

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

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Project Organization Chart



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, 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)		
	Sc	17	1554	\$5,441.88		
	La	La 53 4808				
	Ce	122	10937	\$54.69		
Light	Pr	14	1296	\$115.70		
	Nd	51	4632	\$277.93		
	Sm	11	994	\$16.47		
	Eu	2	155	\$4.66		
	Y	25	2276	\$76.40		
	Gd	10	867	\$173.32		
	Tb	0	44	\$33.35		
	Dy	6	530	\$183.59		
Heavy	Но	2	159	\$9.07		
	Er	5	417	\$11.54		
	Tm	1	83	\$124.99		
	Yb	3	273	\$27.34		
	Lu	0	2	\$1.40		
	Со	23	2106	\$66.48		
Other CN4	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 coalbased 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	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	12.2 35.4						
-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 acidgenerating 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.



Block Flow Diagram



Project Schedule: Budget Period 1 (Four Month No-Cost Time Extension: BP1 end date April 2021)

	Task		Project Month													
ID			2019	9			_		20)20	_				20)21
		0	N	D	JF	M	A	Μ	J	J	A	S	0	1 D	J	FM
	DOE Required Tasks		1		_									_	—	_
1	Project Management & Planning*	_														
2	Finanical Plan for Commercialization*															
3	Techno-Economic Assessment*														Ц	
4	Provide Split Samples*															
5	Feasibility Study*															
	Laboratory Support Tasks	_														
6	Optimization of Physical Separaitons (crush, grind, sort, calicte float)															
7	Optimization of Acid Generation (pyrite recovery, bioreduction)						Х	х	х							
8	Optimizaton of Roasting & Leaching						х	х	Х							
9	Optimization of REE Recovery (selective precip and/or SX)						Х	х	Х							
10	Optimization of CM Recovery (Co/Mn/Sc Precip or SX)						х	Х	Х							
	Pilot-Scale Tasks	_							_							
11	Environmental Monitoring and Management															
12	Pilot Plant Upgrades and Modification (Design, Bidding, procurement, fabrication, installation)					Х	х	х	х							X
13	Feedstock Collection and Preparation					Х	X	Х	Х							
14	Pilot Plant System Shakedown								х							X
15	Pilot Plant Operation and Continuous Improvement															
16	Operational Cost Analysis, Refinement and Optimization															
17	Secondary Feedstock Testing															
18	Decommissioning and Disposition															
	* = DOE Required Task															
	X = one month delay in activity															1

Project Schedule: Budget Period 2 (Project end date June 30, 2022)

	Task		Project Month											
ID					2	021	.1				2022			
			Μ	J	J	Α	S	0	NC)]	FI	MA	M	J
	DOE Required Tasks													
1	Project Management & Planning*													
2	Finanical Plan for Commercialization*											_		
3	Techno-Economic Assessment*													
4	Provide Split Samples*													
5	Feasibility Study*													
	Laboratory Support Tasks													
6	Optimization of Physical Separaitons (crush, grind, sort, calicte float)						_							
7	Optimization of Acid Generation (pyrite recovery, bioreduction)				_									
8	Optimizaton of Roasting & Leaching													
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 (Design, Bidding, procurement, fabrication, installation)				_									
13	Feedstock Collection and Preparation													
14	Pilot Plant System Shakedown				_		_							
15	Pilot Plant Operation and Continuous Improvement													
16	Operational Cost Analysis, Refinement and Optimization													
17	Secondary Feedstock Testing													
18	Decommissioning and Disposition													
	* = DOE Required Task													

Physical Separations Pyrite-Calcite Concentration



Size Exection	Weight		Percentage									
Size Fraction	(%)	Pyrite	Silica	Calcite	Kaolinite	Barite	Montmoril.	Bohmite				
+100 mesh	8.84	6.3	6.4	68.2	4.9			14.2				
100 mesh x 200 mesh	43.72	20.0	14.1	62.8	3.1	0.0						
200 mesh x 325 mesh	14.88	43.3	12.2	35.4	1.1	0.6	7.4					
-325 mesh	32.56	30.1	44.8	21.0	3.7	0.3						
Total	100.00	25.5	23.1	45.6	3.2	0.2	1.1	1.3				

