Recovery of Rare Earth Elements from Coal Byproducts:

Characterization and Laboratory-Scale Separation Tests

by

Roe-Hoan Yoon and Aaron Noble

Center for Advanced Separation Technologies
Virginia Polytechnic Institute & State University
Blacksburg, Virginia, 24061

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12:00-12:30 pm, Wednesday

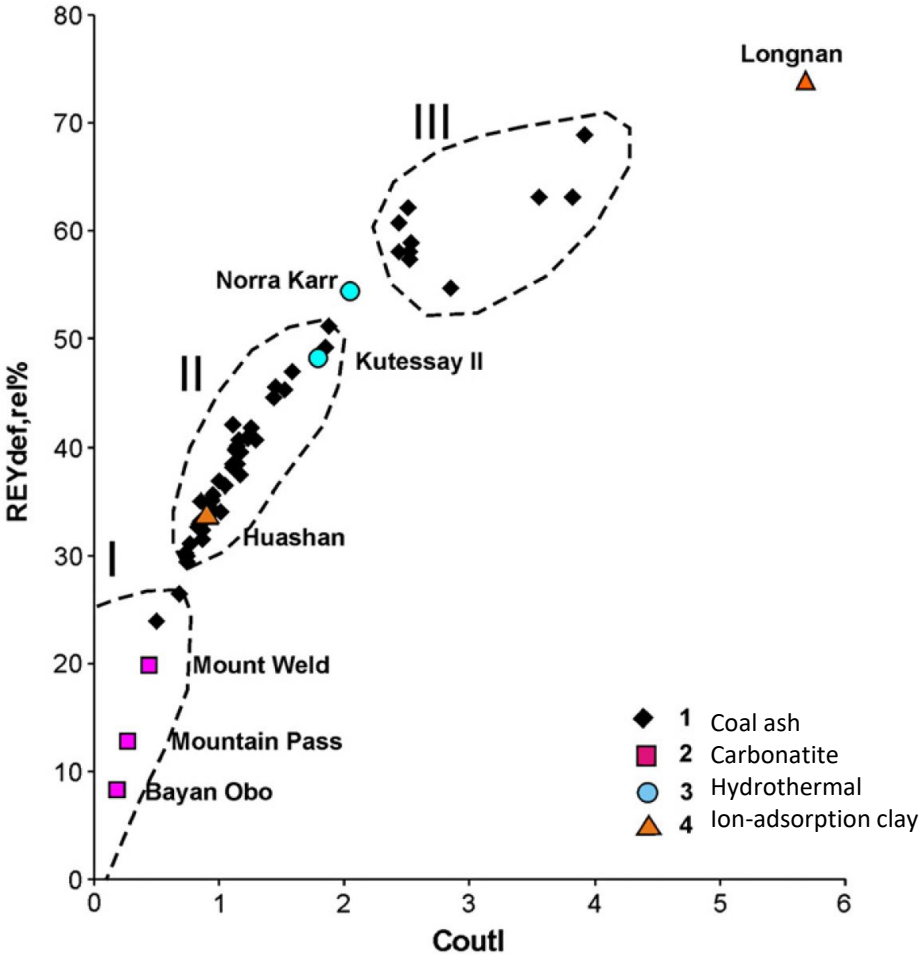
Objectives

- To overcome the challenges in extracting rare earth elements (REEs) from coal byproducts:
  - Low concentration
  - Low separation efficiency

- Approach
  - Extract REEs from the kaolinite present in fine coal refuse by ion-exchange leaching.
  - Extract REEs from the monazite co-present in the refuse to increase the recovery and separation efficiency.

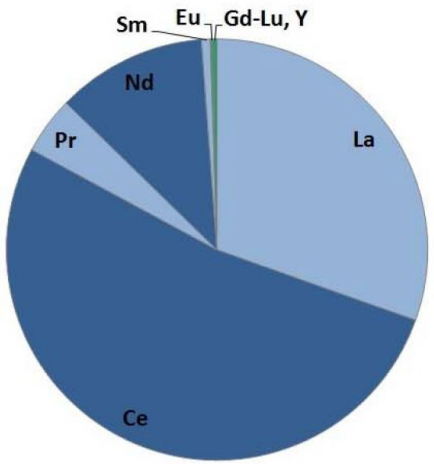
REEs in Coal

Seredin and Dai (2012)

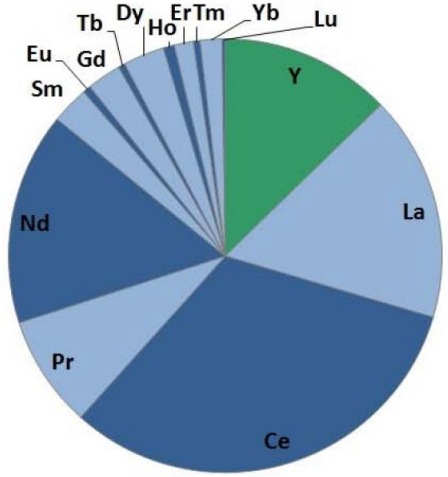


$$C_{outl} = \frac{(Nd + Eu + Tb + Dy + Er)/\sum REY}{(Ce + Ho + Tm + Yb)/\sum REY}$$

Bastnäsite ore, Mountain Pass, California



Central Appalachian Coal

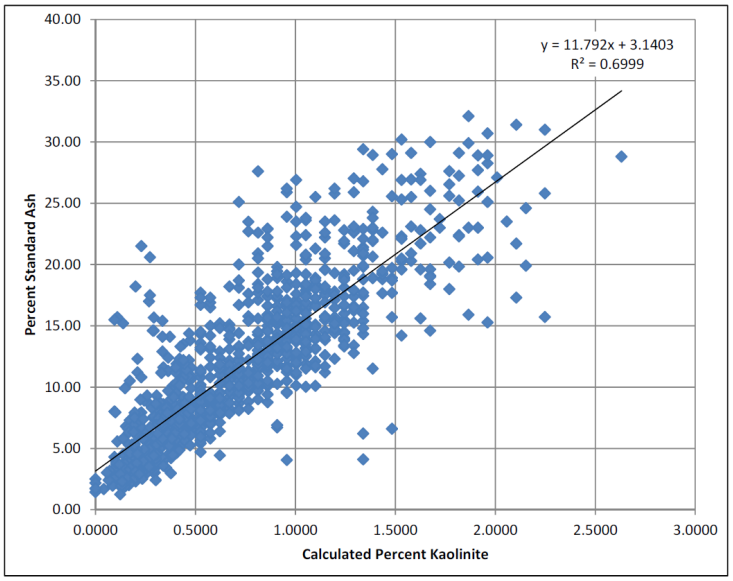


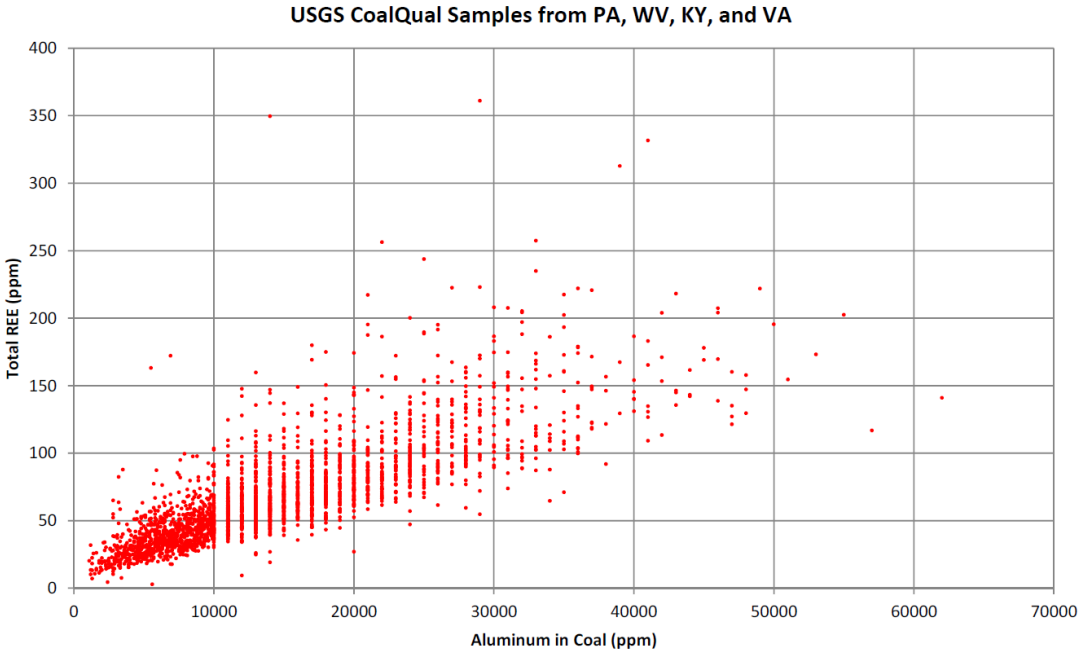
Ekmann and Skone (2013)

