

Feasibility of Recovering Rare Earth Elements from Thickener Underflows

by

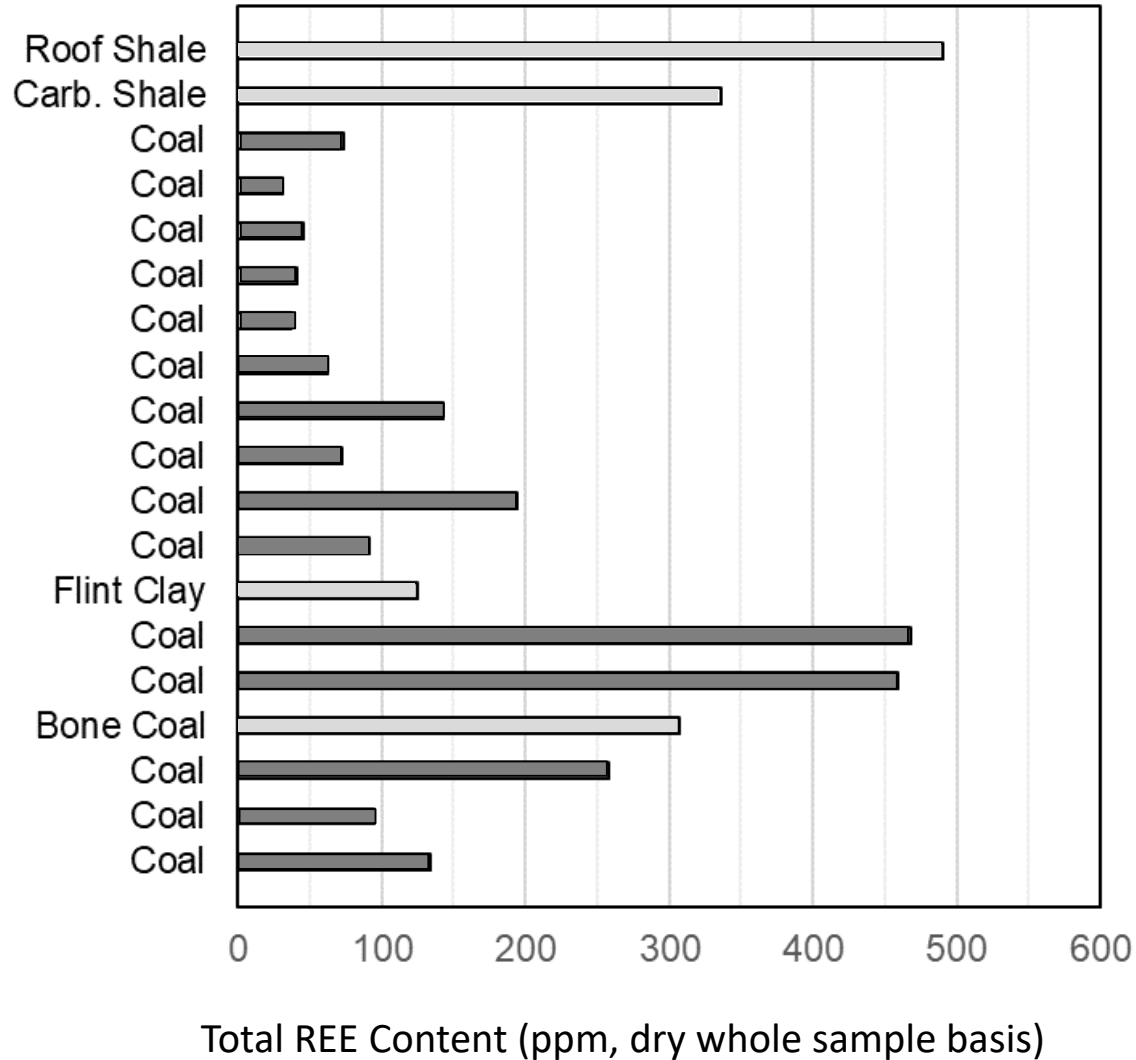
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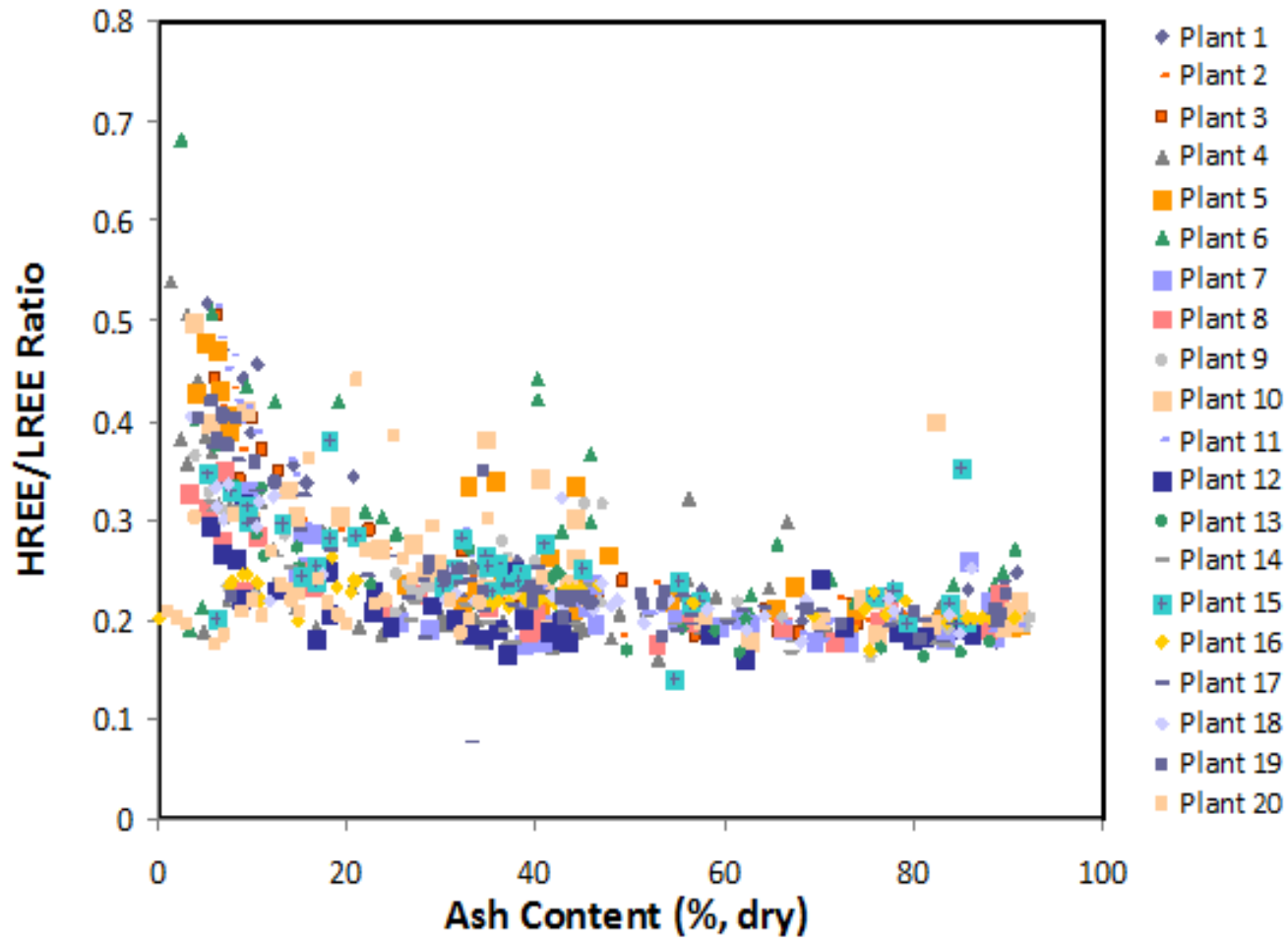
*2019 Project Review Meeting
for Crosscutting Research for Rare Earth Elements
April 9-11, 2019
Omni William Penn Hotel, Pittsburgh, PA*

