Economic Extraction, Recovery, and Upgrading of Rare Earth Elements from Coal-Based Resources

Michael L. Free, Prashant Sarswat, Landon Allen, Wei Liu, Kara Sorensen

Department of Metallurgical Engineering, University of Utah

Aaron Noble, Gerald Luttrell, Daejin Kim, Morgen Leake

Department of Mineral and Mining Engineering, Virginia Tech

Project Overview

The purpose of this project is to technically and economically evaluate new low cost technology to extract and recover an enriched mixed rare earth element (REE) oxide product from REE-bearing, coal-based resources.

This project's technology begins with selective separation of coal waste resources, followed by heap leaching using biooxidized and conditioned solution, and the resulting extracted rare earth elements are concentrated by solvent extraction and recovered by precipitation to produce a product with 2-8 % REE oxide.

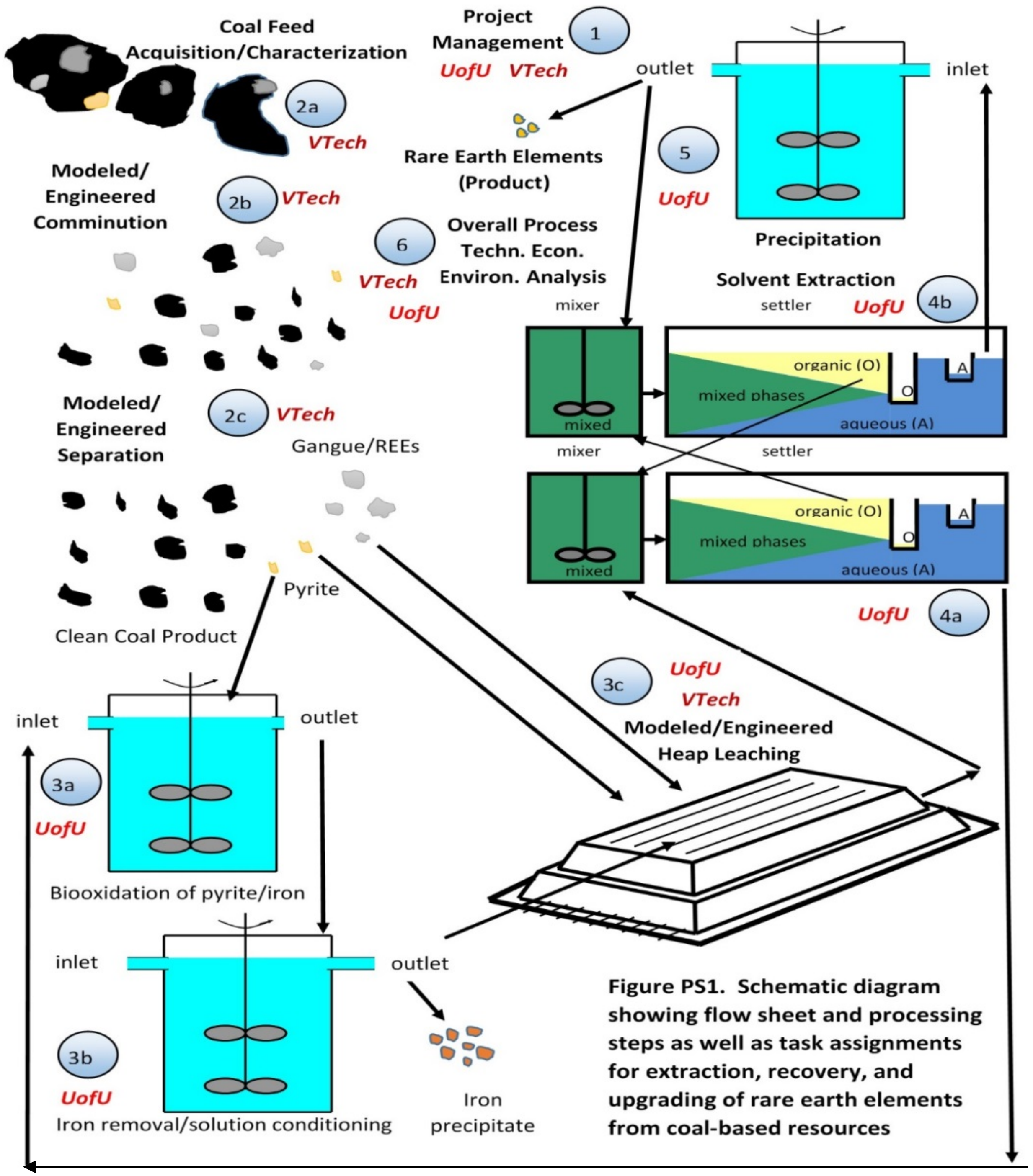

Figure PS1. Schematic diagram showing flow sheet and processing steps as well as task assignments for extraction, recovery, and upgrading of rare earth elements from coal-based resources

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Project Update

- Project updates/accomplishments
  - Industrial participation resulting in 6 different coal waste samples with enriched REE content (total REEs > 190 ppm dry weight basis)
  - Evaluation of separation technologies for rare earth element enrichment in coal waste
  - Demonstration of separation technologies to enrich pyrite for biooxidation
  - Demonstration of heap leaching, combined with biooxidation for extraction of REEs
  - Demonstration of concentration of REEs by solvent extraction
  - Demonstration of iron removal and REEs recovery by precipitation
  - Demonstration of product with 2-8 % mixed REE oxide
  - Presentation of results at Extraction 2018, 2018 AIChE Annual Meeting, and 2019 SME Annual Meeting

Rare Earth Element Resources in Coal Waste Materials

Many coal waste materials contain economically recoverable levels of rare earth elements.

Coal waste resources from many coal producers contain reasonable levels (200-400 ppm) of rare earth elements in large quantities (millions of tons).

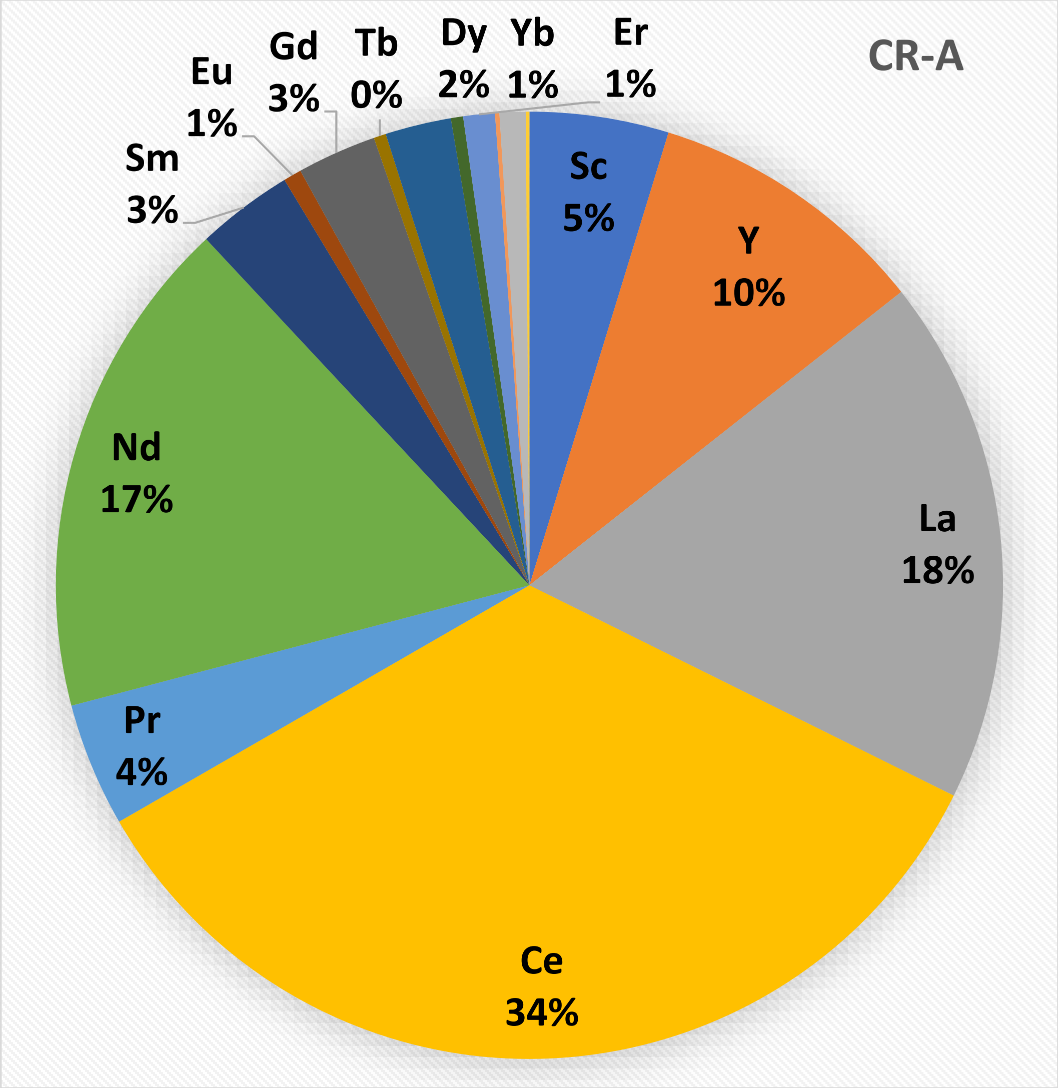
The value of the rare earth elements in coal waste is often greater than $0.05 per kilogram ($45/ton) of coal waste.

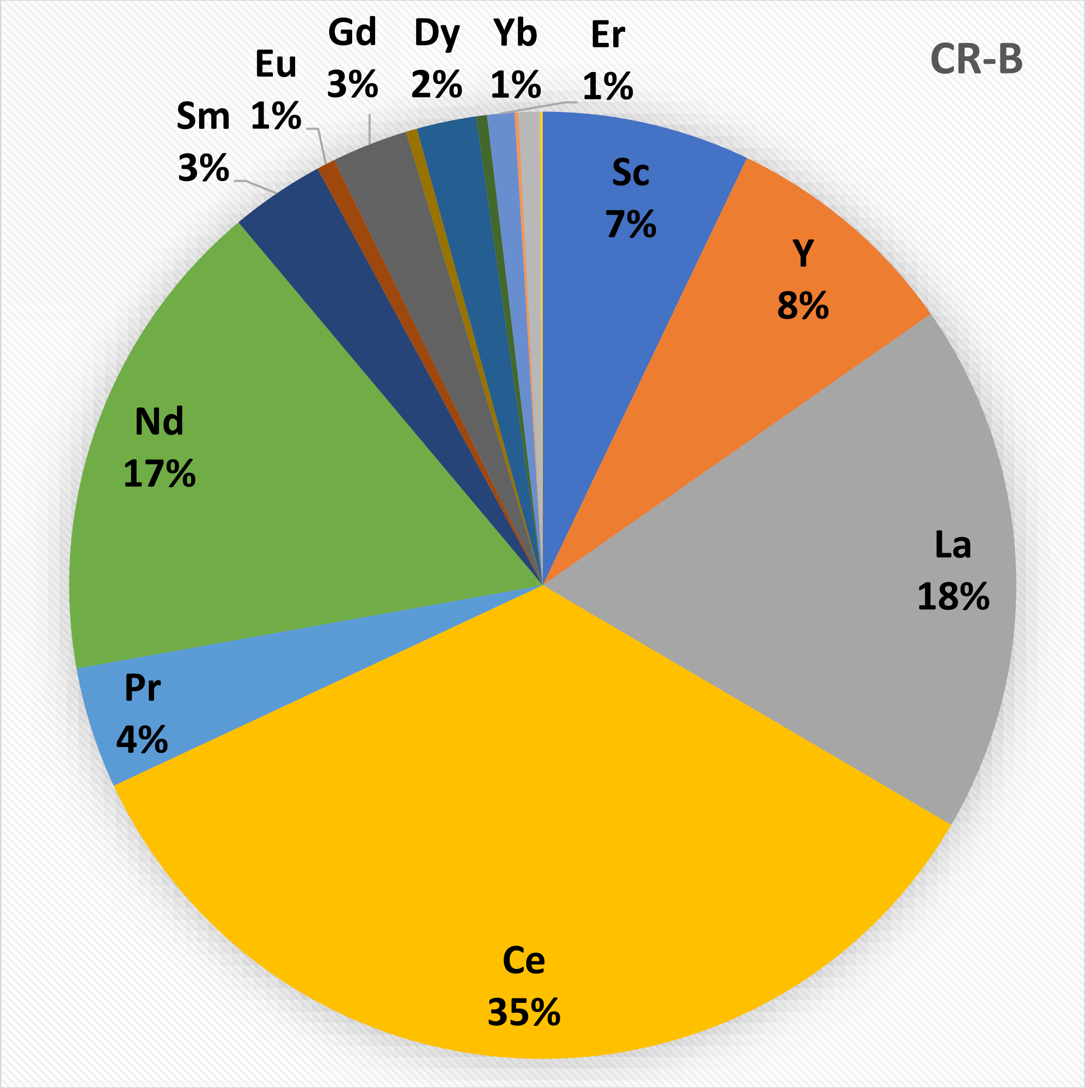
Sample Analysis and Value Estimate

	CR-A	CR-B	CR-C1	Cr-C2	Cr-D1	Cr-D2	Ave	$/kg	Ave.$/ton
Sc (ppm)	11.74	14.18	12.03	11.13	12.15	13.09	12.39	4200	52.02
Y (ppm)	23.80	16.37	21.06	21.46	23.03	23.92	21.61	6	0.13
La (ppm)	44.42	36.27	42.69	41.61	45.06	45.40	42.58	2	0.09
Ce (ppm)	84.96	69.12	79.85	78.11	84.33	84.47	80.14	2	0.16
Pr (ppm)	10.45	8.29	9.91	9.59	10.54	10.49	9.88	52	0.51
Nd (ppm)	42.38	33.38	40.20	39.31	43.18	43.79	40.37	42	1.70
Sm (ppm)	8.17	6.43	7.56	7.51	8.30	8.42	7.73	2	0.02
Eu (ppm)	1.53	1.26	1.40	1.37	1.52	1.55	1.44	150	0.22
Gd (ppm)	6.70	5.20	6.10	6.00	6.60	6.66	6.21	32	0.20
Tb (ppm)	1.04	0.76	0.91	0.91	1.00	1.02	0.94	400	0.38
Dy (ppm)	5.57	4.06	4.97	5.03	5.46	5.55	5.11	230	1.17
Er (ppm)	2.66	1.86	2.41	2.38	2.57	2.70	2.43	34	0.08
Totals	243.42	197.18	229.09	224.41	243.74	247.06	230.82		56.67

Analyses based on microwave digestion using 12 mL reverse aqua regia and 50 mg of solid -80mesh sample. Digested for 20 min @ 185C ICP-MS (Agilent 7900 ICP-MS)

Typical Sample Analysis





Keys to our approach

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Utilize low-cost technologies to enable larger resource utilization.

