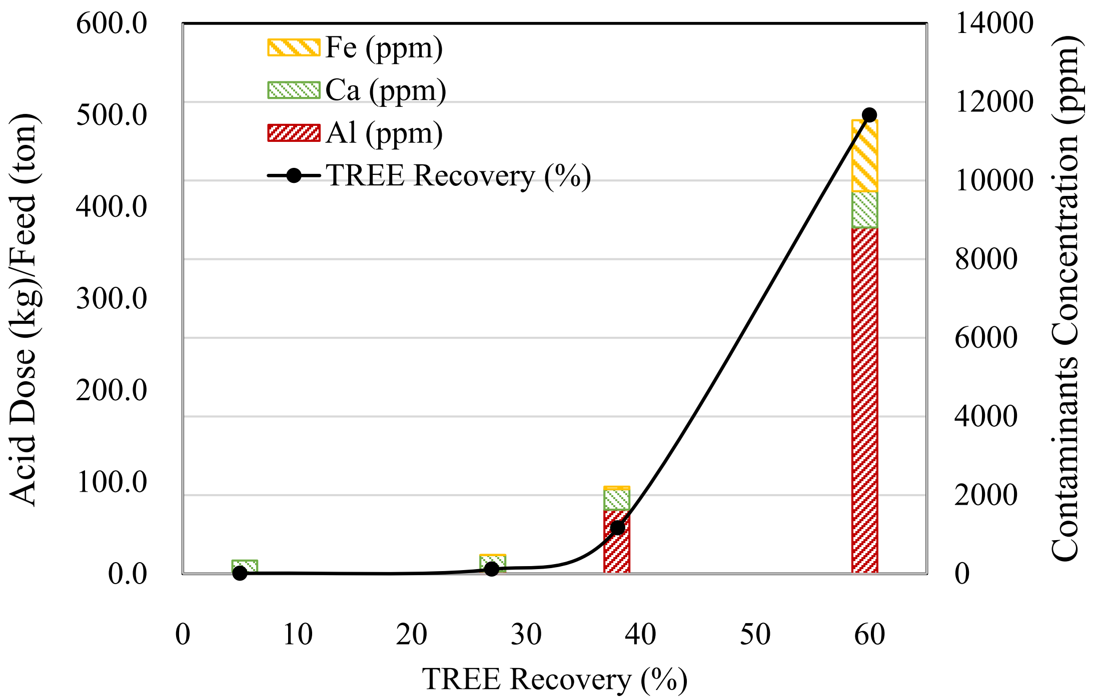


Schematic of the roaster heat zone and discharge overflow weir.

Pilot Plant Flowsheet

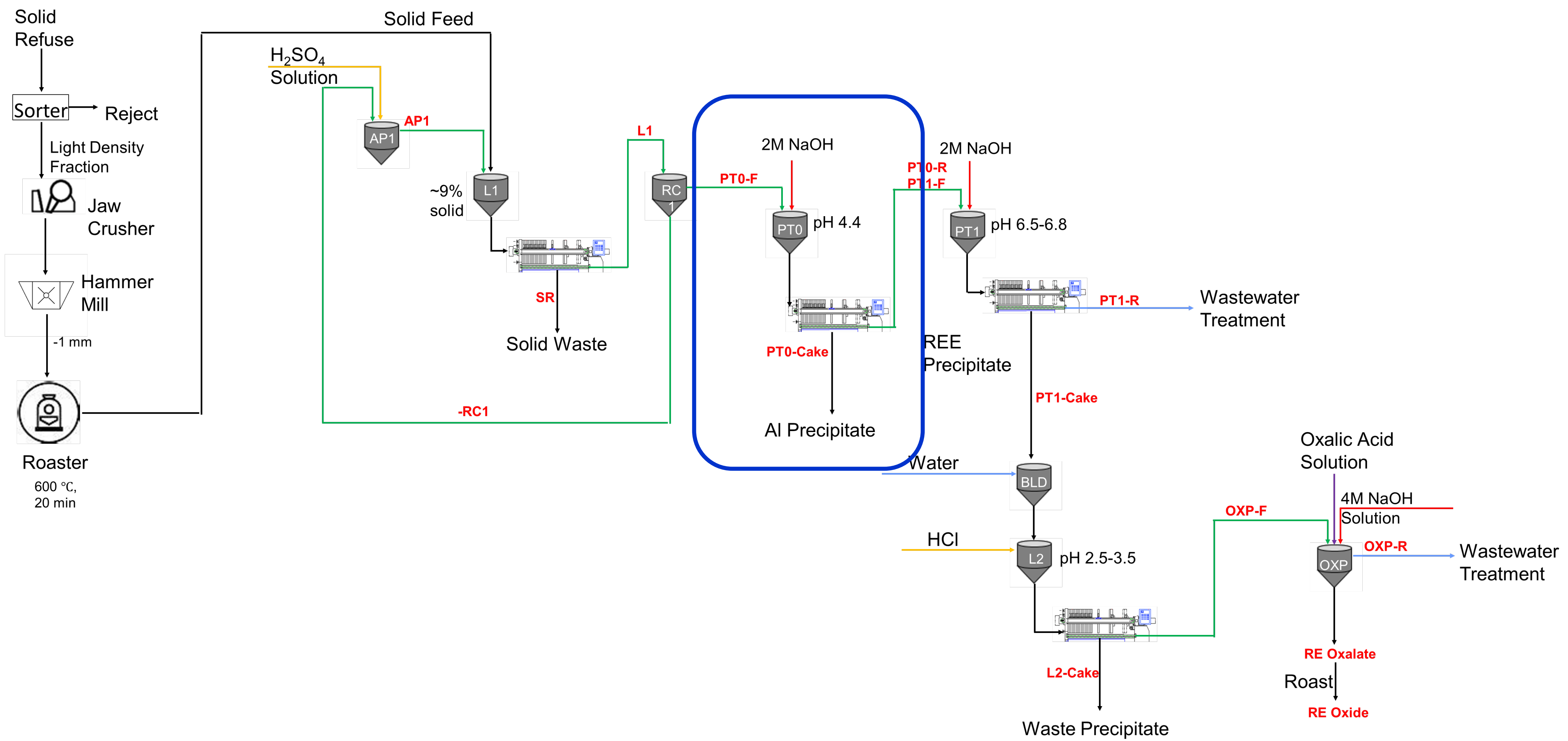


Acid Leaching



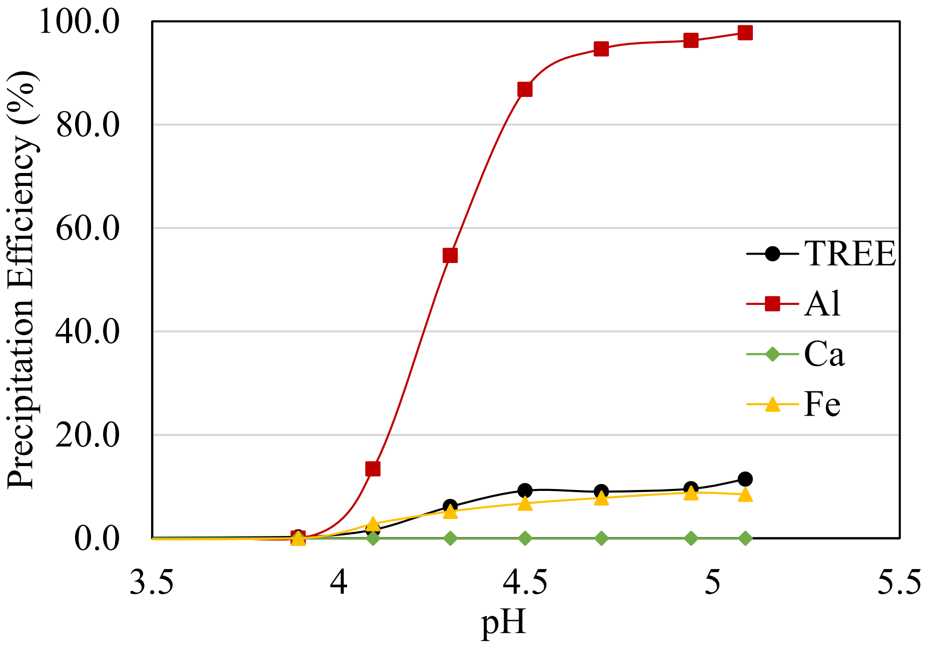
- Leaching with sulfuric acid
  - 0.001 M -1M
  - S/L: 200 g/L
- *Contamination hurts economics*

