Rare Earth Element Production from Coal

Rick Honaker and Jack Groppo
University of Kentucky

Roe-Hoan Yoon and Jerry Luttrell
Virginia Tech

Aaron Noble and John Herbst
West Virginia University

Professional Engineers in Mining (PEM)
Lexington, Kentucky
August 26th, 2016

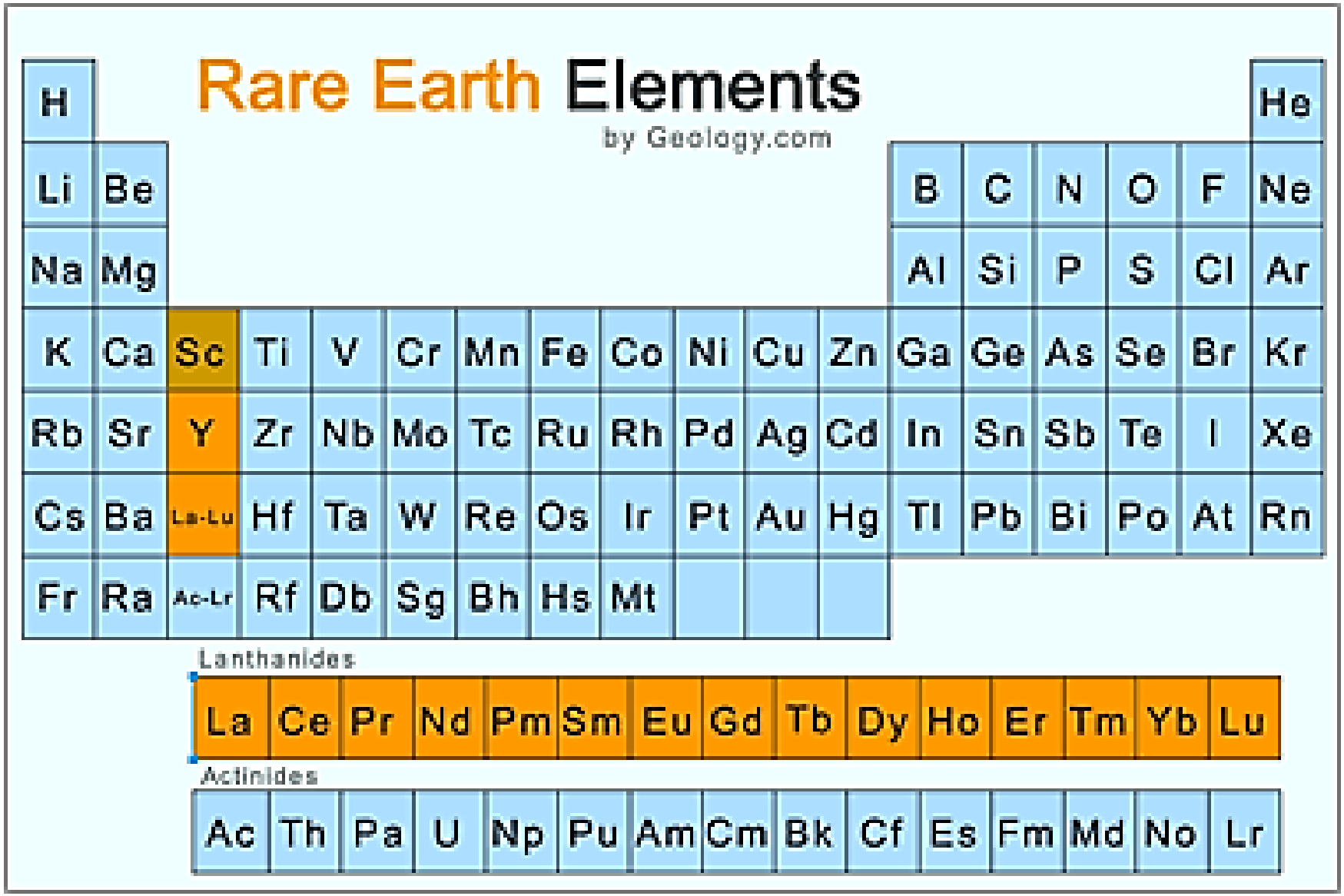
Acknowledgements

- U.S. DOE/NETL
- Blackhawk Mining
- Alliance Coal
- Arch Coal
- Mineral Refining Company (MRC)
- Dr. Ken Han, Hydrometallurgist
- Dr. Cortland Eble, KGS
- Dr. Jason Backus, KGS
- Dr. Jim Hower, CAER
- Graduate Students
  - Wencai Zhang
  - Xinbo Yang
  - Alind Chandra

Outline

- ✓ Background
- REE Value
- REE Forms in Coal
  - Minerals
  - Ion Substitution
  - Organic Association
- REE Concentration

What are Rare Earths?