Analysis of Channel Samples

Fire Clay Coal Seam



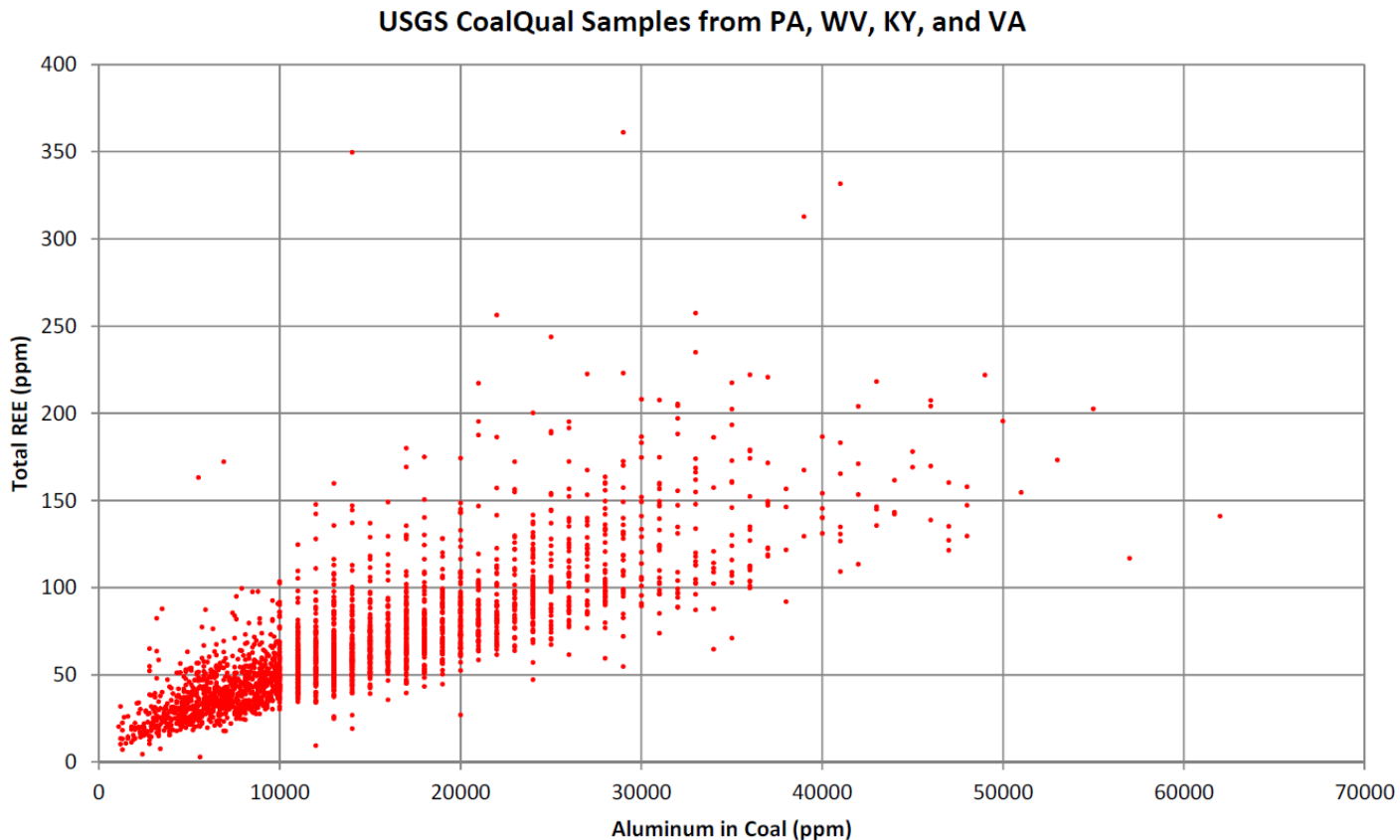
H vs. L REE Ratio



USGS Coal Quality Data Base

(Bryan et al. 2015)

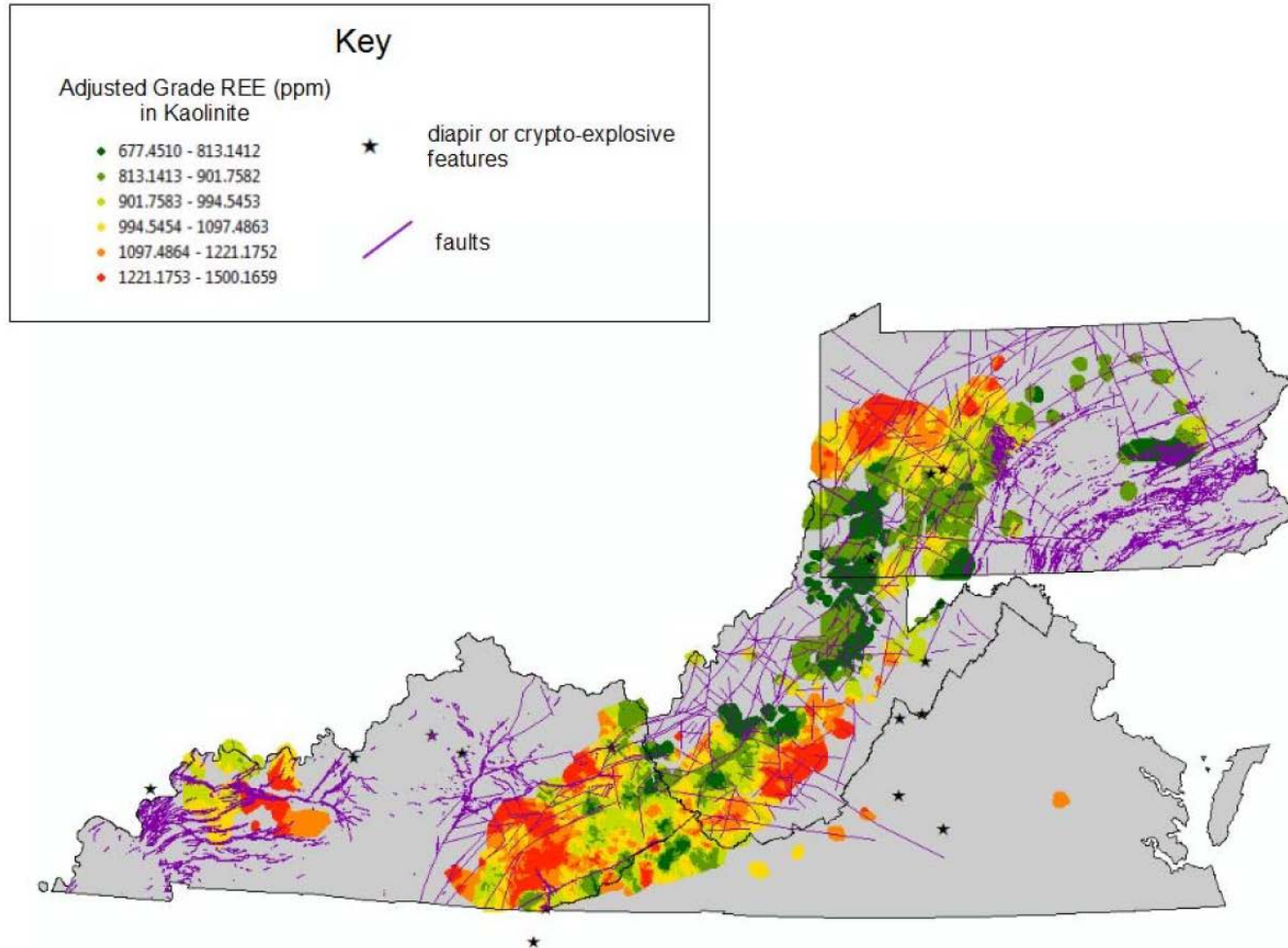
- REEs are mostly associated with kaolinite