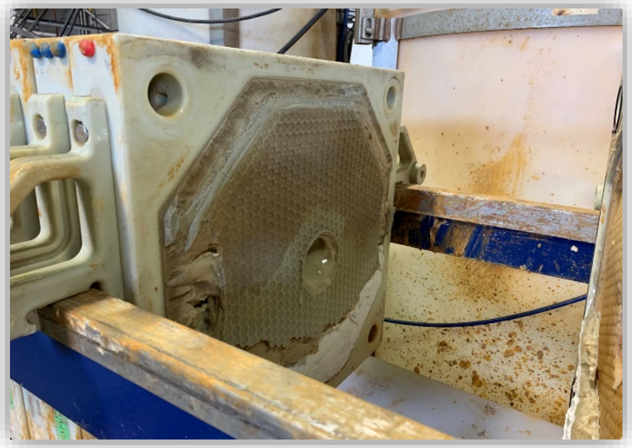
Pilot Plant Flowsheet

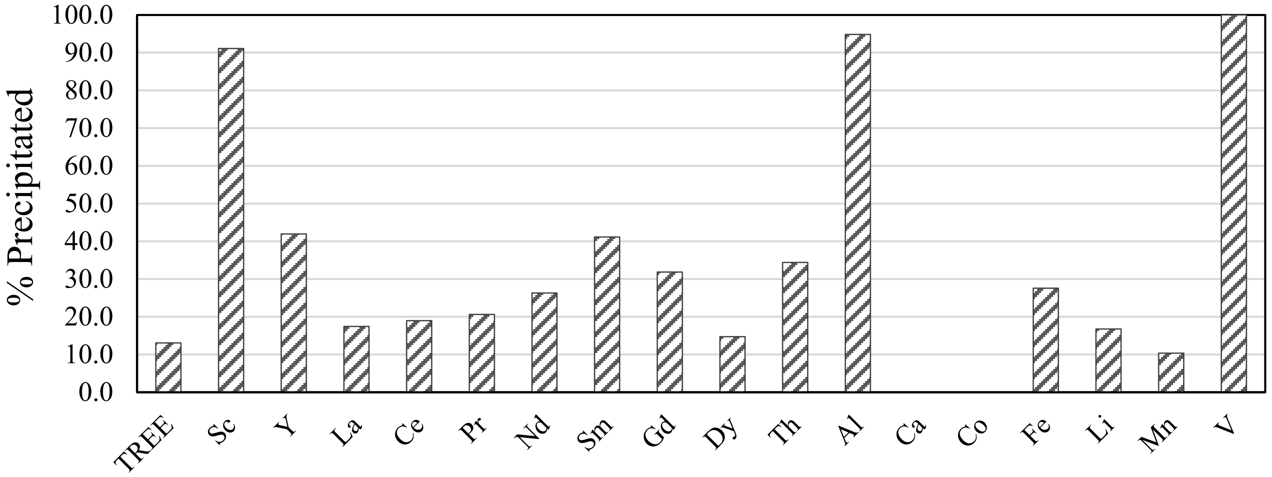


Al Removal

- Al is a major consumer of the oxalic acid due to its ability to form $Al(C_2O_4)_2^-$ and $Al(C_2O_4)_3^{3-}$ complexes
- Al can be removed before RE precipitation by adjusting the pH between 4 to 4.5