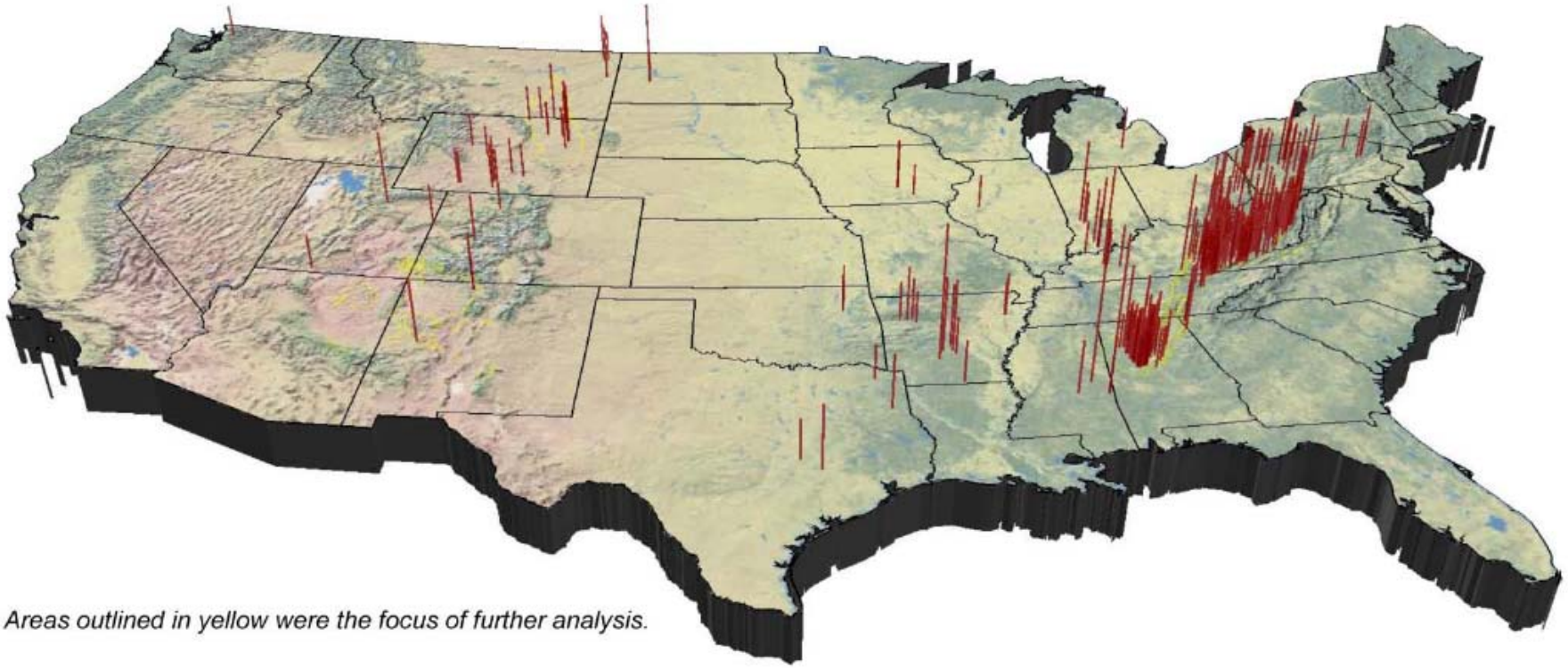


The Significance of Rare Earths

- Numerous high technology applications:
  - Magnets
  - Batteries
  - Phosphors
  - Catalysts

- Used in end products in these sectors:
  - Health care
  - Transportation
  - Green Energy (Wind, Solar, Hybrid Vehicles)
  - Defense
- Rare Earth Chemistry in North America Supports:
  - $329 billion in economic output
  - Associated employment of over 618,000 people

Rare Earth Concentrations > 1000 ppm



Areas outlined in yellow were the focus of further analysis.

Outline

- ✓ *Background*
- ✓ *REE Value*
- REE Forms in Coal
  - Minerals
  - Ion Substitution
  - Organic Association
- REE Concentration