- 10.9 MM tons at 500 ppm cut-off grade

REE Grades in Kaolinite

(Calculated, Bryan et al. 2015)



- REE grades on clay are 5-6 times higher than whole coal.

Ion-Adsorption Clay (IAC)

□ South China

- “Weathered crust elution-deposited rare earth ore”
- 0.05-0.3% REEs
- Physisorbed by double-layer force

□ Low-cost extraction process

- Desorbed by ion-exchange
- Precipitated by oxalic acid and roasted to REOs.

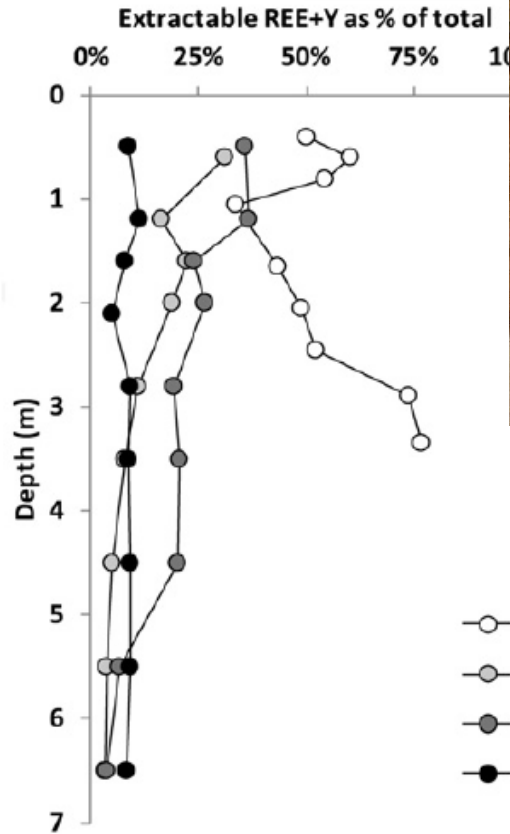
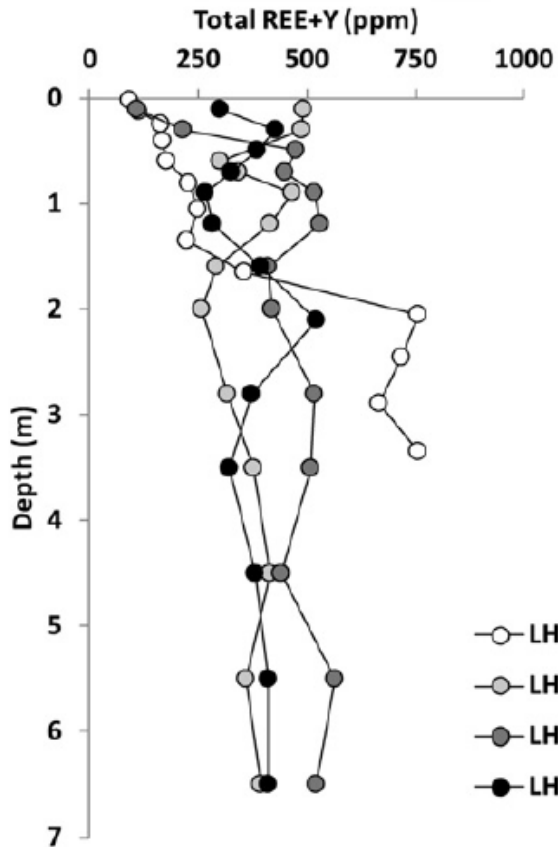
□ >80% of the world’s HREEs

□ >35% of total Chinese REE production



IACs in US?

Bern et al, J. Geochemical Exp. 172, 29 (2017)



