Pilot-scale Testing of an Integrated Circuit for the Extraction of Rare Earth Minerals and Elements From Coal and Coal Byproducts Using Advanced Separation Technologies

PRINCIPAL INVESTIGATOR:
Dr. Rick Honaker
University of Kentucky
504 Rose Street, 230 MMRB, Lexington, KY
E-Mail: rick.honaker@uky.edu

DOE Award Number: DE-FE0027035
Period of Performance: 3/1/2016 – 8/31/2017

2017 NETL Crosscutting Research
Track C: Rare Earth Elements
March 22, 2017

Project Objectives

- Develop, design and demonstrate a pilot-scale processing system for the efficient, low-cost and environmentally benign recovery of high-value rare earth elements (REEs) from coal and coal byproducts.
  - Integrate both physical and chemical separation processes;
  - Pilot-scale circuit will have a dry solids feed rate of ¼-ton/hr (0.23 tonne/hr) and will be capable of producing 5 - 7 pounds (2.3 – 3.2 kg) per hour of combined concentrates with purity levels of at least 2% total REEs by weight;
  - Technical and economic feasibility of the proposed system will be fully evaluated with respect to separation performance, throughput capacity, capital/operating costs, and environmental acceptability.

Project Team

- University of Kentucky
  - Jack Groppo, Jim Hower and Cortland Eble
- Virginia Tech
  - R.-H. Yoon and G.H. Luttrell
- West Virginia University
  - Aaron Noble and John Herbst
- Blackhawk Mining
- Alliance Coal
- Arch Coal
- Eriez Manufacturing
- Mineral Refining Company (MRC)
- Dr. Ken Han, Hydrometallurgist

Outline

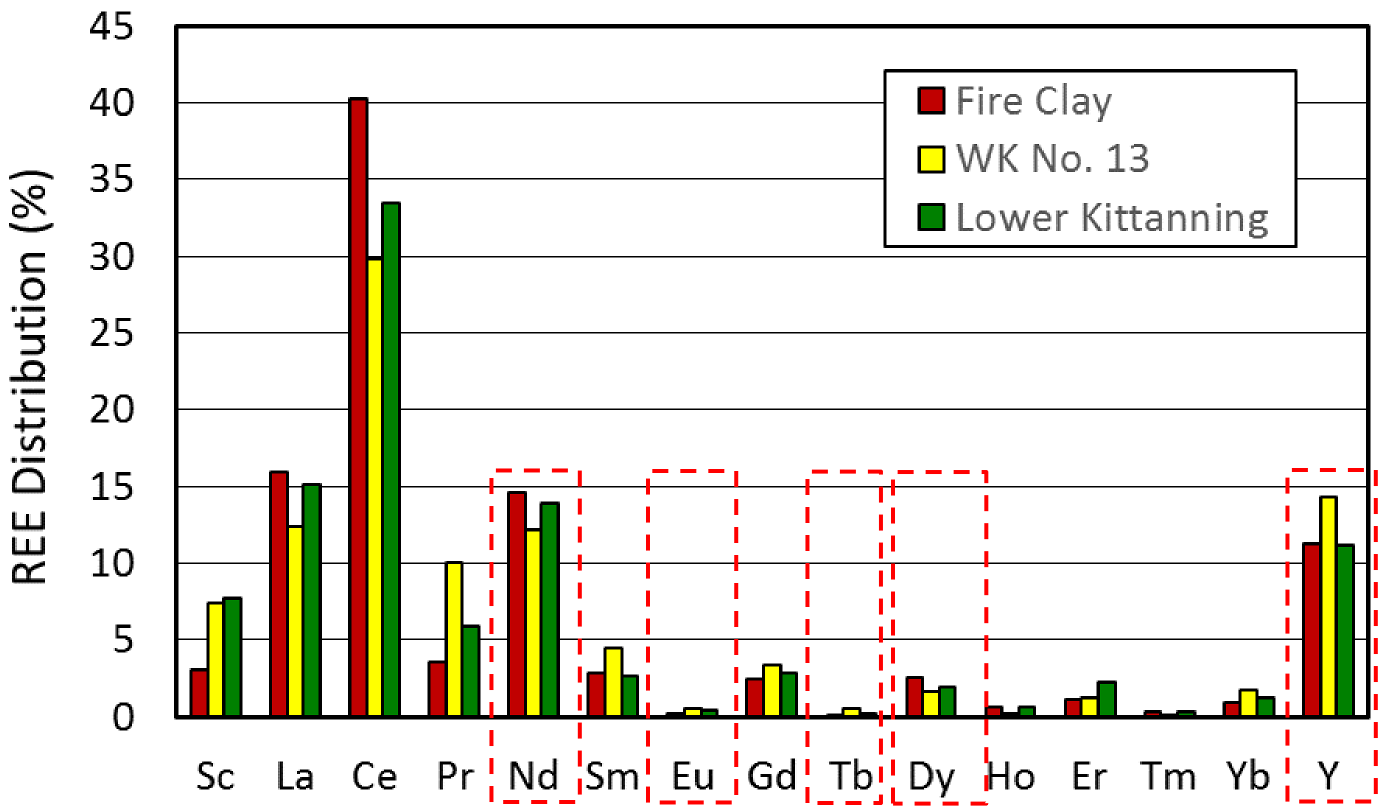
- REE Forms in Coal
  - Minerals
  - Ion Substitution
  - Organic Association
- REE Concentration
  - Physical Concentration
  - Leaching
  - Solvent Extraction
- Conclusions

Feed Stocks Evaluated

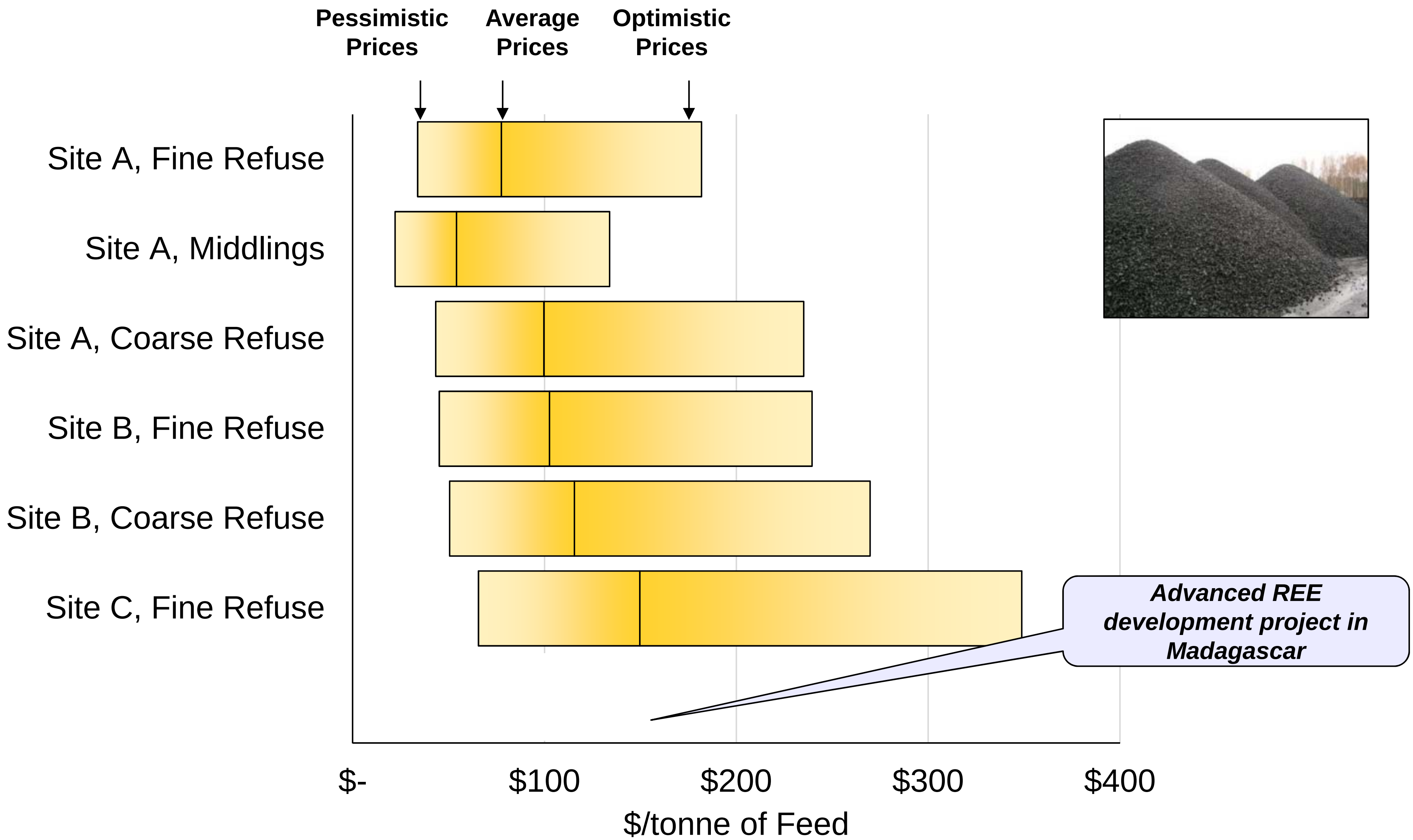
- Coal Sources
  - Fire Clay
  - West Kentucky No. 13
  - Lower Kittanning

- Process Streams
  - Thickener Underflow
  - Middlings
  - Coarse Reject

REE Distribution



In-Situ Value of REE in Coal



Data from 3 CAPP sites

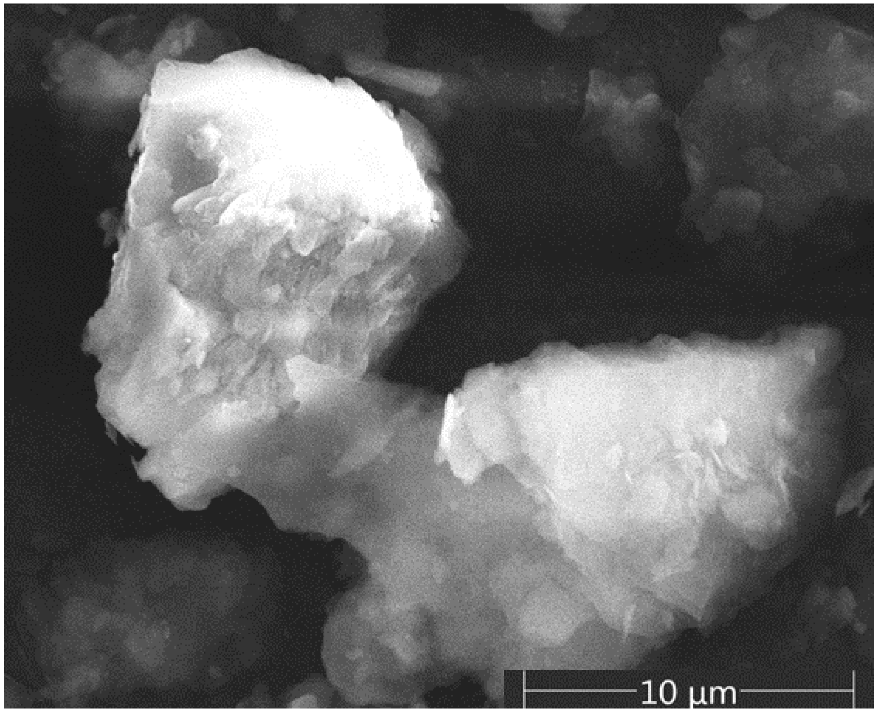
- REE market values are true "maximum," "minimum," and "average" prices, determined element-by-element, over the period 2008 to 2016