USGS Coal Data Base

Bryan *et al.* (2015)

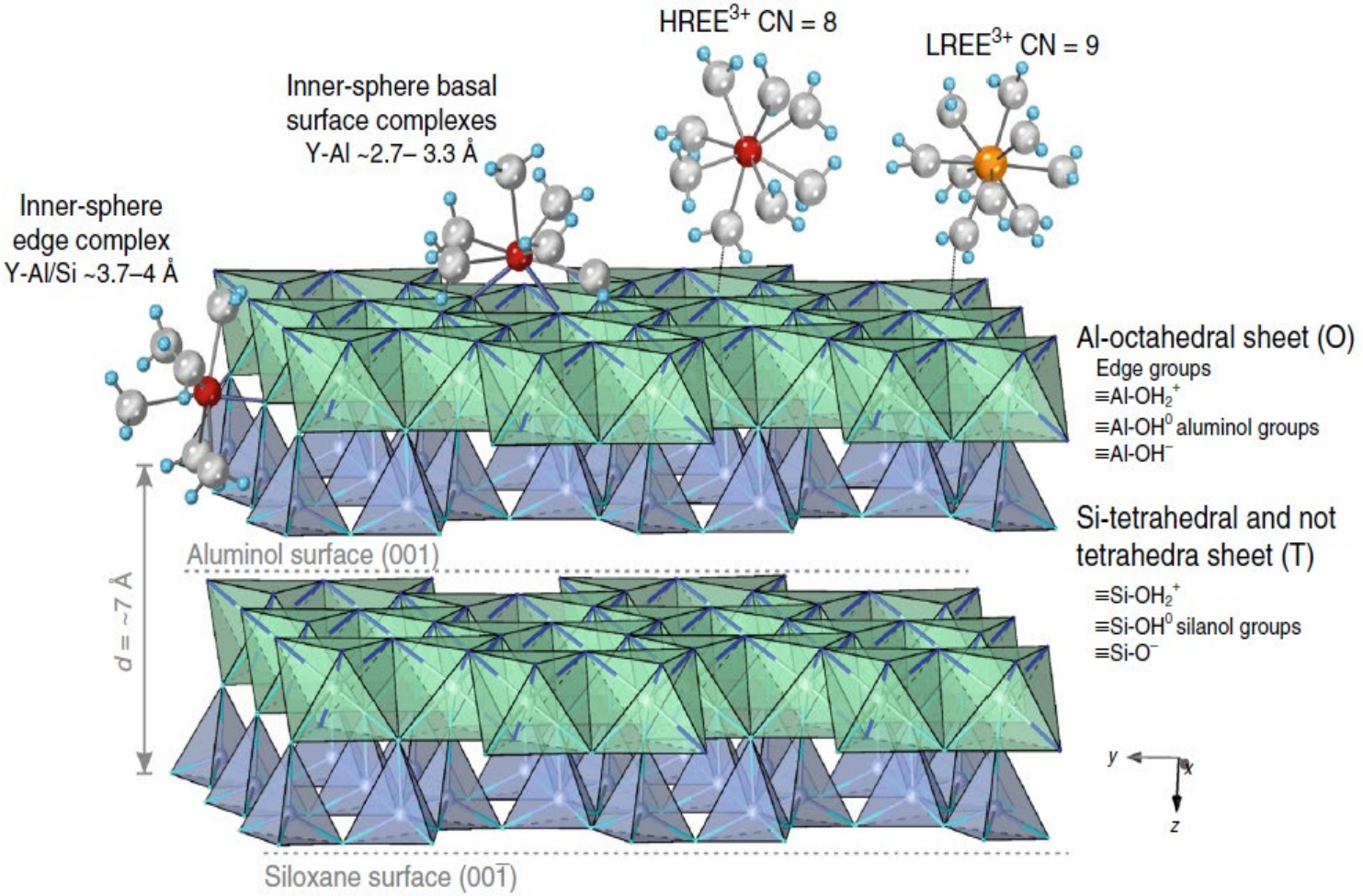
- REEs are in mineral matter
  - 80% from kaolinite
- REEs partition to kaolinite





A Model Based on X-Ray Absorption Studies

Boris *et al.* (Nature, 2020)



- Basal surfaces: *permanent surface charge (outer-sphere complexes)*
- Edge surfaces: *pH-dependent surface charge (inner-sphere complexes)*

Laser-Ablation ICP-MS Analysis of a Single Kaolinite Particle

Before and After Ammonium Sulfate Treatment (Mukai *et al.*, Nature, 2020)

Kaolinitic particle01			
	Before tretment	After treatment	Desorption ratio (%)
Y (ppm)	74.3	23.6	68.2
La (ppm)	61.4	16.2	73.6
Ce (ppm)	629	324	48.5
Pr (ppm)	24.1	7.30	69.8
Nd (ppm)	97.1	32.4	66.6
Sm (ppm)	28.2	9.15	67.6
Eu (ppm)	5.41	2.00	63.1
Gd (ppm)	26.3	8.08	69.2
Tb (ppm)	4.04	1.45	64.2
Dy (ppm)	23.1	10.2	55.6
Ho (ppm)	4.04	1.64	59.5
Er (ppm)	11.7	4.88	58.4
Tm (ppm)	1.72	0.74	56.9
Yb (ppm)	12.4	5.73	53.9
Lu (ppm)	1.68	0.93	45.0
LREE (ppm)	845	391	53.7
LREE[a] (ppm)	216	67.1	69.0
HREE (ppm)	85.0	33.7	60.4
REE (ppm)	985	448	54.5
REE[a] (ppm)	301	101	66.6
REY (ppm)	1059	472	55.4

Chinese IAC industry practice

- 40-70% recovery
- 2,000-4,000 REE ores

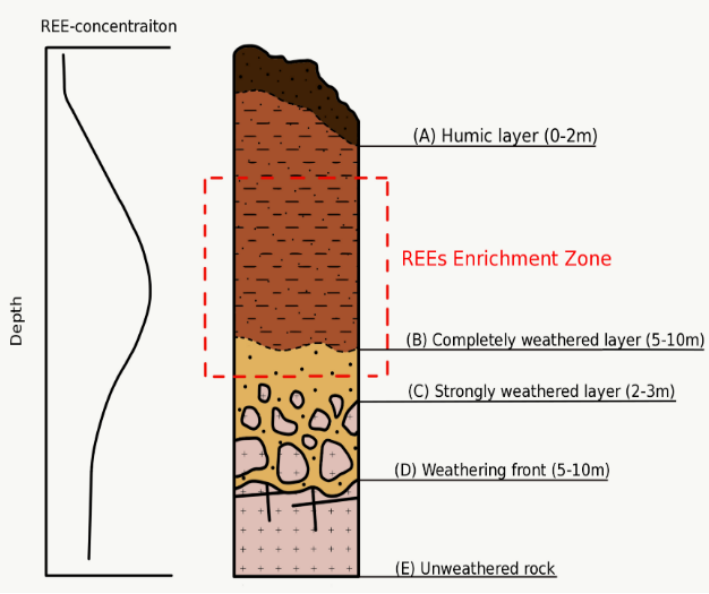
(Schultze *et al.*, 2017)