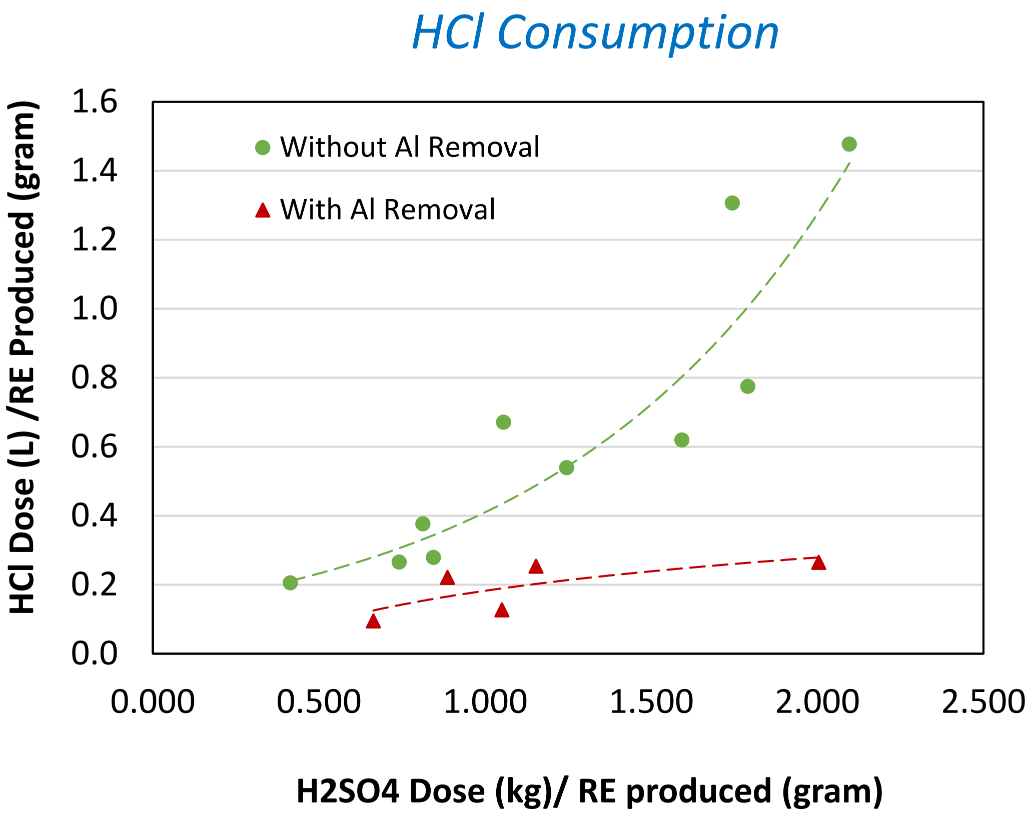


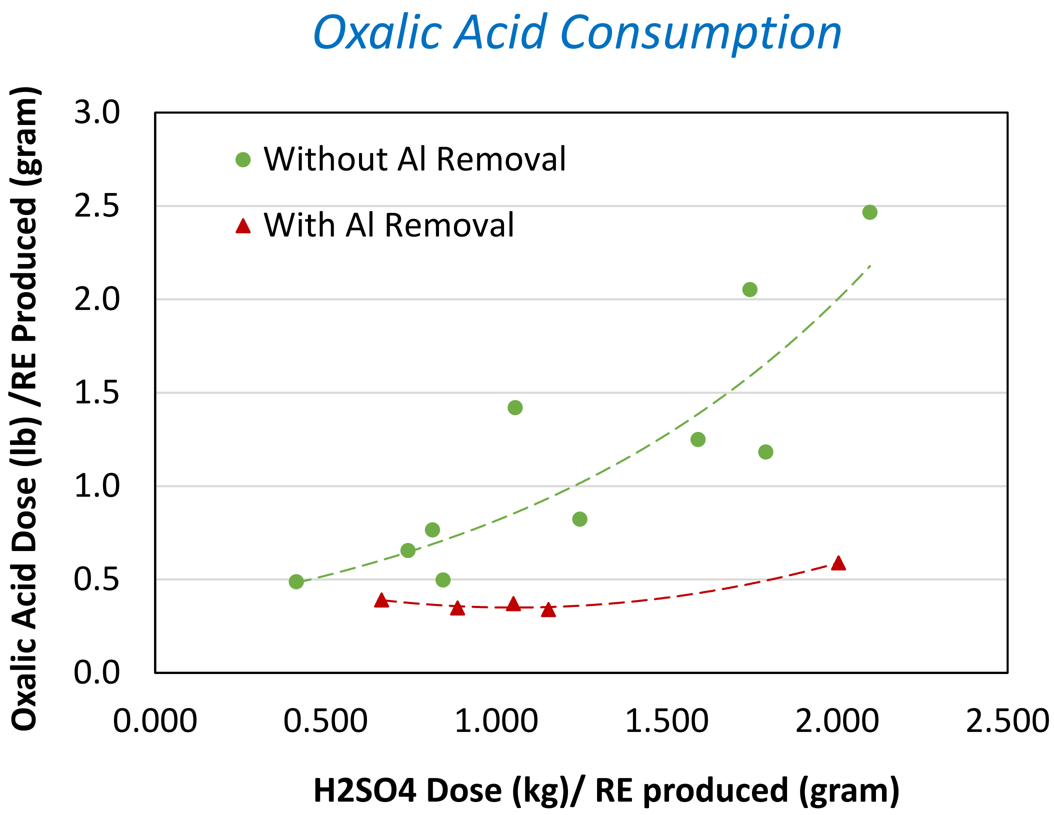




Observed that about 27% of Fe was removed together with Al, which was higher than the lab test results. This is due to the conversion of ferrous hydroxide to ferric hydroxide which shifted the Fe precipitation curve closer to the Al precipitation.