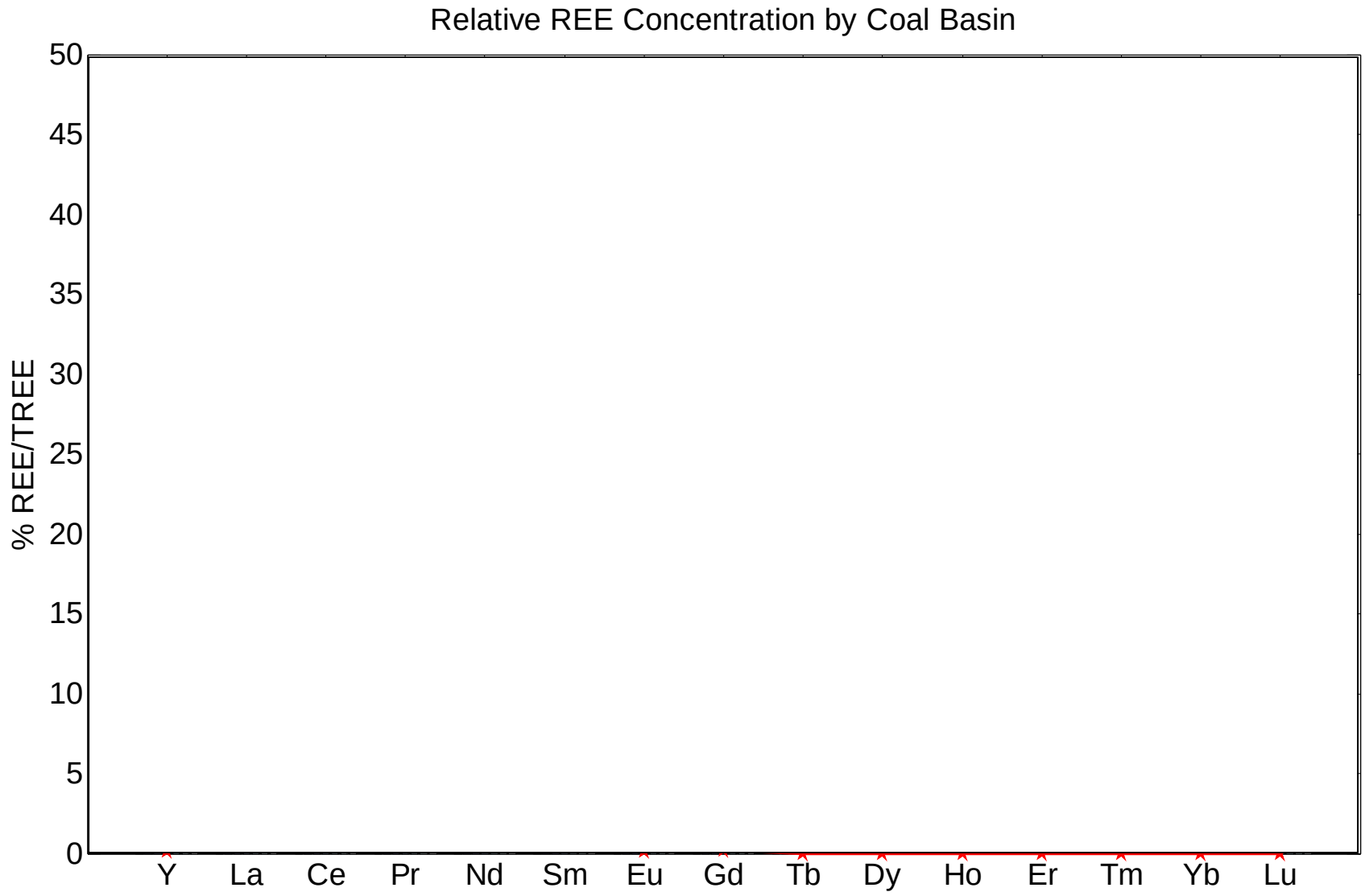
Rare Earth Pricing

However…

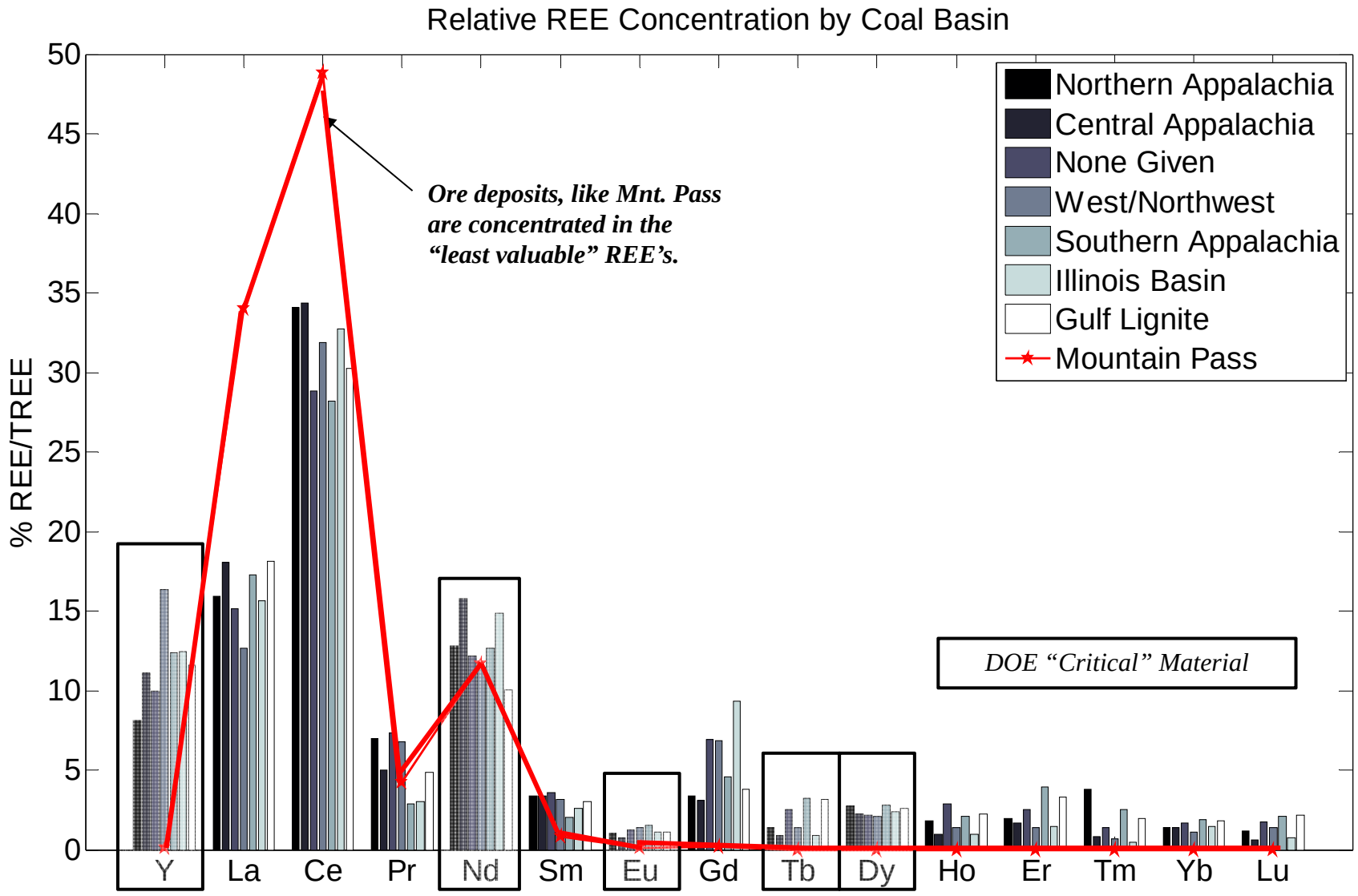
- "Rare Earths" is a plural concept.
- Not all the elements are created equally...
- Not all are equally desired...

	Oxide Price 2009 ($/kg)	Oxide Price 2015 ($/kg)
Lanthanum	30	2.35
Cerium	30	1.9
Praseodynium	38	59
Neodynium	42	41
Samarium	130	1.9
Europium	1600	207
Gadolinium	150	11
Terbium	900	495
Dysprosium	170	235
Holmium	750	38
Erbium	100	39
Thulium	1500	800
Ytterbium	325	24
Lutetium	1800	894
Yttrium	44	5.45