Formation and Passivation of Ion-adsorption Clays

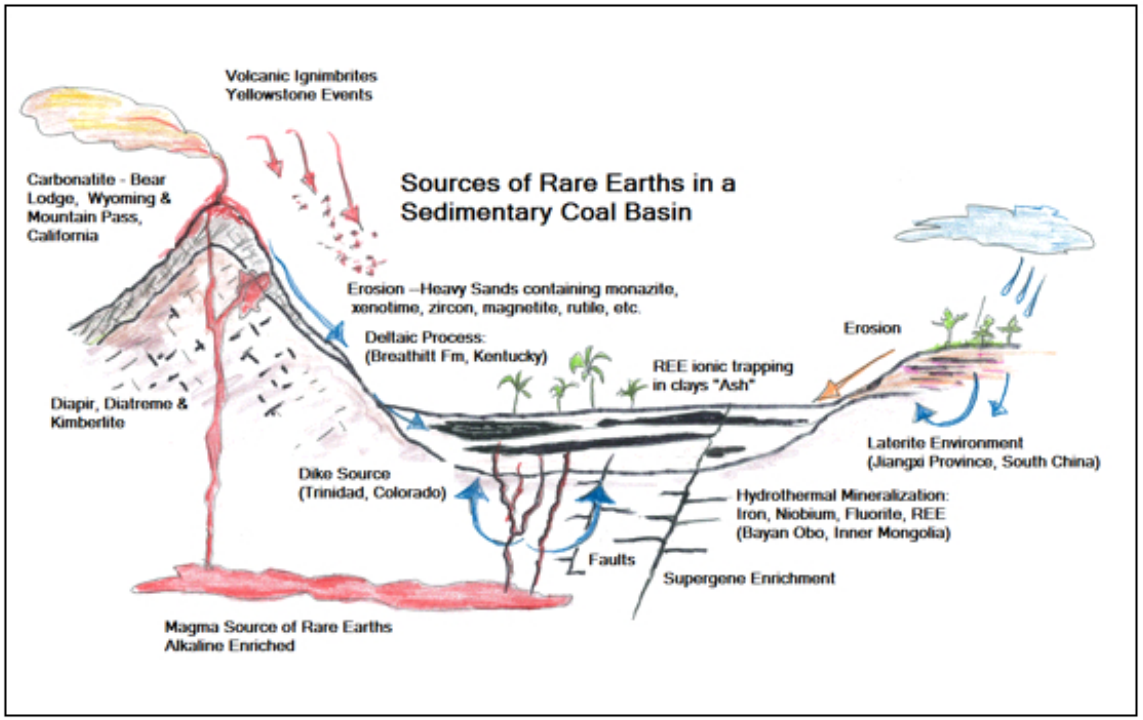
- Weathering of granite
  - Feldspar (>65%)
    - *by meteoric water*

$$2KAlSi_3O_8 + 2CO_2 + H_2O \rightarrow$$
$$Al_2Si_2O_5(OH)_4 + 4K^+ + 4HCO_3^- + 4SiO_2$$

  - REE-bearing accessory minerals
    - *Liberate Ln^{3+} ions into solution*
    - *Adsorb onto kaolinite surface*
    - *Can be passivated by phosphorous*



Li *et al.*, 2017)

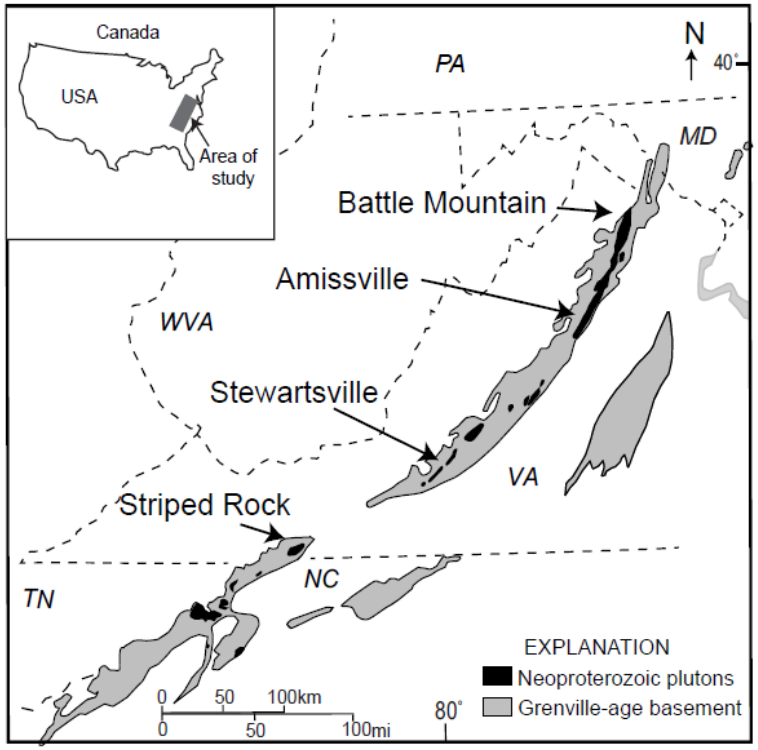


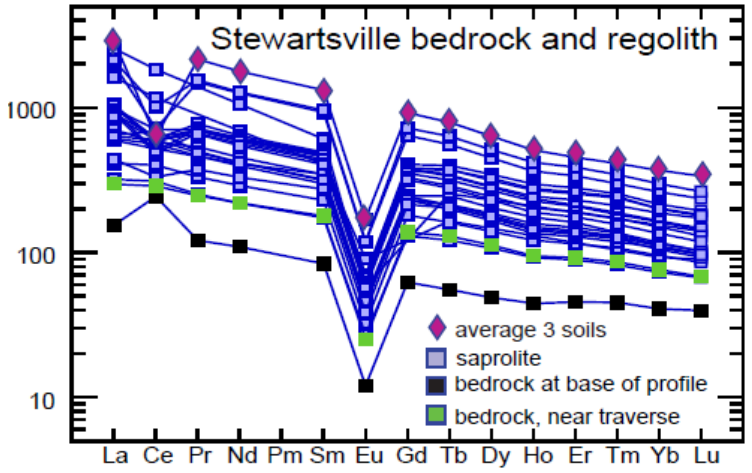
Bryan *et al.*, (2015)

IACs in the U.S.

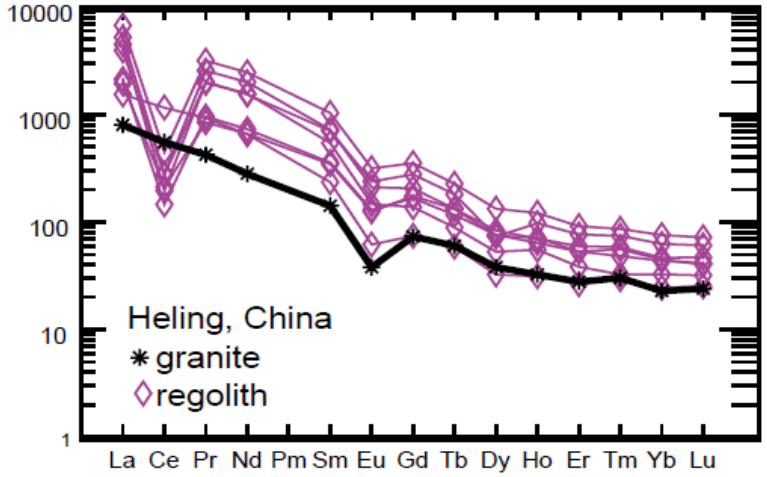
Foley and Ayuso (2015)