Utilize selective separation technologies to upgrade desired feedstock materials (REE and pyrite).

Utilize heap leaching technology for large-scale, low cost extraction.

Utilize biooxidation and pyrite from the coal waste to provide low cost reagents and rapid leaching as well as to remove residual sulfides from future acid rock drainage.

Utilize solvent extraction and precipitation to concentrate and recover a mixed rare earth element rich product.

Perform a technoeconomic analysis to provide investment and commercialization guidance.

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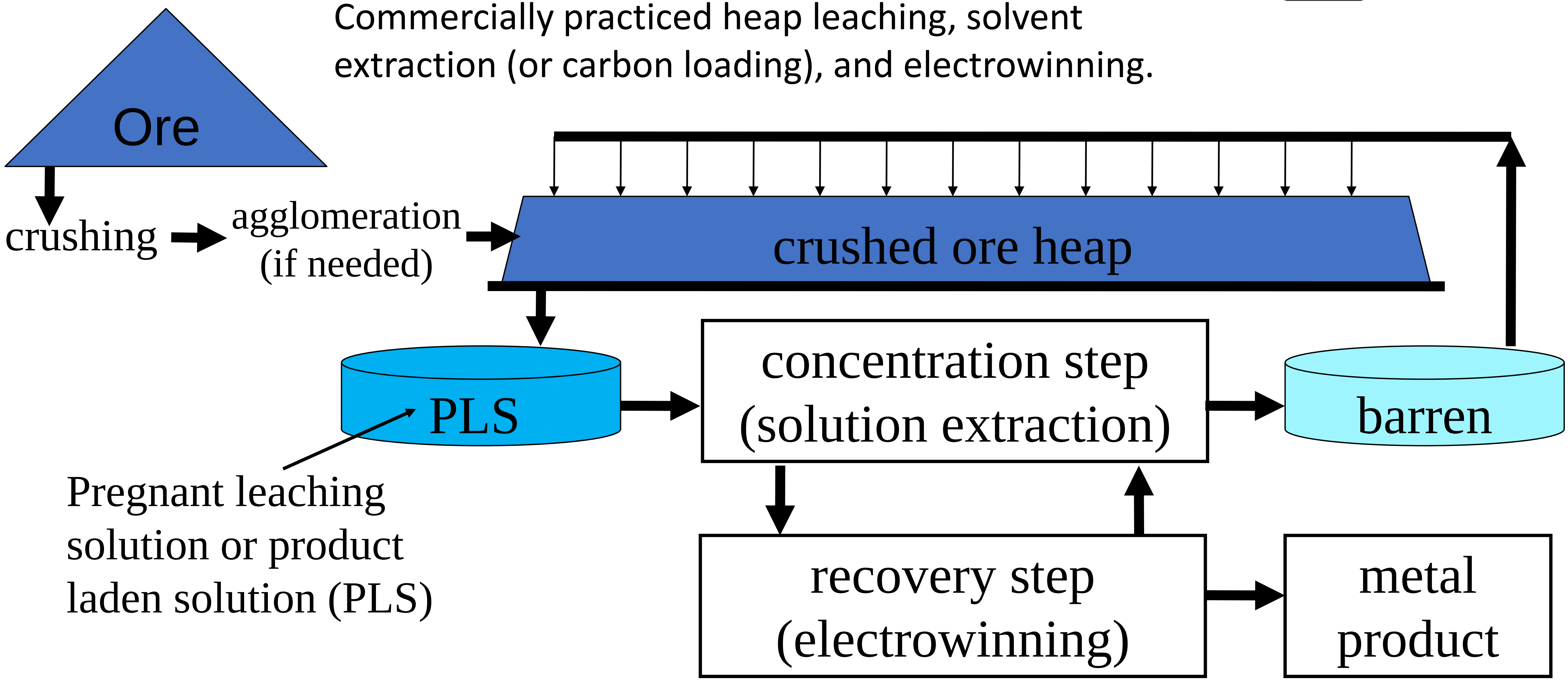
Copper and Gold Processing Scenario

Commercially practiced heap leaching, solvent extraction (or carbon loading), and electrowinning.



How much does it cost?

For Gold Processing, Bald Mountain Run-of-Mine Heap Leaching/Carbon Ads

Total Production (2017): 282,000 oz Au

Total Ore Processed: 34,000,000 tons

Gold value ($1,250/oz) recovered per ton of ore processed: **$10.36/ton**

https://s2.q4cdn.com/496390694/files/doc_presentations/2016/062916-Nevada-Mine-Tour-Presentation-FINAL-PRINTED.pdf

For Copper Processing, Safford Mine Heap Leaching/SX/EW

Total Production (2015): 202,000,000 lb Cu

Total Ore Processed: 36,500,000 tons

Copper value ($2.50) recovered per ton of ore processed: **$13.75/ton**

https://miningdataonline.com/property/88/Safford-Mine.aspx

These are values without considering profit (often >30 %) and mining costs (usually around 35 % of the total, but previously performed for coal waste). Thus, heap leaching/SX/EW of premined material can be done for $5/ton.

Differences to heap leach/SX/EW

No mining (already assumed for coal waste processing)

Additional processing to remove and concentrate pyrite (+$0.5/ton)

Biooxidation using a separate reactor (+$1/ton est. based on BIOX process)

(to generate consistent acid and ferric ions and avoid temperature control issues that arise with sulfide mineral heap leaching that can have large impacts on microbial populations, precipitation and leaching (sulfides are not commonly found in traditional gold and copper ore heap leach processing)

Separate reactor control of iron precipitation (+$0.5/ton est. from ARD work)

(which may otherwise occur in the heap and cause unwanted passivation and pore plugging. This can be effectively the same process as acid mine drainage treatment.)

No electrowinning (-$1/ton est. based on copper industry information)

General Estimated Cost ($5 + 0.5 + 1 + 0.5 – 1) = $6/ton of coal waste

Bioxidation

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Produces acid from sulfide minerals:

$$2Fe^{2+} + 0.5O_2 + 2H^+ \leftrightarrow 2Fe^{3+} + H_2O \qquad \text{(Biotic)}$$

$$FeS_2 + 2Fe^{3+} \leftrightarrow 3Fe^{2+} + 2S_o \qquad \text{(Abiotic)}$$

$$2S_o + 3O_2 + 2H_2O \leftrightarrow 2SO_4^{2-} + 4H^+ \qquad \text{(Biotic)}$$

Can eliminate future acid mine drainage by consuming pyrite in the ore

Provides ferric ion oxidant for leaching as well as to facilitate iron precipitation

Particle Separation Technology

Characterization

Density Based Separation

Flotation

Sorting Technology

Spiral Concentrator

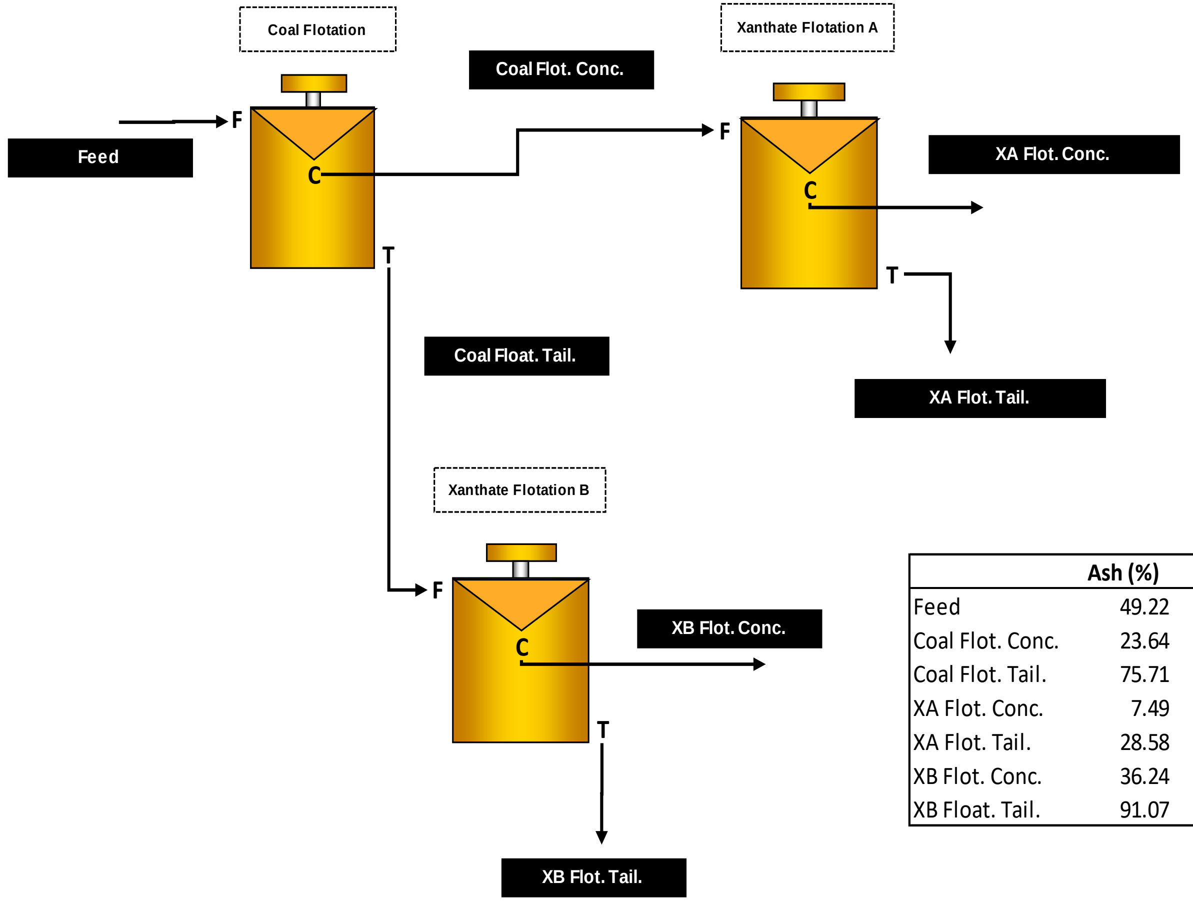
Preliminary results show sulfur upgrading to 6.9 % is feasible for ore CR-B

CR-B spiral concentration feed and product characterization

	Sulfur (%)	Iron (%)	Ash (%)
Feed	6.51	6.17	80.90
Conc.	6.87	6.71	84.24
Tail.	4.35	5.28	73.27

Flotation

Preliminary results show sulfur upgrading to 8.4 % is feasible for ore CR-B



	Ash (%)	Fe (%)	S (%)
Feed	49.22	3.23	3.92
Coal Flot. Conc.	23.64	2.47	5.66
Coal Flot. Tail.	75.71	3.66	2.36
XA Flot. Conc.	7.49	2.07	8.36
XA Flot. Tail.	28.58	2.77	5.36
XB Flot. Conc.	36.24	3.90	5.75
XB Float. Tail.	91.07	3.14	1.07

X-Ray-Based Sorting

Blue color is higher density (generally high in iron), green is intermediate density (most of the material – coal waste), and orange is lower density (mostly cleaner coal).