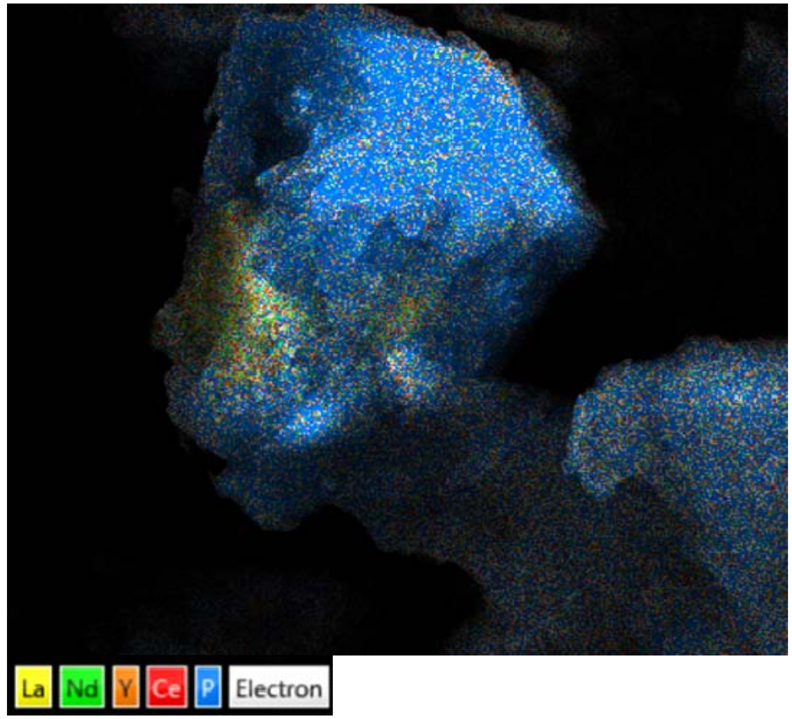
REE Forms in Coal

- Mineral association
  - monazite $(Ce,La,Pr,Nd,Th,Y)PO_4$
  - xenotime YPO_4
  - bastnaesite $(Ce, La)CO_3F$
  - other
- Clay adsorbed REEs
- Aluminum octahedron association in clays
- Organic affinity

Element Mapping Energy Dispersive Spectroscopy

Fire Clay Thickener Underflow

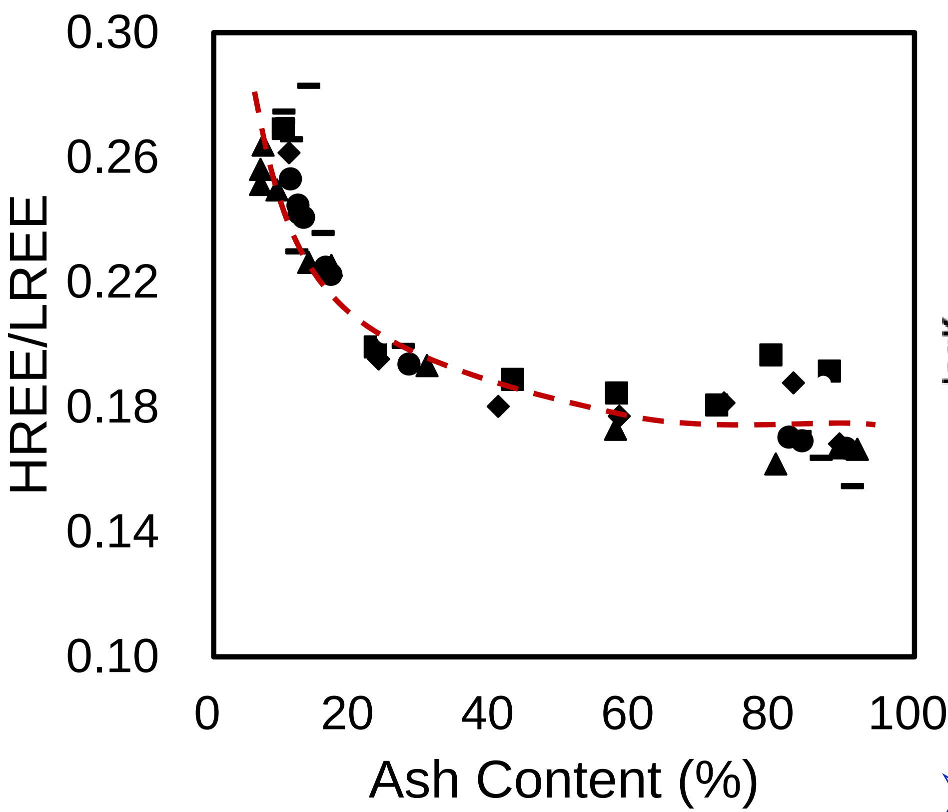




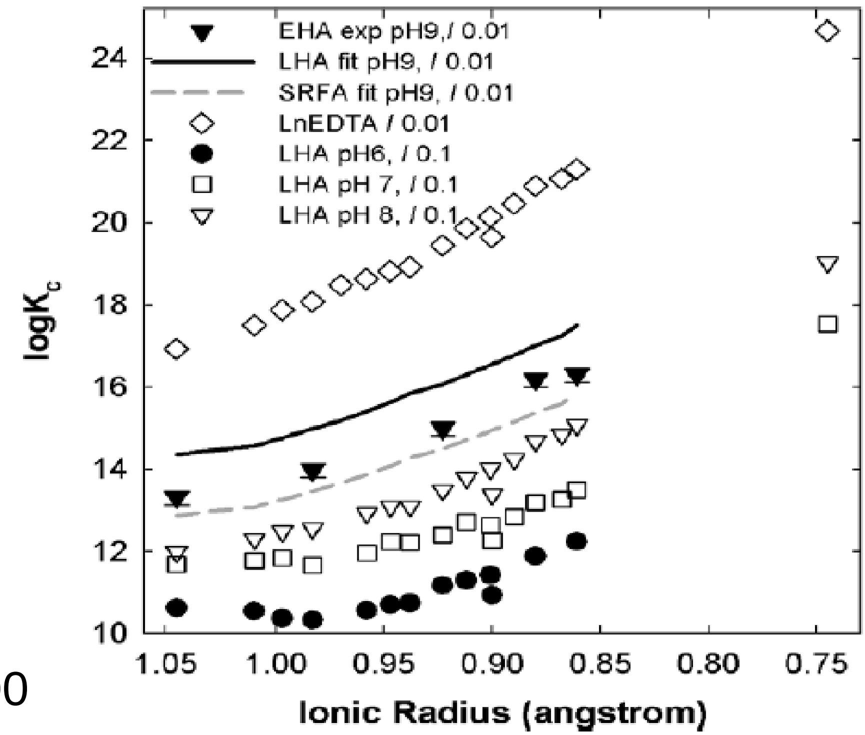
- RE mineral particles have a top size of around 10 microns and a bottom size of around 150 nm.

Organic Association

HREE/LREE



Binding Constant



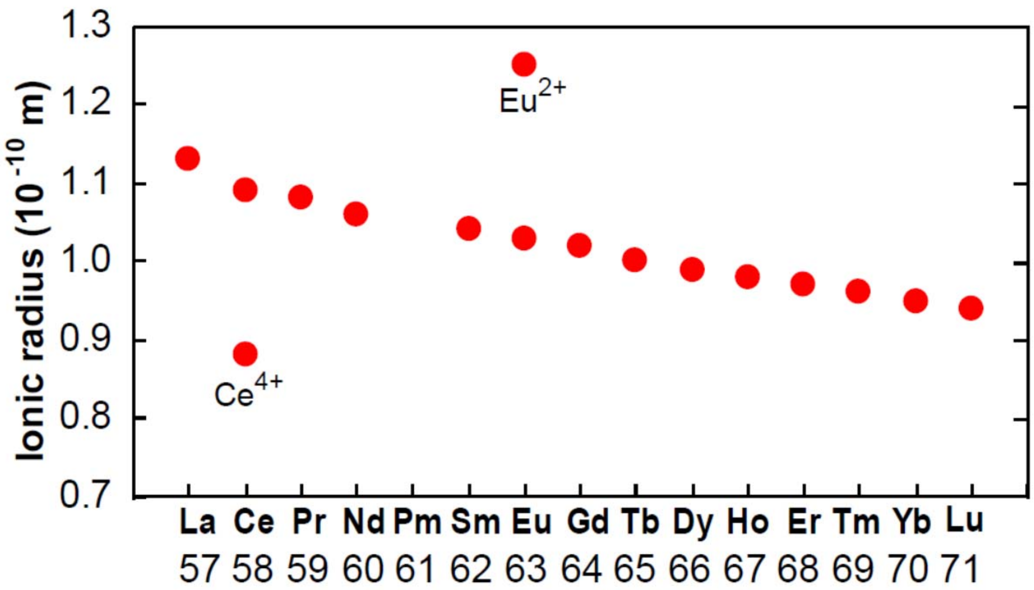
- HREEs associated with clean coal

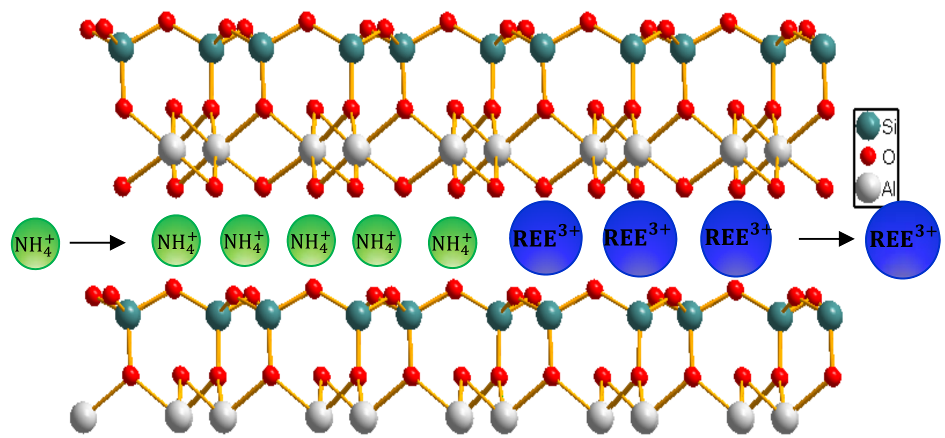
- Binding Constant HREEs>LREEs
- Coalification
- High rank coal?