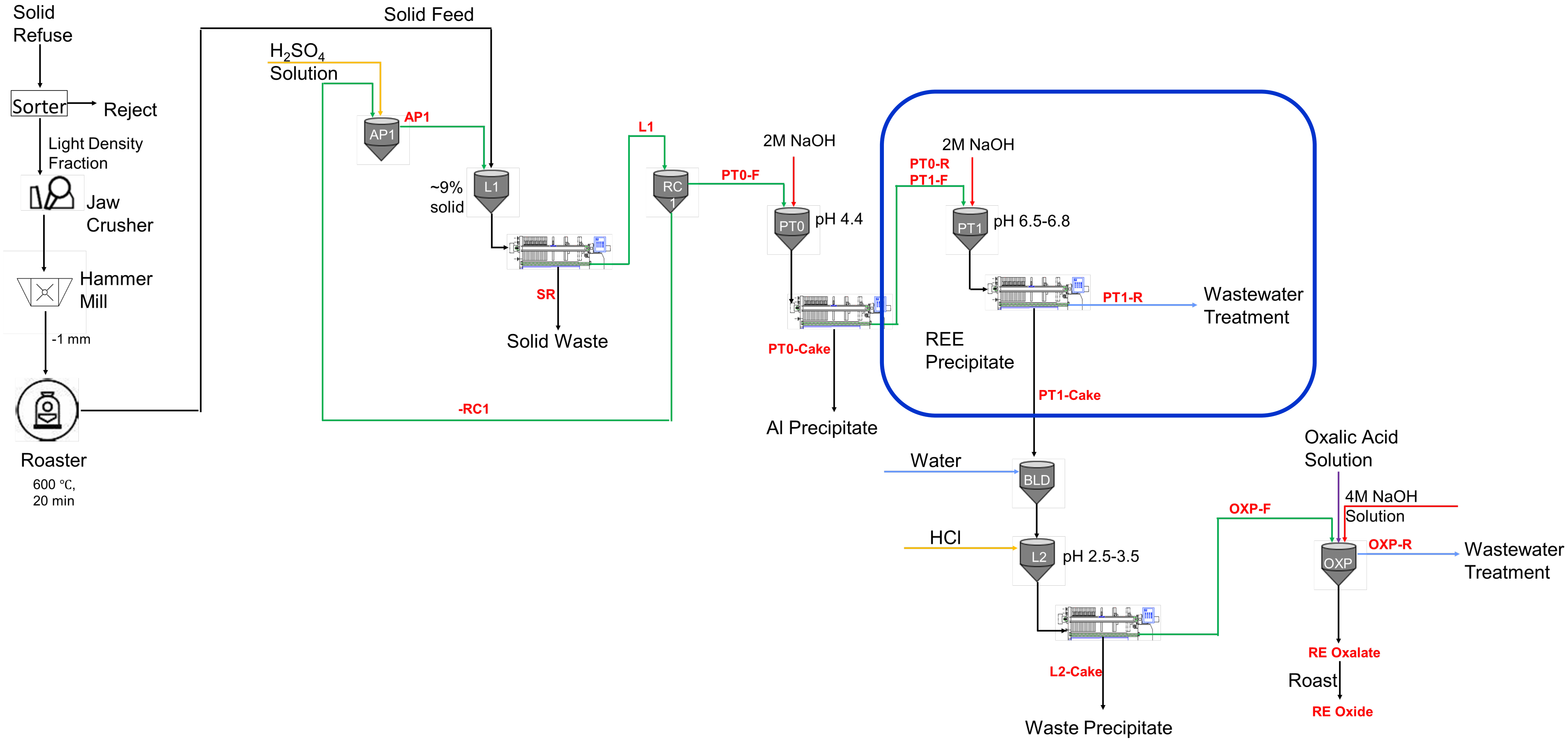
Economic Assessment



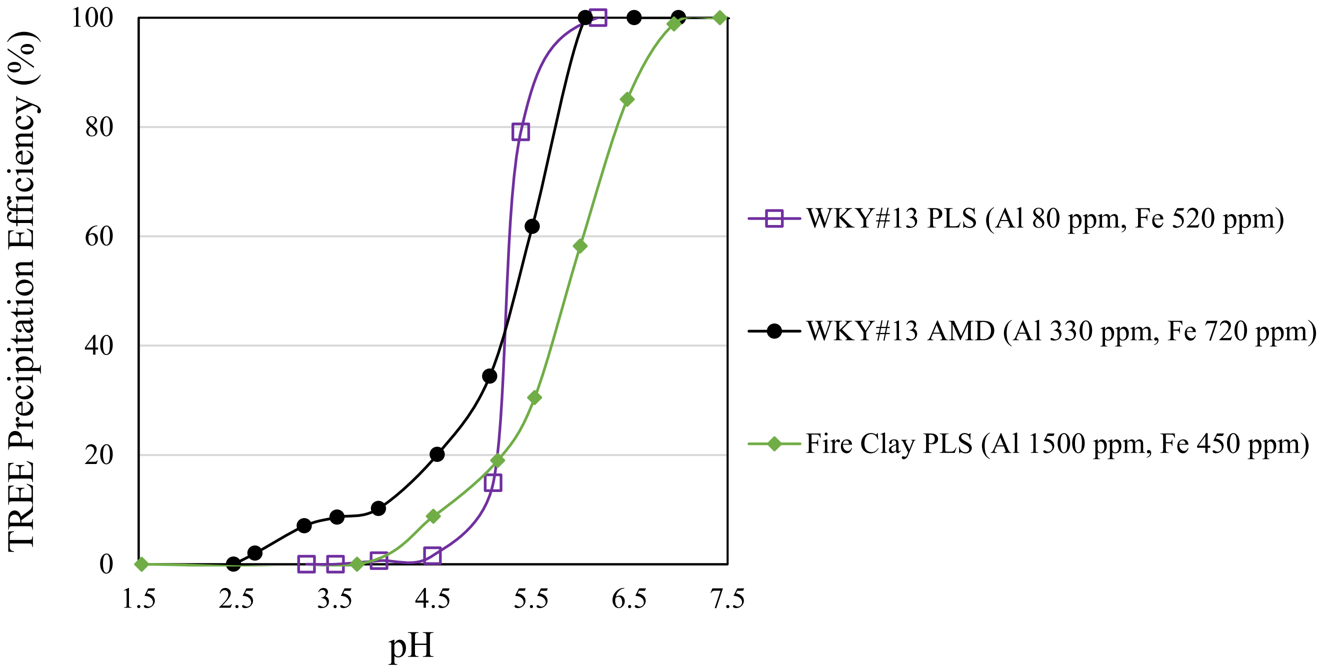


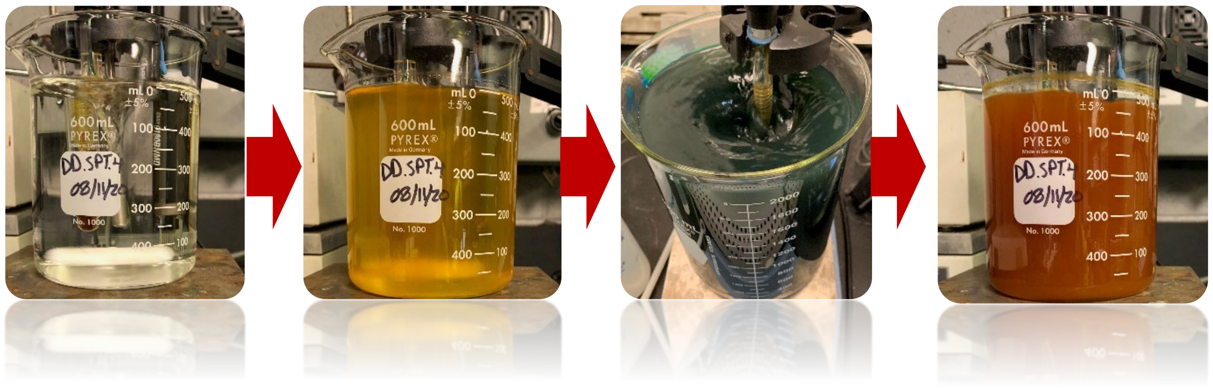
- ❑ *Increased acid dosage in the leaching process resulted in an increased contamination level in downstream process;*
- ❑ *Adding an Al removal step significantly reduced the downstream chemical consumption.*

Pilot Plant Flowsheet



Rare Earth Precipitation

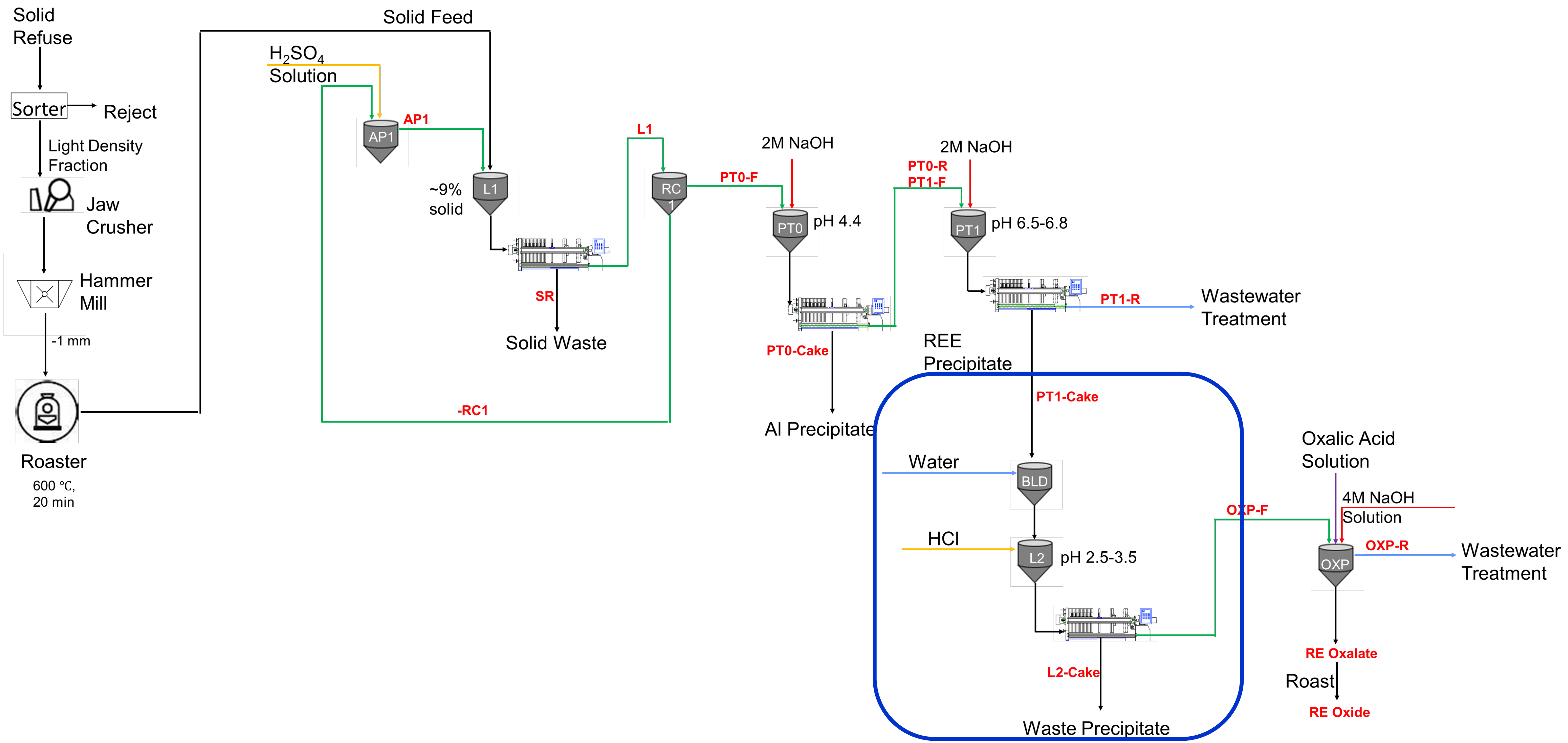




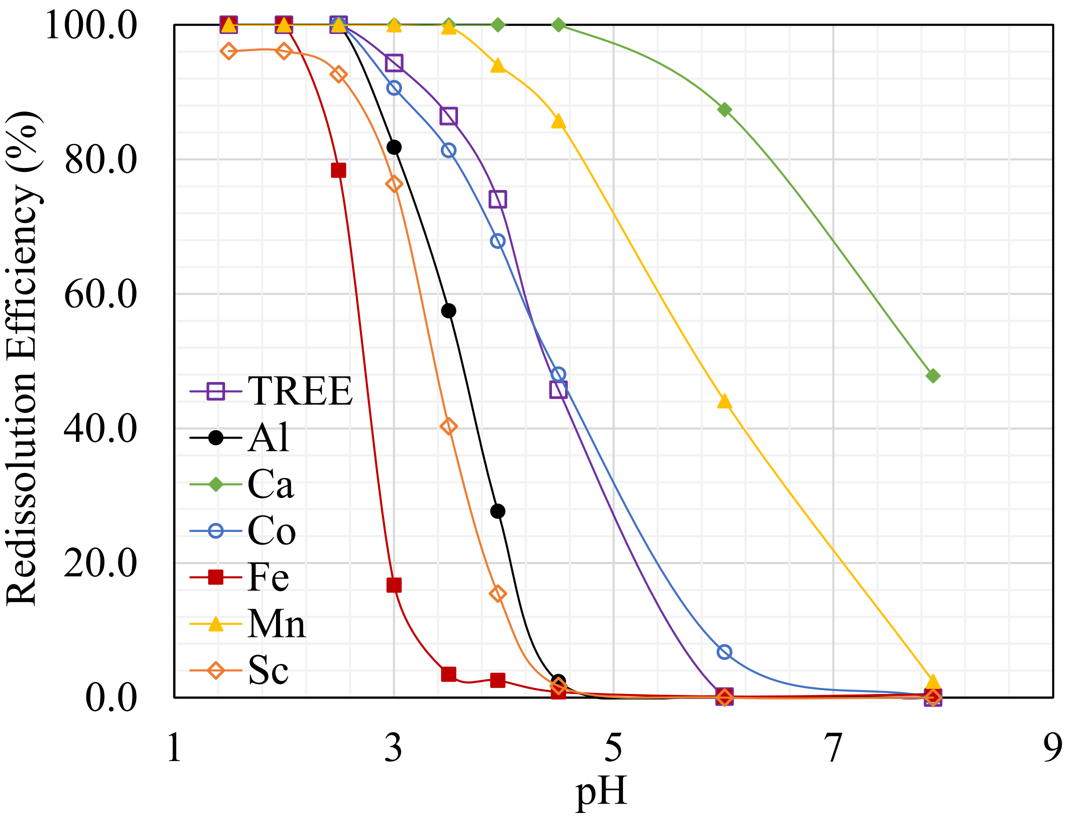
RE Precipitation Cake Produced in Pilot Plant