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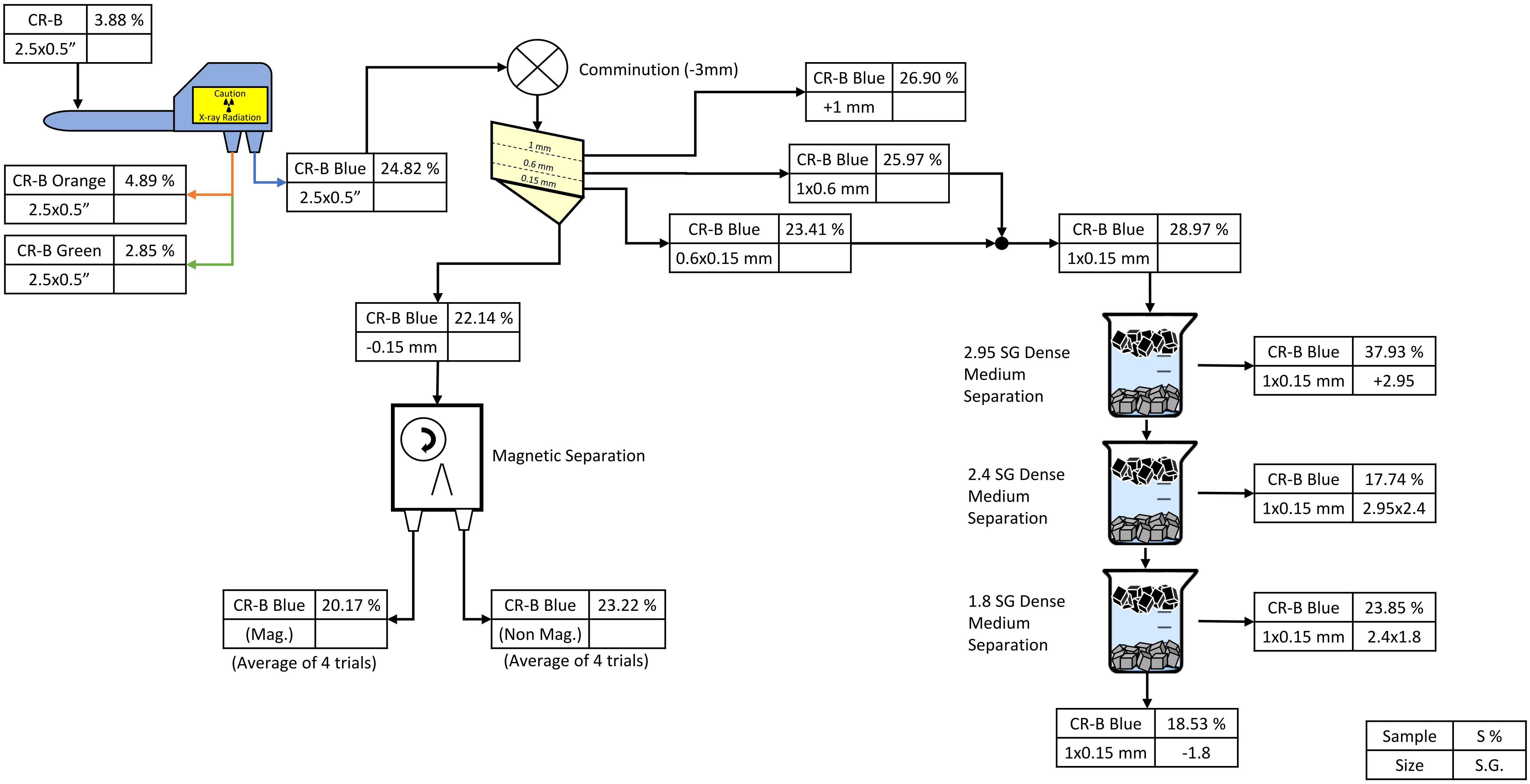
	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Th	U
Sample	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
CR-B																		
Blue	8.84	13.80	19.99	44.74	5.54	21.85	5.00	1.00	4.38	0.59	3.11	0.55	1.38	0.19	1.10	0.16	6.55	1.68
Green	16.52	19.88	37.77	78.84	9.26	35.54	7.31	1.47	6.16	0.85	4.52	0.82	2.12	0.28	1.69	0.24	12.84	2.03
Orange	12.27	17.15	34.56	78.68	9.26	36.40	7.92	1.58	6.49	0.85	4.23	0.73	1.89	0.24	1.47	0.21	9.80	2.53
CR-C1																		
Blue	13.78	23.87	24.73	52.48	6.32	24.47	5.64	1.21	5.65	0.84	4.74	0.90	2.46	0.33	2.08	0.30	7.57	1.47
Green	14.26	23.78	44.52	90.21	10.88	41.11	8.18	1.55	6.70	0.93	5.10	0.95	2.50	0.33	2.04	0.29	12.46	1.91
Orange	12.52	20.51	33.32	69.07	8.13	30.87	6.42	1.26	5.51	0.78	4.37	0.79	2.17	0.30	1.86	0.26	11.24	2.46
CR-C2																		
Blue	14.77	26.24	32.38	68.25	8.16	31.96	6.88	1.42	6.50	0.92	5.23	0.99	2.69	0.36	2.34	0.35	8.48	1.41
Green	12.98	26.00	44.26	90.24	10.77	41.48	8.08	1.52	6.89	0.98	5.35	1.00	2.67	0.36	2.21	0.31	12.24	1.93
Orange	10.32	20.52	33.37	69.49	8.06	30.05	6.11	1.13	5.16	0.74	4.12	0.75	2.03	0.27	1.68	0.24	12.92	2.49
CR-D1																		
Blue	10.09	20.50	19.24	41.67	5.03	20.15	4.58	0.95	4.68	0.68	4.00	0.76	2.11	0.29	1.82	0.26	6.06	1.26
Green	13.02	23.21	46.19	94.71	11.34	43.40	8.17	1.51	6.60	0.91	4.97	0.90	2.43	0.33	1.95	0.28	11.98	1.82
Orange	9.69	18.04	28.32	58.87	6.69	24.31	5.02	0.96	4.44	0.66	3.81	0.71	1.79	0.25	1.49	0.21	16.74	4.11
CR-D2																		
Blue	13.28	26.22	23.25	50.81	5.98	23.72	5.46	1.13	5.62	0.84	5.04	0.96	2.72	0.38	2.38	0.35	7.21	1.62
Green	13.66	25.70	45.40	93.10	11.14	42.94	8.36	1.56	6.92	0.97	5.43	1.00	2.76	0.37	2.24	0.32	12.31	2.15
Orange	9.33	17.24	25.42	53.26	6.23	23.67	4.89	0.96	4.42	0.65	3.73	0.68	1.85	0.26	1.57	0.22	9.77	3.48

X-Ray-Based Sorting

Blue color is 15-20 % iron, green color is around 5 % iron. Hand sorting can give 20 % sulfur content in product


CR-B 3.88 %
2.5x0.5”
Caution
X-ray Radiation
CR-B Orange 4.89 %
2.5x0.5”
CR-B Green 2.85 %
2.5x0.5”
CR-B Blue 24.82 %
2.5x0.5”
Comminution (-3mm)
1 mm
0.6 mm
0.15 mm
CR-B Blue 26.90 %
+1 mm
CR-B Blue 25.97 %
1x0.6 mm
CR-B Blue 23.41 %
0.6x0.15 mm
CR-B Blue 28.97 %
1x0.15 mm
CR-B Blue 22.14 %
-0.15 mm
Magnetic Separation
CR-B Blue 20.17 %
(Mag.)
(Average of 4 trials)
CR-B Blue 23.22 %
(Non Mag.)
(Average of 4 trials)
2.95 SG Dense Medium Separation
CR-B Blue 37.93 %
1x0.15 mm +2.95
2.4 SG Dense Medium Separation
CR-B Blue 17.74 %
1x0.15 mm 2.95x2.4
1.8 SG Dense Medium Separation
CR-B Blue 23.85 %
1x0.15 mm 2.4x1.8
CR-B Blue 18.53 %
1x0.15 mm -1.8
Sample S %
Size S.G.

Float-Sink Test Procedure Images

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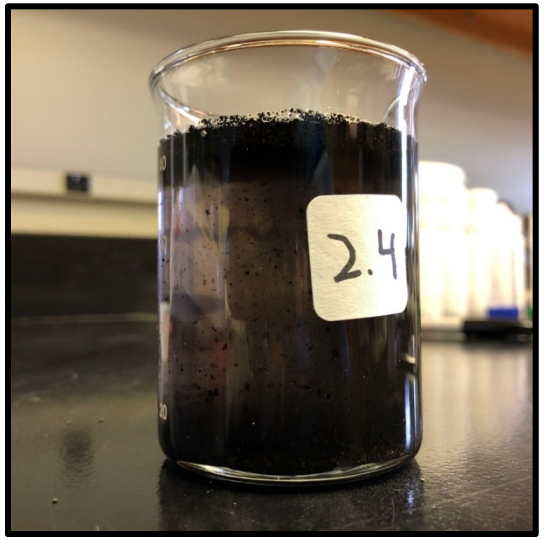
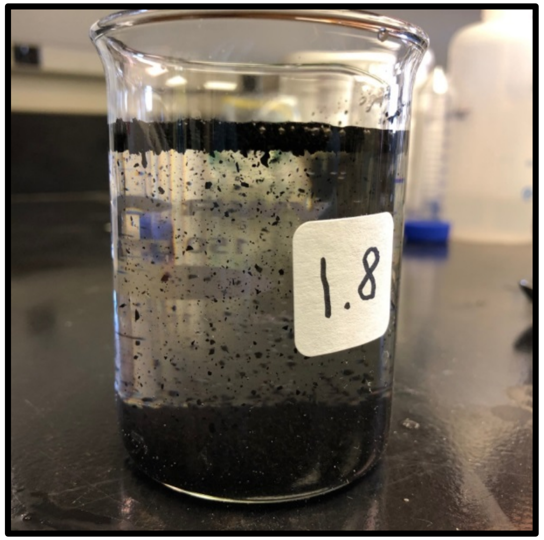
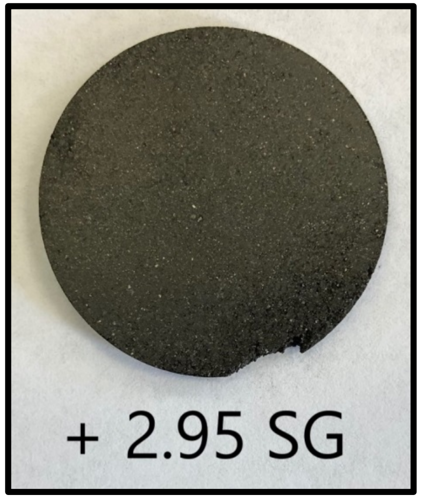
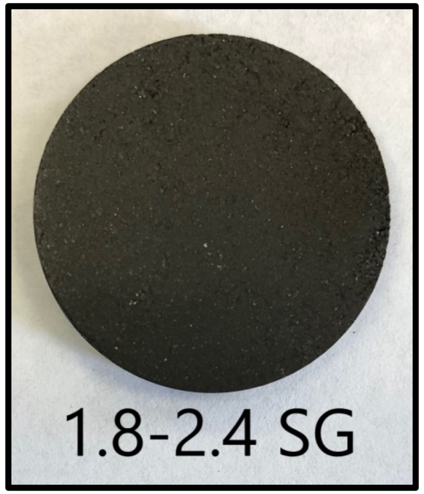
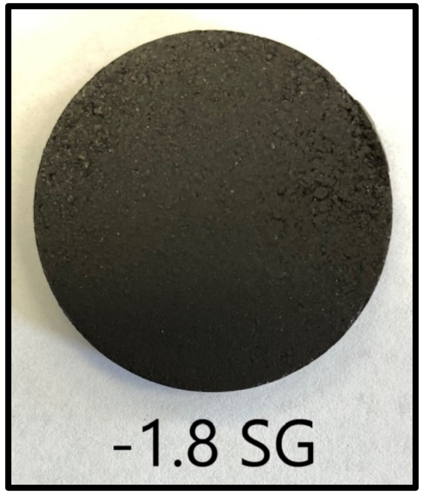










Balanced Mass, Ash, and Sulfur

CR-B Blue 0.15x1 mm	Mass (g)	Ash (%)	S (%)
Feed	32.46	64.87	28.78
-1.8	2.31	25.87	18.53
1.8-2.4	3.88	56.79	23.85
2.4-2.95	9.79	75.15	17.74
+2.95	16.48	66.14	37.93

Balanced Sulfur Data

Dens. Class	Yield	S-Grade	S-Rec.
+2.95	50.77%	37.93%	66.92%
-2.95/+2.4	30.15%	17.74%	18.59%
-2.4/+1.8	11.95%	23.85%	9.91%
-1.8	7.13%	18.53%	4.59%