Calcite-Pyrite Circuit Analyses

Sample	Density (g/cm ³)	Ca (ppm)	Fe (ppm)	Si (ppm)	% Pyrite	% Calcium Carbonate
CYC.100920.OF.X20.	2.24	2.400	4.310	0.670	8.83	5.74
CYC.102020.OF.X20.	2.70	4.28	7.85	0.275	16.21	10.31
CYC.SOLID(2.0).O/F.3.X20.	2.65	6.696	9.924	0.188	21.06	16.57
CYC.SOLID(2.0).O/F.2.X20.	2.65	7.530	10.585	0.149	22.35	18.55
CYC.101420.OF.X20.	2.65	9.632	12.722	0.191	26.06	23.02
CYC.SOLID(2.0).FEED.2.X20.	3.28	4.800	16.471	0.069	35.01	11.90
SCREEN.OF.LMT.FLOAT.X20.	2.86	15.462	18.860	0.286	39.97	38.23
CYC.101520.OF.X20.	3.29	7.668	19.601	0.126	41.46	18.92
CYC.100920.FEED.X20.	2.94	7.526	21.177	0.286	41.94	17.39
CYC.101420.FEED.X20.	2.83	7.05	21.078	0.118	44.81	17.49
CYC.101620.FEED.X20.	3.23	6.035	22.506	0.099	45.07	14.10
CYC.BARREL.2.X20.	3.12	8.611	22.682	0.114	45.64	20.21
CYC.101620.UF.X20.	3.42	7.724	23.679	0.091	47.47	18.06
CYC.BARREL.3.X20.	3.42	8.218	24.106	0.071	50.05	19.91
CYC.102020.FEED.X20.	3.43	6.579	24.709	0.119	50.62	15.72
CYC.101520.FEED.X20.	3.47	5.38	26.232	0.111	51.66	12.36
CYC.100920.BARREL.1.X20.	3.38	8.535	25.495	0.091	52.08	20.34
CYC.SOLID(2.0).FEED.3.X20.	3.10	7.252	26.671	0.119	52.97	16.80
CYC.BARREL.1.X20.	3.54	6.536	27.062	0.053	55.28	15.58
CYC.100920.UF.X20.	3.45	7.499	26.941	0.102	55.72	18.10
CYC.102020.UF.X20.	3.79	5.884	27.968	0.067	58.47	14.35
CYC.101320.UF.X20.	4.07	6.115	28.104	0.074	59.10	15.00
CYC.101520.UF.X20.	3.89	4.161	29.38	0.069	60.83	10.05
CYC.101420.UF.X20.	3.64	6.431	29.432	0.035	62.63	15.97
CYC.SOLID(2.0).U/F.3.X20.	3.85	6.689	30.719	0.042	64.60	16.41
CYC.SOLID(2.0).U/F.2.X20.	3.76	5.506	32.096	0.030	65.50	13.11
SCREEN.OF.LMT.SINK.X20.	4.12	3.077	36.800	0.016	77.62	7.57

Sulfuric Acid Generation by Biooxidation

- Concentrated pyrite is used as feed to a bio-oxidation reactor.
- Bacteria is used to drive the oxidation reaction converting Fe²⁺ to Fe³⁺.
- 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



(9)Water bath (10) Leachate reservoir



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 I/min, which was changed to 0.2 I/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







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 I/min, which was changed to 0.2 I/min later. After that, when Eh reached to 600mV, pyrite feeding was started.
- Other restarting parameters were similar to previous one.



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

Coal Waste Bioleaching

Two samples of coal waste (Fire Clay coarse refuse roaster feed and WK 13 coarse refuse roaster feed) were tested to evaluate their potential for heap bioleaching using bioleaching solution accumulated from other bioreactors.