Liberty Hill, South Carolina



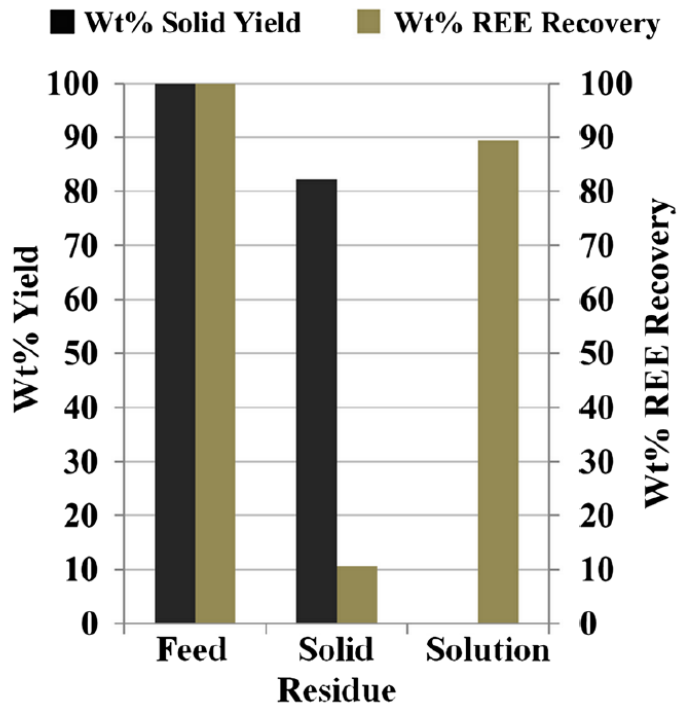
Stewartville, Virginia

Upper Kittanning Coal, PA

Ion-Exchange Leaching

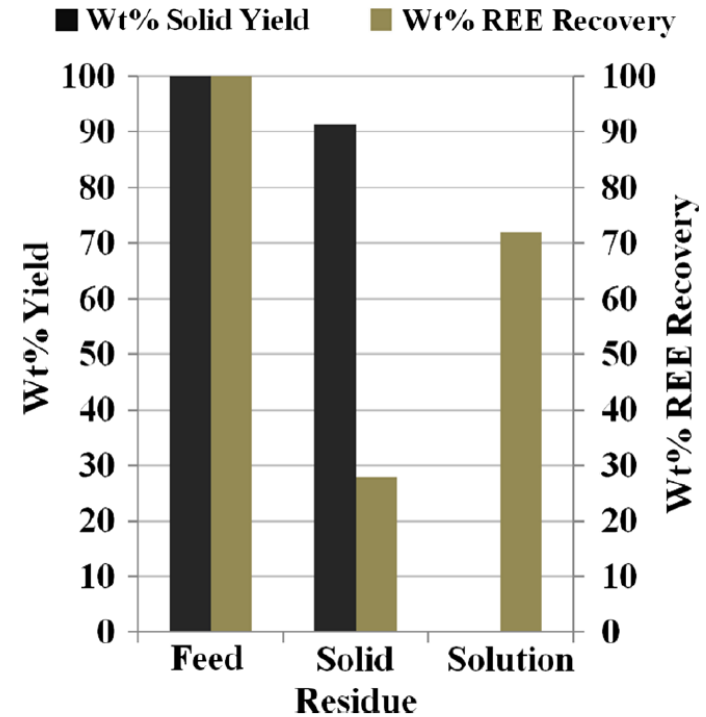
Sample A

- Top of the coal seam



Sample B

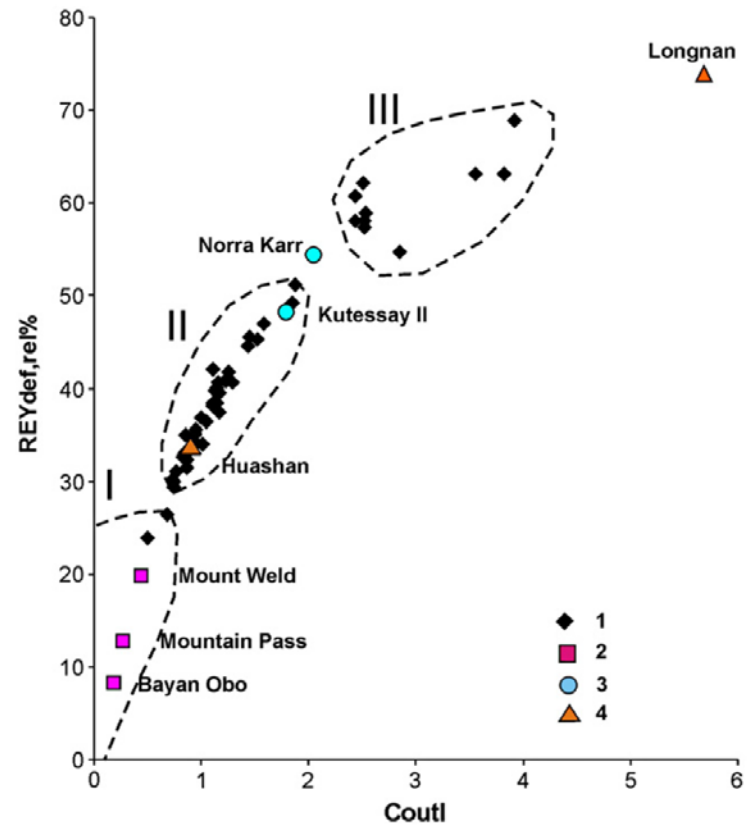
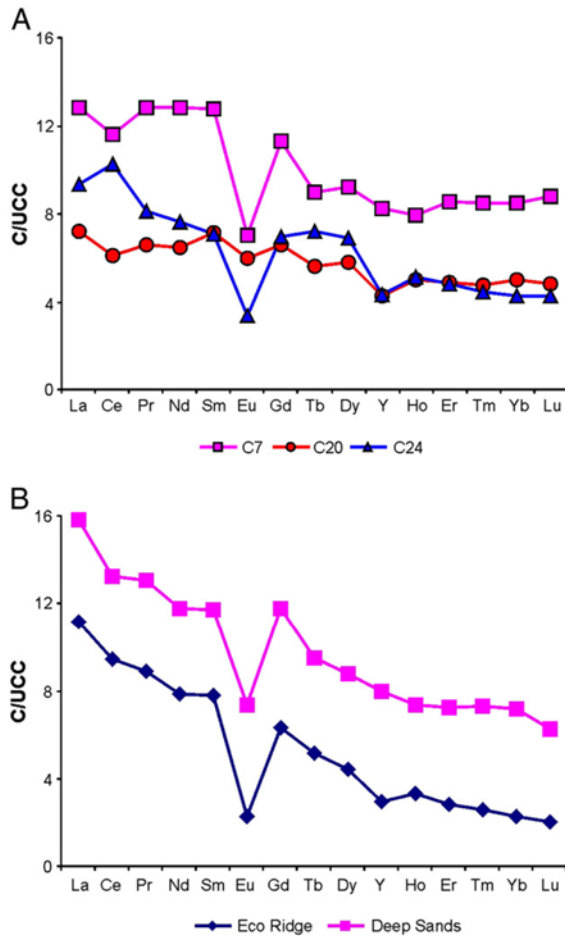
- Just below Sample A



595x10 μm sample in 1 M $(\text{NH}_4)_2\text{SO}_4$
1 hr contact time

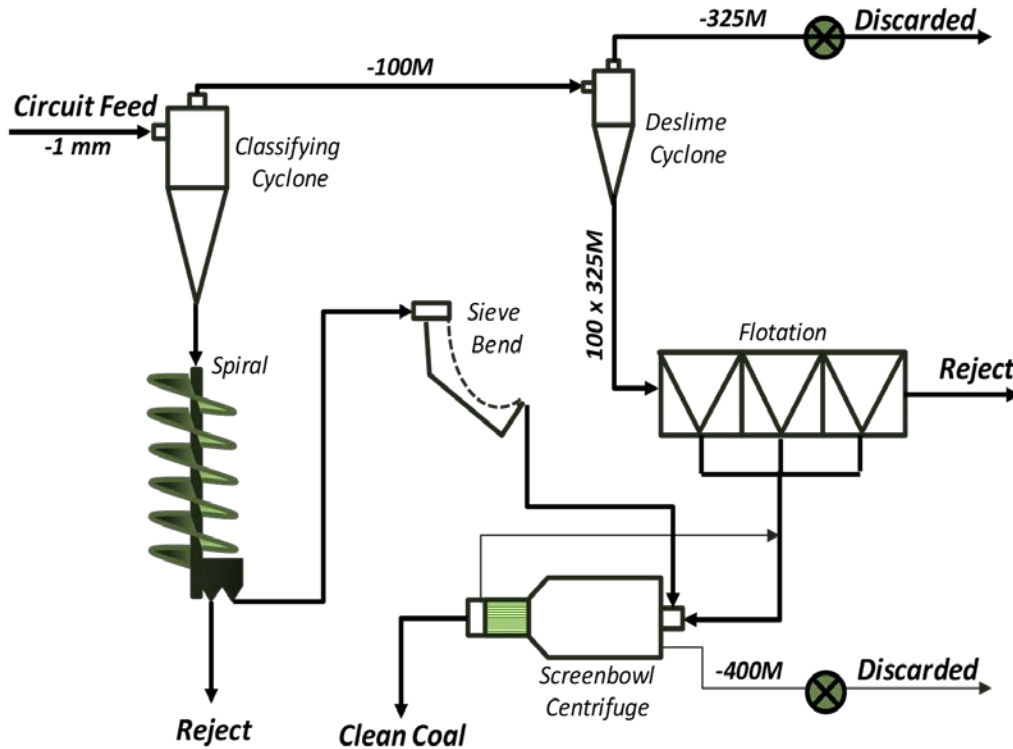
Mineral Matter in Coal: A Rich Source of HREEs