- Mass balancing of sulfur increased feed % and decreased +2.95 class %

Extraction, Concentration, Recovery

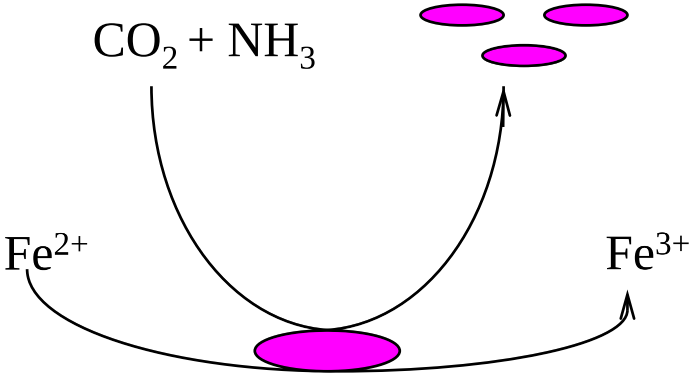
Biooxidation

Leaching

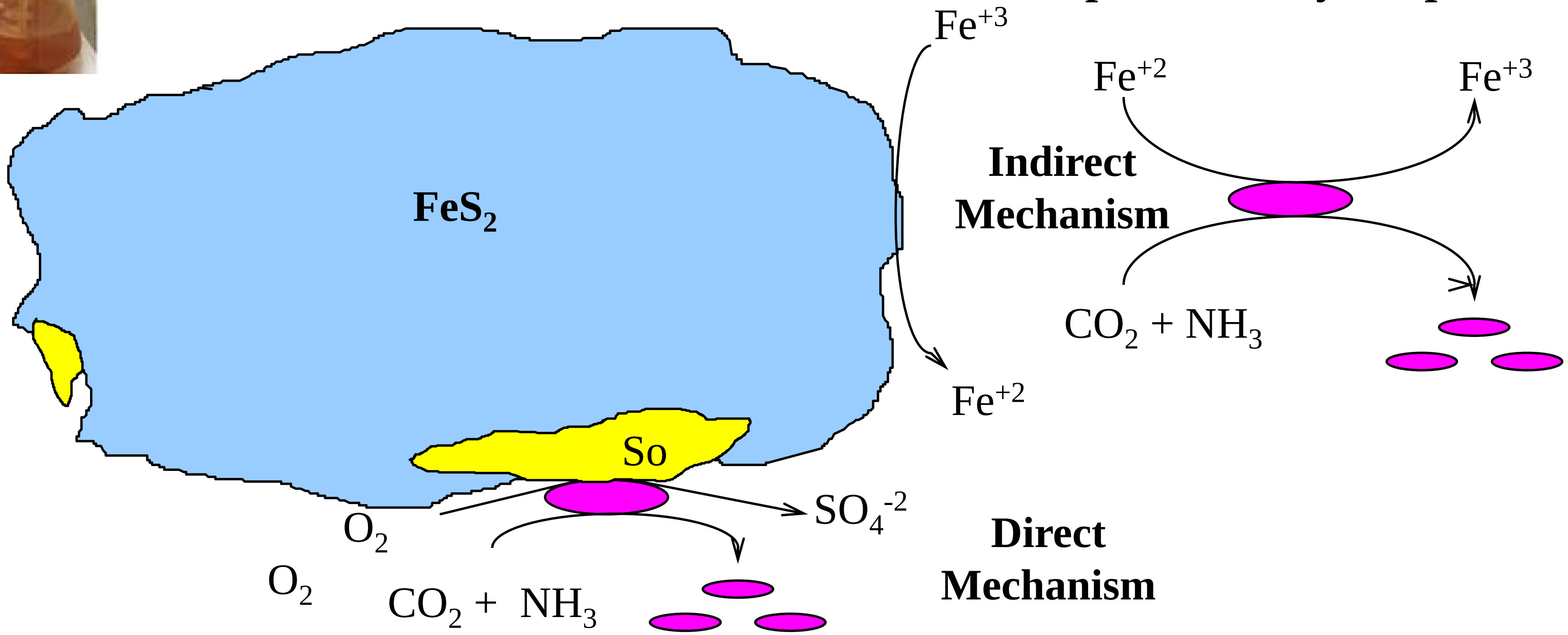
Solvent Extraction

Precipitation

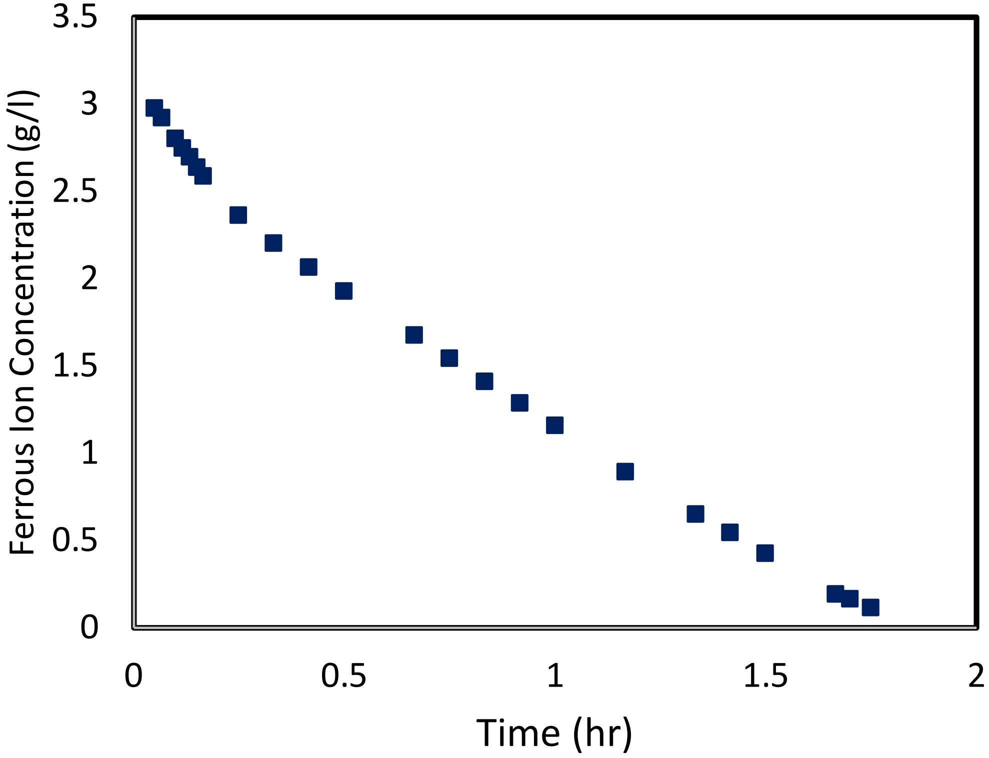
Biooxidation



Biooxidation scenario for pyrite using bacteria such as *Acidithiobacillus ferrooxidans*. Note that the dominant mechanism involves indirect leaching. Bacteria are represented by the pink ovals.

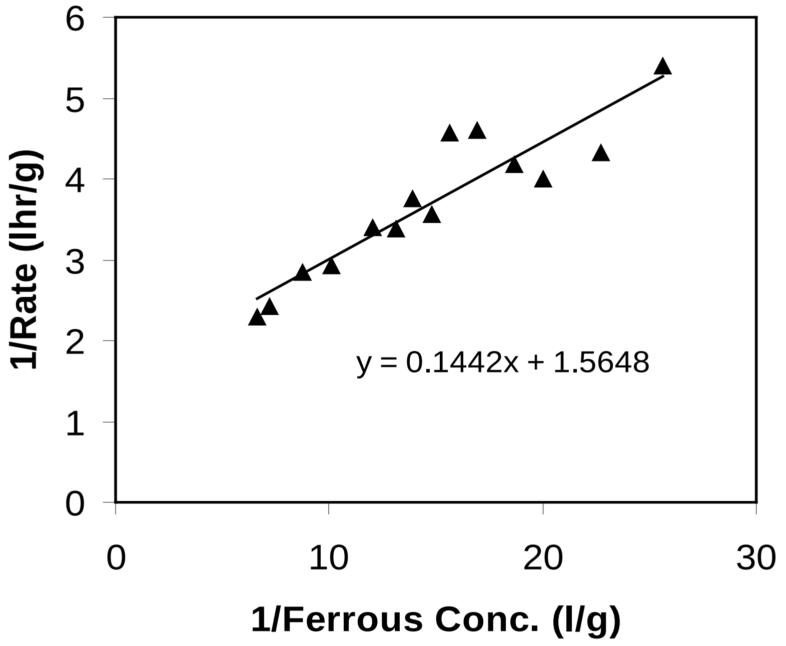


Rate of biooxidation



$$R_{Fe+2ox.} = \frac{C_{cells}\mu_{\max}C_{Fe+2}}{Y_c(C_{Fe+2}+K_m)}$$

$$\frac{1}{R_{Fe+2ox}} = \frac{Y_cK_m}{\mu_{\max}C_{cells}C_{Fe+2}} + \frac{Y_c}{\mu_{\max}C_{cells}}$$

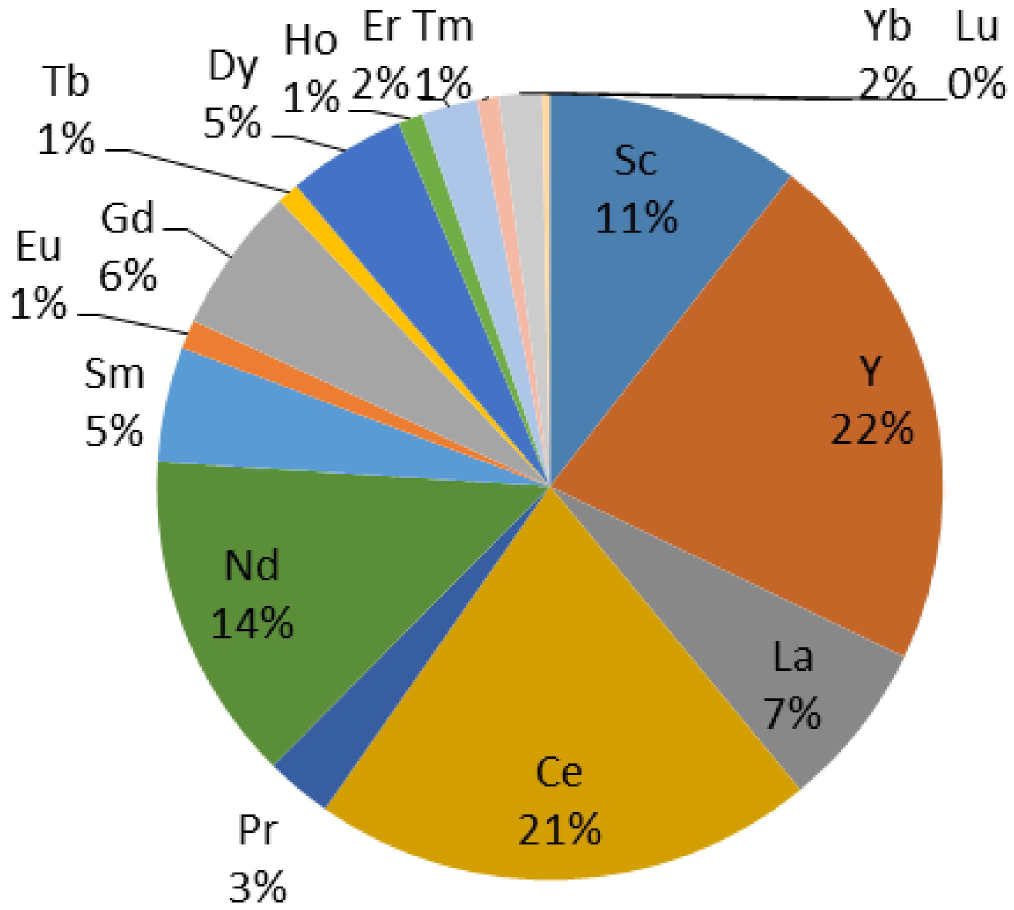


Rates are about 2 grams of ferrous iron oxidized per liter of solution per hour, which results in large reagent savings

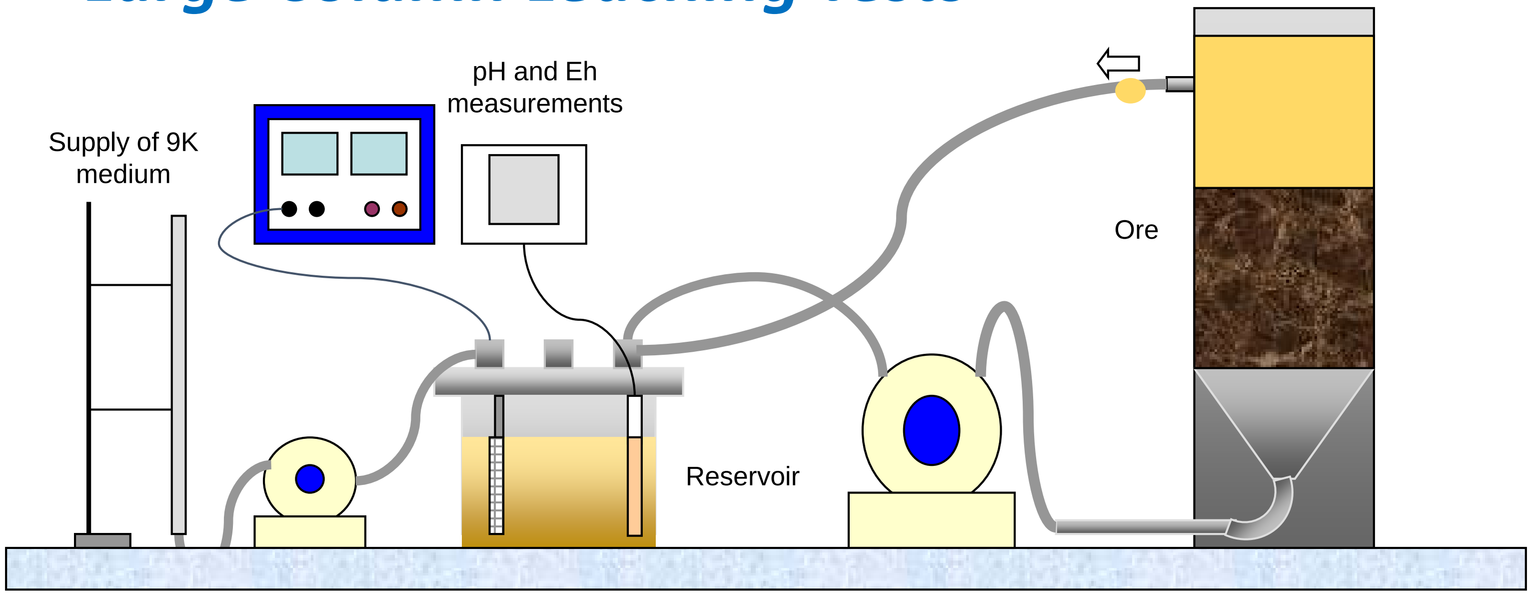
Michaelis-Menton kinetics analysis is performed to evaluate performance and equation constants.

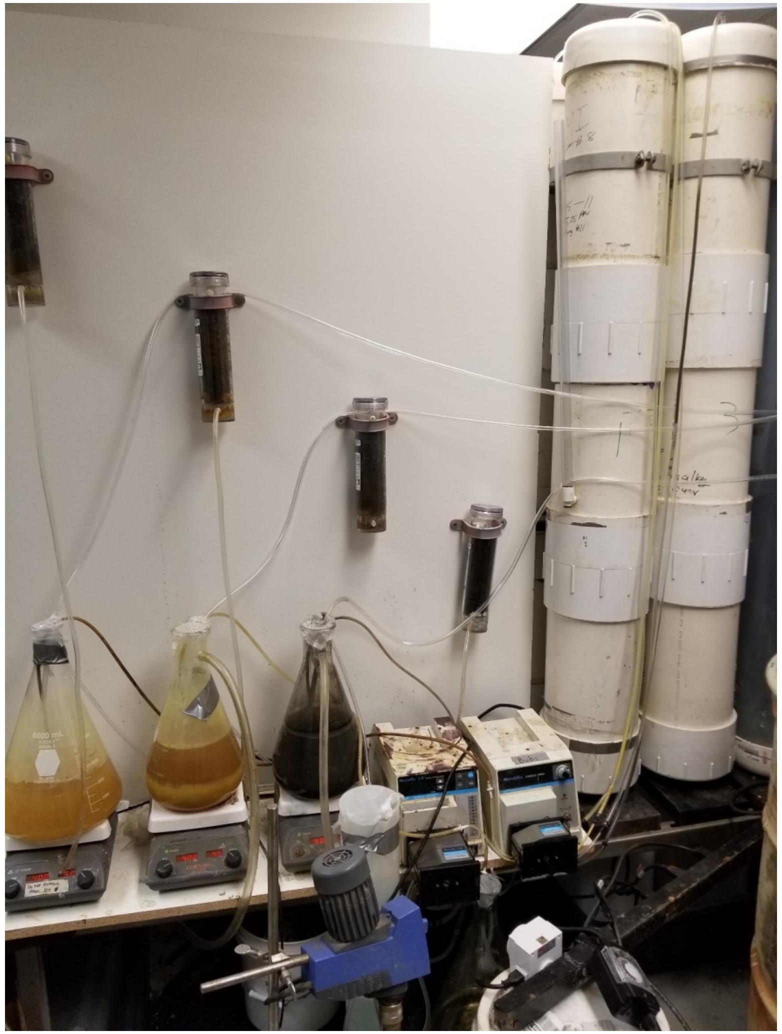
14-day small column leaching tests

Preliminary short-term small column leaching results show the anticipated extracted constituents of waste coal using biooxidation based leaching from one source (CR-A).



Large Column Leaching Tests





A schematic diagram showing leaching of coal waste using the large column; and picture of actual leaching solution that is being circulated in column. In few cases leaching solution is not continuously recycled through column. In these cases Eh of the solution is kept maintained and that solution is continuously fed in to the column from top and collected from the bottom.

Large columns are 5 ft. tall, 8 inches in diam. (right side of image).

Each column was filled with ~ 60 kg of crushed coal waste sample.

The bottom portion of the column was filled with glass spheres.

The flow rate of leaching solution was ~ 500 ml/day.

A fabric filter was also placed on top of the column to distribute the leaching solution.

Large Leaching Column Conditions

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Column 1: Bacterial leaching solution prepared using 9k media is being circulated continuously. In this case similar solution is collected and sent back again for leaching.