Pourret et al., 2007

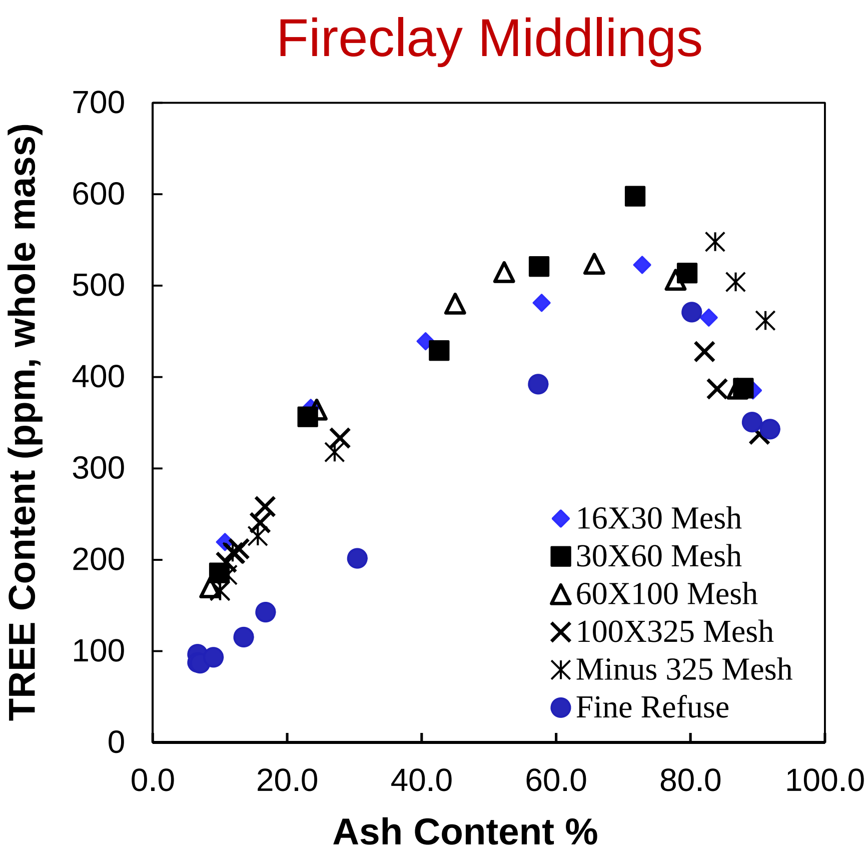
REE Clay Adsorption

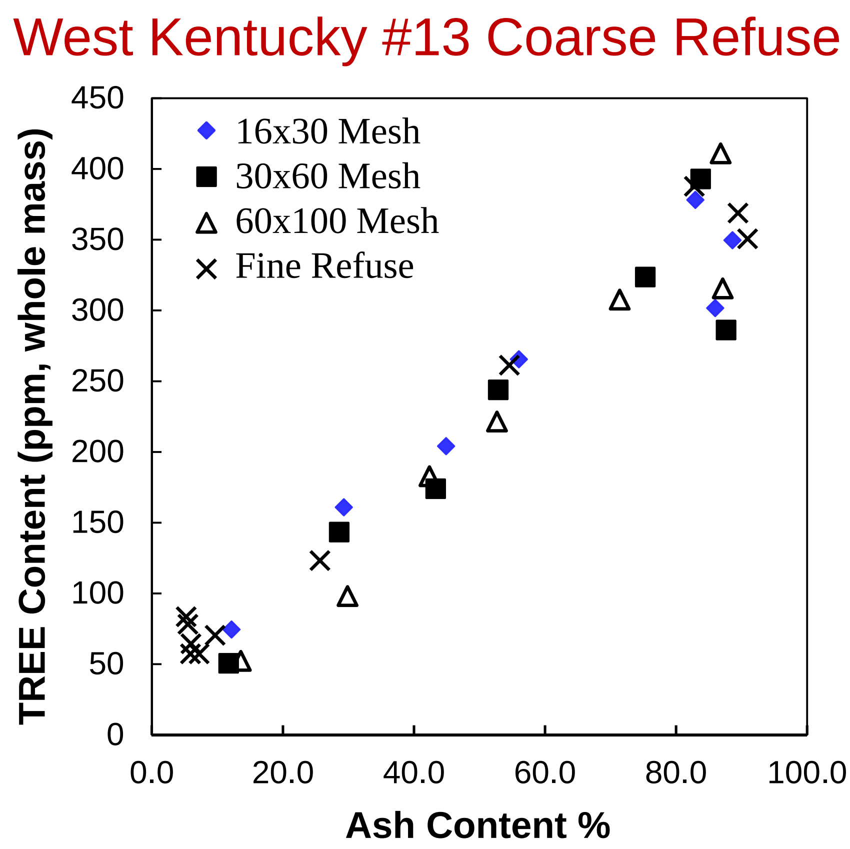
- Ionic radii decreases with increasing atomic weight.
- RE ions adsorbed in interlayer regions of clay minerals.
- RE ions are more hydrated in solution.
- Hydration Energy >> Electrostatic Energy
- NaCl or $(NH_4)_2SO_4$





REE Distribution in Coal





- Similar trend was observed at 20 coal processing plant located across the nation (R. Honaker, 2014)

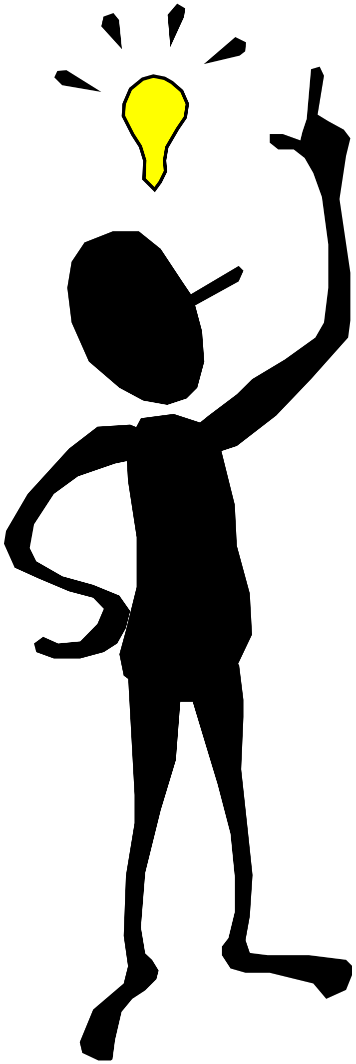
Fire Clay Seam REE Distribution

ID	Description	Lithology	REE (ppm, ash-basis) TREE	LREE	HREE	REE (ppm, whole-basis) TREE	LREE	HREE	HREE /LREE
B1	Roof Shale	Roof Shale	545.23	490.92	70.04	476.69	429.21	61.24	0.14
B2	Carb. Shale	Carb. Shale	647.06	571.92	93.24	326.19	288.31	47.00	0.16
B13	Flint Clay	Flint Clay	144.95	129.94	21.28	117.74	105.55	17.29	0.16
B16	Bone Coal	Bone Coal	590.91	506.48	100.82	298.59	255.92	50.94	0.20
		Total Rock	431.5	383.5	60.9	319.8	284.3	45.1	0.16
B3	Coal	Coal	381.10	290.06	103.84	71.61	54.50	19.51	0.36
B4	Coal	Coal	1412.40	902.75	559.19	29.52	18.87	11.69	0.62
B5	Coal	Coal	1085.94	800.40	320.46	44.52	32.82	13.14	0.40
B6	Coal	Coal	1118.73	877.30	277.08	39.49	30.97	9.78	0.32
B7	Coal	Coal	1418.14	1149.21	312.34	36.02	29.19	7.93	0.27
B8	Coal	Coal	1195.89	978.74	256.48	60.03	49.13	12.88	0.26
B9	Coal	Coal	1848.52	1484.24	412.52	139.01	111.61	31.02	0.28
B10	Coal	Coal	1570.75	1264.77	350.81	70.84	57.04	15.82	0.28
B11	Coal	Coal	1561.83	1351.89	247.64	189.14	163.71	29.99	0.18
B12	Coal	Coal	1532.12	1084.51	494.79	88.40	62.58	28.55	0.46
B14	Coal	Coal	1964.52	1740.24	270.65	457.54	405.30	63.03	0.16
B15	Coal	Coal	3450.96	2947.80	591.06	447.59	382.33	76.66	0.20
B17	Coal	Coal	2635.21	2253.41	444.66	251.66	215.20	42.47	0.20
B18	Coal	Coal	1695.85	1281.78	469.17	92.08	69.60	25.48	0.37
B19	Coal	Coal	663.34	505.36	179.61	130.08	99.10	35.22	0.36
		Total Coal	1457.2	1197.4	299.8	187.0	156.7	35.3	0.22

Outline

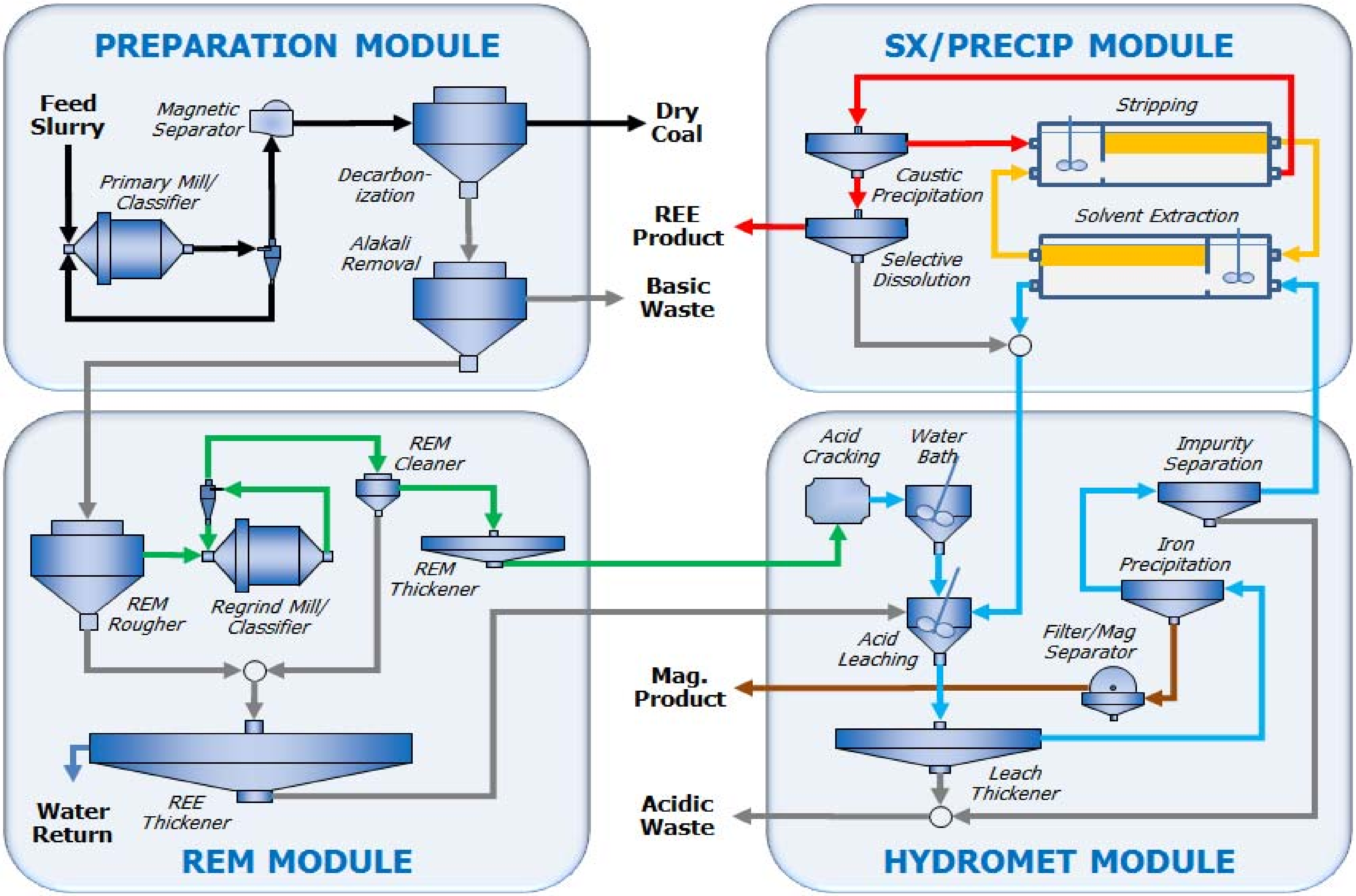
- ✓ *REE Forms in Coal*
  - ✓ *Minerals*
  - ✓ *Ion Substitution*
  - ✓ *Organic Association*
- ✓ REE Concentration
  - ✓ Physical Concentration
  - Leaching
  - Solvent Extraction
- ❑ Conclusions