- Stewartsville



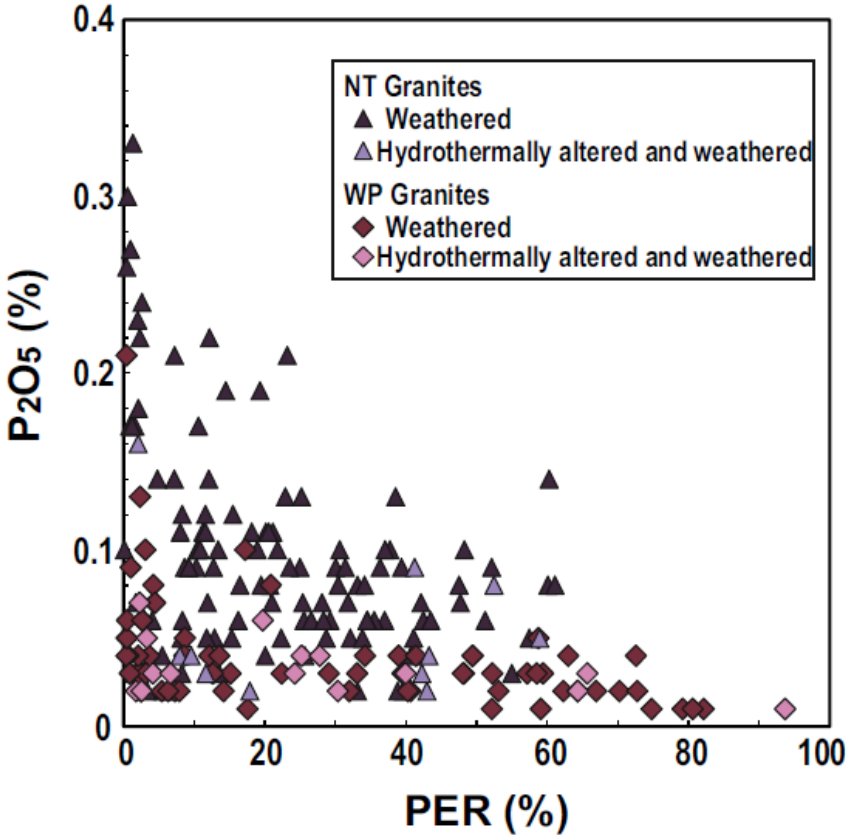


- Heling, China



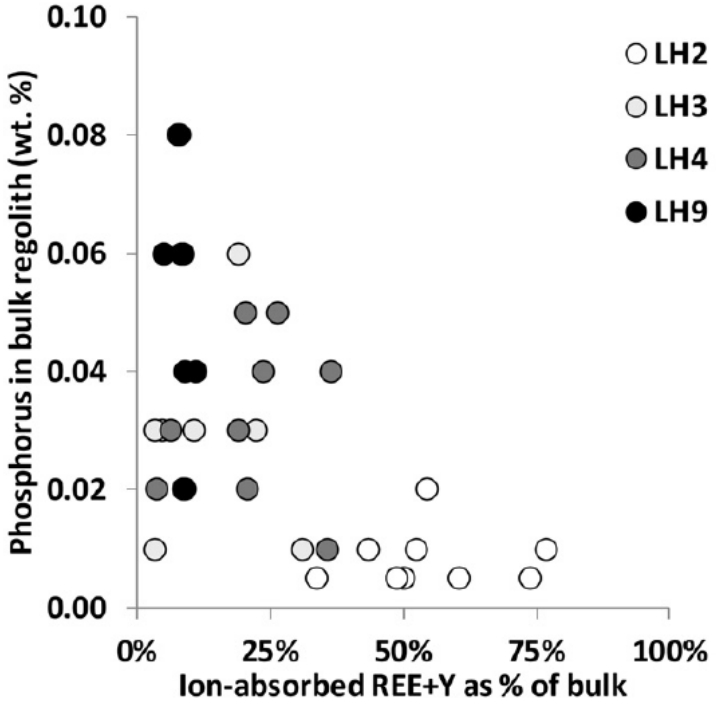
Effect of Phosphor on Ion-Exchange Leaching

- Sanematsu *et al*. (2015)



PER: ion-exchangeable rare earths

- Bern *et al*. (2017)

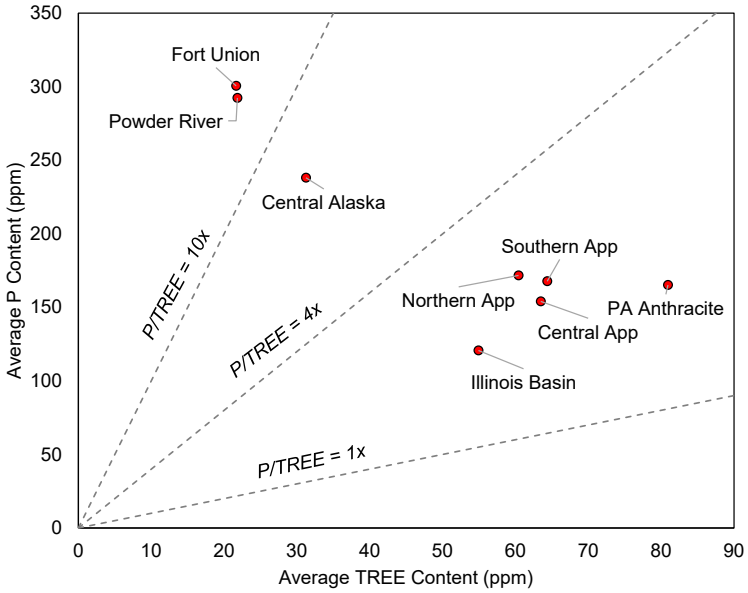


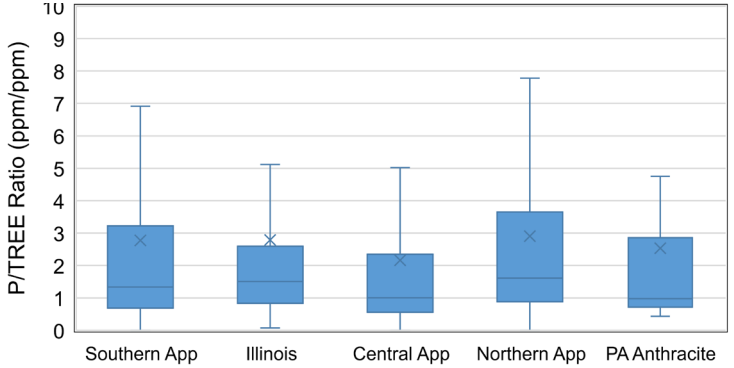
Phosphate minerals scavenge Ln^{3+} ions from solution during IAC formation.

Phosphate in US Coal

USGS COAL Database

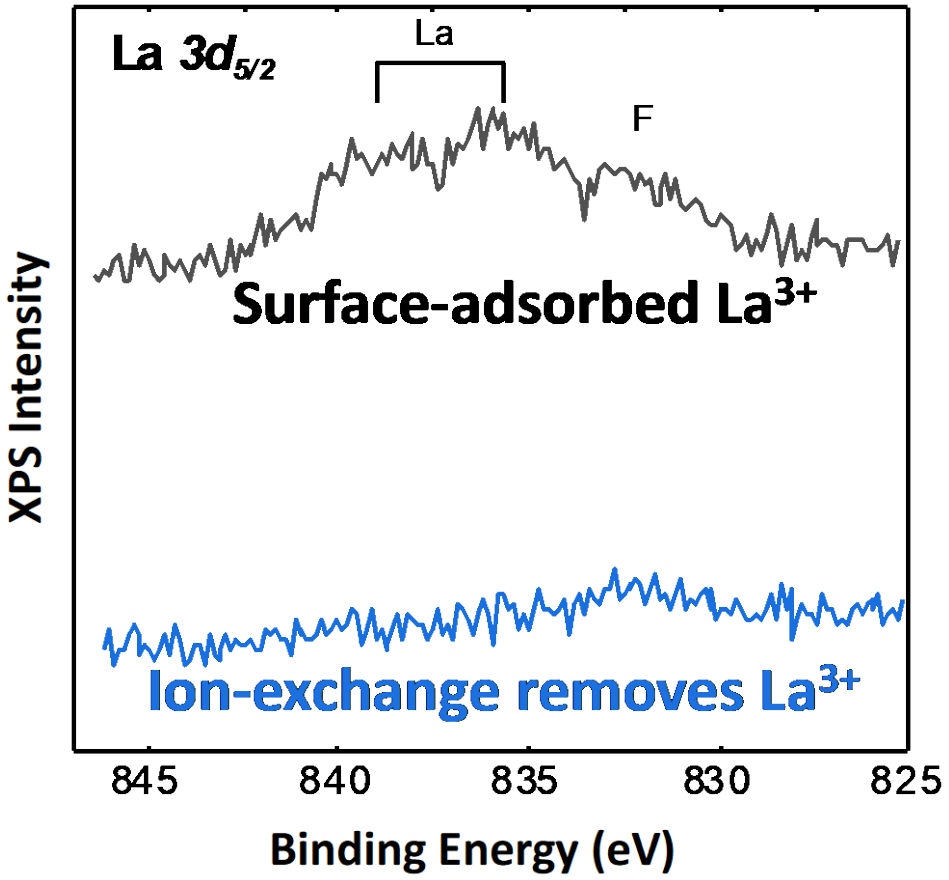
- P content and/or P/TREE ratio may be used to identify promising feedstocks.
  - Eastern coals, P/TREE = 1 to 4
  - Western coals, P/TREE > 10
- Some Appalachian coal seams have nearly negligible P content.
- Further investigations will be useful.