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**

Pilot Plant Flowsheet



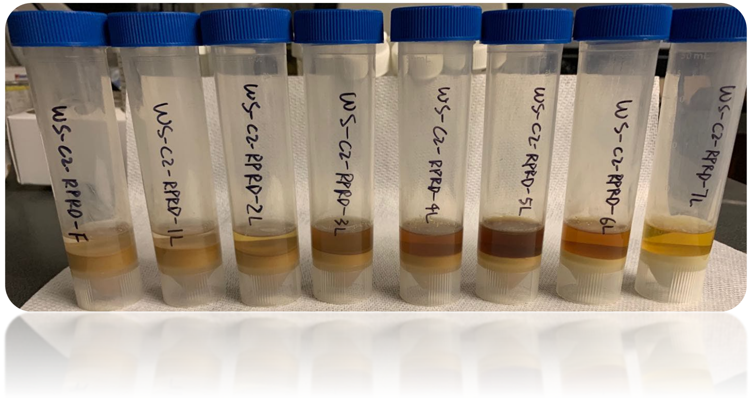
RE Redissolution



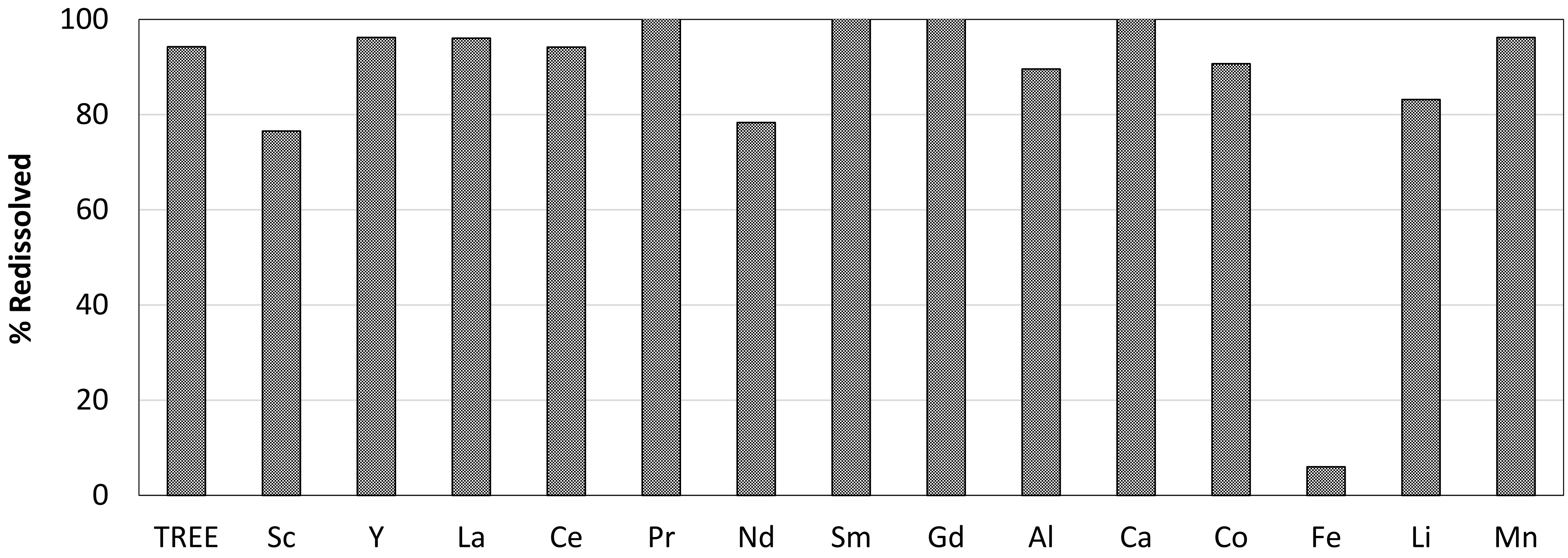
Redissolution efficiency of REEs, Al, Ca and Fe at various pH