REEs is a “Plural” Term

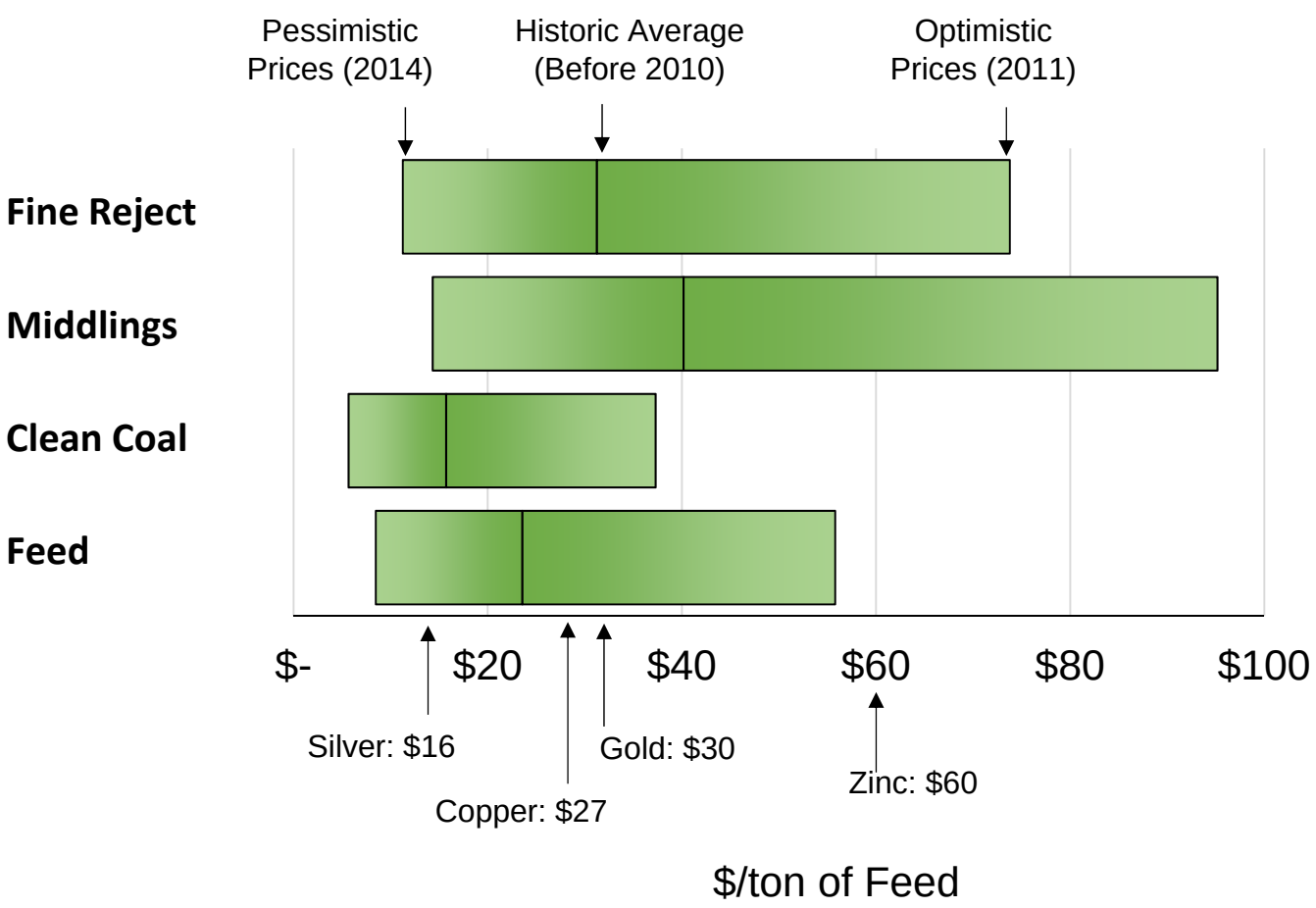


REEs is a "Plural" Term



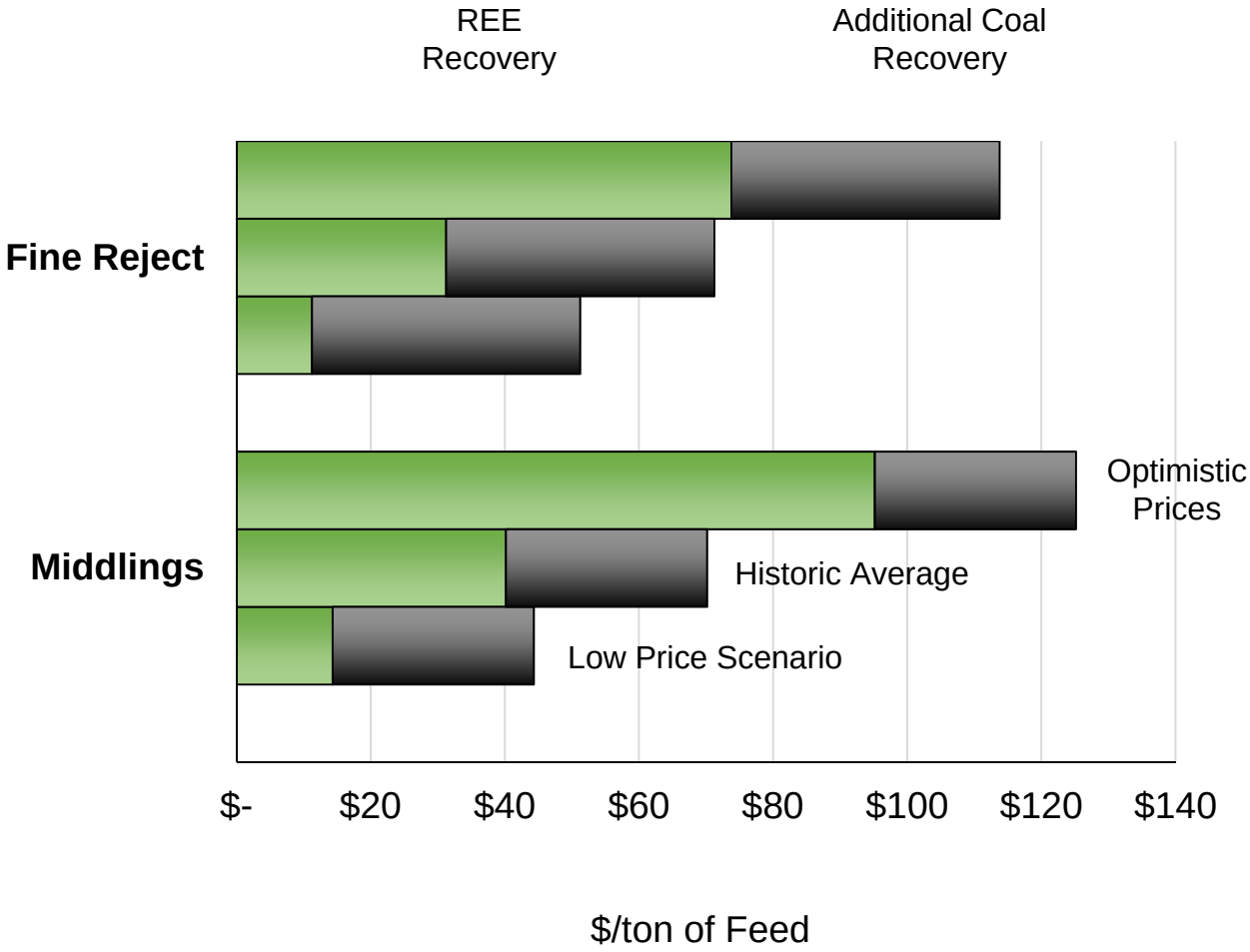
Fire Clay Coal Sample

Contained Value of REEs in 1 Ton of Material



Effect of Additional Coal Recovery

Contained Value of REEs in 1 Ton of Material



Outline

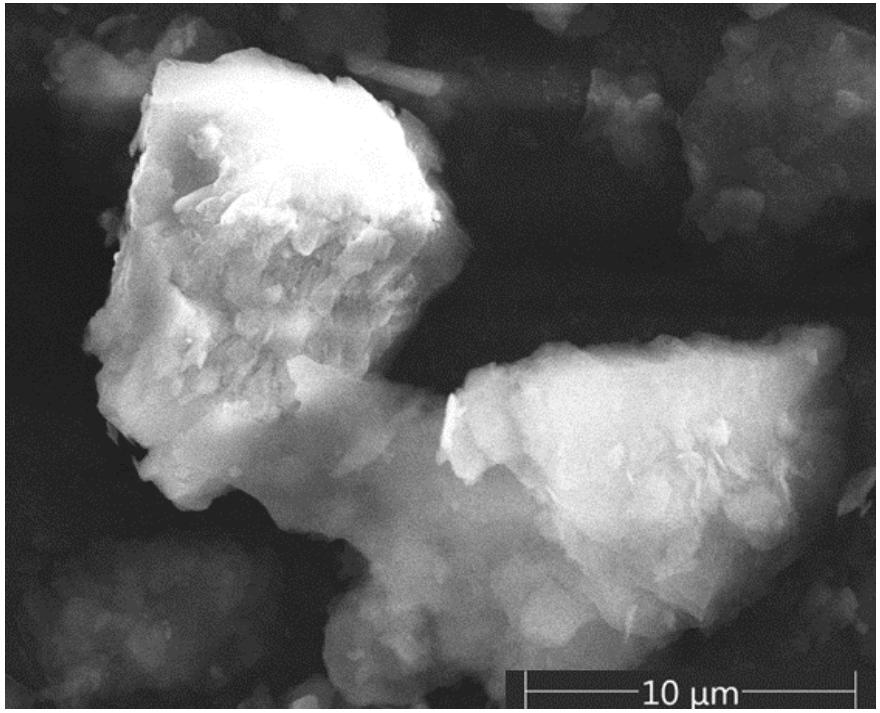
- ✓ *Background*
- ✓ *REE Value*
- ✓ REE Forms in Coal
  - Minerals
  - Ion Substitution
  - Organic Association
- REE Concentration