(Serendin and Dai, 2013)

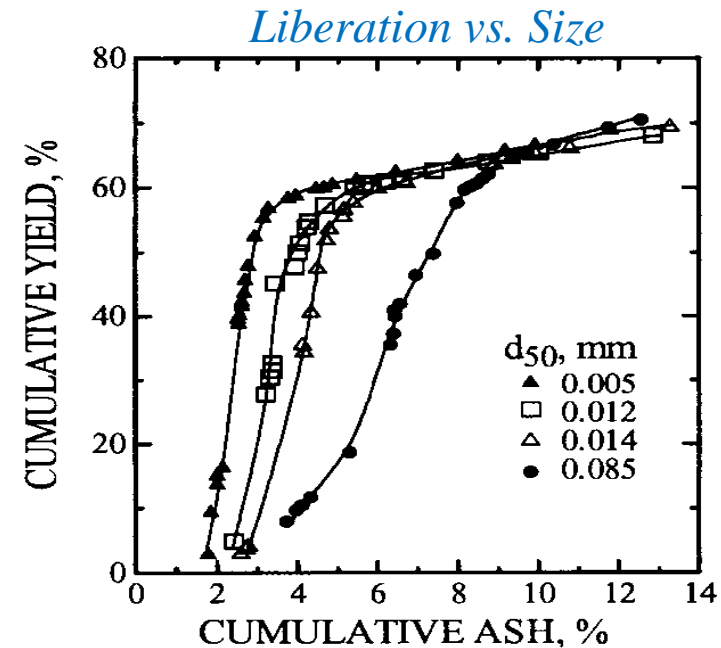


HREEs have higher adsorbabilities on clay than LHRs.

Fine Coal Cleaning in US



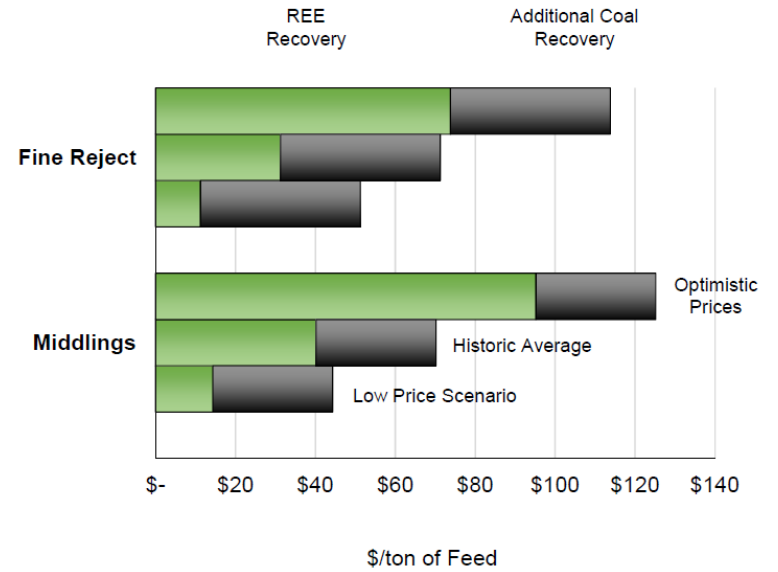
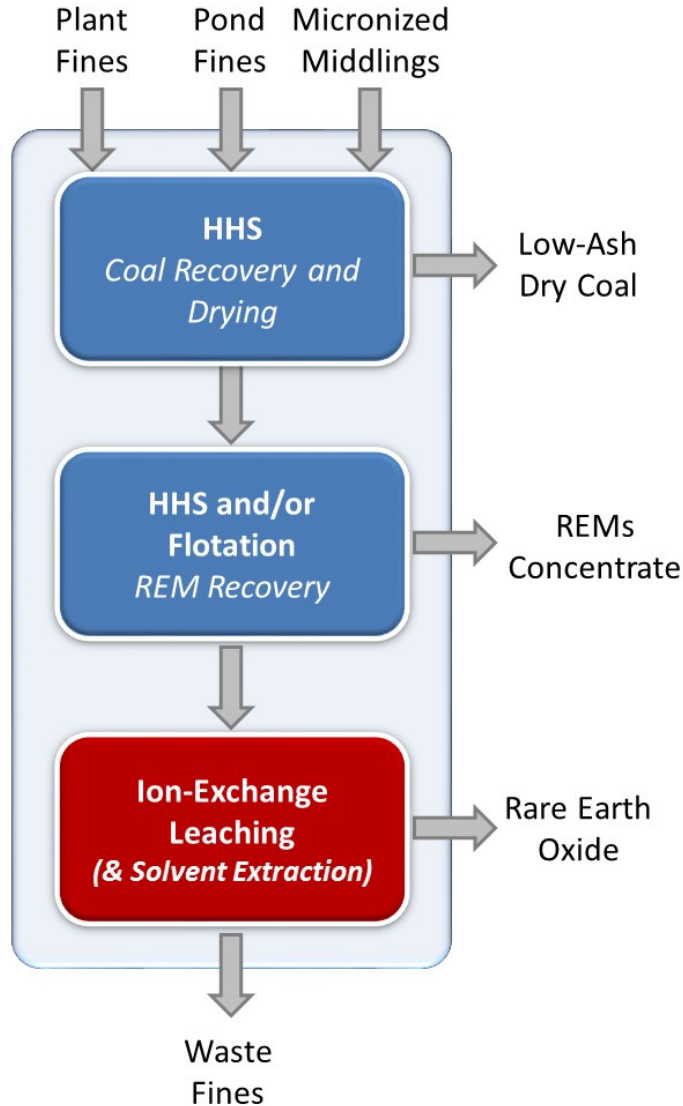
>4 billion tons in impoundments