Ferrous

Ferric

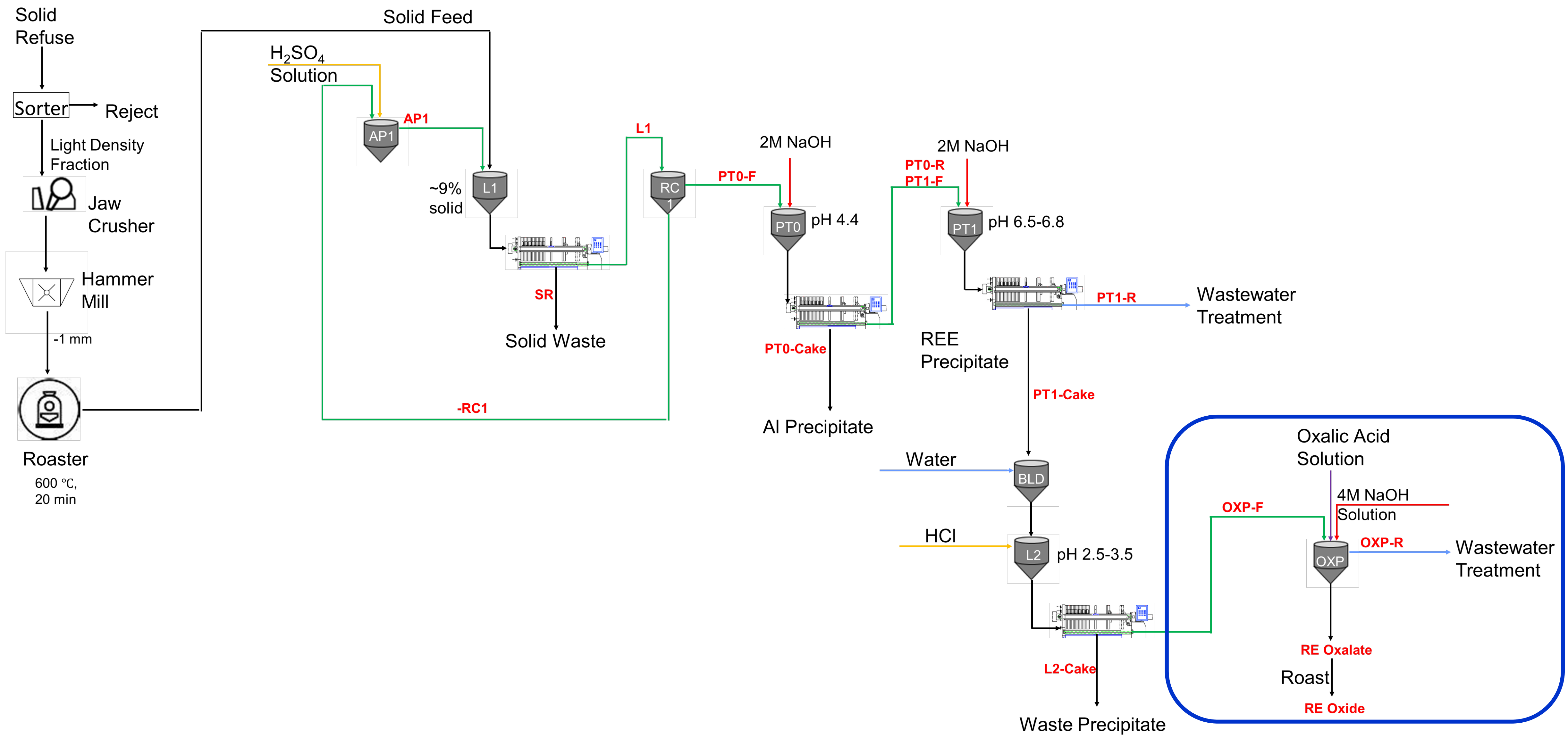


RE Redissolution

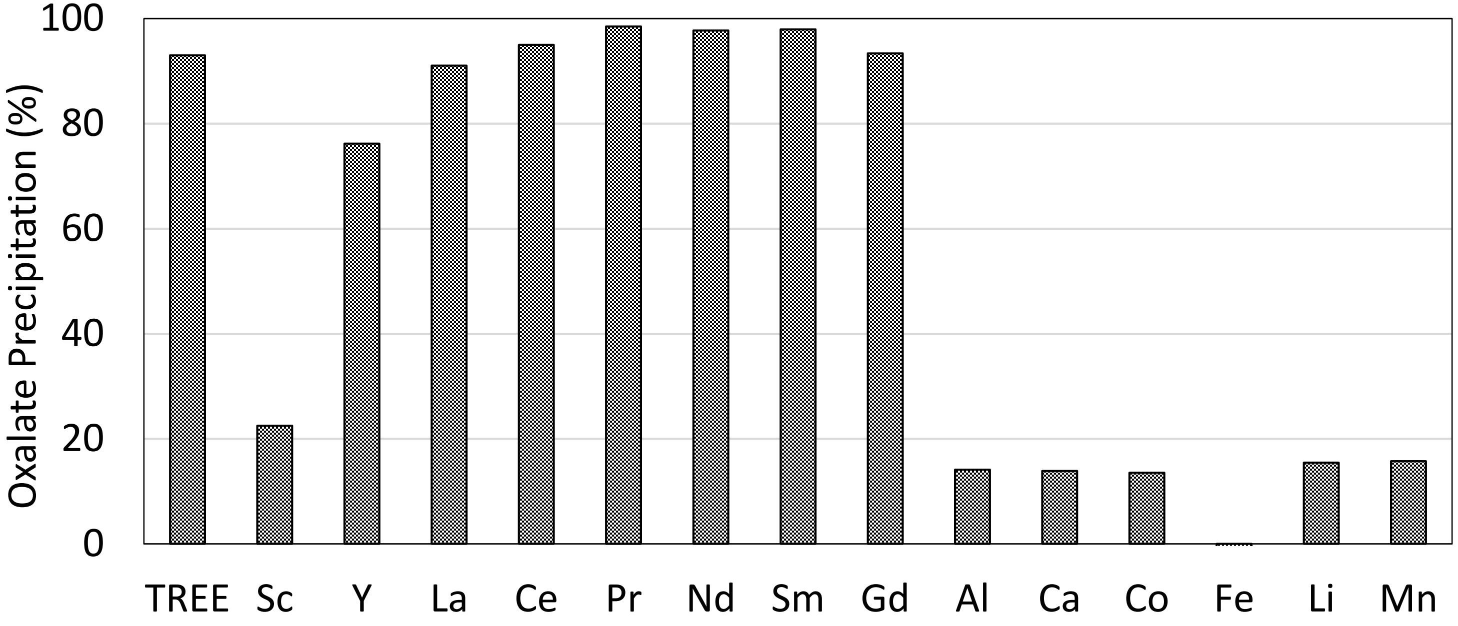


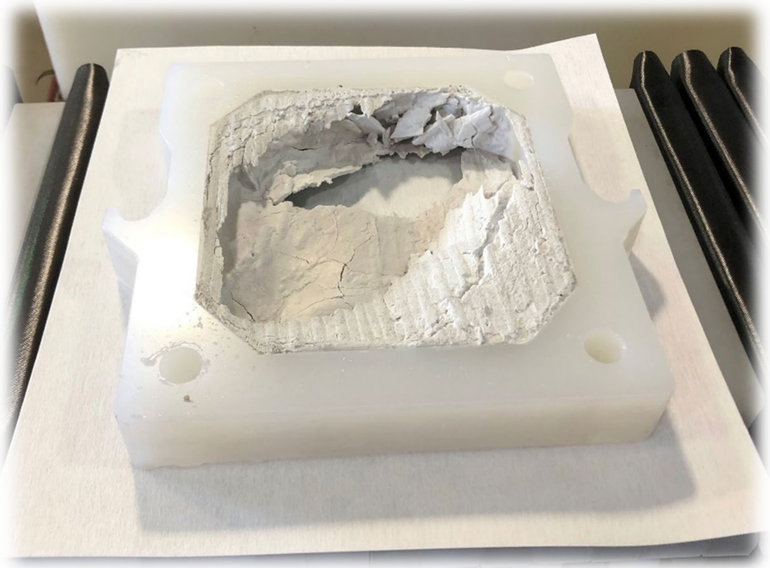
Redissolution efficiency of rare earth elements and major contaminants (pilot scale).
(pH=2.5, hydrochloric acid)

Pilot Plant Flowsheet



RE Oxalate Precipitation





Oxalic precipitation efficiency (pilot scale, feed rate 1 gpm, pH 1.5, Oxalic Dosage: 6.4g/L

Final REO Products

Test No.	Sample Source	Percent Concentration (%)																
		Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Total REO
1	WK 13 Acid Drainage	0.00	36.44	0.55	7.80	4.15	10.01	7.11	2.24	11.54	1.94	9.24	1.52	3.06	0.17	0.66	0.06	96.48
2	WK 13 Coarse Refuse	0.05	2.27	12.22	31.73	4.24	15.45	2.78	0.44	1.55	0.00	0.58	0.10	0.27	0.00	0.14	0.02	71.83
4	WK 13 Coarse Refuse	0.04	2.73	16.81	44.08	4.36	15.39	2.34	0.38	1.58	0.00	0.90	0.52	0.24	0.23	0.17	0.07	89.86
5	WK 13 Coarse Refuse	0.02	3.60	14.96	43.61	4.63	17.42	3.01	0.48	2.29	0.00	1.25	0.55	0.30	0.23	0.19	0.06	92.61
7	WK 13 Coarse Refuse	0.02	3.37	17.78	45.01	4.44	15.78	2.47	0.41	1.89	0.00	1.04	0.57	0.28	0.24	0.19	0.07	93.57
4	Fire Clay Coarse Refuse	0.01	3.99	15.00	45.02	4.87	16.87	3.79	0.47	2.31	0.00	1.54	0.22	0.29	0.04	0.21	0.08	94.68
5	Fire Clay Coarse Refuse	0.01	3.72	11.85	43.46	4.54	16.15	3.38	0.50	2.43	0.00	1.42	0.41	0.29	0.04	0.24	0.09	88.52
6	Fire Clay Coarse Refuse	0.00	3.32	15.61	43.32	4.43	15.45	2.57	0.41	1.87	0.00	1.27	0.49	0.28	0.04	0.20	0.08	89.34