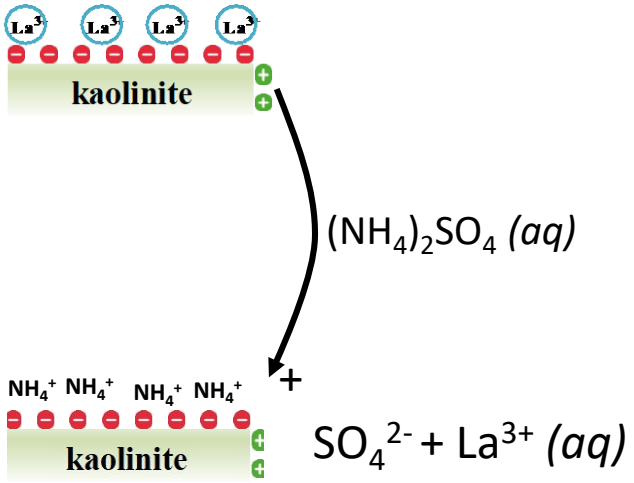




Ion-exchange Leaching of La^{3+} from Kaolinite

In the Absence of Phosphate

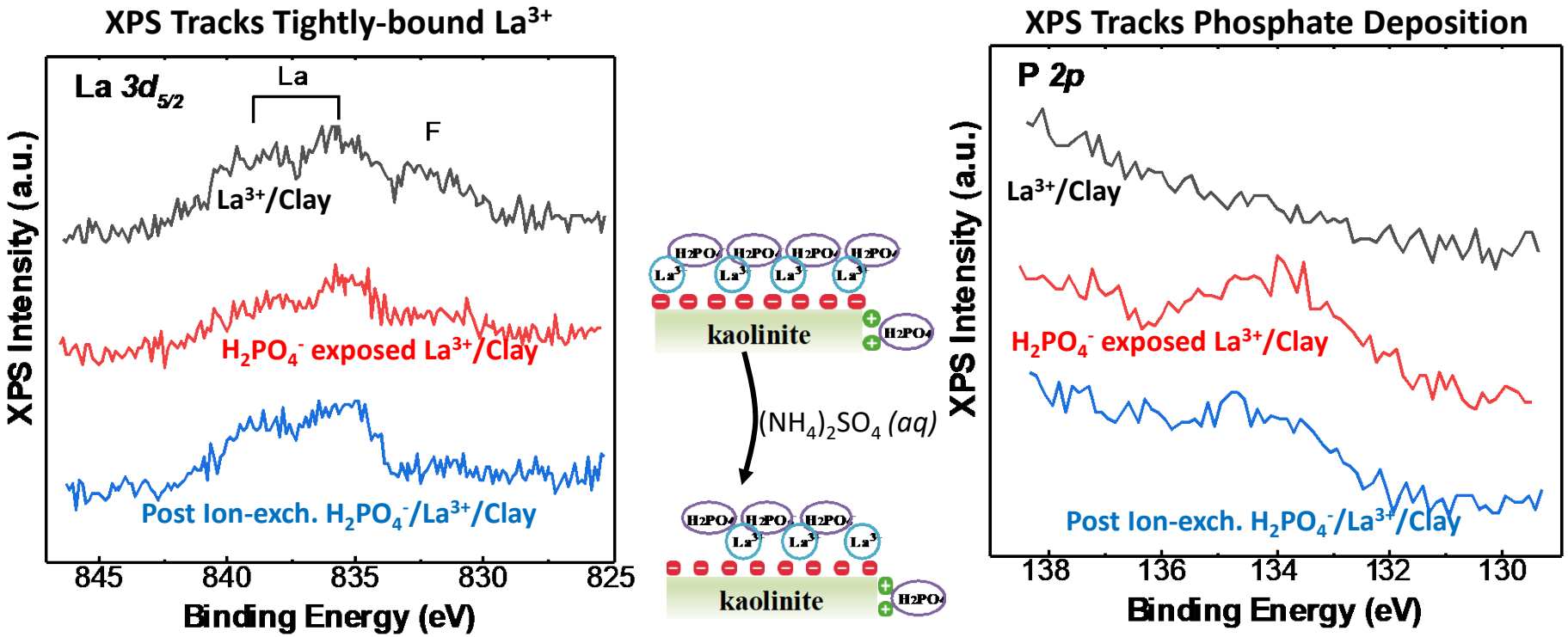




95% of La^{3+} ions have been removed.

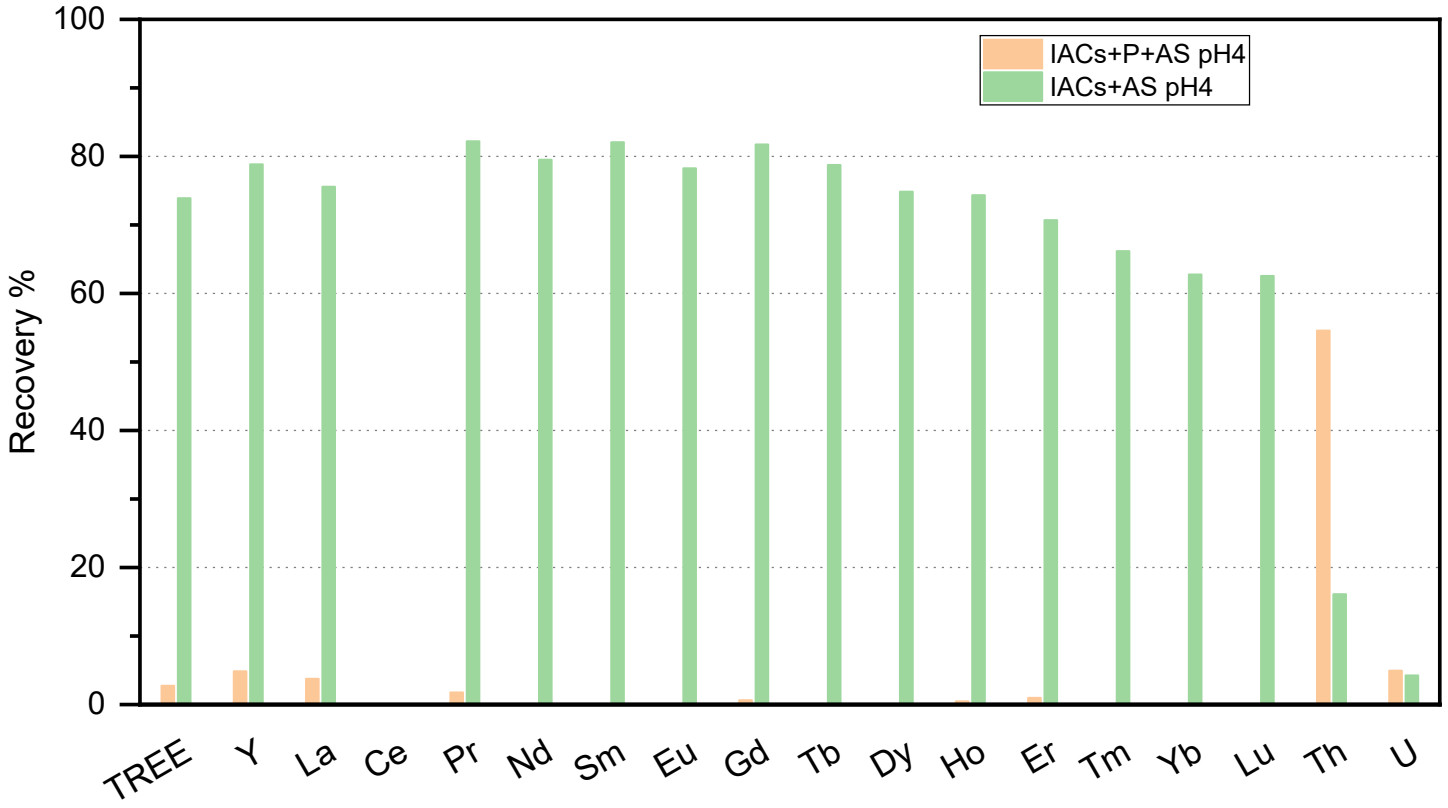
Ion-exchange Leaching of La^{3+} from Kaolinite

In the Presence of Phosphate



18% of La^{3+} ions have been removed.