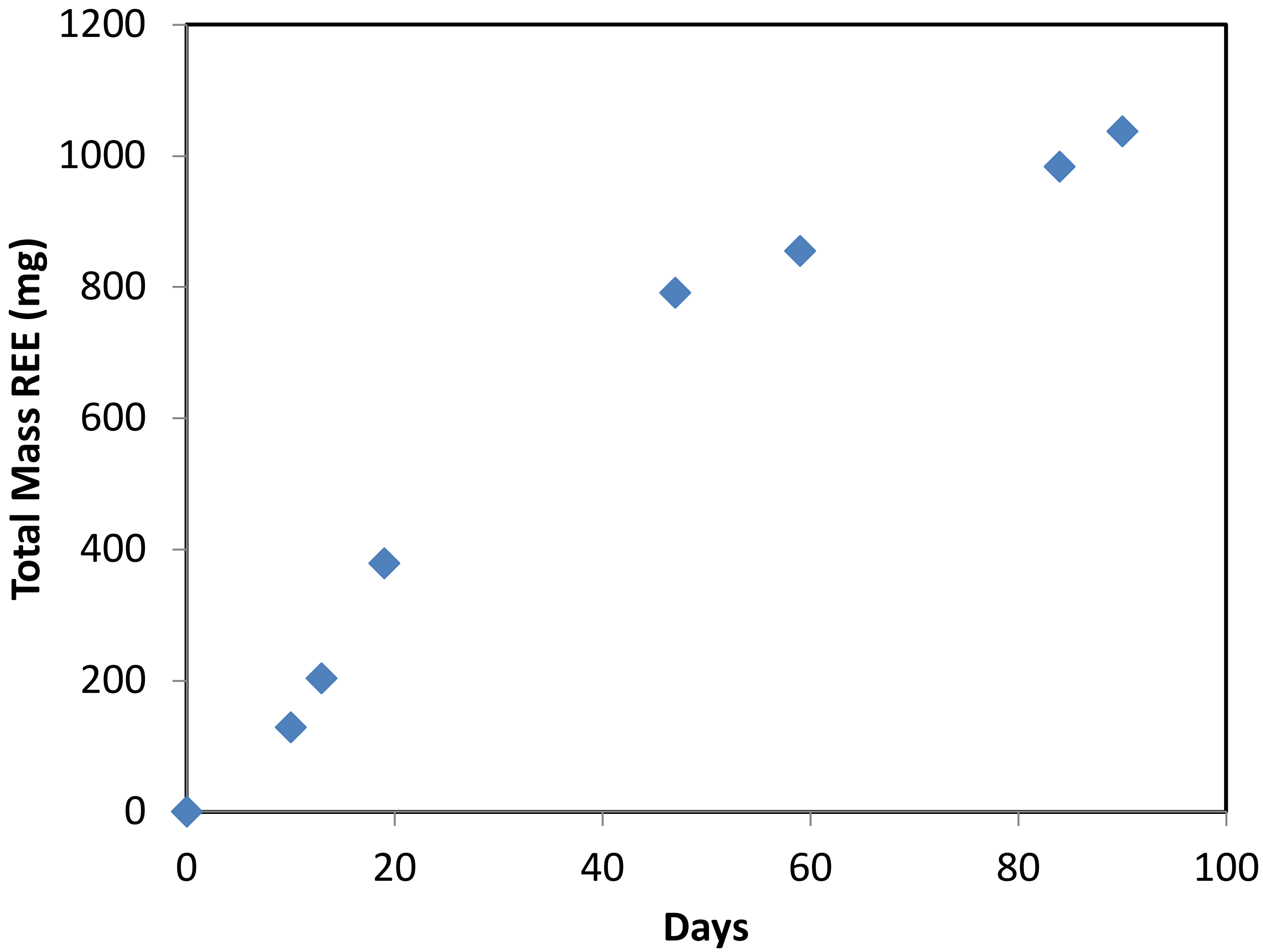
Column 2: In this column also, bacterial leaching solution prepared using 9k media is being circulated. However, in this case the solution is not recycled.

Column 3: In this column also, bacterial leaching solution was used, but pyrite blend nutrient was used. Here the details of such solution:

Name of the salt/species	Concentration
Potassium Sulfate	0.88 g/l
Ammonium Sulfate	0.9 g/l
Potassium Phosphate	0.25 g/l
Magnesium Sulfate	0.5 g/l
Pyrite from Mine sites	100 g/l
Sulfuric Acid	Added up to pH 1.5

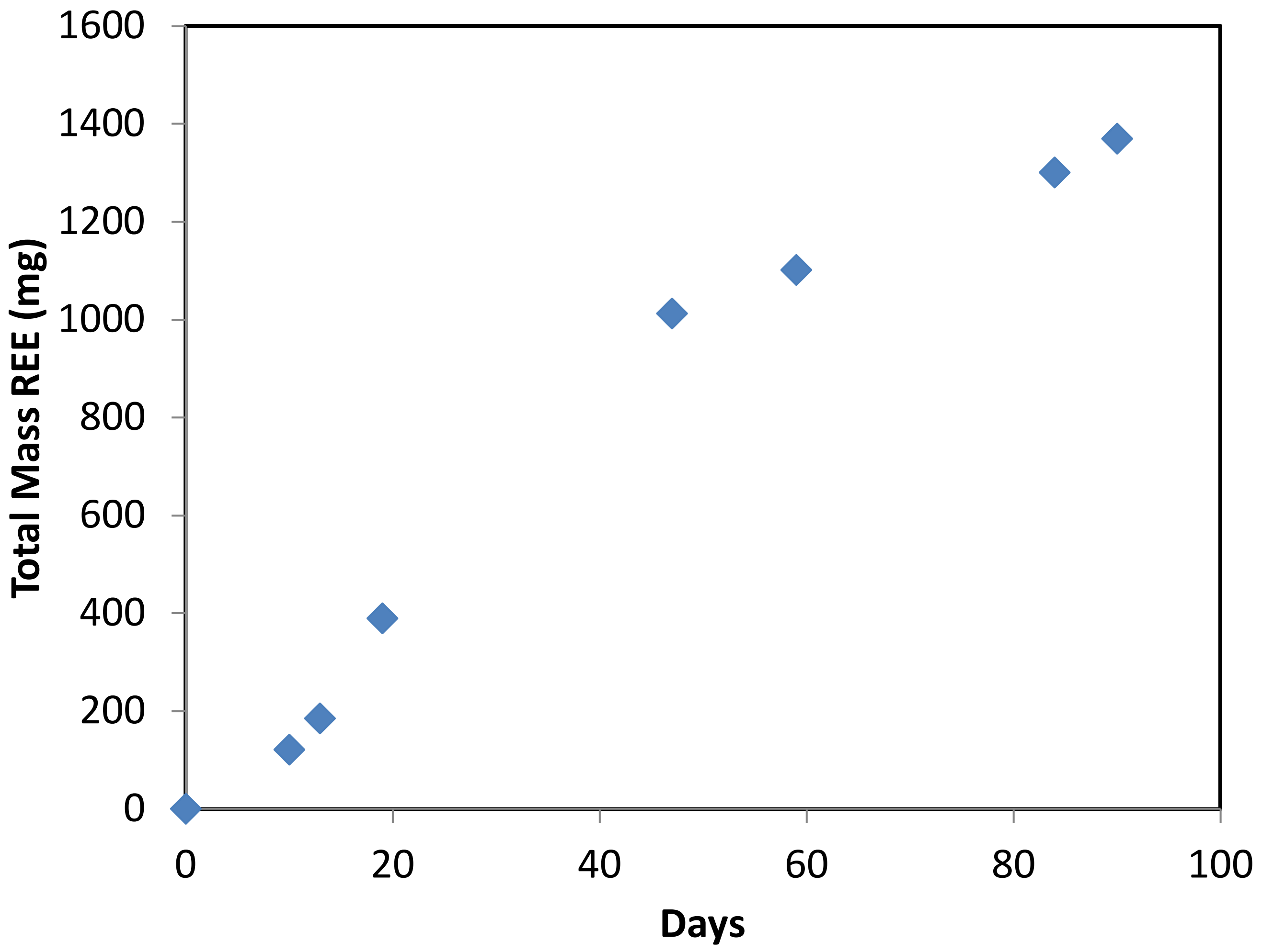
Column 4: In this column 20g/l ferric sulfate solution was recirculated. In this case no 9k media was used. In order to adjust Eh, hydrogen peroxide was used. Initial Eh was ~ 600 mV and pH was ~ 1.5. This is a control test for the chemical oxidation without bacteria.

Large Column Leaching Results



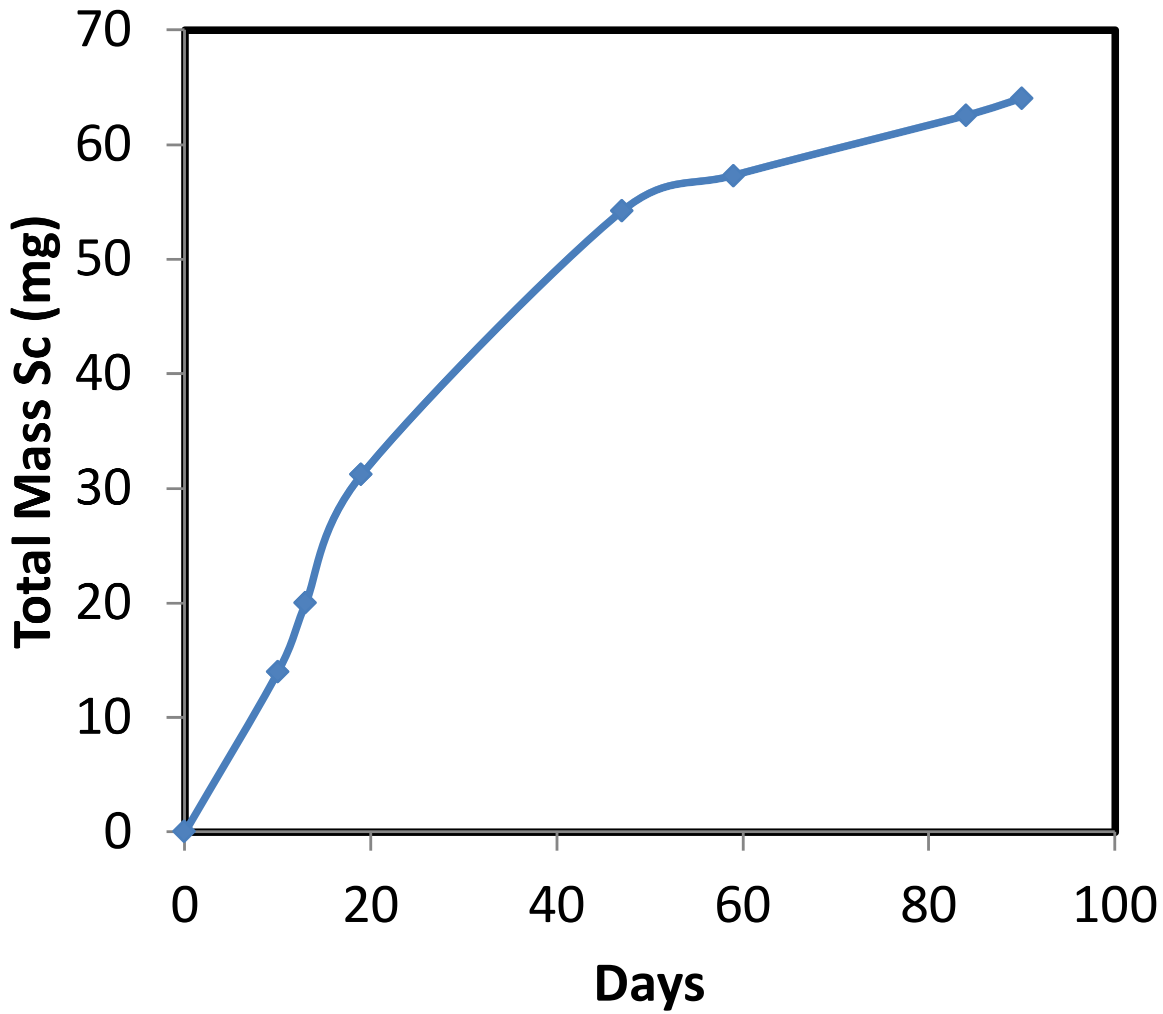
Leaching extraction for large column (60kg coal waste) fed by biooxidation reactor (35^{o}C) fed using 9K medium with air sparging.

Large Column Leaching Results



Leaching extraction for large column (60kg coal waste) fed by biooxidation reactor (35^oC) fed using pyrite enriched (7 % pyrite) coal waste with air sparging.