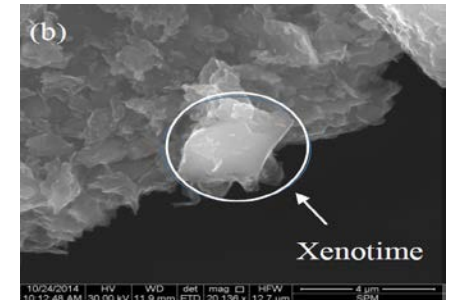
Thickener/Impoundment



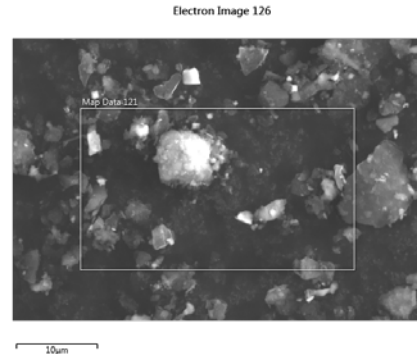
Simple Approach



Feed



Product

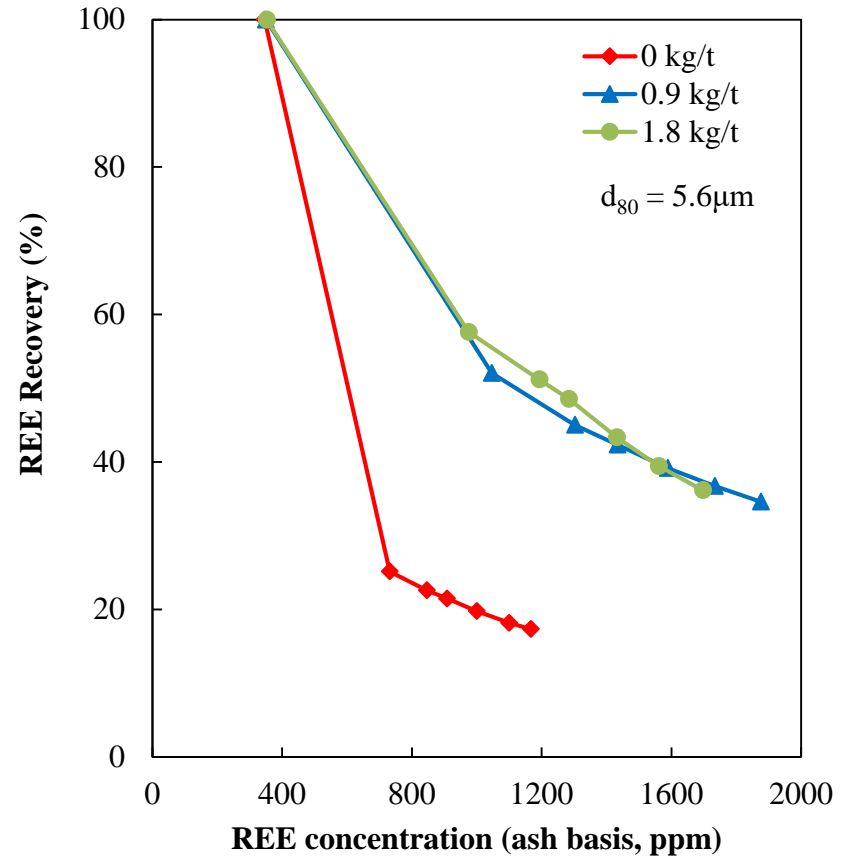
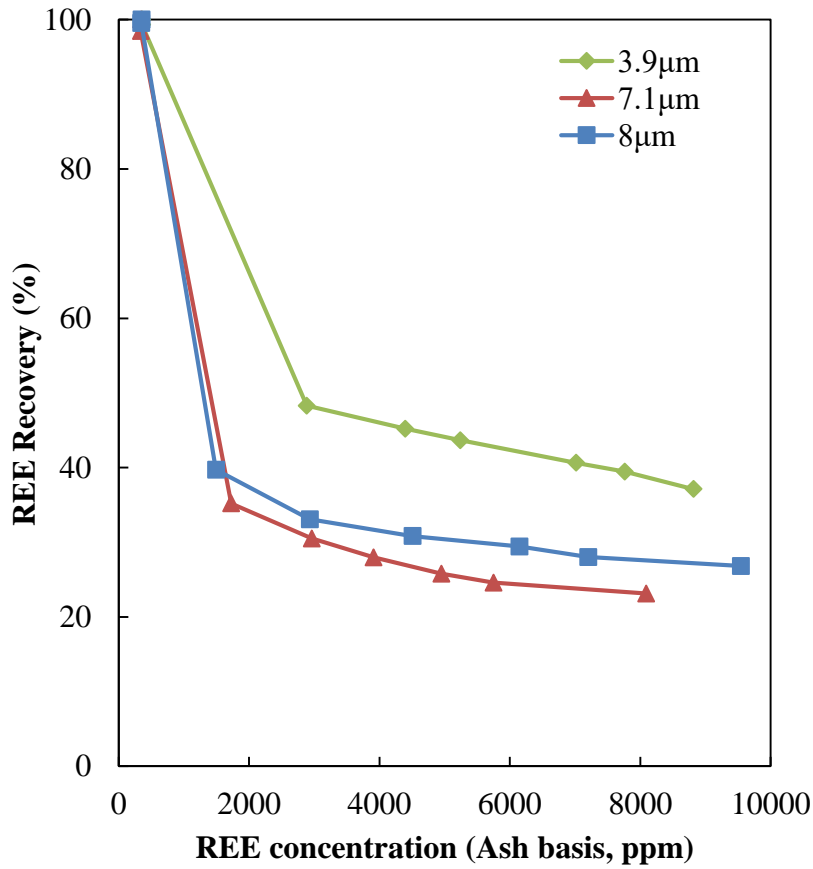


HHS Pilot Plant



No binder

Leatherwood Thickener U/F



Artificial Ores

□ Chalcopyrite ($d_{80} = 4 \mu\text{m}$)

Grade (%Cu)				Cu Recovery (%)
Feed	Tailings	Concentrate		
		Two-Liquid Flotation	HHS ¹	
22.07	0.06	27.8	34.11	99.9
12.82	0.18	24.3	34.14	99.3
4.18	0.06	22.27	33.86	98.9

□ Monazite ($d_{80} = 3 \mu\text{m}$)

Products	Weight	REE (%)	
	%	Grade	Recovery
Conc.	3.14	62.57	93.1
Tail	96.86	0.15	6.9
Feed*	100.00	2.11	100.0