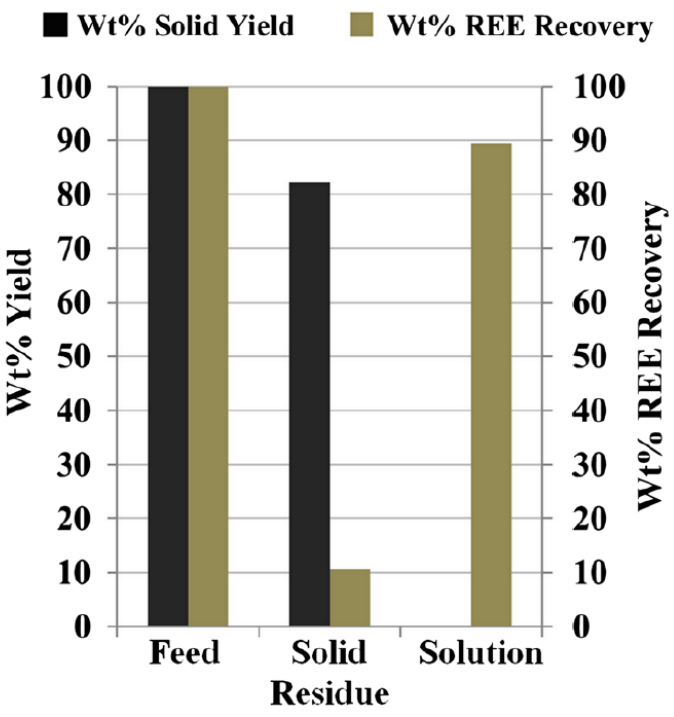
Passivation of an IAC Sample from South China by Phosphate



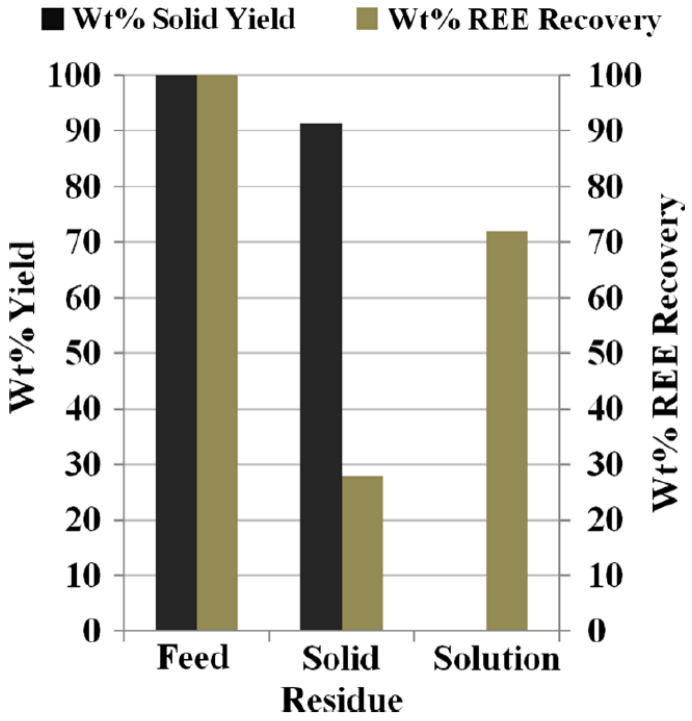
Ion-exchange Leaching of Upper Kittanning Coal, PA

Rozelle *et al.* (2016)

- Sample A
  - Top of the coal seam

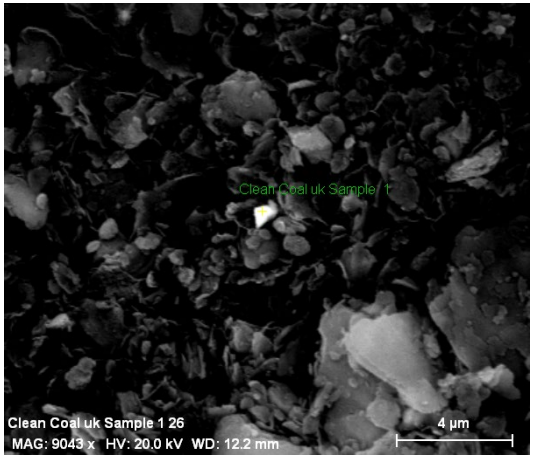


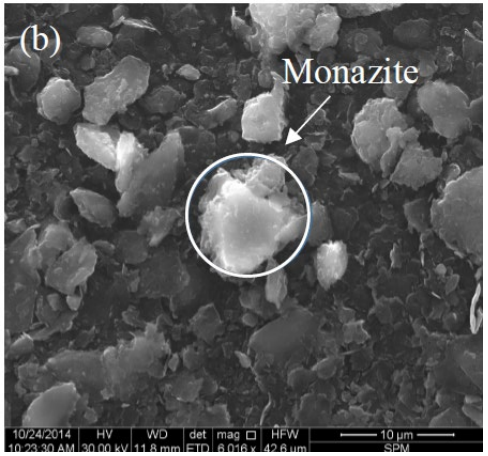
- Sample B
  - Just below Sample A

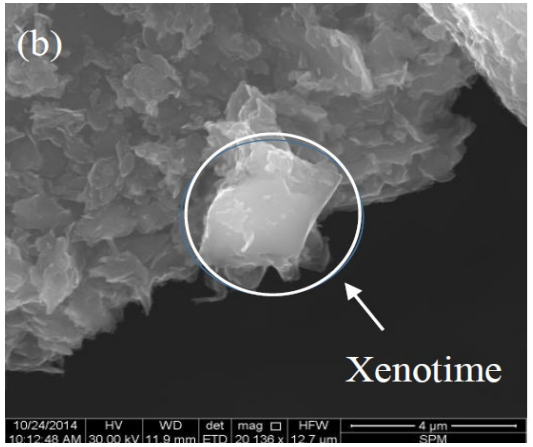


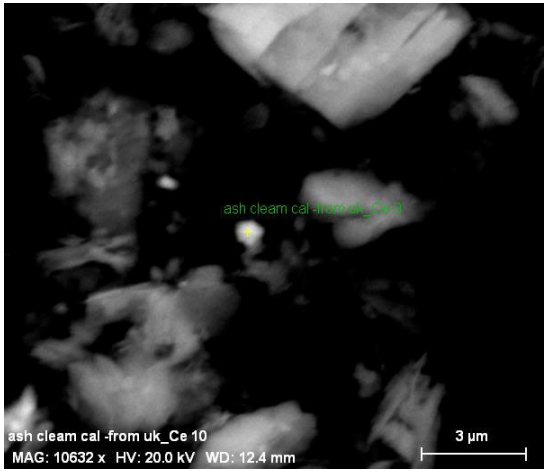
595x10 µm sample in 1 M $(NH_4)_2SO_4$
1 hr contact time