Large Column Leaching Results



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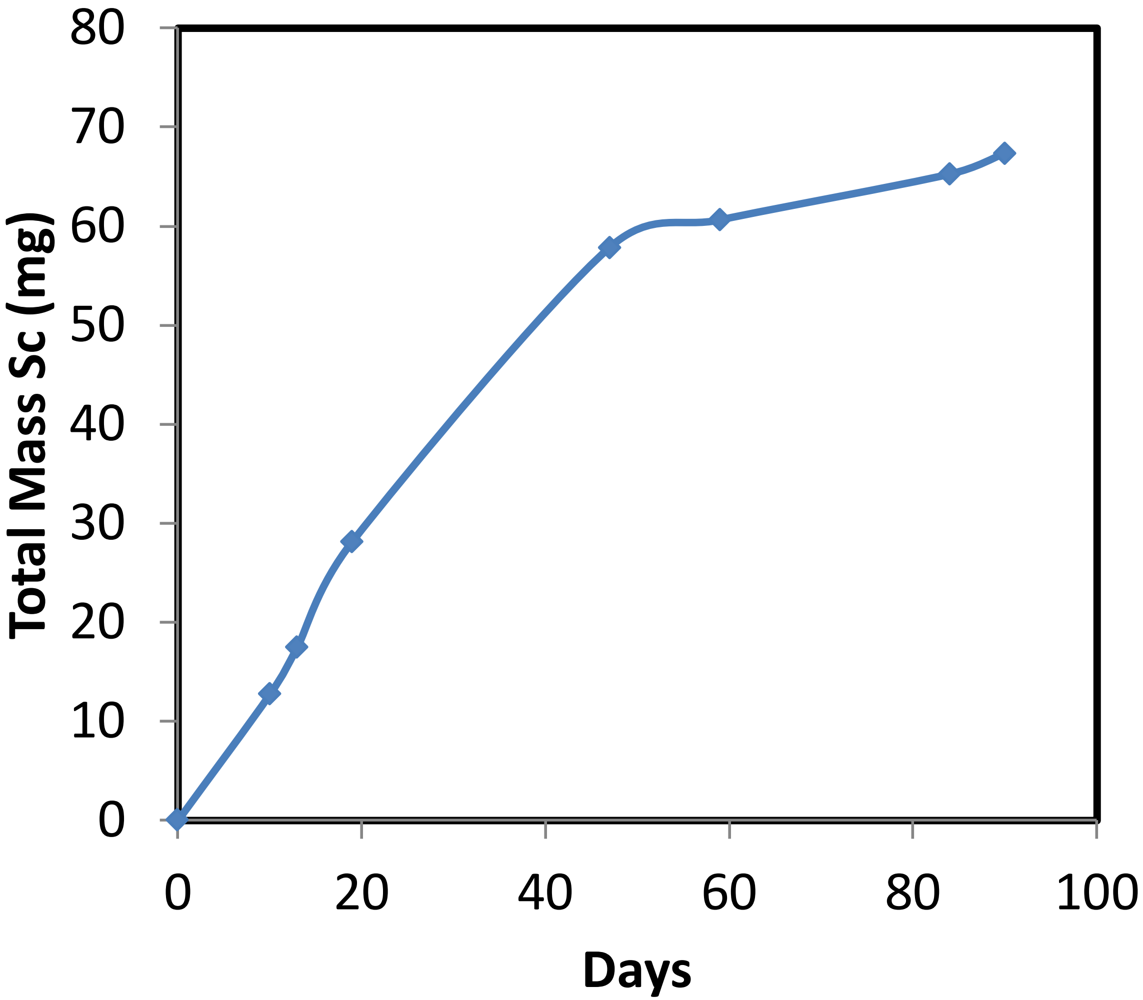
Large Column Leaching Results



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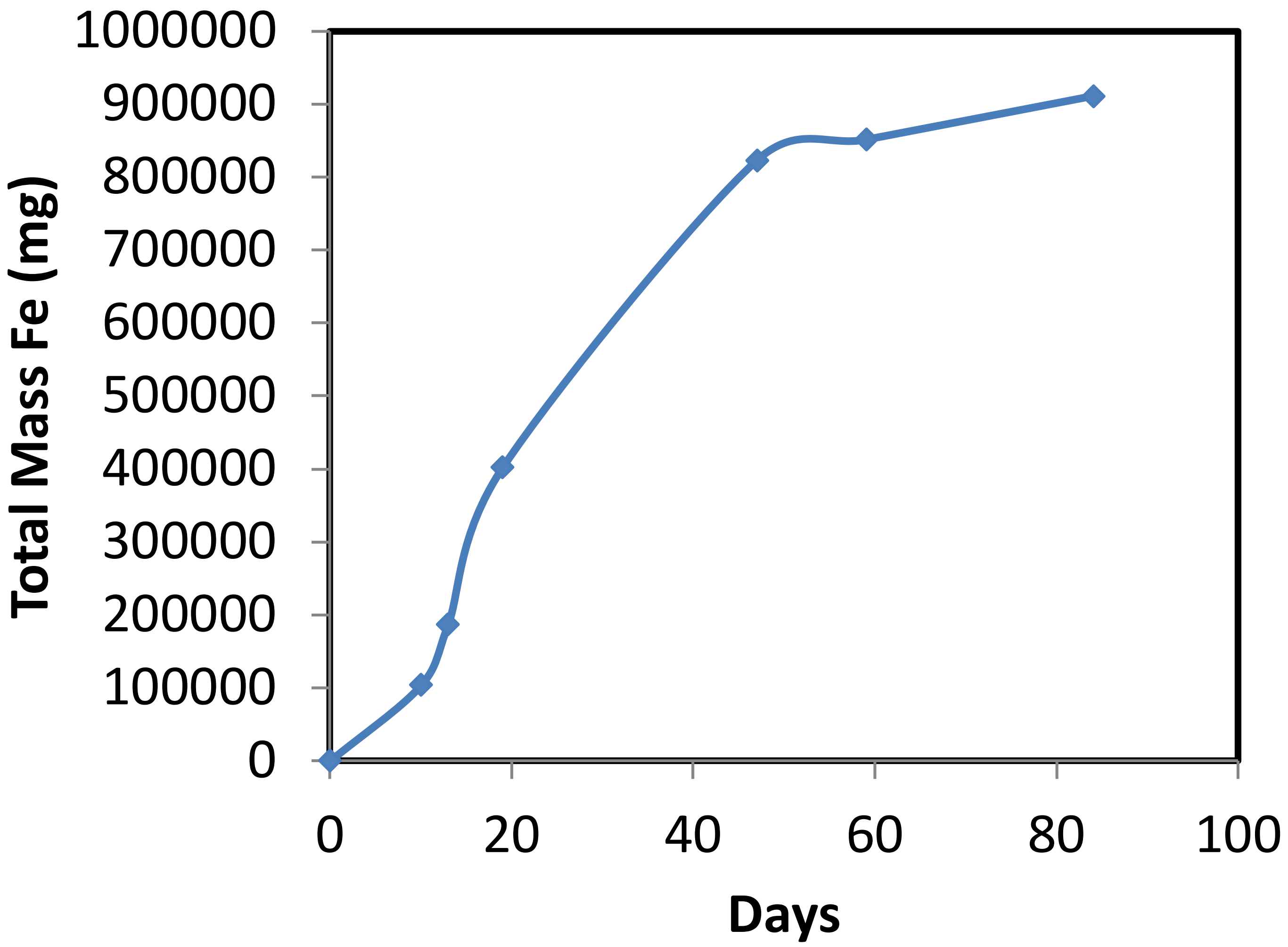
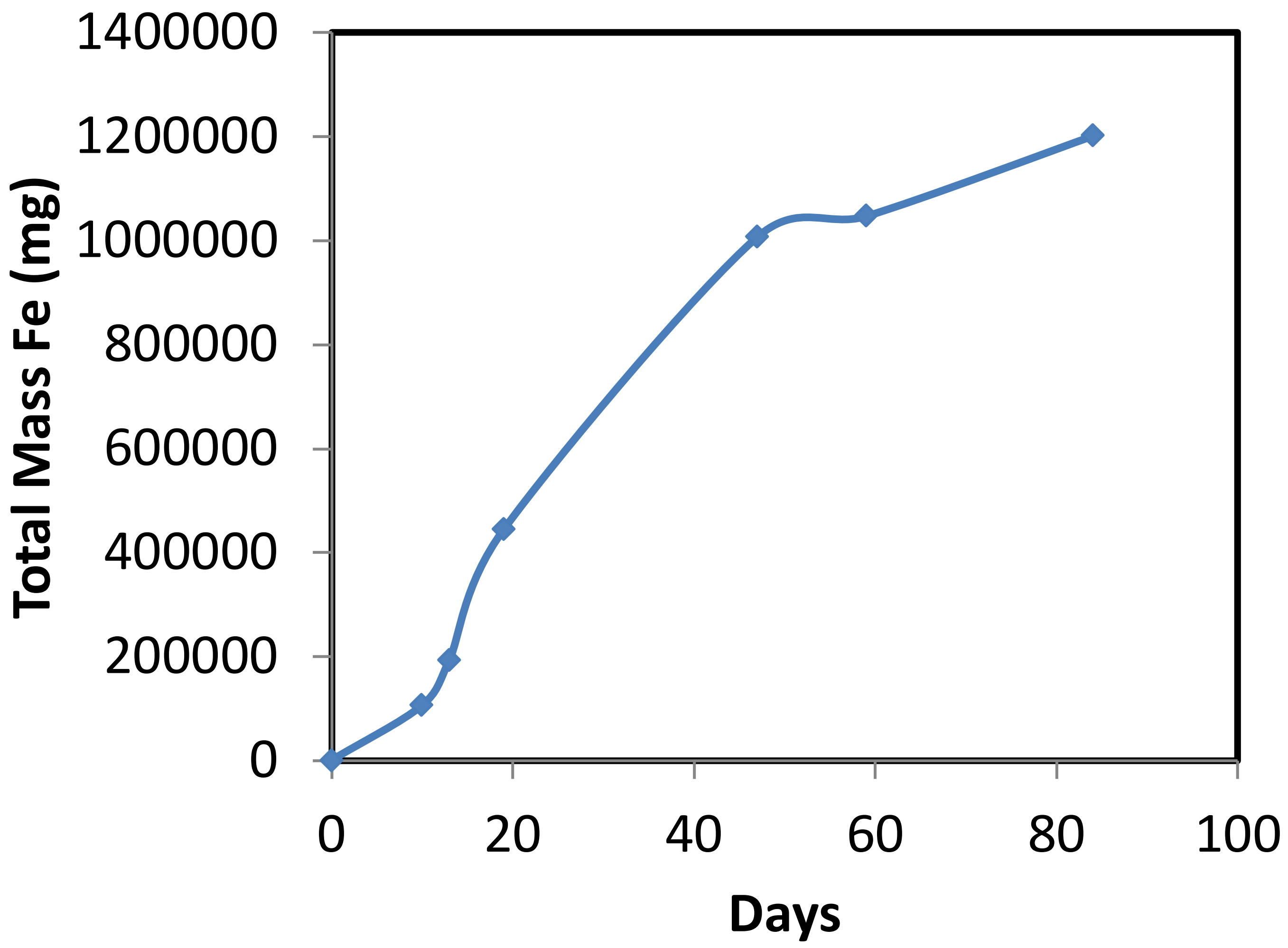
Large Column Leaching Results



Leaching extraction for large column (60kg coal waste) fed by biooxidation reactor (35^{o}C) fed using 9K medium with air sparging. Approximately 5 % of the total iron came from the feed solution. The rest came from pyrite dissolution.

Large Column Leaching Results



Leaching extraction for large column (60kg coal waste) fed by biooxidation reactor (35^oC) fed using pyrite enriched (7 % pyrite) coal waste with air sparging. Approximately 30 % of the total iron came from the feed solution. The rest came from pyrite dissolution.

Large Column Leaching Results

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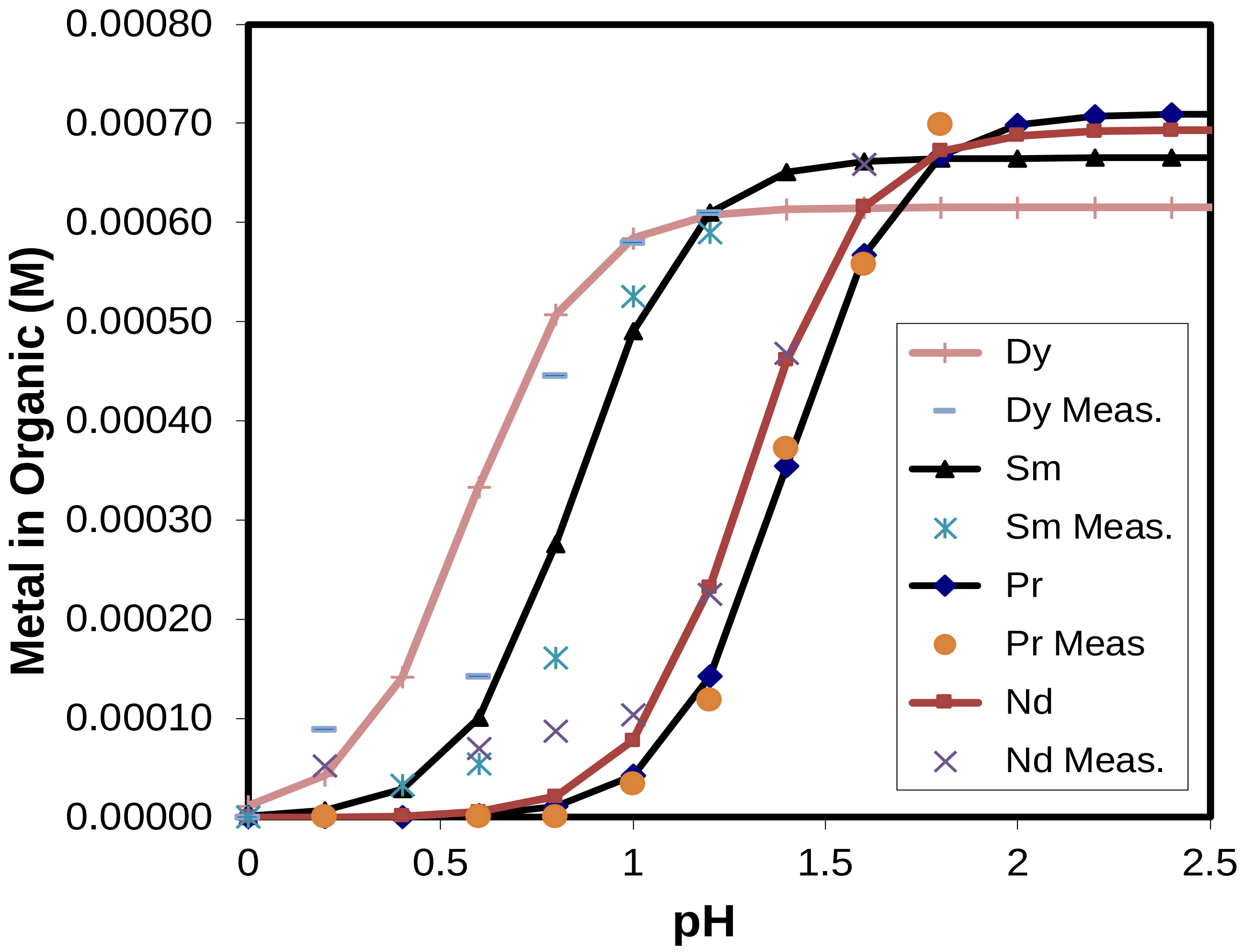
Leaching of REEs from coal waste is slow in heaps using biooxidation. It may take one year to reach 30 % recovery ($17 value/ton) under current test conditions, *which have not been optimized*. We believe we can increase the extraction rates and recoveries significantly. Note that finer particles will dramatically increase rates and recoveries, but much finer particles will also make the heaps mechanically unstable, and therefore be more feasible in stirred tank reactors.