Ion-Exchange Leaching

- Thickener U/F
 - At 50°C

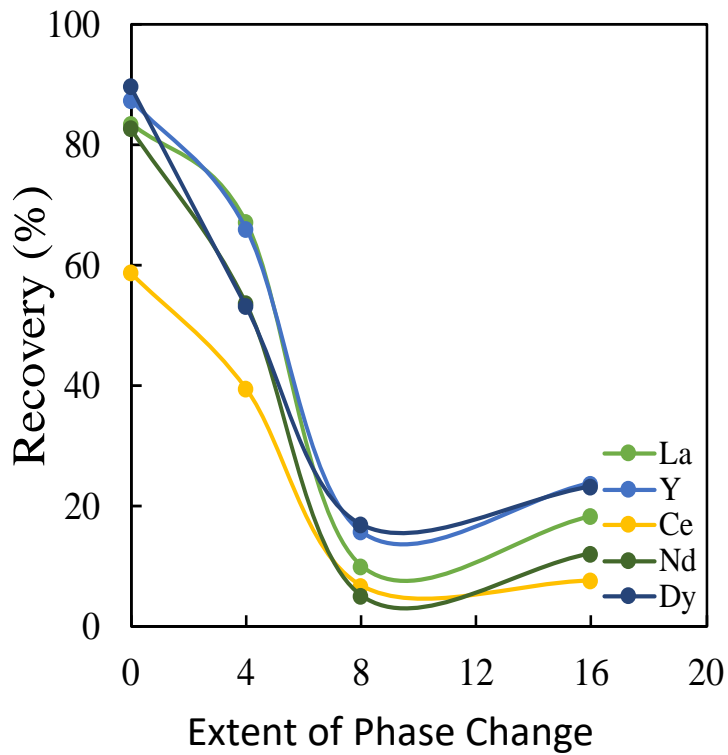
Lixiviant	Conc. (moles/l)	Feed			Solid Residue			REE Recovery (%)
		Ash (% wt)	REE (ppm)	Wt. (g)	Ash (% wt)	REE (ppm)	Wt. (g)	
(NH ₄) ₂ SO ₄	0.5	92.03	234.58	30.0	90.85	232.05	29.2	3.7
A	0.5	92.03	234.58	30.0	90.01	198.79	28.1	20.6
B	0.5	92.03	234.58	30.0	89.51	227.96	29.2	5.4

- Artificial Ion-Exchange Clay at 25°C

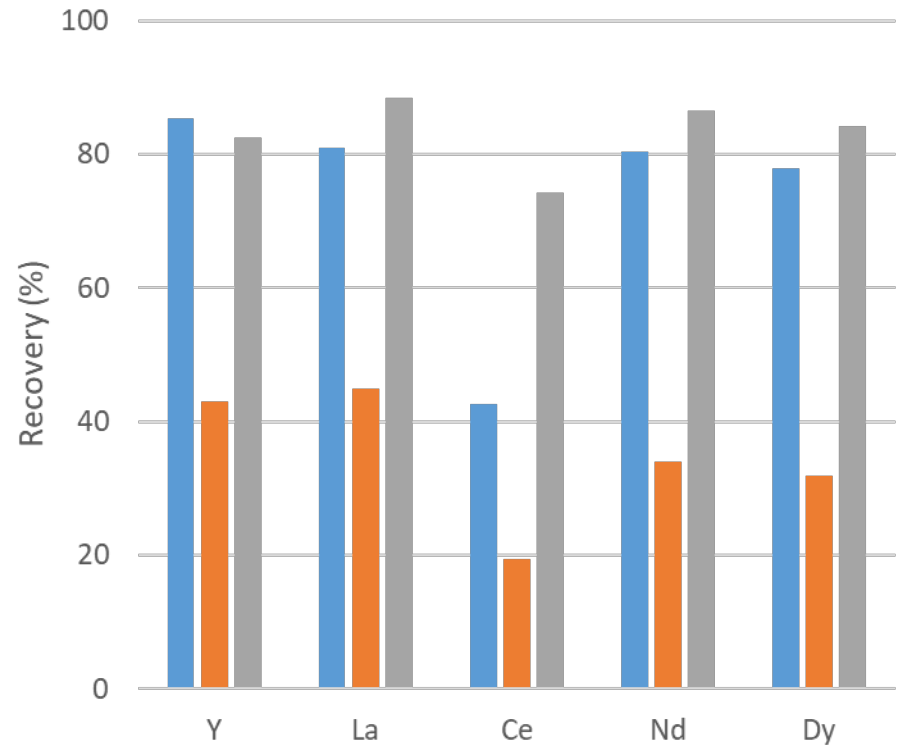
Lixiviant	Conc. (moles/l)	Feed		Solid Residue		REE Recovery (%)
		REE (ppm)	Wt. (g)	REE (ppm)	Wt. (g)	
(NH ₄) ₂ SO ₄	0.5	1812.5	15.0	726.8	14.9	60.1
A	0.5	1812.5	15.0	932.9	14.9	48.7
B	0.5	1812.5	15.0	1235.9	14.8	32.9
C	0.05	1812.5	15.0	643.3	14.4	65.9

Problem & Solution

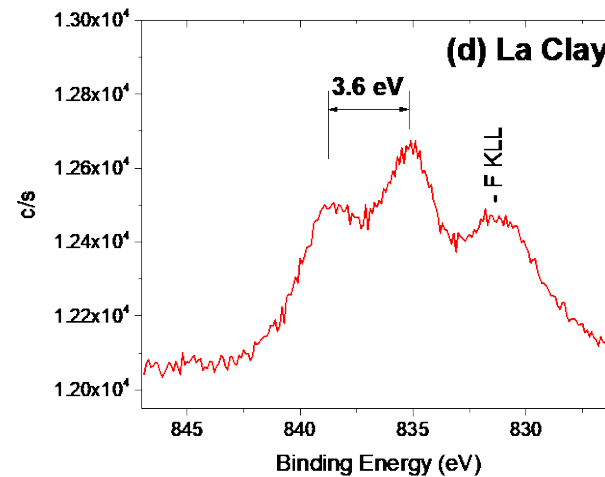
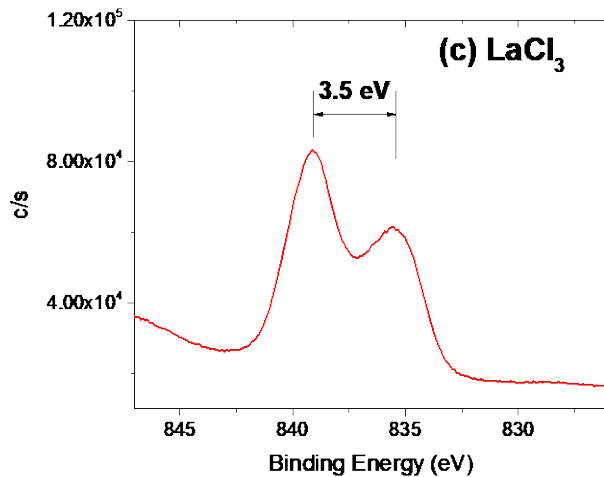
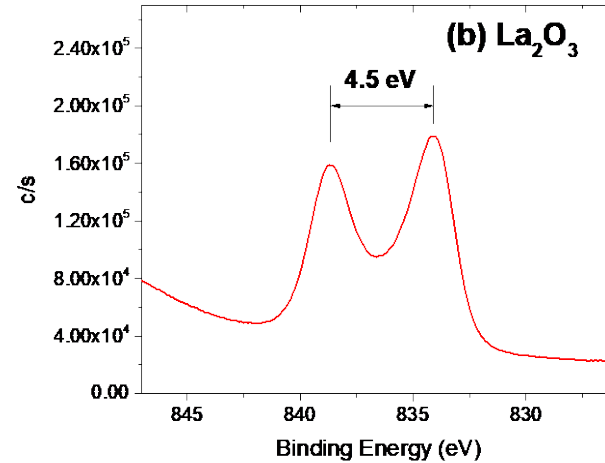
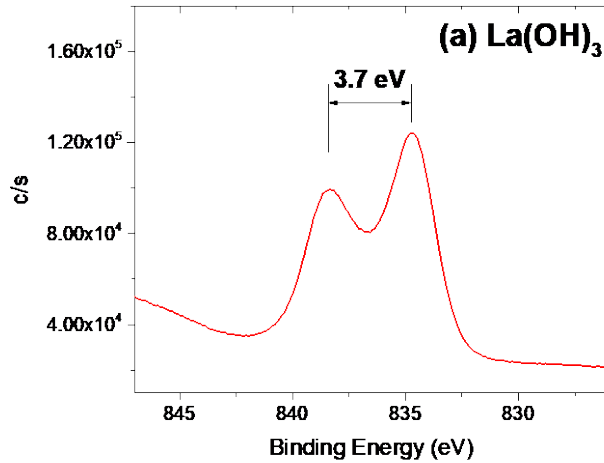
Colloidal phase