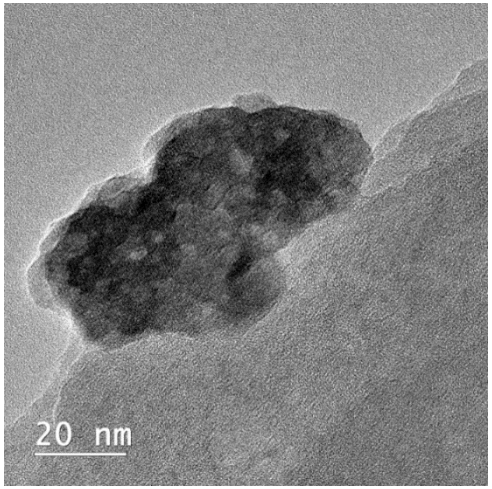
Rare Earth Minerals in Appalachian Coal

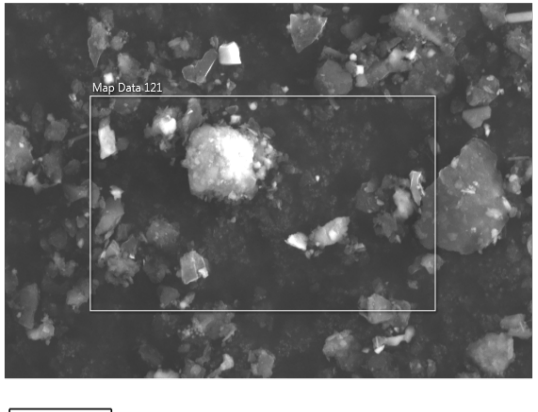






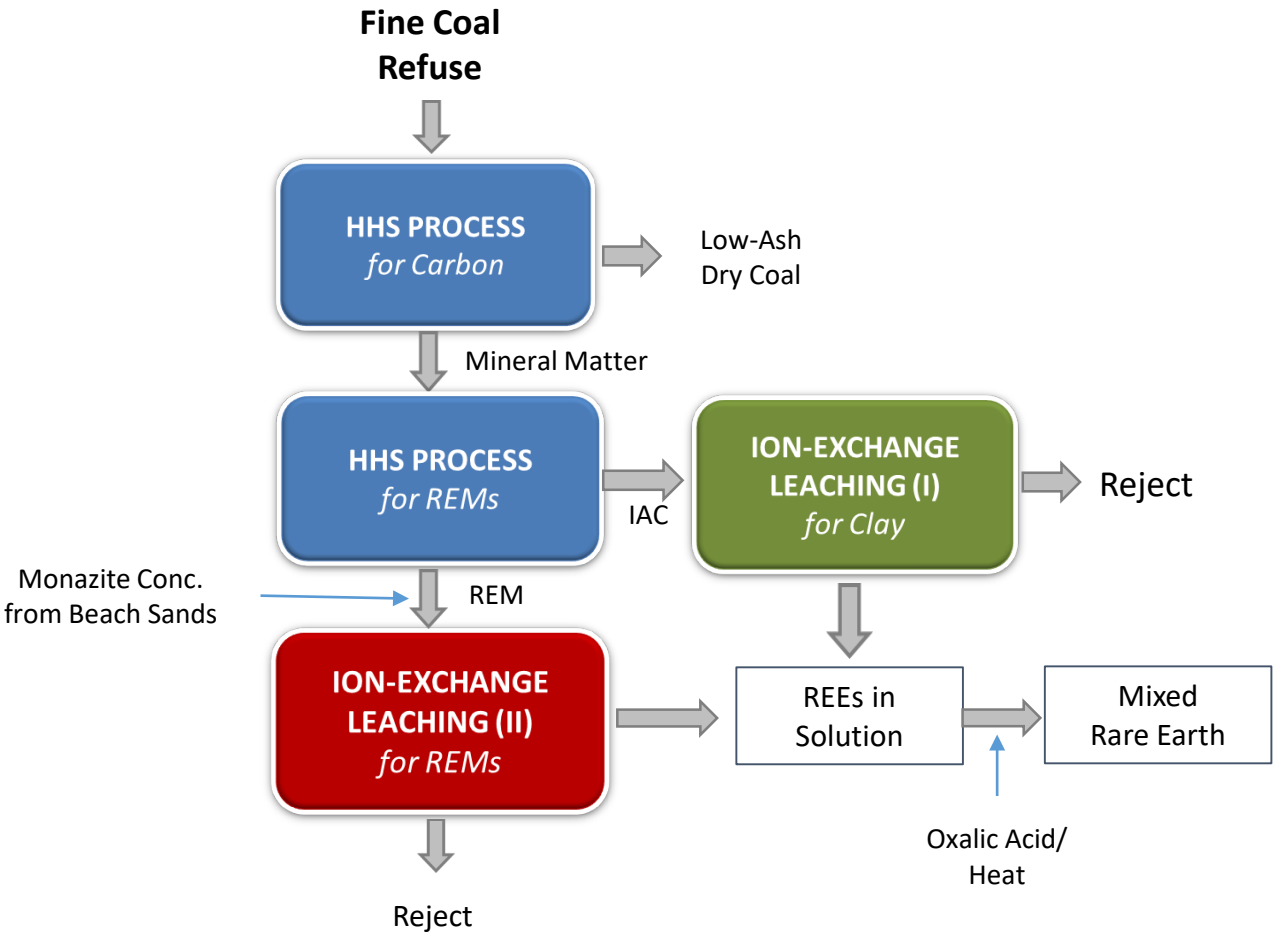






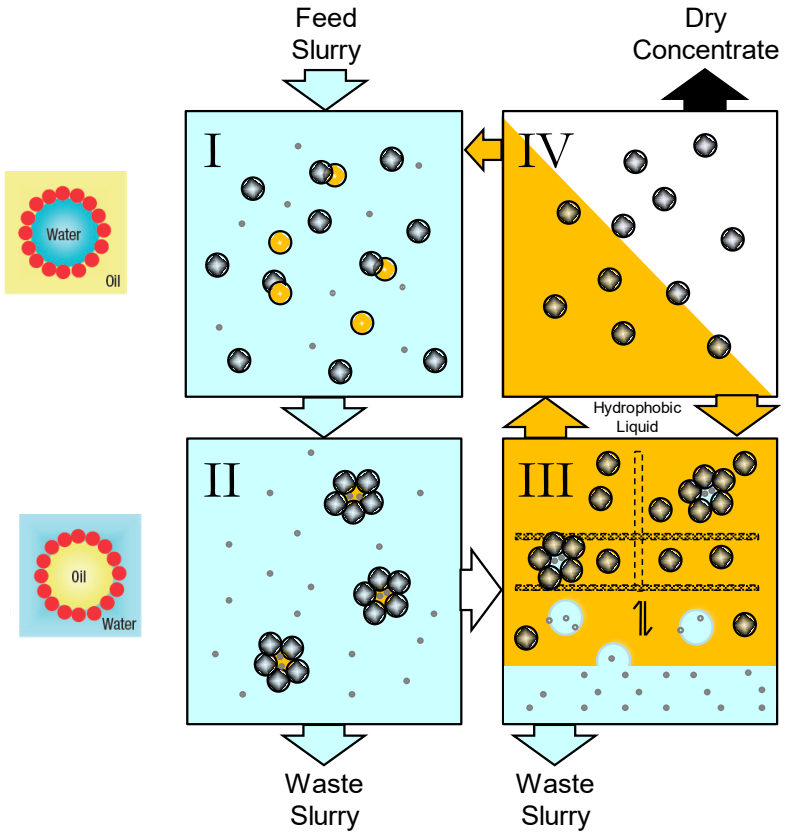
HHS Product

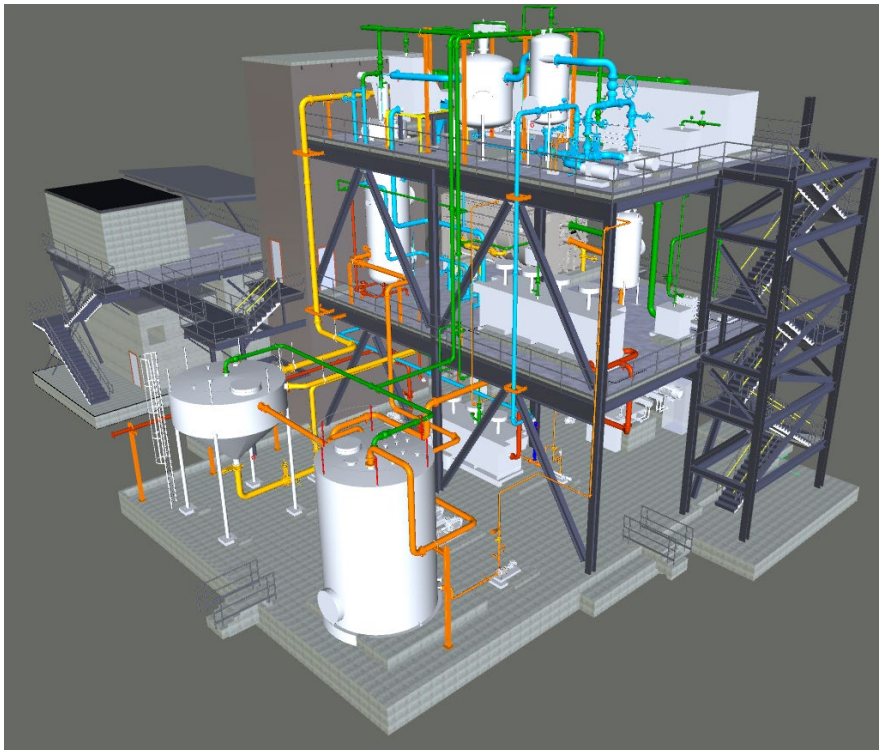
REE Recovery from Fine Coal Refuse: New Approach