Pathways to Commercialization
Alternative Strategies

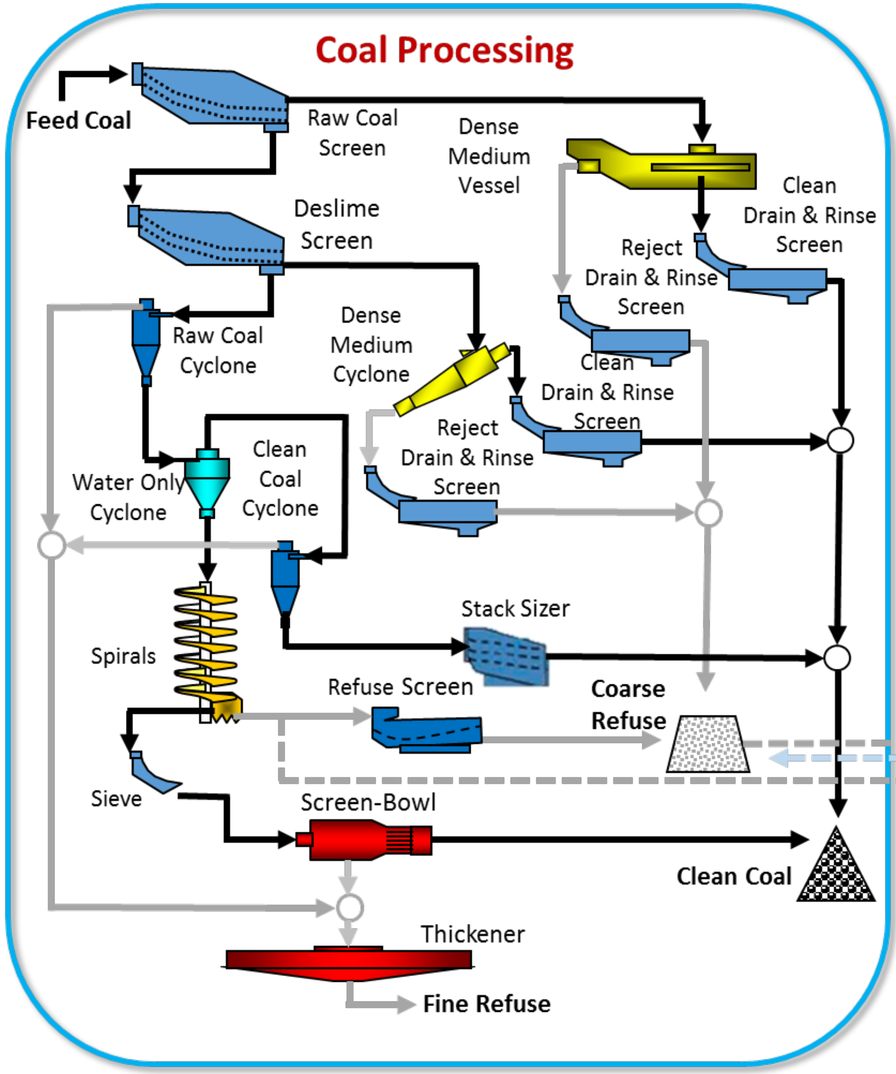
- Direct recovery from acid mine drainage
- Heap leaching of coarse refuse.
- Tank leaching of FBC residuals.

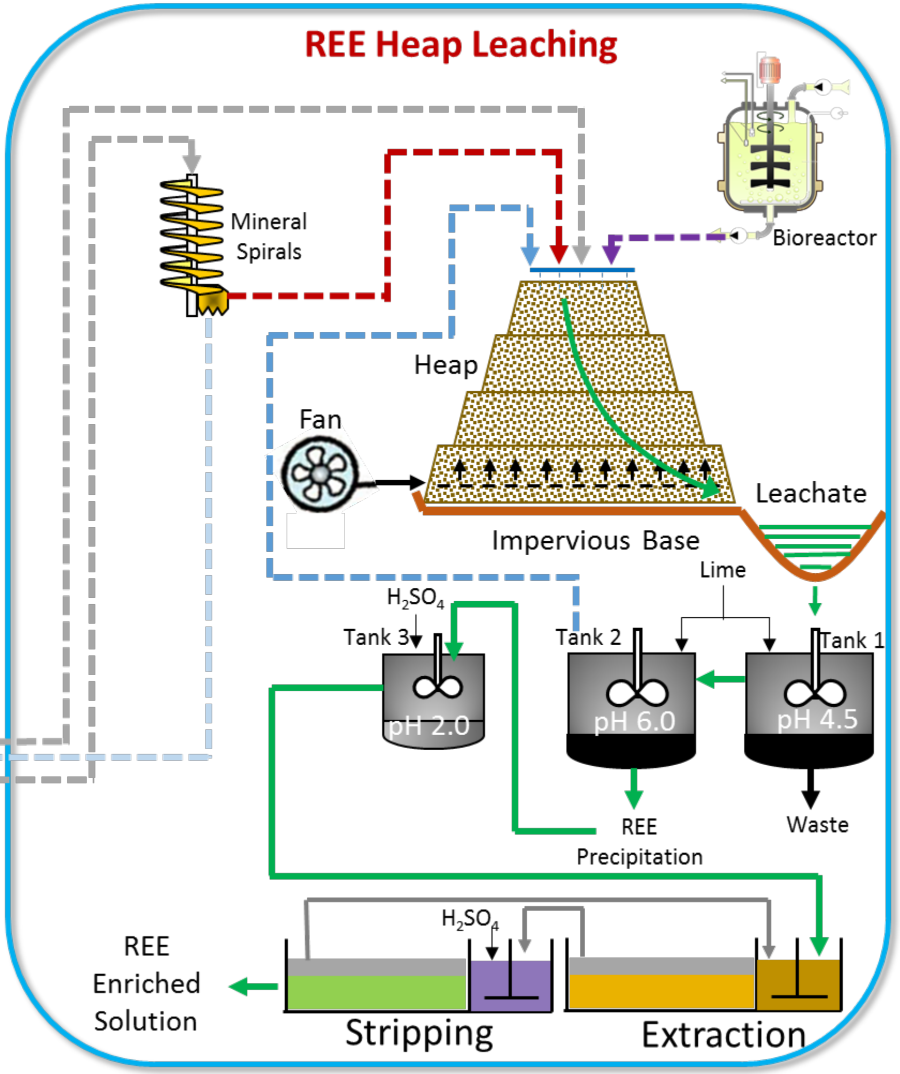
Coarse Refuse Heap Leach Solution

Element	PPM
Sc	0.78
Y	3.90
La	0.31
Ce	2.25
Pr	0.88
Nd	1.09
Sm	0.62
Eu	0.19
Gd	2.65
Tb	0.29
Dy	0.95
Ho	< 0.003
Er	0.01
Tm	0.09
Yb	0.31
Lu	0.14
Total	**14.45**

All based on strategic implementation of the technologies being developed in this project.

Pathways to Commercialization
Heap Leach Approach





Pathways to Commercialization

FBC + Heap Leach Approach

SG	Wght (%)	Total Sulfur (%)	Btu/lb
1.40 FL	35.2	3.13	13246
1.60 FL	12.3	4.94	12173
1.80 FL	4.0	7.49	10137
2.00 FL	2.3	8.18	7941
2.20 FL	1.4	7.63	5766
2.30 FL	1.0	6.74	4008
2.40 FL	3.5	3.04	1684
SINK 2.40	40.4	3.89	407