Sample Characterization Findings

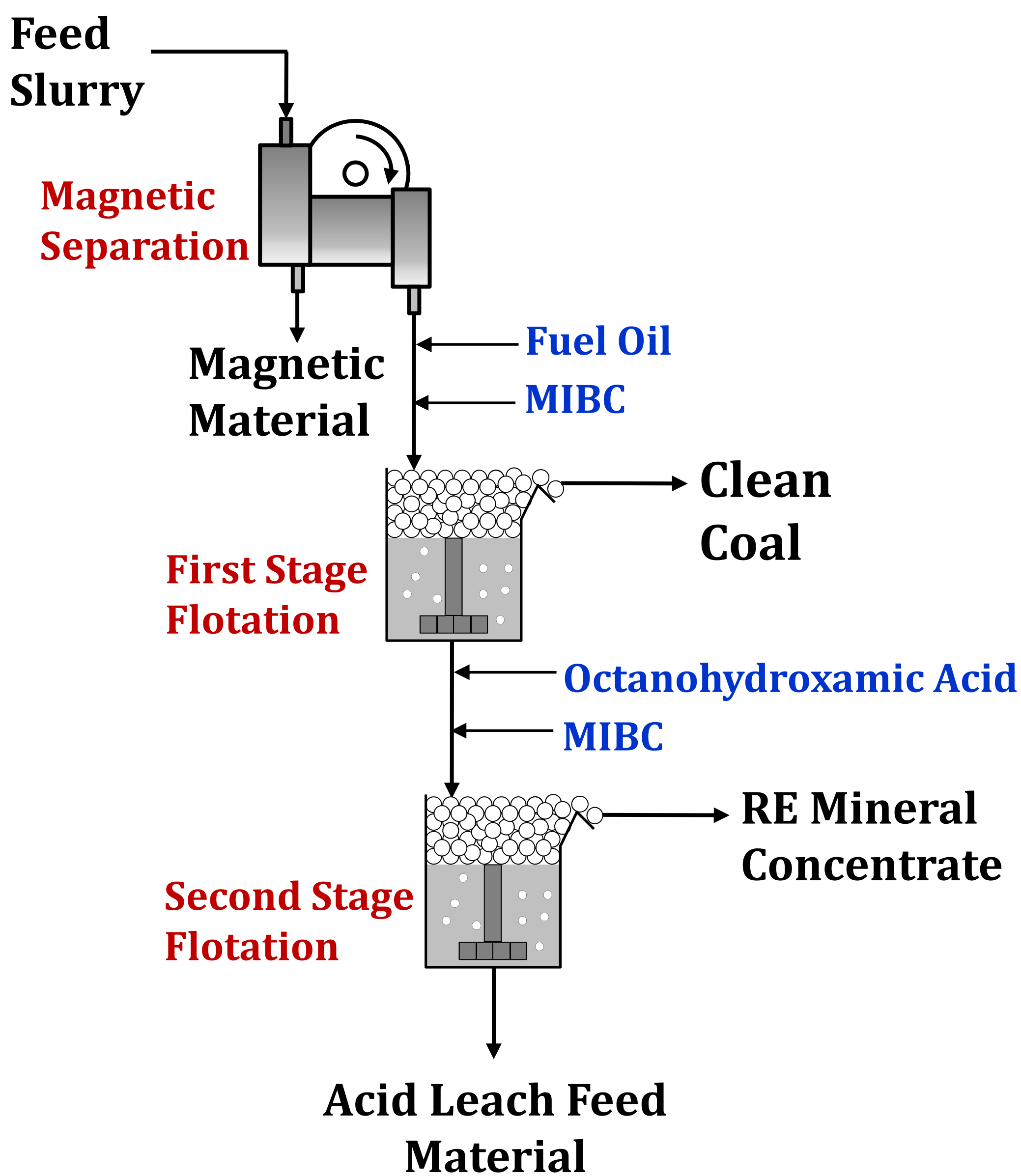


- Although the heavy REEs are concentrated in the low density fractions, crushing and grinding the material to liberate the mineral matter from the fraction is uneconomical.
- Ultrafine waste processing stream
  - Least amount of energy required for liberation purposes.
- The 1.60 x 2.00 SG fraction
  - Typically rejected to meet coal quality specs
  - Approximately 5% to 10% of total plant feed.
  - Crushing and grinding liberates both coal and RE minerals.
  - Heavy REE concentrations are significant.

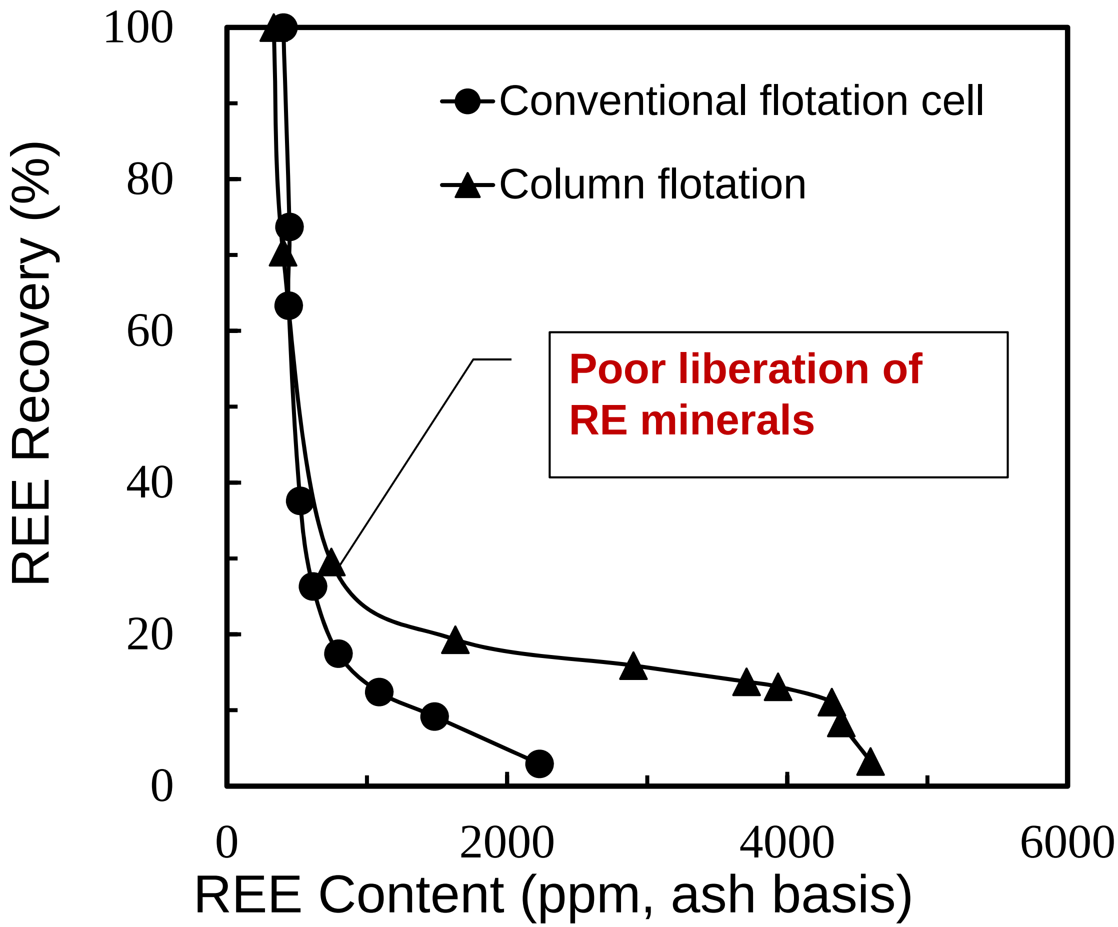
REE Recovery Flowsheet



REM Concentration by Flotation

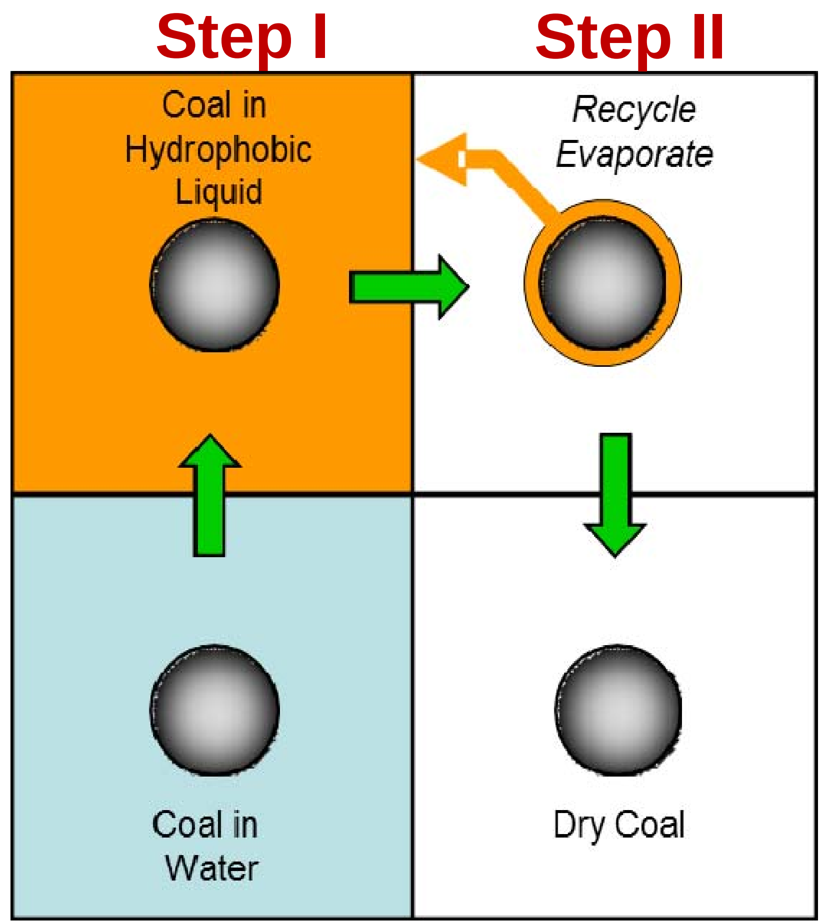


REM Concentration by Flotation

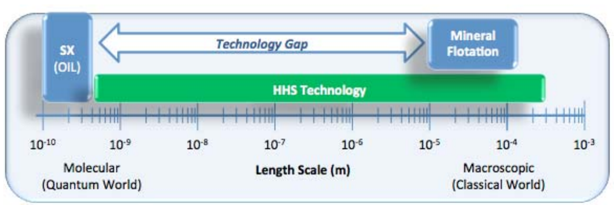


Hydrophobic Hydrophilic Separation (HHS)