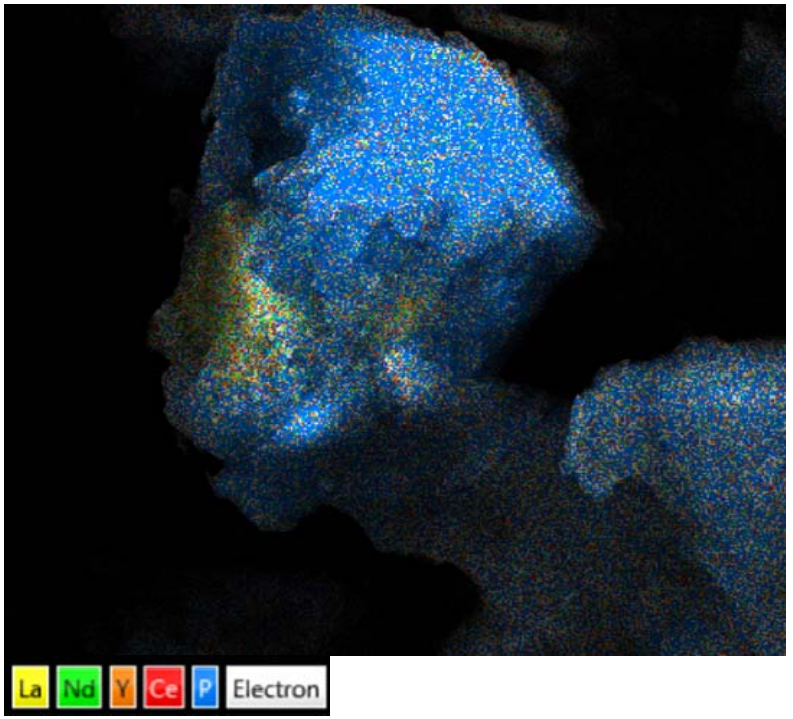
REE Forms in Coal

- Mineral association
  - monazite $(Ce,La,Pr,Nd,Th,Y)PO_4$
  - xenotime YPO_4
  - bastnaesite $(Ce, La)CO_3F$
  - other
- Ion substitution in clay
- Organic association

Element Mapping Energy Dispersive Spectroscopy

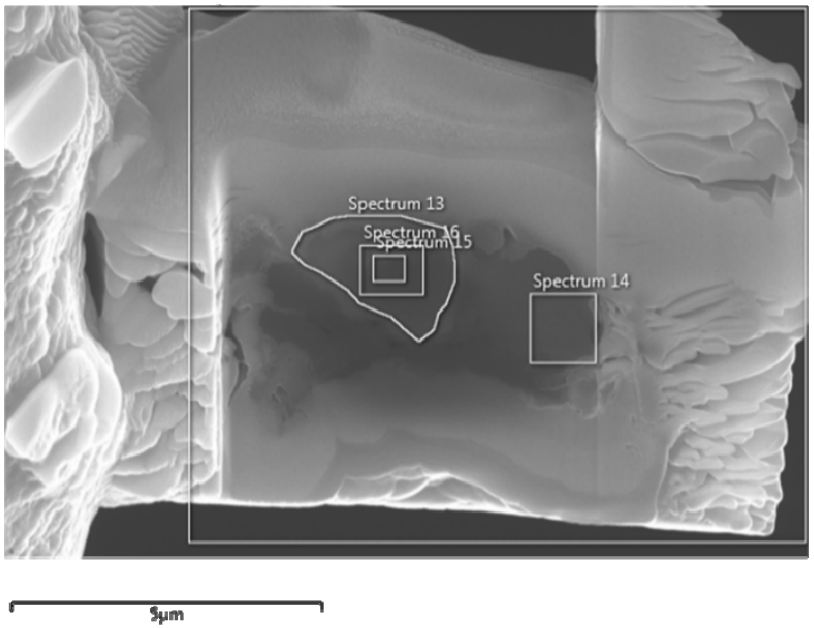
Fire Clay Thickener Underflow

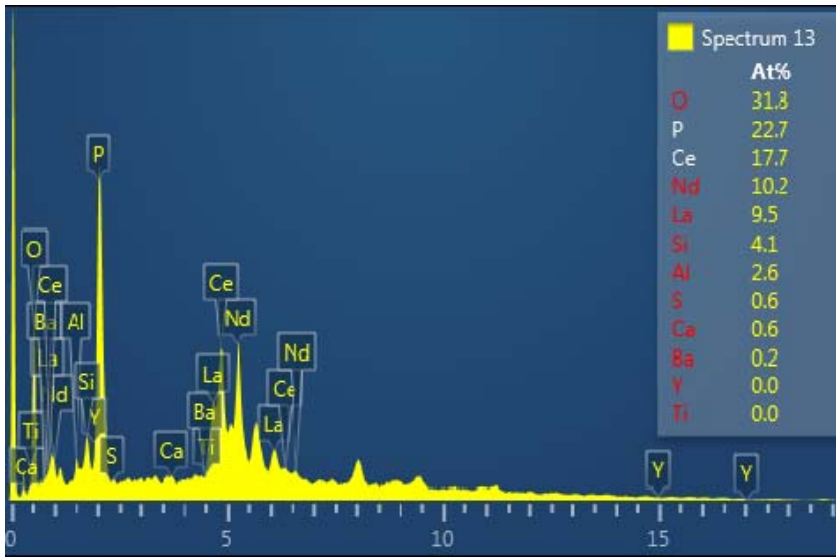




- RE mineral particles have a top size of around 10 microns and a bottom size of around 150 nm.