õ

1000



and (b) WK 13 refuse leaching test.

Bioreactor restarting procedure

Bio-oxidation Reactor Scaling

250-gallon Biooxidation Reactor



Three 3000-gallon Biooxidation Reactors



3-liter Biooxidation Reactor

Leaching Characteristics of Bio-oxidation Acid

- Leaching performed ٠
- Peak recovery of TREES achievable in short leaching time.
- Prevents Al leaching thus reduce downstream chemical consumption.
- Reduction of Na and Fe indicated the formation of Na-• jarosite (XRD confirmed).
- Data comparison between ICP-OES and ICP-MS.



240

300

300

240



Leaching condition: Bioleach Acid, S/L=1/5 (w/v), 75 °C. Solid feed: Dotiki pile minus 1.5-inch, hammer milled, roast at 600 °C 20 minutes. Solid weight gained 12% after 5 hours leaching.

Leaching Characteristics of Bio-oxidation Acid



- Ce peak occurs at 1 hour, La peak occurs at 30 minutes.
- Pr and Nd showed a slightly head down after 90 minutes of leaching.
- Light REEs coprecipitation occurred with the formation of gypsum (CaSO4).
- Heavy REEs not affected.
- REE recovery reached peak at 30-60 minutes, whereas recovered value of REEs and critical elements increased with prolonged leaching time.

Leaching Characteristics of Bio-oxidation Acid Particle Size Effect



Leaching Characteristics of Bio-oxidation Acid

Solid-to-liquid Ratio Effect







Leaching Characteristics of Bio-oxidation Acid

Counter Current Leaching



Optimization of Rare Earth Recovery by Pre-Leach Roasting TGA-DSC Studies



- Leaching Recovery by Roasting Temperature
- Pronounced Effect on Light Elements
- Fe Reduction by Magnetic Material Removal

REE leaching recoveries for roasting products of 2.20 sink density fraction of WK No.13 material. (1.2 M H2SO4, 75°C for 5 hours)

Optimization of Rare Earth Recovery by Pre-Leach Roasting

LECO TGA-Fire Clay (volatiles removed at 600°C, ashed at 600°C)



Optimization of Rare Earth Recovery by Pre-Leach Roasting

LECO TGA-WK-13 (volatiles removed at 600°C ashed at 600°C)



Optimization of Rare Earth Recovery by Pre-Leach Roasting

Inert Roasting Effects at 1000°C: Fire Clay

Leaching at 1.2M sulfuric acid at 75°C for 1 hours at 1% solids



Optimization of Rare Earth Recovery by Pre-Leach Roasting Acid Baking using sulfuric acid

- The results shown in the figure compare the recoveries obtained from 1st and 2nd stage acid baking with the blank roasting using the same acid molarity in leaching.
- The blank roasting performed at 600°C yields only 35.92% REE recovery, with HREEs being approximately 22%.
- The acid baking performed at 250°C recovered approximately 33% TREEs while obtaining 35.68% in HREEs.



A: Blank roasting at 600°C followed by 0.5M H₂SO₄ leaching,
B:1st stage acid baking using 1:1 acid to coal ratio and leaching with DI water, C:Two-Stage acid baking at 250°C using 1:1 acid to coal ratio and leaching with DI water (Each leaching operation was performed at 5% S/L, 75 °C, and 2hrs)

Optimization of Rare Earth Recovery from PLS

Precipitation using NaOH

50 min leaching filtrate



Leachate Solution pH: 1.708 Eh: 717.9 RmV

TREE: 14.41 ppm Al: 1650 ppm Ca: 747 ppm Fe: 6723 ppm

NaOH Dose at pH 4.5: 22.49 g/L

3 hour leaching filtrate



Leachate Solution pH: 2.091 Eh: 691.6 RmV

TREE: 12 ppm Al: 3595 ppm Ca: 718 ppm Fe: 1071 ppm

NaOH Dose at pH 4.5: 15.25 g/L



5 hour leaching filtrate



Leachate Solution pH: 2.339 Eh: 412.1 RmV

TREE: 10.69 ppm Al: 4033 ppm Ca: 775 ppm Fe: 538 ppm

NaOH Dose at pH 4.5: 14.62 g/L





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.)