- Step I
  - Hydrophobic particles are transferred to a hydrophobic liquid
    - Spontaneous process
- Step II
  - Hydrophobic particles are separated from hydrophobic liquid
    - Solid/liquid separation
    - Vaporization/condensation
  - Spent hydrophobic liquid is recycled

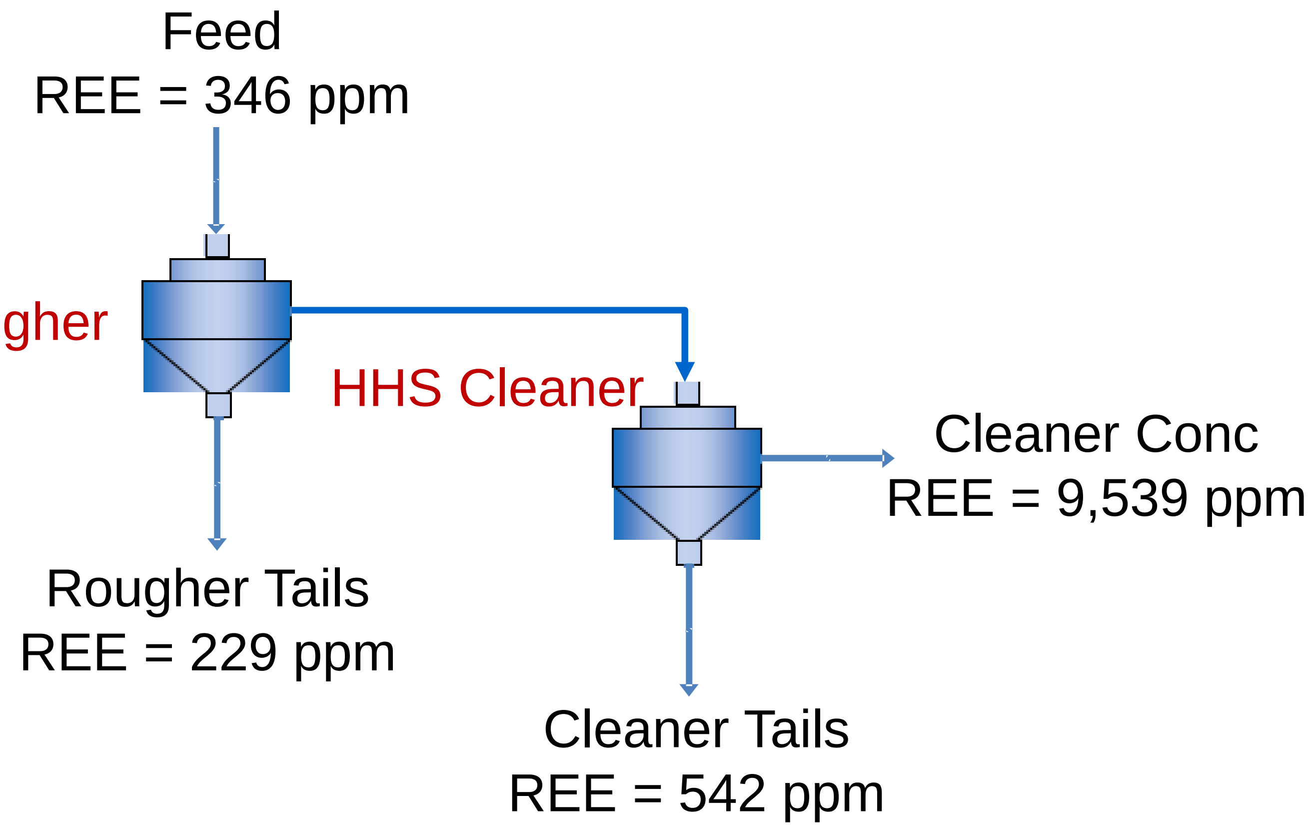


$\Delta G_t < 0$ $\Delta G_e > 0$



MRC
MINERALS REFINING COMPANY

HHS REE Concentration



Process Stream	Ash (%)	REE Assays (ppm)		Mass Yield (%)	REE Recovery (%)
		Ash Basis	Whole Mass		
Cleaner Concentrate	48.7	9539	4644	1.8	26.9
Cleaner Tails	90.0	542	487	8.3	13.0
Rougher Tails	91.4	229	210	89.8	60.1
Feed	90.5	346	313	100.0	100.0

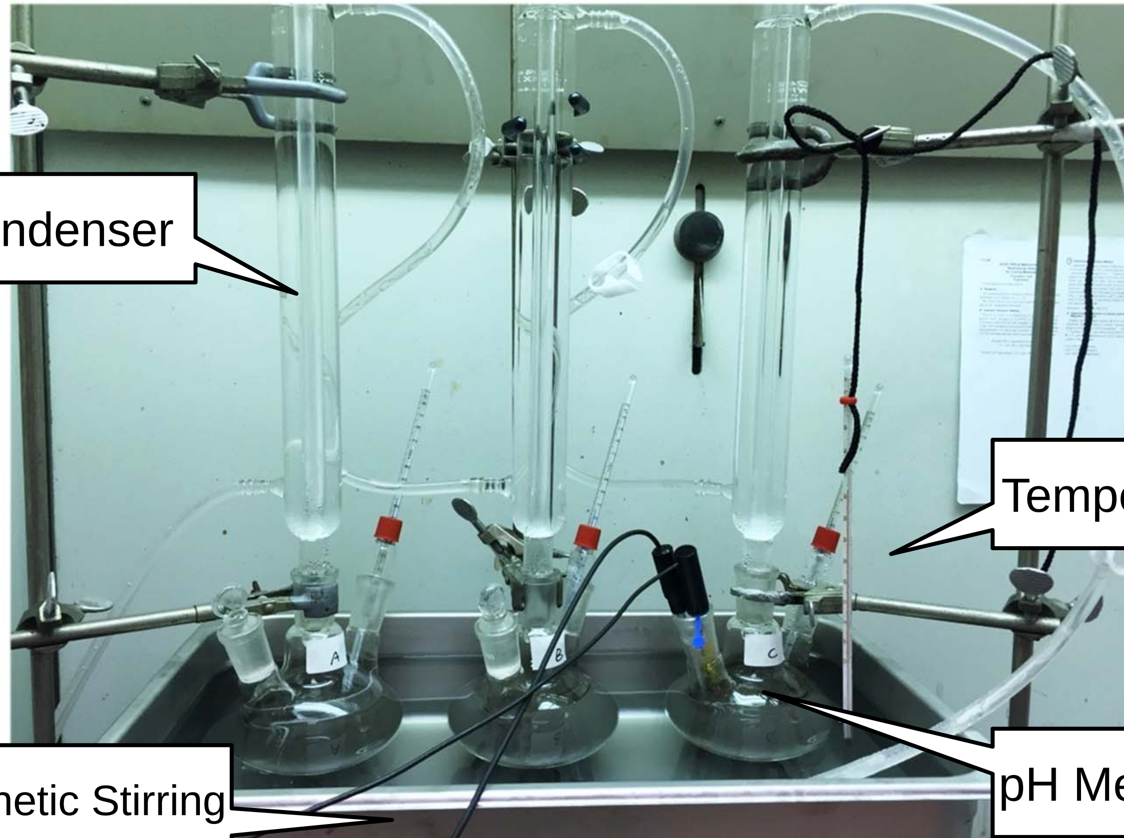
Recent HHS REE Concentration

Process Sample	Weight (%)	Ash (%)	TREE Content (ppm, ash basis)
Rghr/Clnr Conc	0.7	15.1	17,428
Rghr/Clnr Conc Tail	1.3	75.4	5,155
Rghr/Clnr Tail	11.8	91.0	581
Scvgr/Clnr Conc	0.3	51.4	11,478
Scvgr1/Clnr Conc Tail	3.7	89.6	548
Scvgr1/Clnr Tail	3.9	92.5	251
Scvgr 2/Clnr Conc	2.5	91.9	572
Scvgr2/Clnr Conc Tail	2.5	90.3	235
Scvgr2/Clnr Tail	3.7	92.6	197
Rghr/Scvgr1/Scvgr2 Tail	69.5	93.1	156
Feed	100.0	91.7	331

Outline

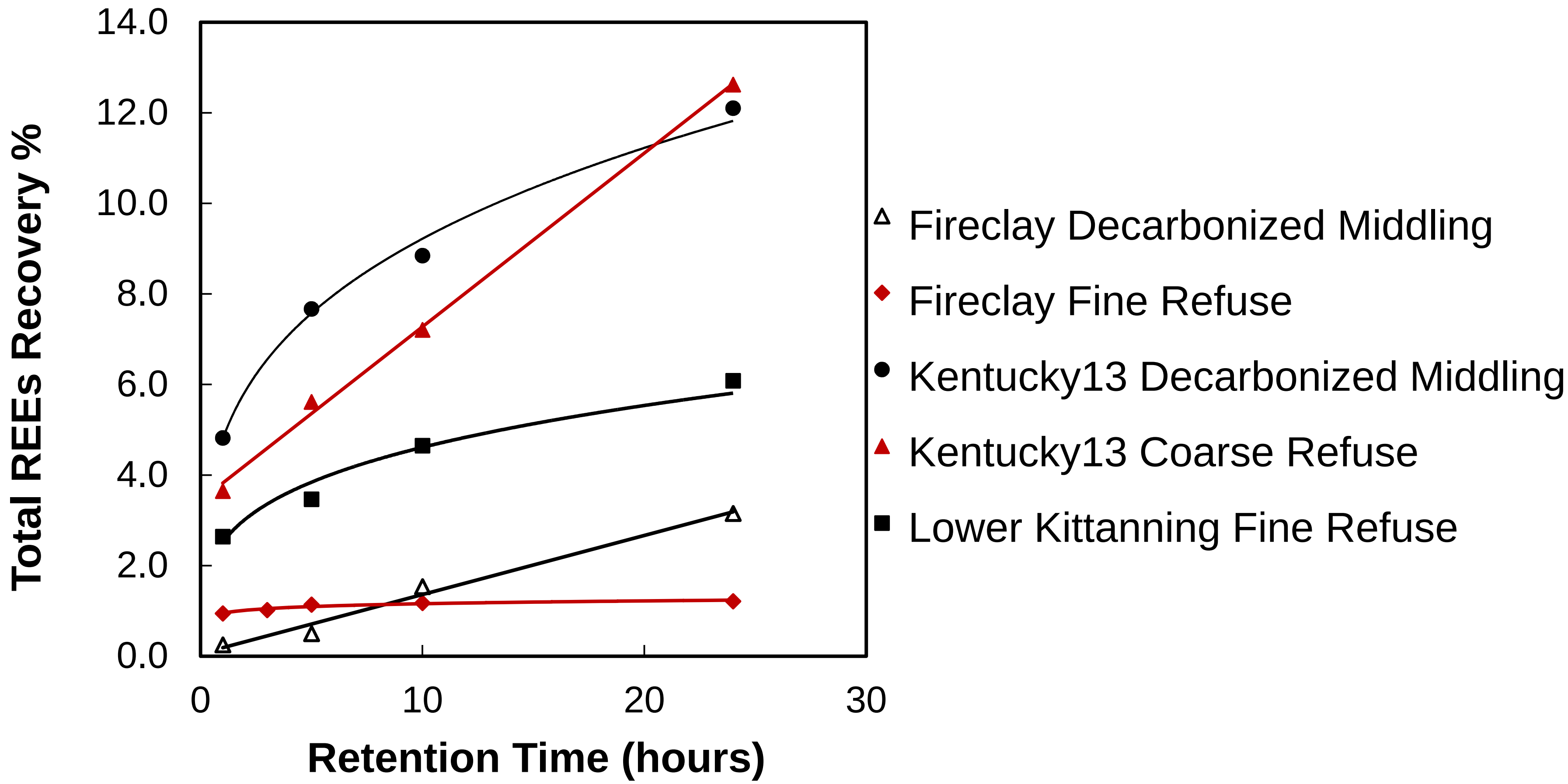
- ✓ *REE Forms in Coal*
  - ✓ *Minerals*
  - ✓ *Ion Substitution*
  - ✓ *Organic Association*
- ✓ REE Concentration
  - ✓ *Physical Concentration*
  - ✓ Leaching
    - ✓ Ion Exchange
    - ▪ REE Leaching
  - • Solvent Extraction
- ❑ Conclusions