REE Minerals in Coal

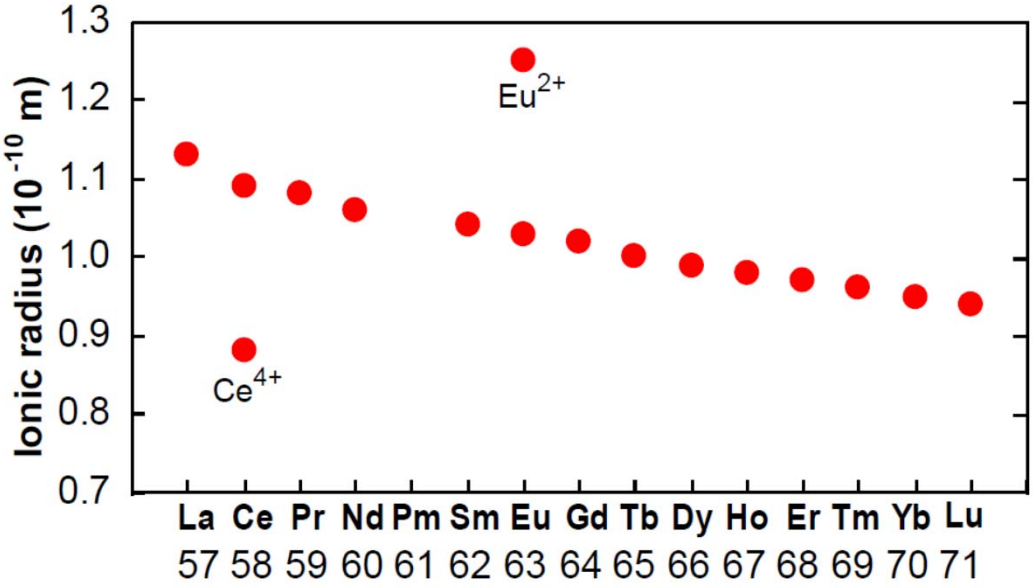


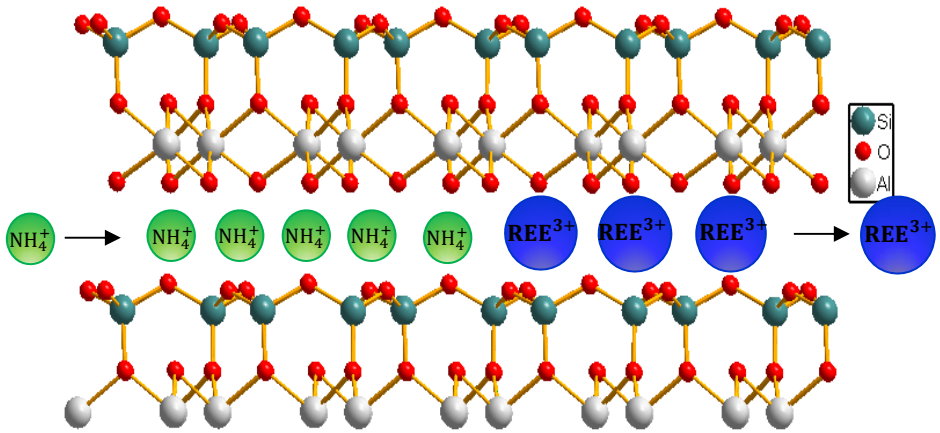


- Ce + La + Nd = 36.7%
- High phosphorus content indicates nearly pure monazite mineral
- Confirmed by TEM.

REE Substitution

- 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 $(NH_4)_2SO_4$



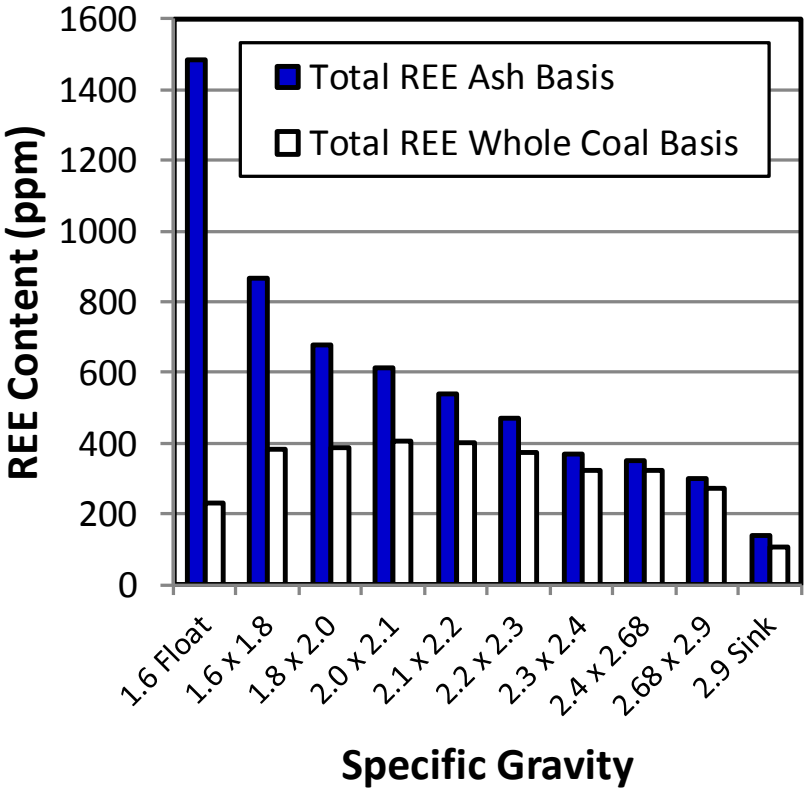


Outline

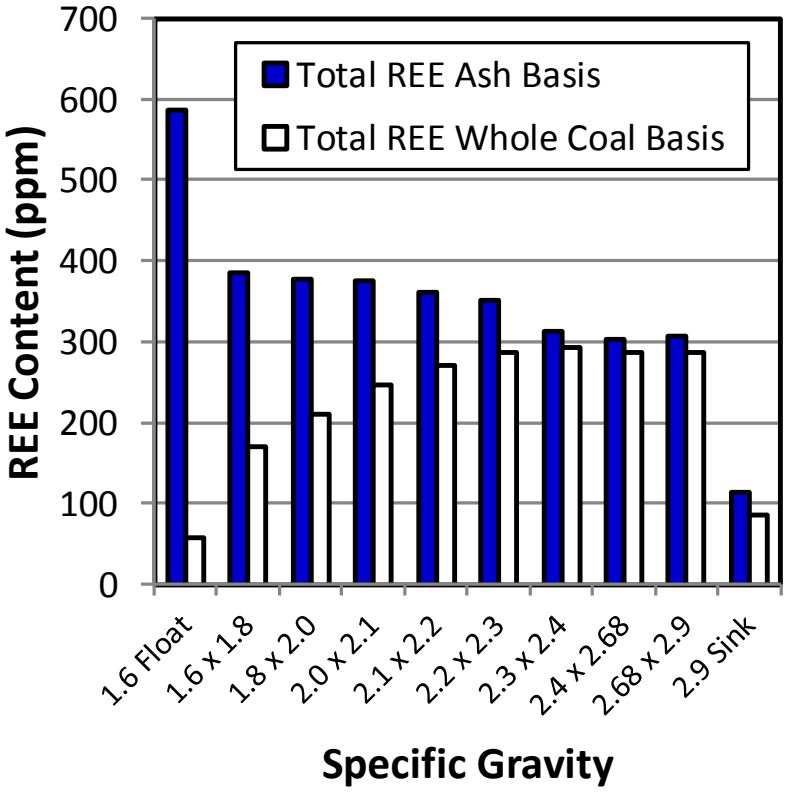
- ✓ *Background*
- ✓ *REE Value*
- ✓ *REE Forms in Coal*
  - *Minerals*
  - *Ion Substitution*
  - *Organic Association*
- ✓ REE Concentration