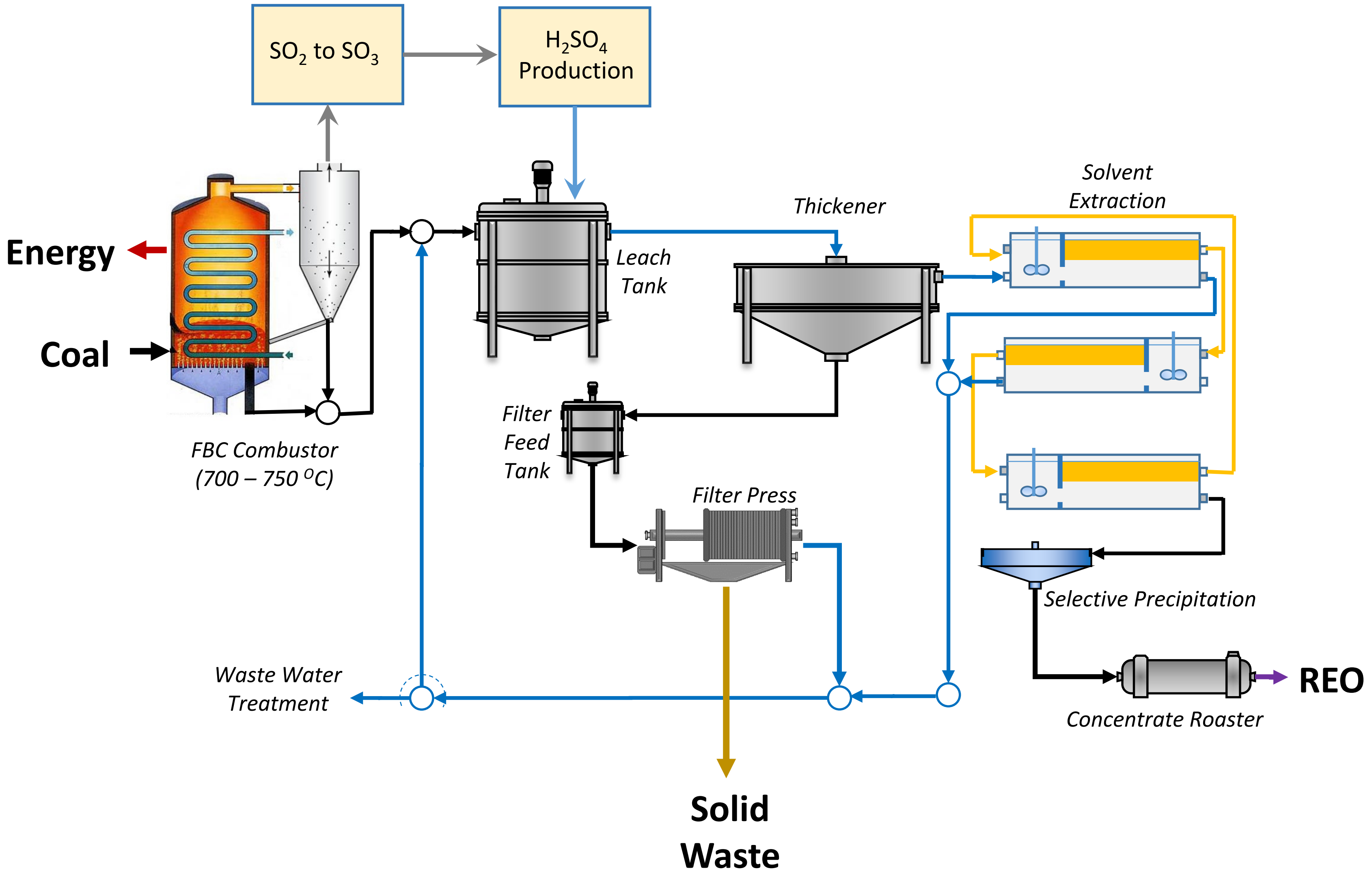
Utility Market (47.5% total wght, 12,968 Btu, 408 ppm REE)

FBC Feed (7.4% total wght, 8686 Btu, 7.72% Sulfur, 417 ppm REE)

Heap Leach Material (44.9% total wght, 587 Btu, 360 ppm REE)

Pathways to Commercialization

FBC + Heap Leach Approach

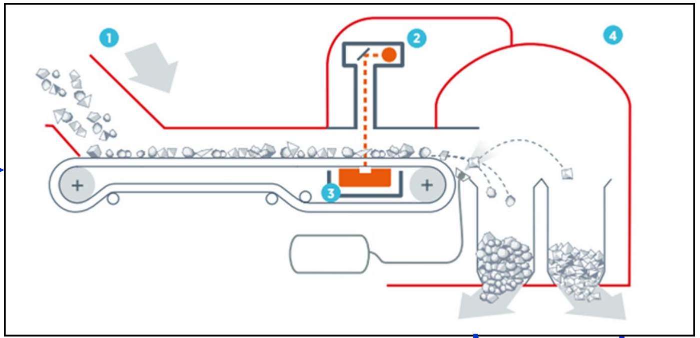


Pathways to Commercialization
FBC + Heap Leach Approach

Coarse Refuse Stream or Storage

1.6 SG Sink

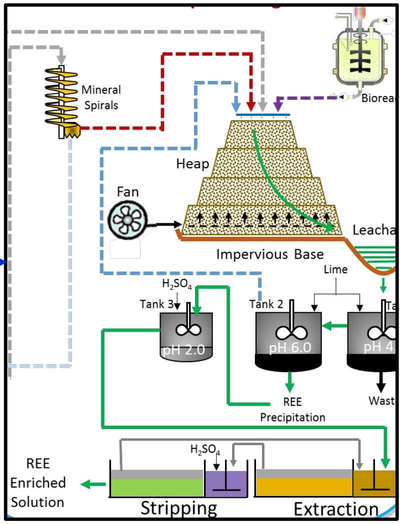
Low-Cost Density-Based Separator



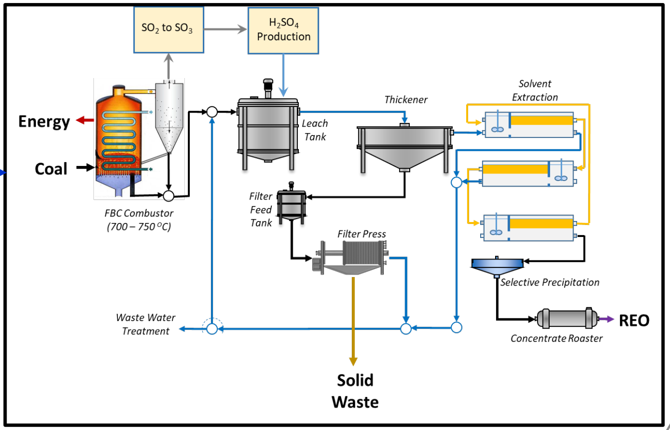
2.2 SG Sink

1.6 x 2.2 SG

Heap Leach System



FBC Generator & CM Recovery



Techno-Economic Analysis Scenarios

		Flowsheet Components				
Scenario	Feedstock	Preparation	Extraction	Concentration	Source Data	Comment
	Primary Scenarios					
1	Fire Clay Coarse Refuse	Sorting, Roasting	Acid Leaching	Solvent Extraction, OA Precipitatic	Pilot Data	
2	Fire Clay Coarse Refuse	Sorting, Roasting	Acid Leaching	Selective Precipitation	Pilot Data	
3	West KY #13 Coarse Refuse	Sorting, Roasting	Acid Leaching	Selective Precipitation	Pilot Data	
4	West KY #13 Heap Leachate	None	Natural Leaching	Selective Precipitation	Pilot Data	
	Option Scenarios					
5	Fire Clay Thickener Underflc	Decarbonization, REM Recovery	Acid Cracking	Selective Precipitation	Pilot + Lab	Potential of mineral recovery
6	Fire Clay Middlings	Grinding, Decarbonization	Acid Leaching	Selective Precipitation	Lab Data	Evaluate grinding as preparation strategy
7	Fire Clay 1.4 x 1.8	Fluidized Bed Combustion	Acid Leaching	Selective Precipitation	Lab Data	FBC for energy generation, see energy and fuels paper
8	West KY #13 1.4 x 1.8 Fractioı	Fluidized Bed Combustion	Acid Leaching	Selective Precipitation	Lab Data	FBC for energy generation, see energy and fuels paper
9	West KY #13 Coarse Refuse	Sorting	Acid Leaching	Selective Precipitation	Maybe Pilot?	Compare to #3, but without roasting
10	Fire Clay Coarse Refuse	Sorting	Acid Leaching	Selective Precipitation	Maybe Pilot?	Compare to #2, but without roasing
11	West KY #13 Coarse Refuse	Sorting	Acid Leaching	Solvent Extraction, OA Precipitatic	Lab Data	Similar to #1, but with W. KY rather than FC.

Summary

- A rare earth pilot plant consisting of pre-concentration, acid leaching, purification and waste treatment modules has been designed, constructed and tested over a 3-year performance period.
- The plant was operated continuously at a rate of 100 lbs/hr solids and produced 10 – 100 grams per day of > 90% REO mix.
- High purity REO mix products were generated from multiple feed types and sources.
- Several alterations were applied and tested in an effort to minimize cost:
  - Pre-leach roasting;
  - Contaminant element removal steps using selective precipitation;
  - Elimination of solvent extraction.
- Detailed TEA & feasibility study underway.

Questions and comments?