Solvent Extraction



$$LnR_3 = \frac{Ln_{Total}K\frac{[RH]^3}{[H^+]^3}}{1 + K\frac{[RH]^3}{[H^+]^3}}$$

100 ppm Rare Earth Elements, using D2EPHA.

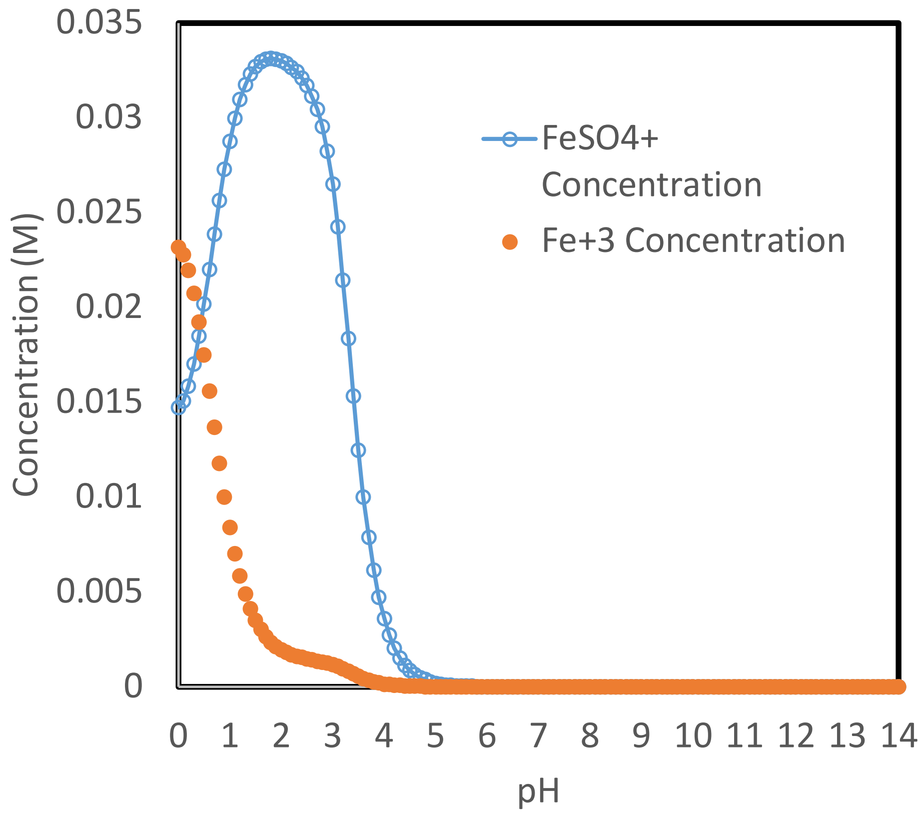
Precipitation

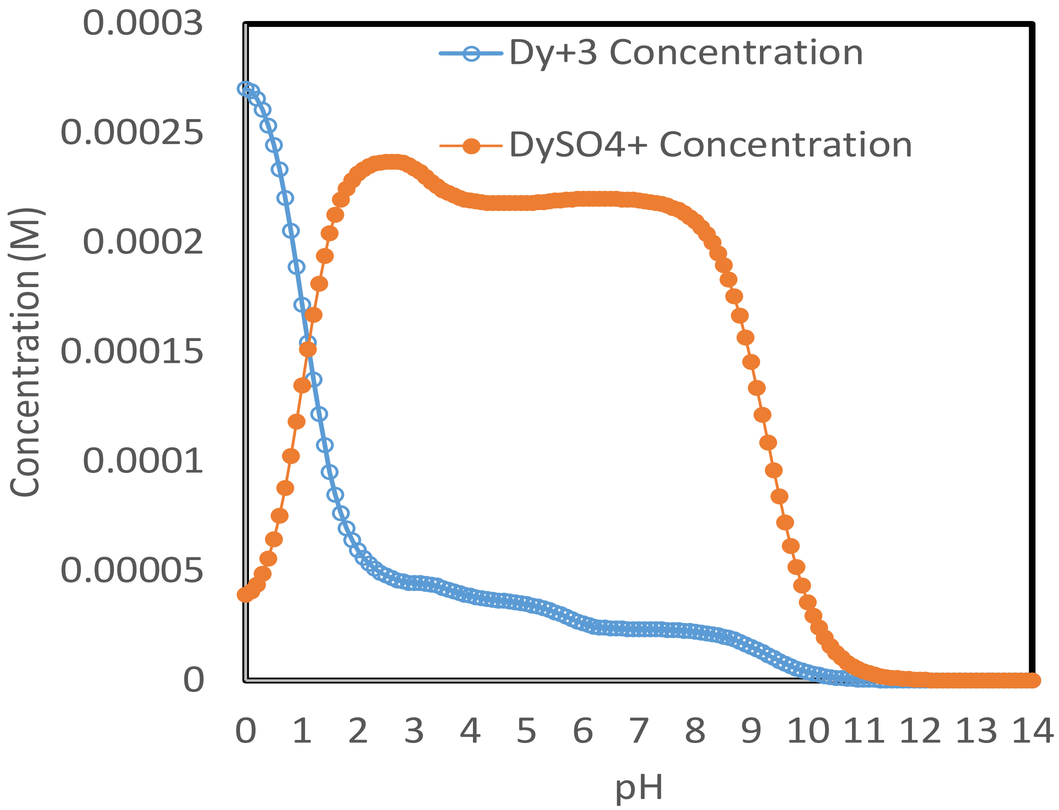
The primary soluble species with significant concentration levels at pH 0 are metal ions and metal sulfate ions (Fe^{3+}, $FeSO_4^+$, Dy^{3+}, $DySO_4^+$, La^{3+}, $LaSO_4^+$). As the pH rises, the reducing concentration of H^+ ions, makes sulfate more available to complex with the metal ions as indicated in Equation 1:

$$H^+ + SO_4^{2-} \leftrightarrow HSO_4^- \qquad (1)$$

Precipitation

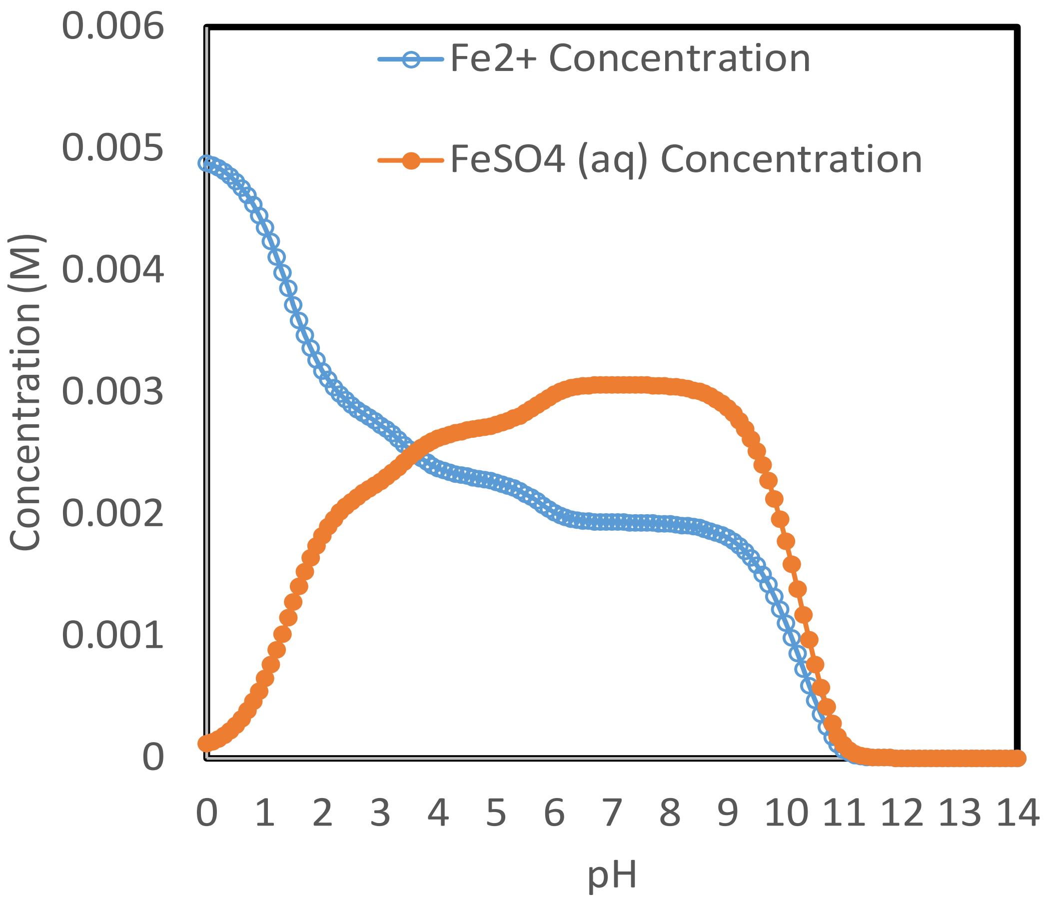
50 ppm Rare Earth Elements, 2000 ppm Fe.
Visual Minteq 3.1 Simulation

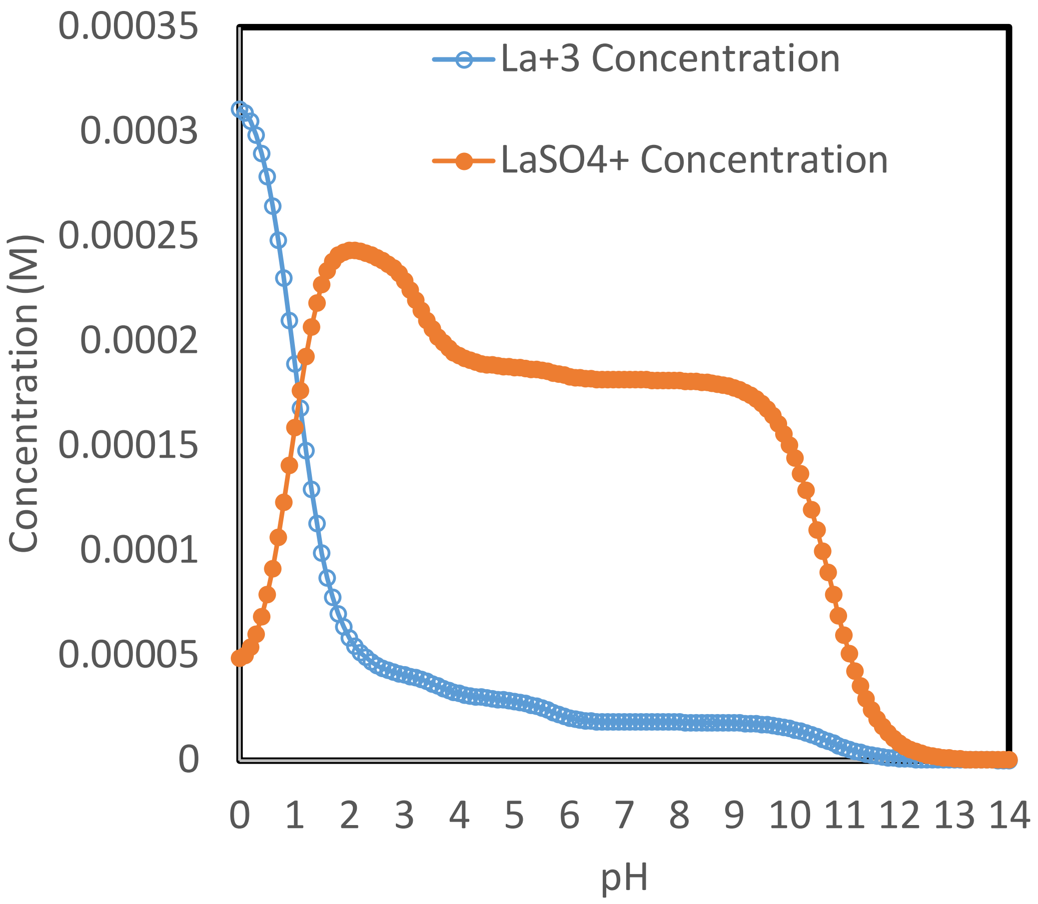




Precipitation

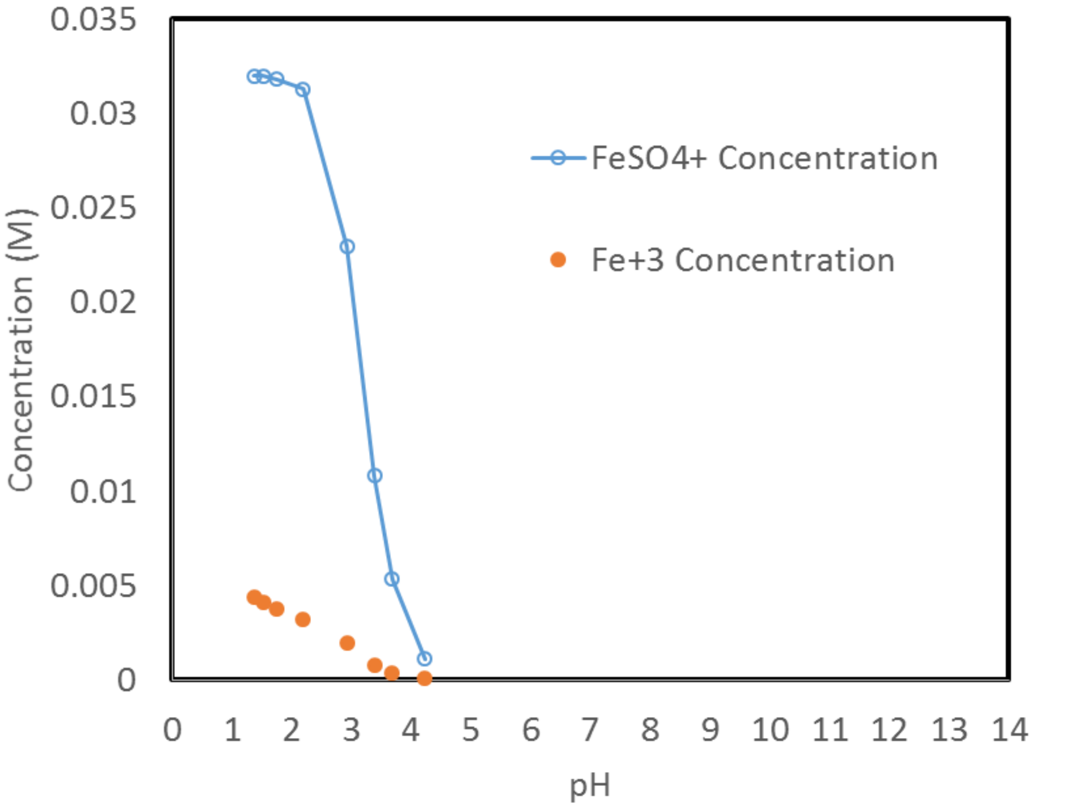
50 ppm Rare Earth Elements, 2000 ppm Fe.
Visual Minteq 3.1 Simulation