REE Density Partitioning

Fire Clay Coal



Eagle Coal



REE Concentration Considerations

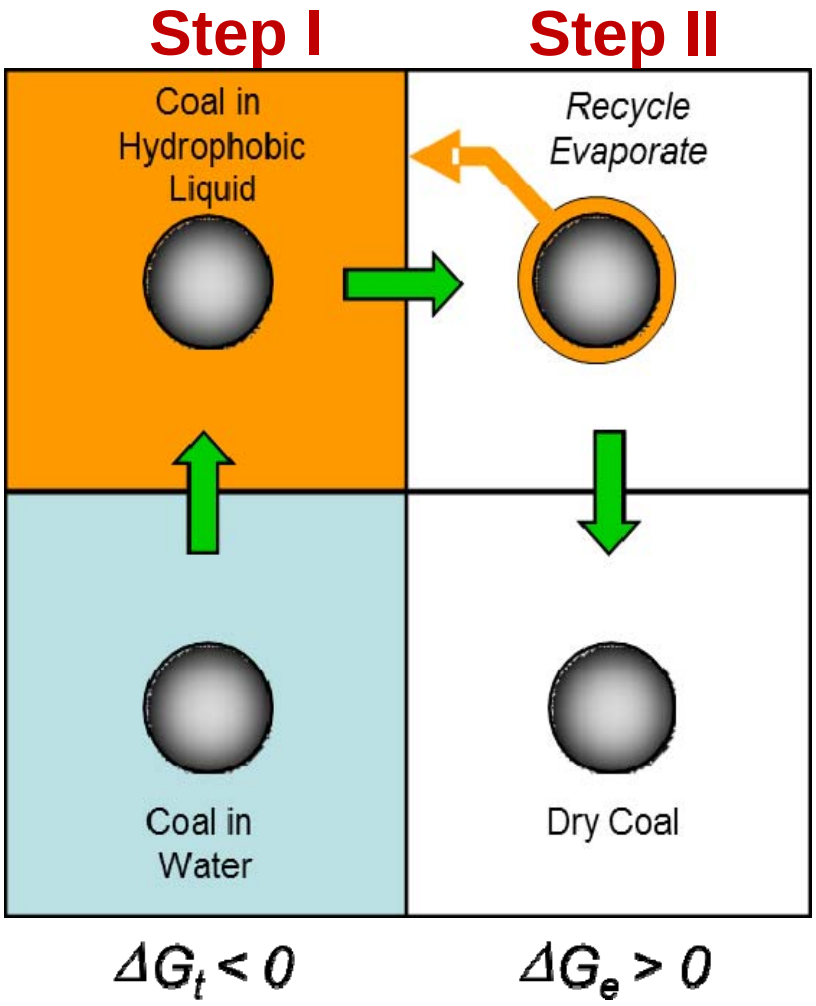
- Coarse reject streams
  - Uneconomical to crush and grind the entire material.
- The lowest density fractions
  - Uneconomical to crush and grind the entire material.
- Ultrafine waste processing stream
  - Least amount of energy required for liberation purposes.
- The 1.60 x 2.00 SG fraction
  - Typically rejected to meet coal quality specs
  - Typically ~ 5% to 10% of total plant feed.
  - Crushing and grinding liberates both coal and RE minerals.
  - Heavy REE concentrations are significant.

Feed Stocks Evaluated

- Coal Sources
  - Fire Clay
  - West Kentucky No. 13
  - Lower Kittanning
- Process Streams
  - Thickener Underflow
  - Middlings
  - Coarse Reject