Ion-Exchange Experiments



- $(NH_4)_2SO_4$ = 0.1 mol/L
- Solution pH of 5 adjusted using HNO_3
- Solid : Liquid = 1 : 20 (w:v)
- Temperature: 75 ºC

Ion Exchange



- West Kentucky 13 seam showed the best potential;
- However, REE recovery was low;
- The response using Fireclay coal sources was the lowest.

Ion-Exchange Using Novel Lixiviant

- Thickener U/F @ 50°C

Lixiviant	Conc. (moles/l)	Feed			Solid Residue			REE Recovery (%)
		Ash (%wt)	REE (ppm)	Wt. (g)	Ash (%wt)	REE (ppm)	Wt. (g)	
$(NH_4)_2SO_4$	0.5	92.03	234.58	30.0	90.85	232.05	29.2	3.7
A	0.5	92.03	234.58	30.0	90.01	198.79	28.1	20.6
B	0.5	92.03	234.58	30.0	89.51	227.96	29.2	5.4

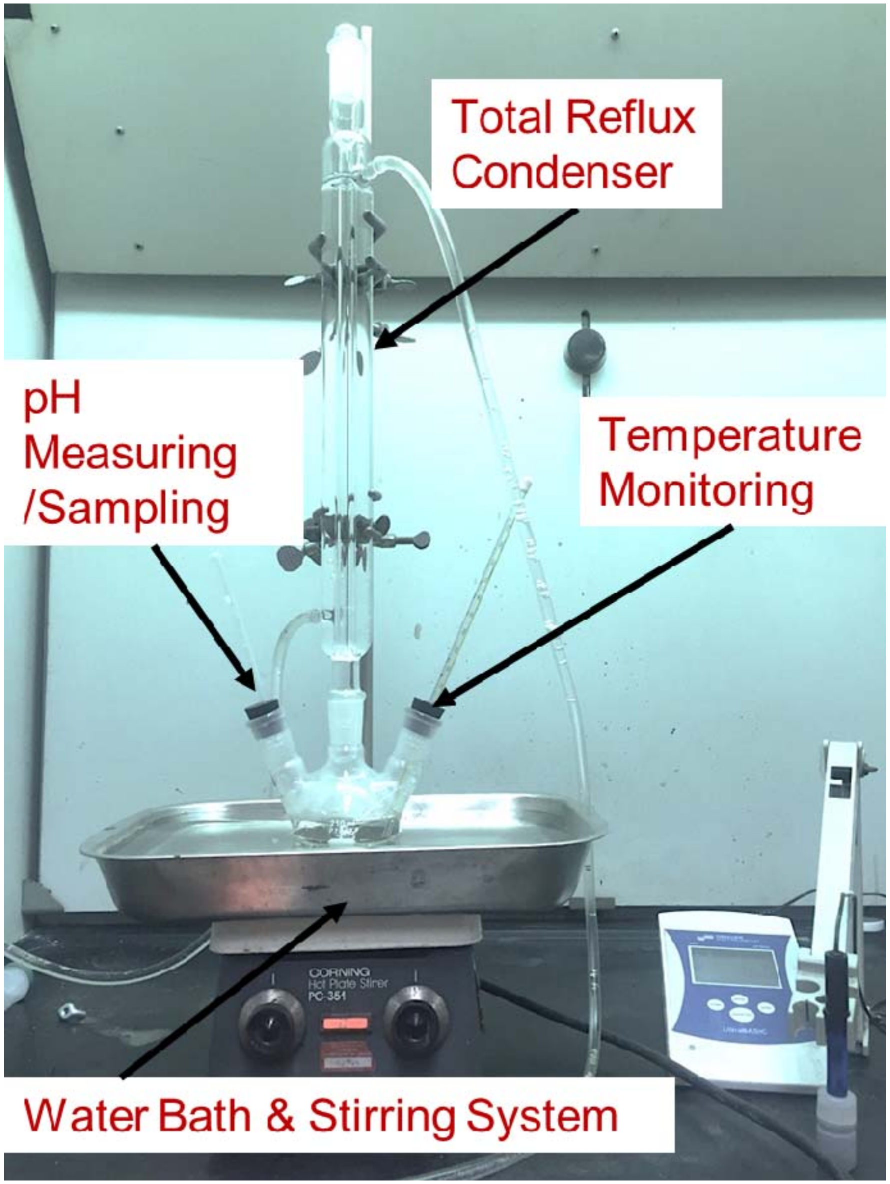
- Artificial Ion-Exchange Clay at 25°C

Lixiviant	Conc. (moles/l)	Feed		Solid Residue		REE Recovery (%)
		REE (ppm)	Wt. (g)	REE (ppm)	Wt. (g)	
$(NH_4)_2SO_4$	0.5	1812.5	15.0	726.8	14.9	60.1
A	0.5	1812.5	15.0	932.9	14.9	48.7
B	0.5	1812.5	15.0	1235.9	14.8	32.9
C	0.05	1812.5	15.0	643.3	14.4	65.9

Outline

- ✓ *REE Forms in Coal*
  - ✓ *Minerals*
  - ✓ *Ion Substitution*
  - ✓ *Organic Association*
- ✓ REE Concentration
  - ✓ *Physical Concentration*
  - ✓ Leaching
    - ✓ *Ion Exchange*
    - ✓ REE Leaching
  - Solvent Extraction
- ❑ Conclusions

Acid Leaching System



Objective:

To determine ion-exchangeable REE in coal refuse.

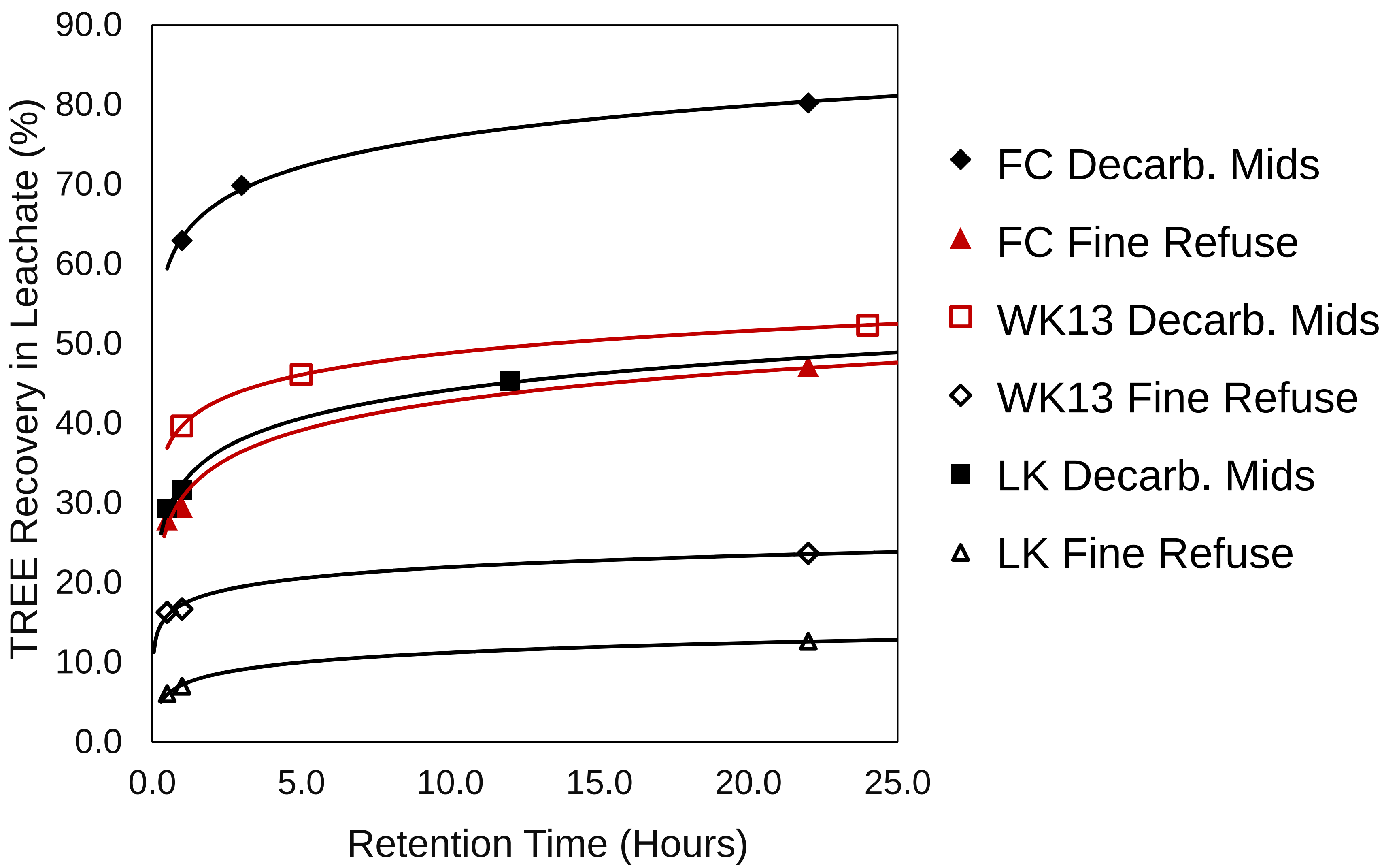
Conditions:

Leaching Solution: 1% Nitric Acid (pH =1.0)
Temperature: 80 ºC
Solid Concentration: 1%~5%
Analytical Method: ICP-OES