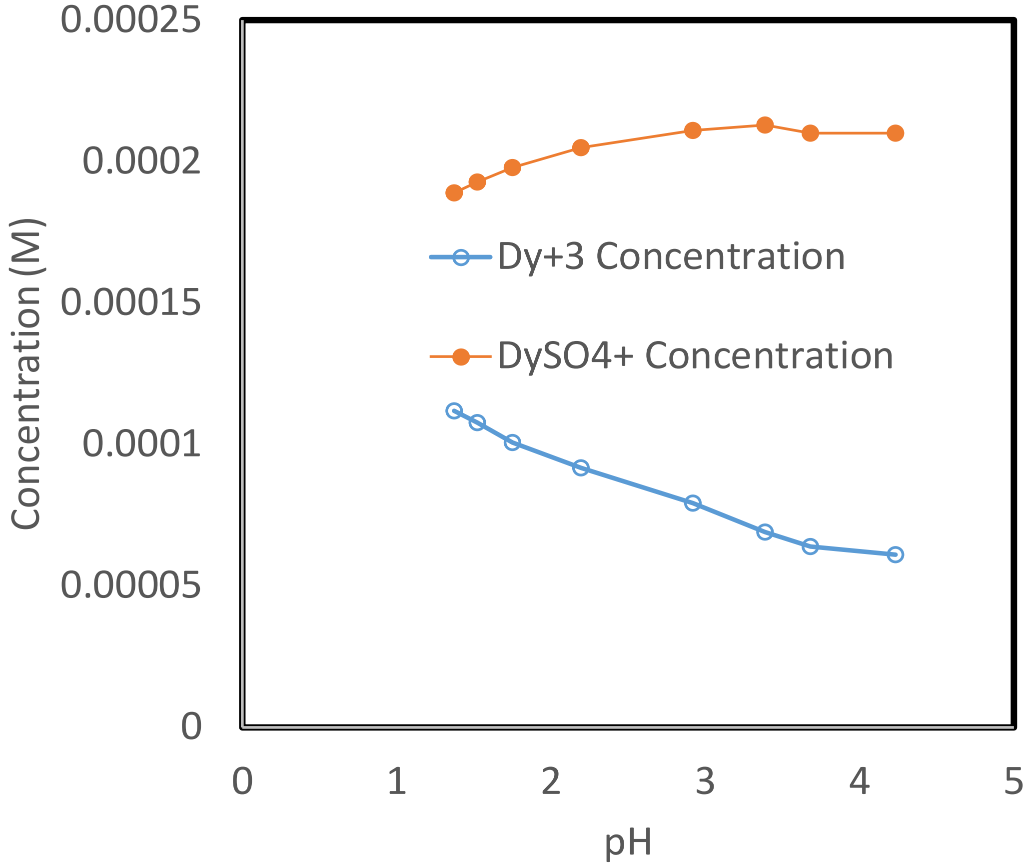




Precipitation

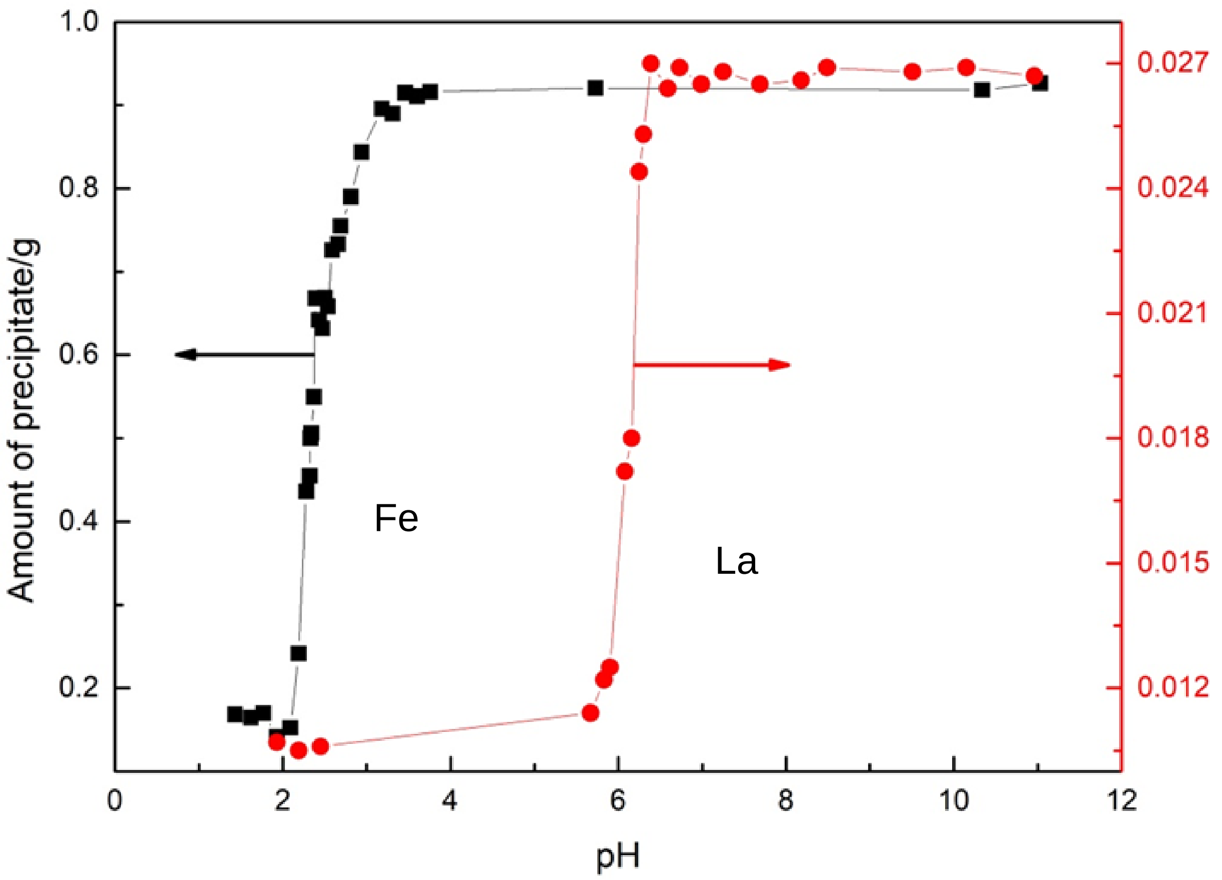
50 ppm Rare Earth Elements, 2000 ppm Fe.
Visual Minteq 3.1 Simulation using $MgCO_3$

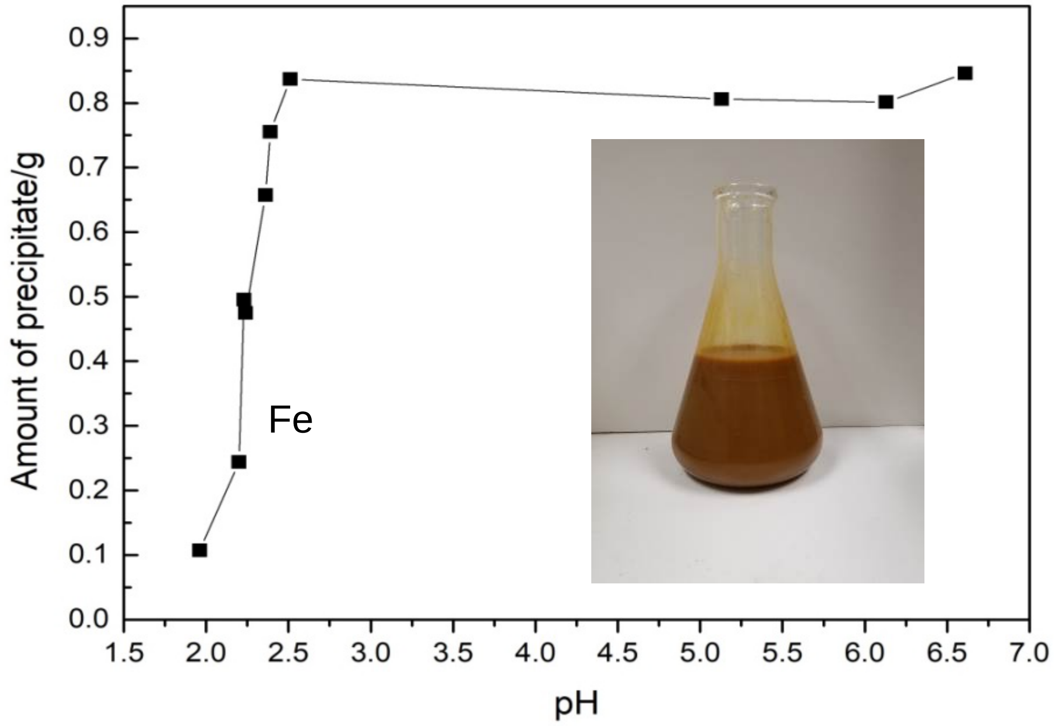




Precipitation

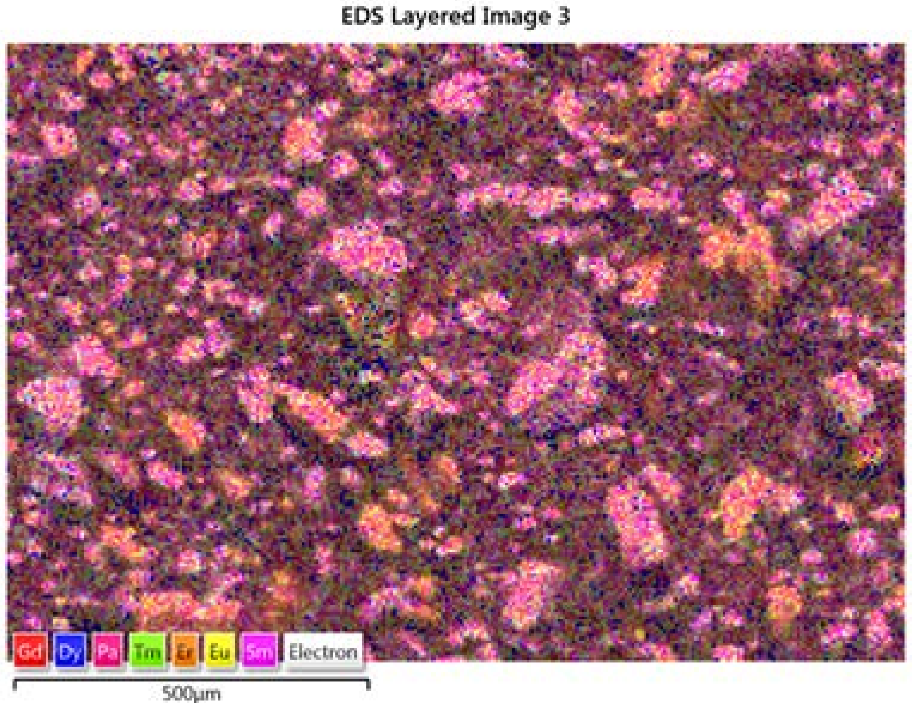
50 ppm Rare Earth Elements, 2000 ppm Fe. Measured data using ferric sulfate and 100 ppm lanthanum sulfate with titration using NaOH (left) $MgCO_3$ below

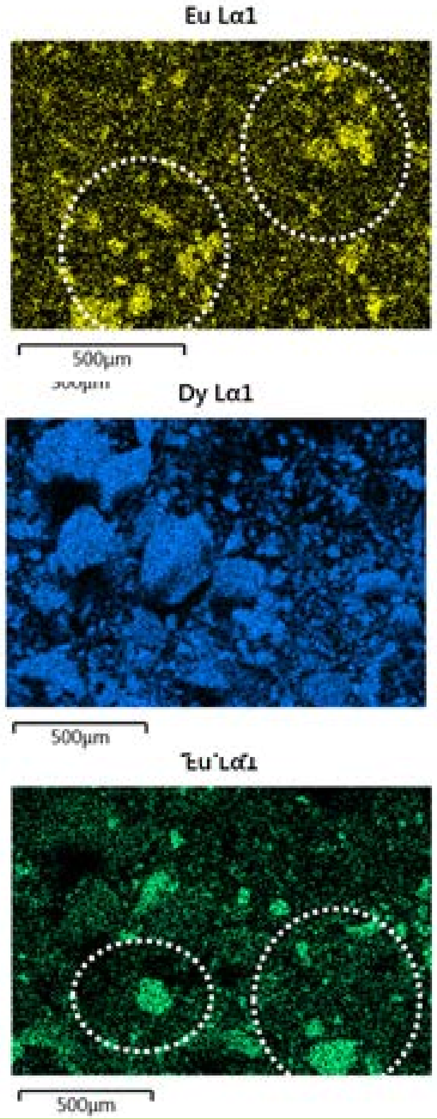




Precipitation

Initial precipitate after removing iron shows enriched rare earth elements.





More than half of the rare earth elements can be recovered by precipitation without solvent extraction.

Summary

NATIONAL ENERGY TECHNOLOGY LABORATORY

Rare earth elements can be recovered in significant quantities from coal waste using low cost technologies that are commercially used on large scales in the gold and copper industries.

Additional testing and analyses are being performed to estimate economic and technical viability, but preliminary results show significant potential.

Preparing Project for Next Steps

Market Benefits/Assessment

- This project addresses low cost technologies to extract and recover REEs from coal-based resources with modest levels of REEs
- This program could lead to large scale production of REEs from REE-enriched coal-based resources, which are estimated to be in the hundreds of millions of tons.

Technology-to-Market Path

- Additional testing at a pilot-scale should be performed to refine the process and obtain a more precise estimate of the cost of the process in order to encourage large-scale demonstration and future, widespread industrial utilization
- The next technological challenge is to design the lowest cost flow sheet and scale-up.
- New research includes using this technology to reprocess tailings.
- Although we have involved industry for samples, partners are needed for scale-up.