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

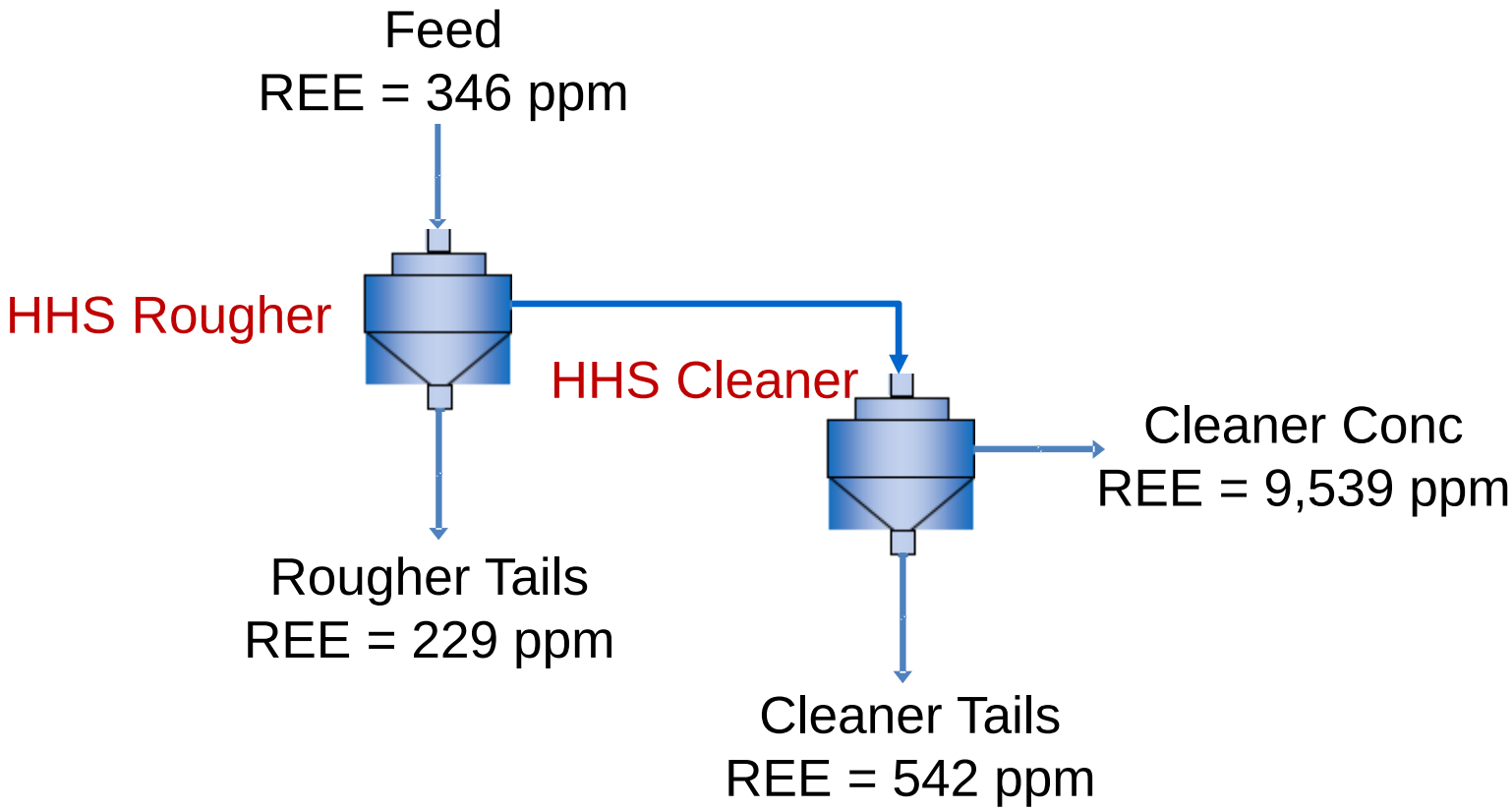


MRC
MINERALS REFINING COMPANY

HHS Process Photos

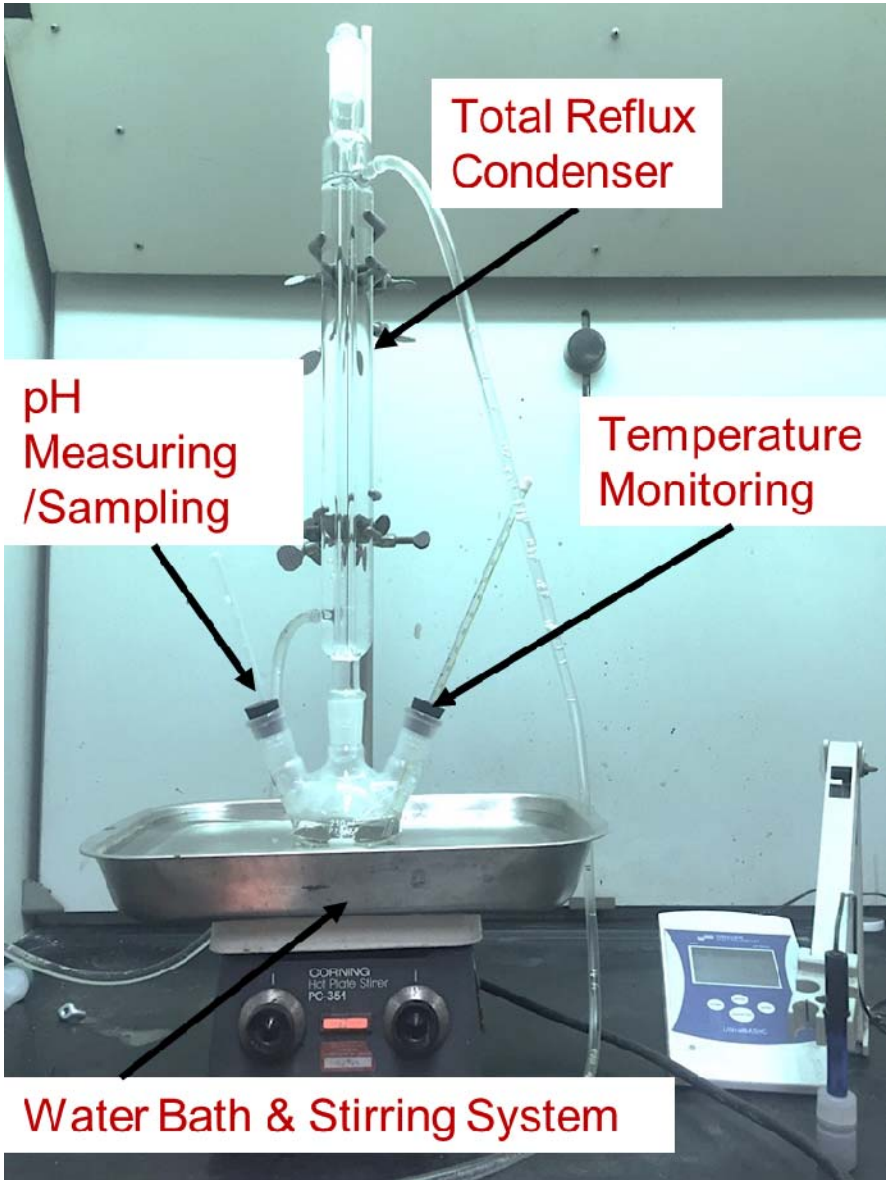
MRC
MINERALS REFINING COMPANY

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

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:

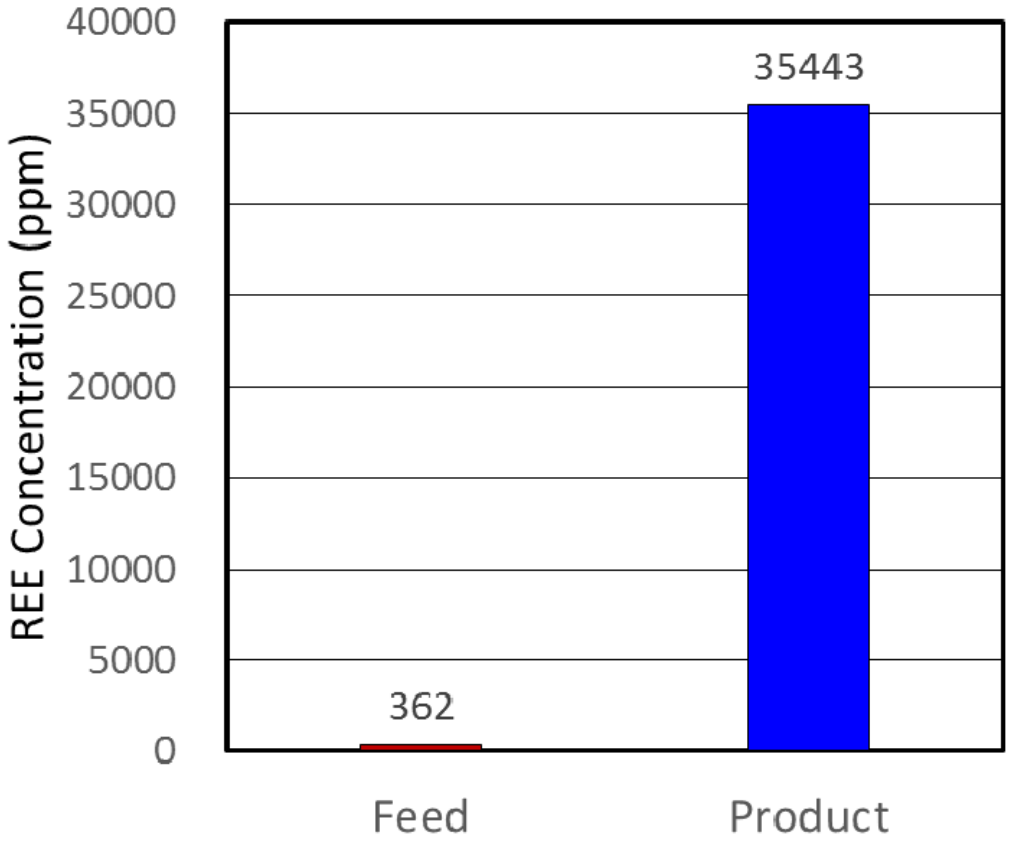
Leaching Time

Leaching Recovery

Fire Clay Middlings

P80 (microns)	Total REE Recovery (%)	LREE Recovery (%)	HREE Recovery (%)
8.7	83.7	86.9	64.8
7.3	84.3	87.7	65.0
6.5	83.6	87.1	63.2
5.0	82.3	85.9	62.1
0.9	82.0	86.2	59.2

Recent REE Concentration Results



Concentration Ratio = 98

Recent REE Concentration Results

Stream	Light Rare Earth Element Content (ppm)					
	Sc	Sm	La	Ce	Pr	Nd
Feed	21	12	60	135	19	53
Product	34	2063	3834	16228	1723	7446
Ratio	2	179	64	121	89	140

Stream	Heavy Rare Earth Element Content (ppm)									
	Y	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Feed	32	2	10	1	6	2	6	1	4	NA
Product	1200	173	1283	3	935	112	269	114	7	20
Ratio	37	99	127	4	161	74	48	94	2	NA

Summary

- REEs exist in mineral and ion exchange form in high rank coals with compositions of each varying significantly.
- RE minerals of monazite, xenotime and bastnasite have been identified with grain sizes from a couple hundred nanometers to ten microns.
- Thickener underflow and middlings material offers an excellent opportunity for coal and REE recovery.
- HHS process has successfully concentrated REE minerals from 346 ppm to 9,539 ppm.
- Solvent extraction produced a REE oxide concentrate containing 35,443 ppm .