Optimization of Critical Material Recovery

CoS Precipitate Re-dissolution



Dissolution tests (calcination impact) 1.2 M HCl; room temperature



Roasting at appropriate temperature increased the dissolution of cobalt sulfide.



593.67

Zn

39.60

NiO

Process Flow Sheet



Process Flow Sheet (Co/Mn Flowsheet)



Completed REE/CM Pilot Plant



Pilot Plant Upgrades and Modification PLC









Complete PLC and power box shown.

Both PLC Control Panels are wired and labeled. (Shown 1 of 2 PLC Control Panels).

Process Economics Feasibility Study

- Feasibility study analyzed the commercial production of REEs and CM from coarse refusing (500 tph feed) utilizing technology components from the project:
 - Roasting
 - Biooxidation
 - Selective Precipitation
 - Dedicated Scandium Recovery
 - Dedicated Co and Mn Recovery
- Output production is estimated at around 300 Mt annually of total rare earth oxide, 18 Mt Sc, 32 Mt Co and 405 Mt Mn.

Feedstock Material Coarse Refuse Performed by DE-FE003182 Checked by Total Plant 500 TPH REE Feed Grad minal Plant Size 12000 TPD (unit conversion Project NPV (335,709,839 1000000 lb/h (unit conversion Process Code PM1 Feed Preparation Operating Labo PM2 Technical Labor Roasting TL. PM3 Power/Utilities Leaching PM4 Al Precipitat Lease Agreement PM5 **REE** Precipitation Consumables/Reagents Al Wash Waste Disposa DM7 **RE-Redissolutio** OF Plant Overhead DM/R **REE Oxalate Precipitation** CS/ General Sales, and Administration PM9 Biooxidation Circuit PM10 Sc SX Separation PM11 CM Recovery Circuit PM13 Received PM13 Reserved PM14 Reserved PM15 Reserved

REE-Econ: Techno-Economic Assessment Tool for Coal-Based REE Recovery

Excel-Based TEA Model

Process Economics Biooxidation Cost Analysis

- The biooxidation unit is a large cost component, but it shows notable cost advantages over raw acid leaching.
- Total acid production cost = \$0.05 /kg, a reduction of approximately 75% vs. bulk sulfuric acid.
- Largest cost components = mixing, temperature management, capitalization costs (~81% of total).

Total cost = $0.05 / \text{kg H}_2\text{SO}_4$ equivalent



Process Economics Feasibility Study

- Key Findings:
 - 1. Plant capital cost = \$137 million. Biooxidation circuit = $\sim 1/3$ of total capital expenditure.
 - 2. Achieved project objective of 50% operating cost reduction versus existing pilot plant. Contributing factors = bioxidation, use of coal calcite, and use of Al wash.
 - 3. Highest single line item cost = neutralization base.
 - 4. Under the baseline conditions evaluated, the project was found economically viable; however, this viability is very sensitive to the scandium price.
 - 5. The overall system recovery is very low, and even modest improvements to recovery could greatly increase the economic robustness of the process.



Summary

- Biooxidation using concentrated ultrafine coal pyrite can produce a 0.2 M H₂SO₄ solution at 25% of the cost of commercial acid.
- Biooxidation acid can be used to effectively leach REEs and CMs from coarse coal refuse.
- Magnetic iron oxide can be produced by roasting at 400°C.
- Acid baking after roasting provides leach recoveries of HREEs and LREEs greater than 80%.
- Sc and Co/Ni/Zn/Mn circuits have been developed providing well over 2% product grades.