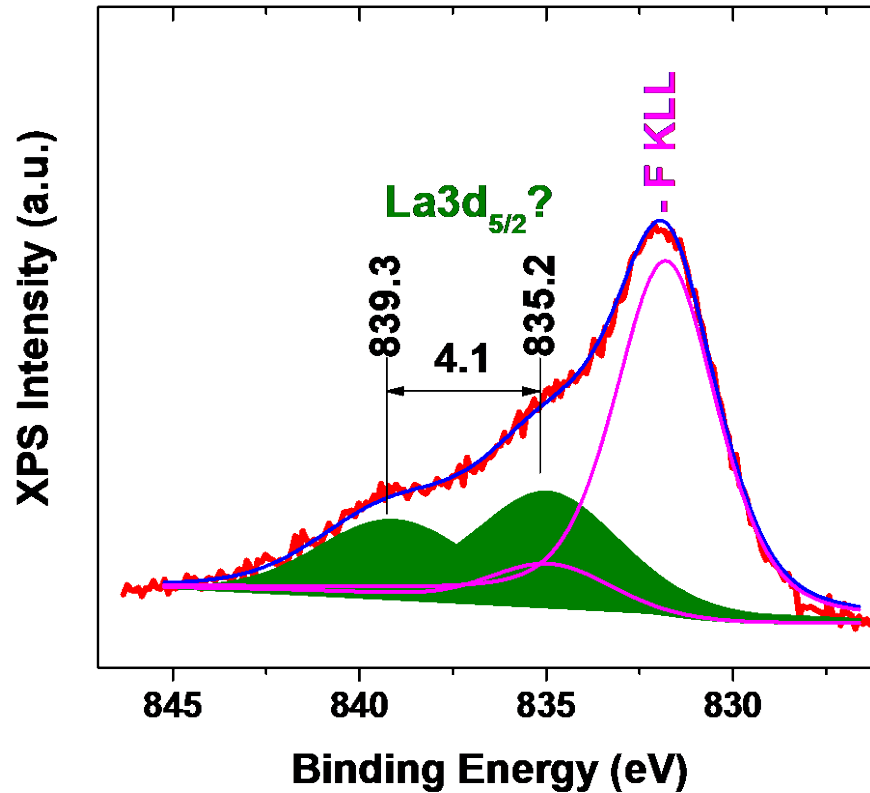
Solution



XPS Spectra of La on Artificial IAC



XPS Spectra of a Mineral Matter of a Middling Sample



Implication

□ LTI Project (2014)

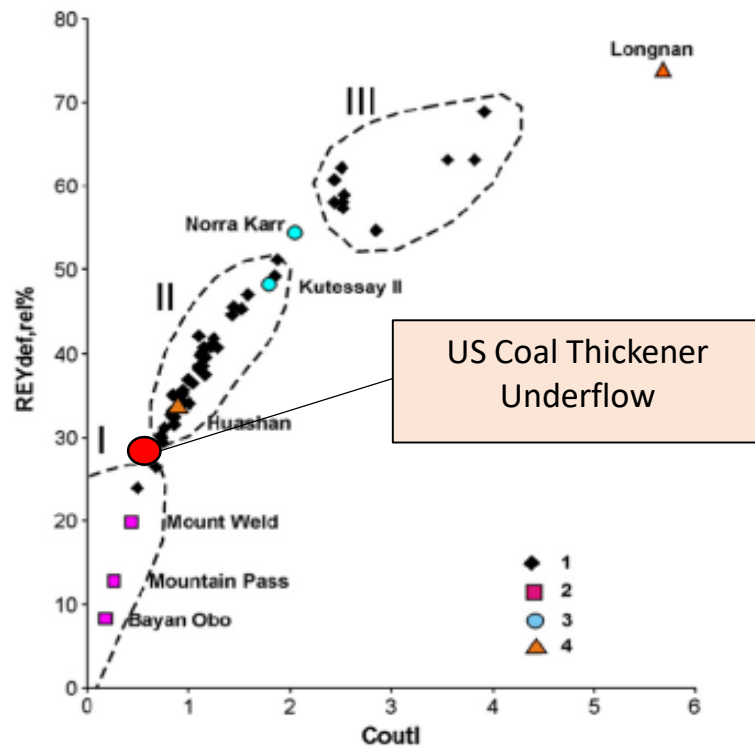
- Audited 15 coal beneficiation plants in Central Appalachia
- Fine coal refuse produced 1,313 TPY REE.

Table 3. Production of mass, ash and REEs for 15 coal processing facilities.

Stream	Mass TPY	Ash TPY	REE TPY	REE/Whole	REE/Ash
Plant Feed	78,567,376	36,986,176	9,899	126	268
Clean Coal	36,697,676	3,435,608	1,620	44	472
Coarse Refuse	33,279,712	28,160,683	6,285	189	223
Fine Refuse	8,589,993	5,227,936	1,313	153	251

- Thus, each of the 15 plants produced 87 TPY REE.
- Multiplying this number with 248, the number of operating plants, gives 21,700 TPY
- *Assuming 50% recovery*, US beneficiation plants can produce 10,850 TPY REE.
- In 2018, US consumed 9,500 tons.

Comparison with Other REE Sources



HHS Mobile Pilot-Plant



Summary

- ❑ Clay minerals in coal are rich sources of heavy REEs.
- ❑ Clay minerals congregate to thickener underflows.
- ❑ Heavy and critical REEs can be readily recovered at low cost and with minimal disruption.
 - produce salable coal from waste streams
 - ~4 billion tons of pond fines can be an additional source
- ❑ XPS studies showed evidence for ion-adsorption clays in US coal byproducts
 - most likely in colloidal phase
 - makes IX leaching difficult
 - characterization and extraction studies ongoing