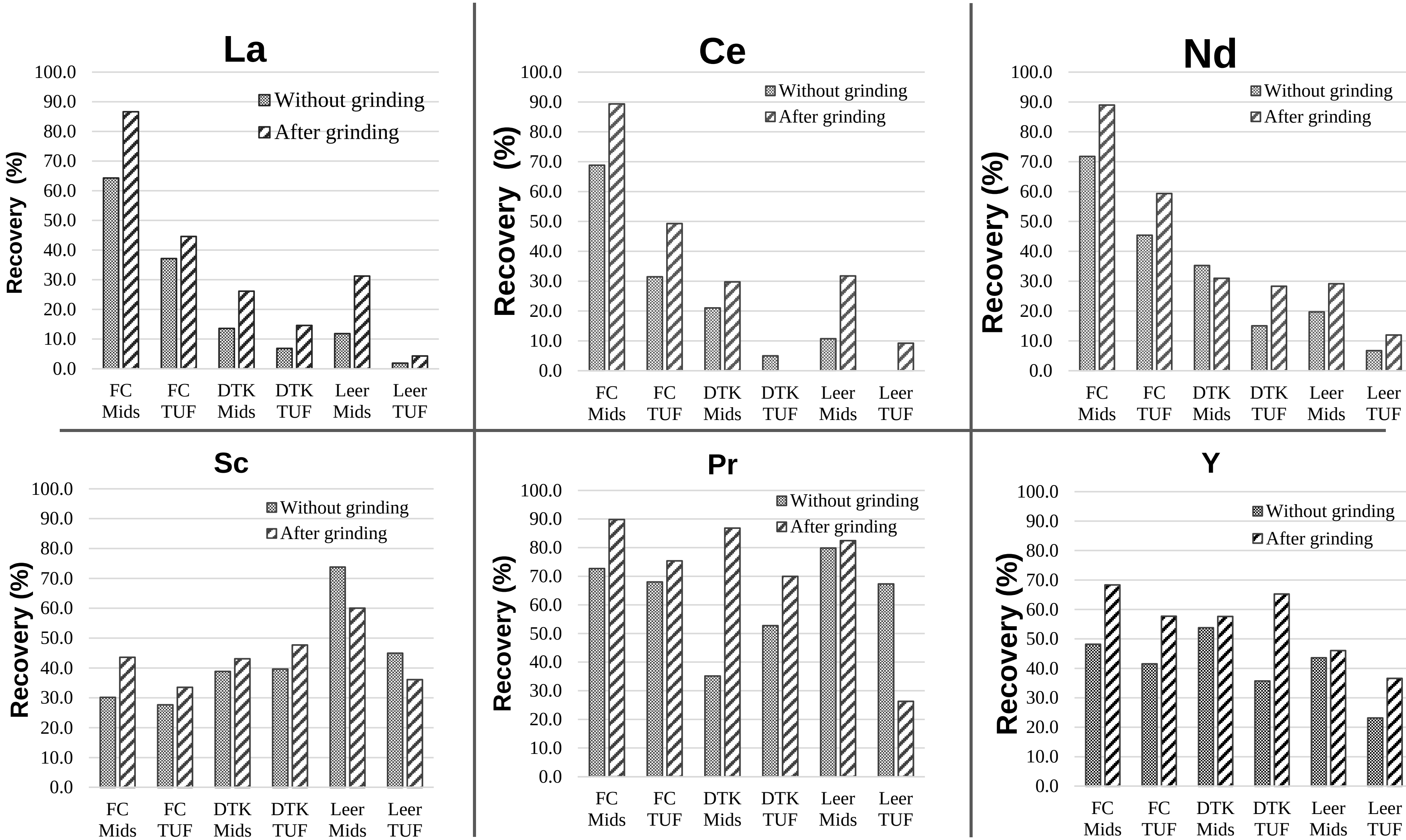
Variable:

Leaching Time

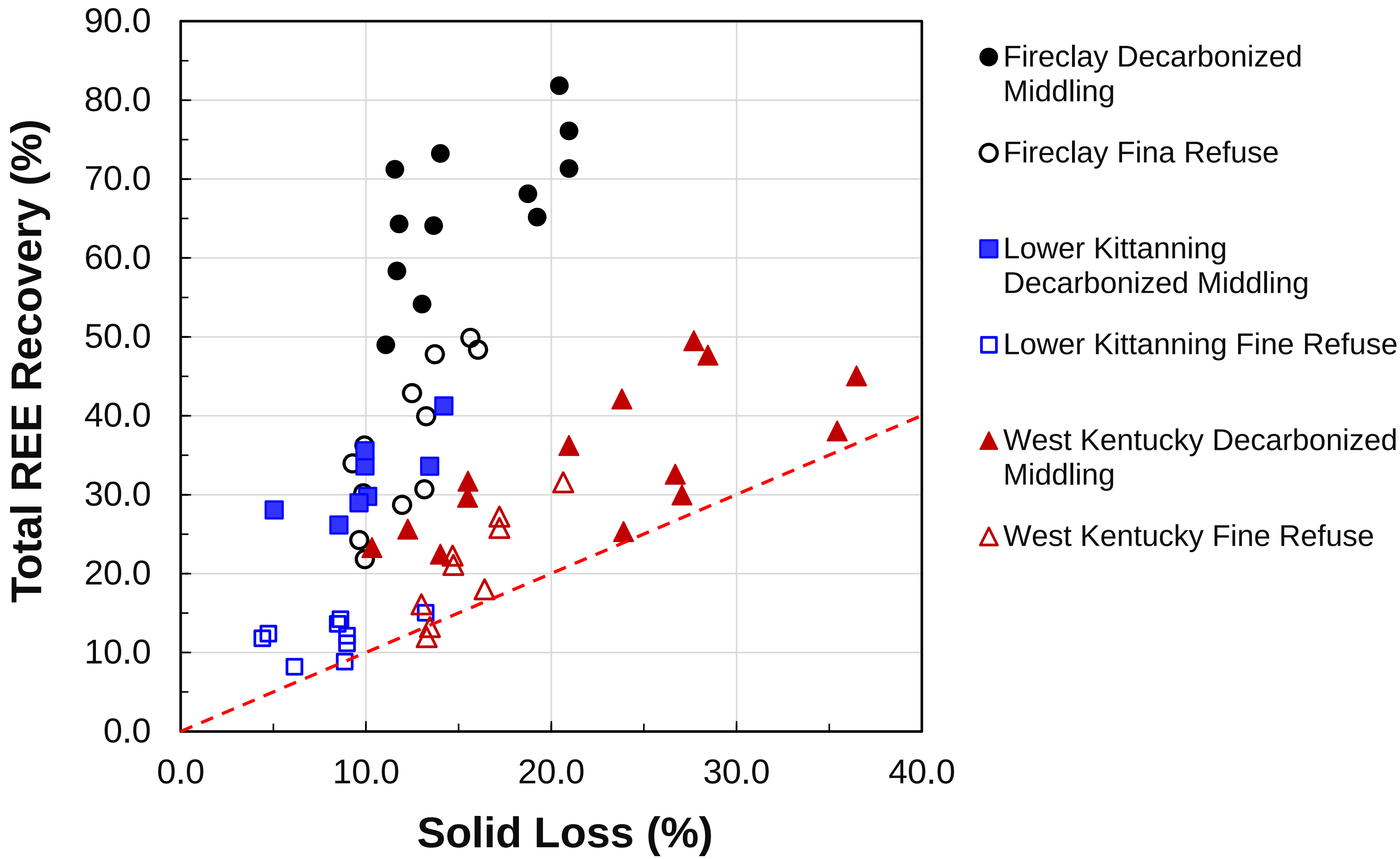
Leaching Kinetics



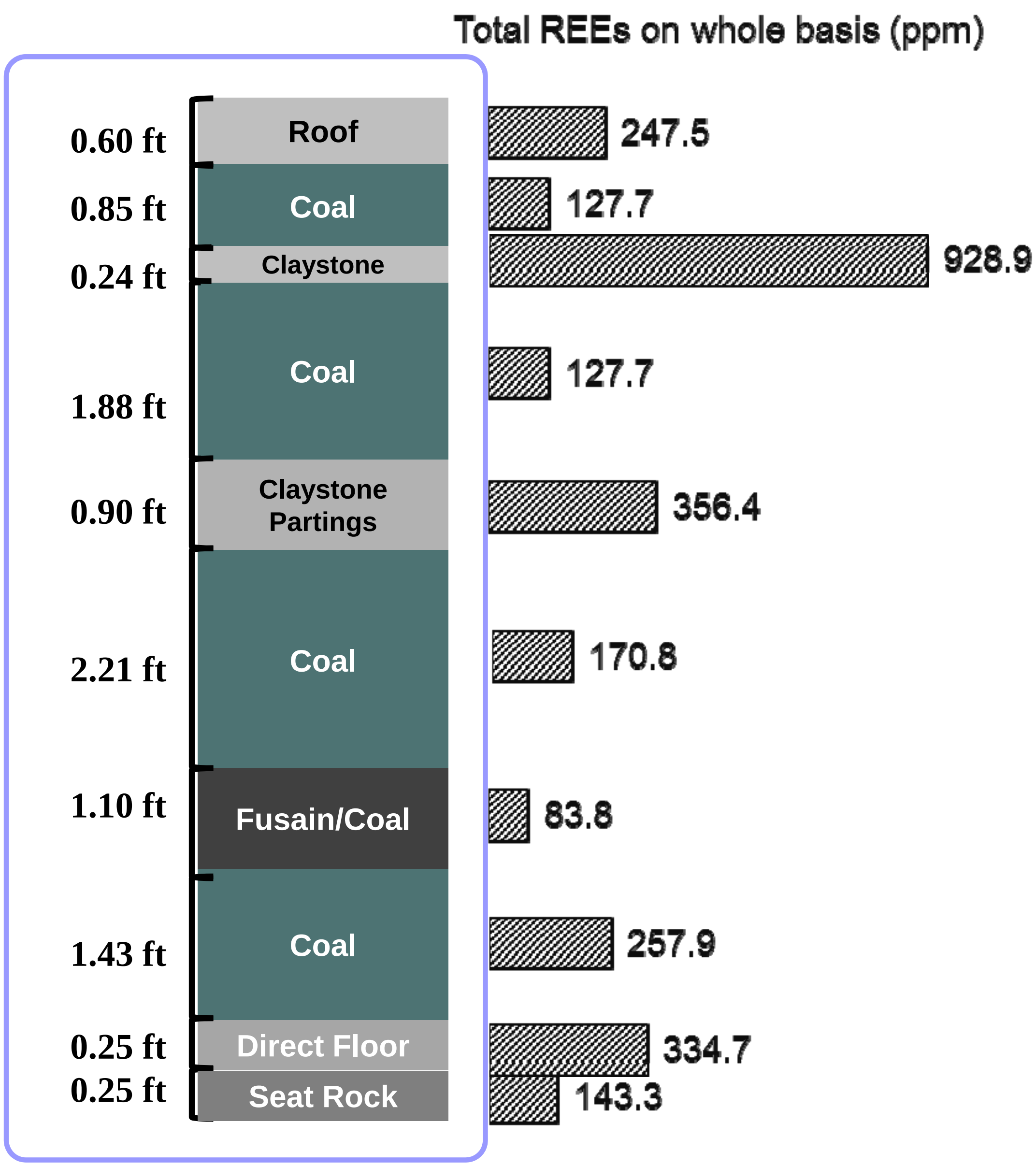
Differential REE Leaching



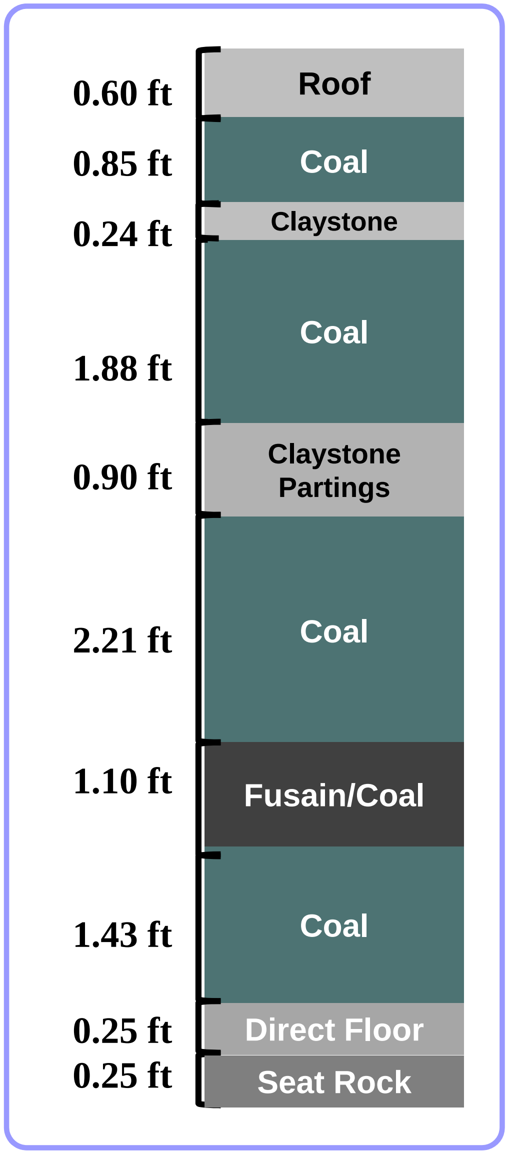
Leaching Selectivity



West Kentucky #13 Core



West Kentucky #13 Core

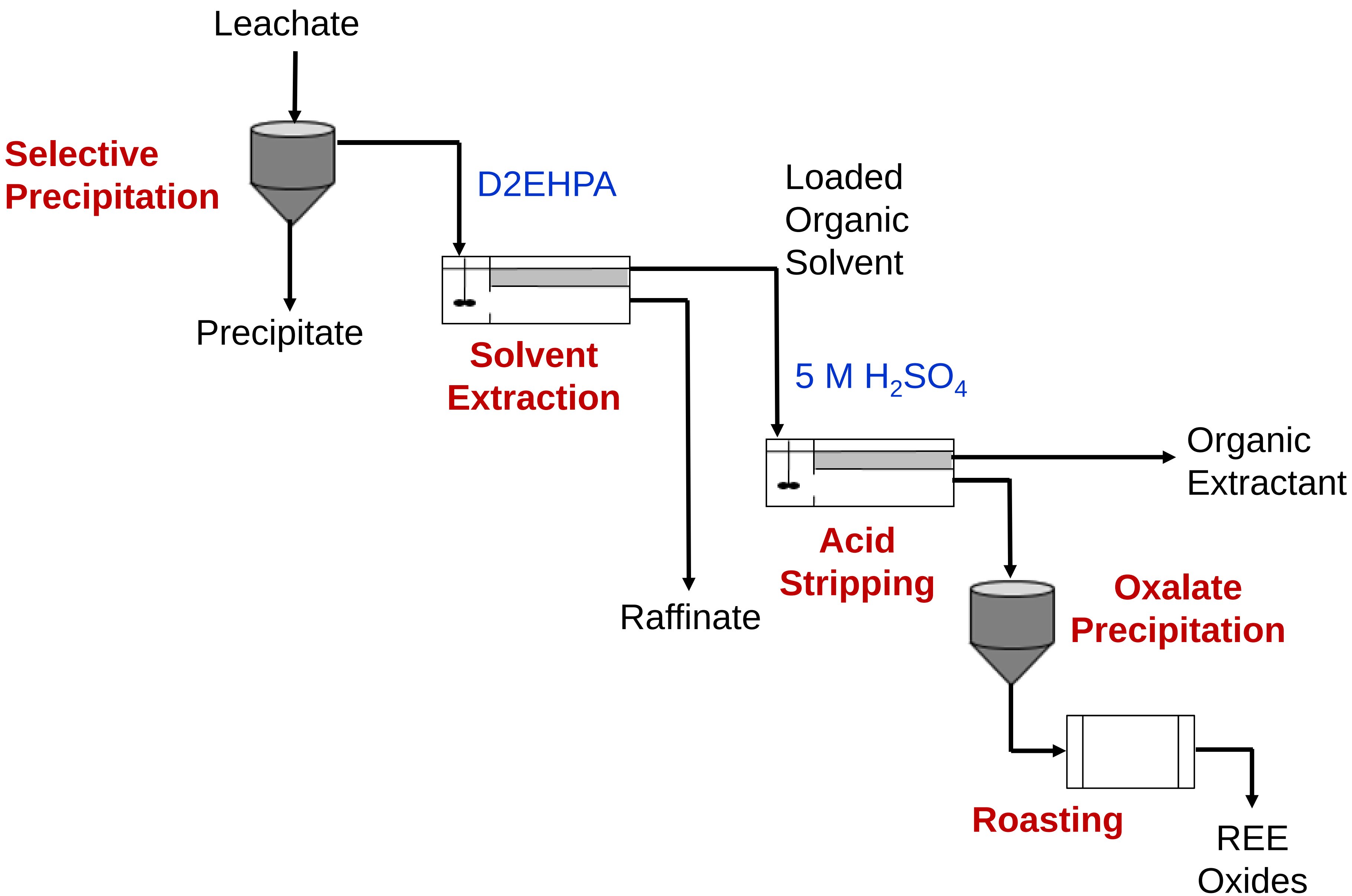


Description	Leaching Recoveries %		
	Total	LREE + Sc	HREE + Y
Roof	26.96	21.22	48.76
Coal	87.76	89.77	83.76
Claystone	53.10	34.12	88.39
Coal	87.76	89.77	83.76
Claystone Partings	9.61	6.67	22.42
Coal	75.68	67.73	94.82
Fusain	46.56	38.99	69.73
Coal	72.91	68.21	88.89
Direct Floor	60.53	48.40	83.02
Seat Rock	20.01	16.77	31.38

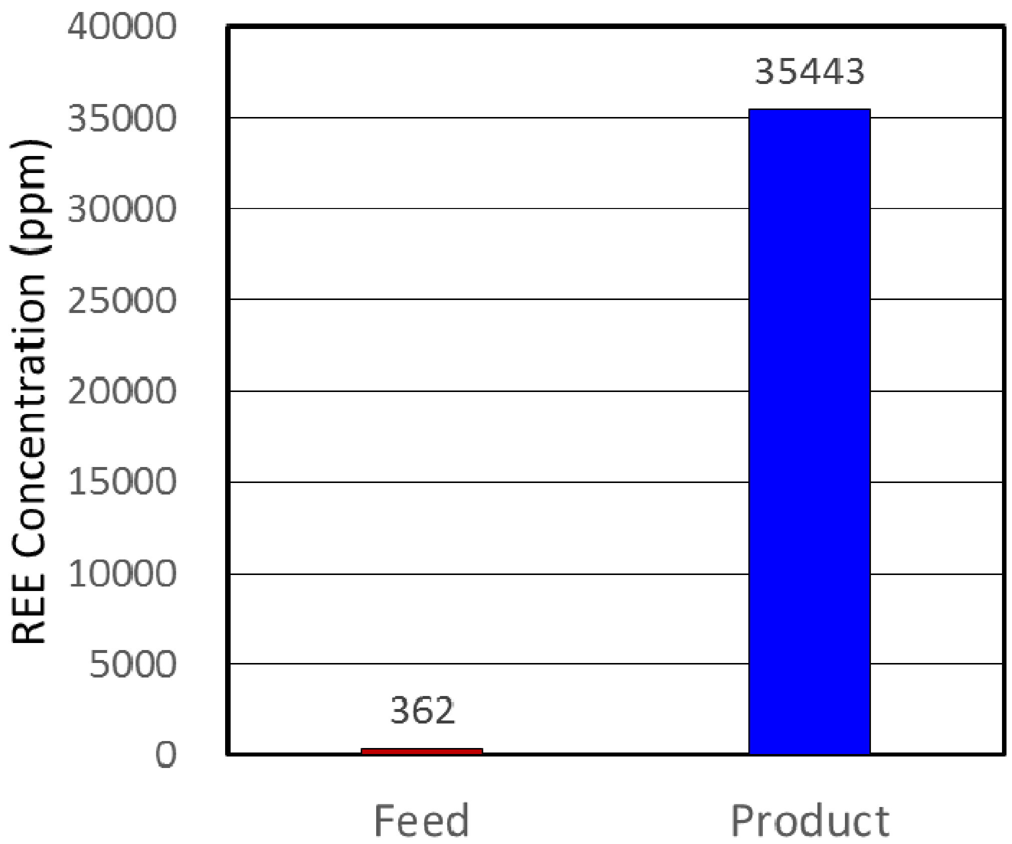
Outline

- ✓ *REE Forms in Coal*
  - ✓ *Minerals*
  - ✓ *Ion Substitution*
  - ✓ *Organic Association*
- ✓ REE Concentration
  - ✓ *Physical Concentration*
  - ✓ *Leaching*
  - ✓ Solvent Extraction
- ❑ Conclusions

REE Recovery from Leachate



Recent REE Concentration Results



Concentration Ratio = 98

Solvent Extraction Products

Rare earth content (ppm, dried mass basis)						
Rare Earth Element	Dotiki TUF	Dotiki Middling	Fireclay TUF	Fireclay Middling	Leer TUF	Leer Middling
Scandium	0	0	0	0	92	84
Yttrium	22579	34438	12126	22050	2446	177
Lanthanum	128	757	4146	28	6	85
Cerium	1694	7586	28615	527	2057	285
Praseodymium	465	1142	5200	150	188	150
Neodymium	3441	6021	20615	545	645	181
Samarium	3277	4610	8466	375	487	53
Europium	1083	1380	777	98	141	15
Gadolinium	8280	9152	6909	950	842	95
Terbium	1413	1519	851	360	135	10
Dysprosium	11295	11883	6312	4475	1107	75
Holmium	1268	1388	689	727	139	9
Erbium	2306	3149	1145	2392	295	17
Thulium	269	603	128	442	65	5
Ytterbium	329	1558	102	1228	149	9
Lutetium	23	171	35	123	22	2
Total	57852	85357	96117	34470	8816	1250

Outline

- ✓ *REE Forms in Coal*
  - ✓ *Minerals*
  - ✓ *Ion Substitution*
  - ✓ *Organic Association*
- ✓ REE Concentration
  - ✓ *Physical Concentration*
  - ✓ Leaching
    - ✓ Ion Exchange
    - ✓ REE Leaching
  - ✓ Solvent Extraction
- ❑ Conclusions

Summary

- Coal waste materials at three mining operations located in different coal basins were found to contain rare earth elements having significant contained REE values.
- Physical concentration of RE minerals from a thickener underflow was achieved using the HHS process. The TREE content increased from 0.033% ppm to 1.74%.
- Selective leaching of the TREEs in middling sources was successful with REE recovery values up to around 85%.
- Solvent extraction produced RE oxide products from each coal waste source. TREE concentrations up to 10% was achieved from around 300 ppm feedstocks.