Hydrophobic-Hydrophilic Separation (HHS) Process

Yoon, R.-H., US Patent 9,518,241 (2016)





- No lower particle size limit
- No entrainment
- Dry products

- Construction in progress for coal recovery

Monazite Recovery by HHS

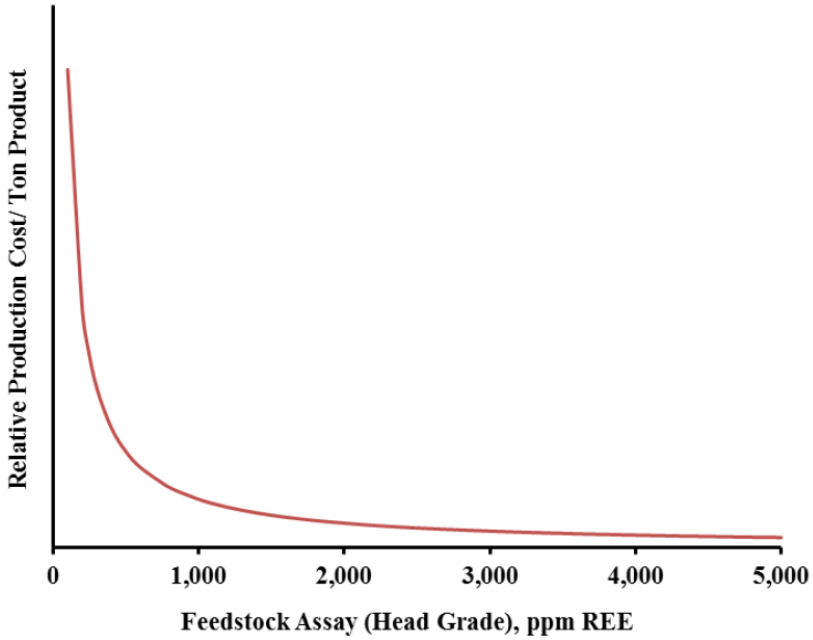
- Preliminary test results
  - *Oil washing*

Test	Particle Size	Conc Grade, % (Total)	Overall Recovery, %
HHS 4	5.0	0.55%	6.6%
HHS 8	3.0	0.29%	1%

  - *Water washing*

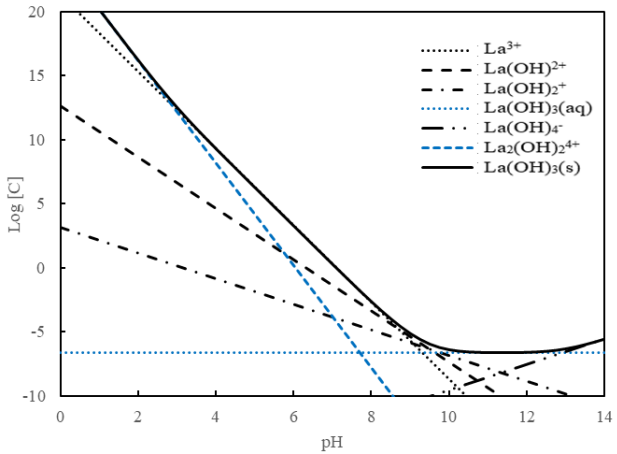
Test	Particle Size	Conc Grade, % (Total)	Conc Grade, % (Dry Ash Basis)	Overall Recovery, %
HHS 4	2.2	6.34%	56.14%	14.2%
HHS 8	3.0	3.73%	-	4.54%

- Rozelle *et al*. (2019)
  - *Leonardo Technologies, Inc.*
  - *DOE report*

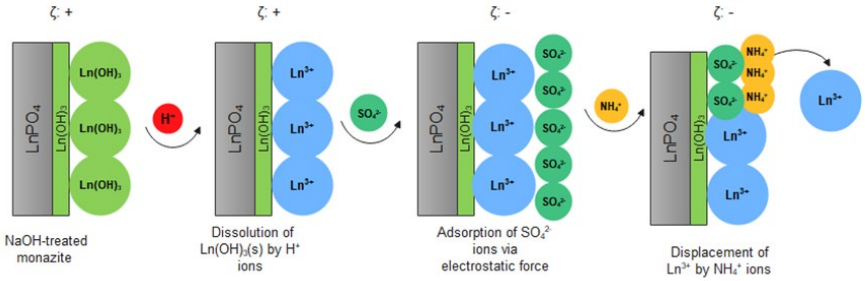


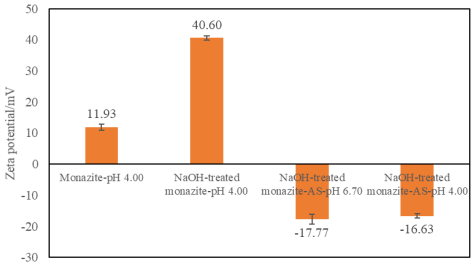
Ion-Exchange Leaching of Monazite

- Solubility diagram

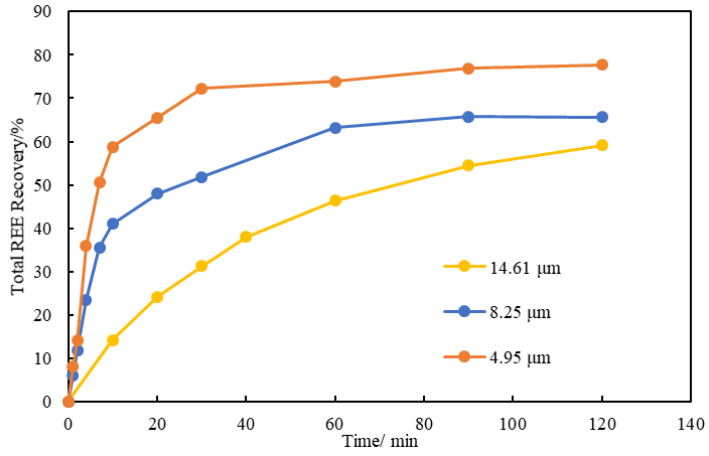


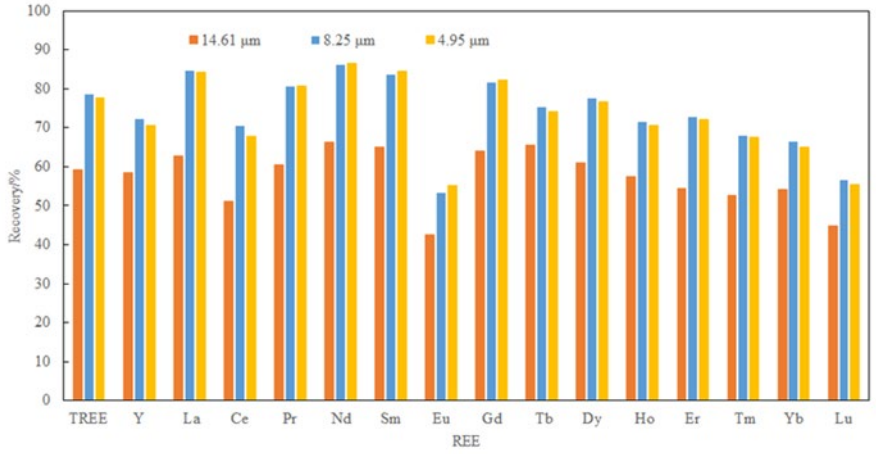
- Model





- Leaching experiment
  - *50% NaOH, 80°C, 24 hrs, Ion-exchange leaching at pH 4*

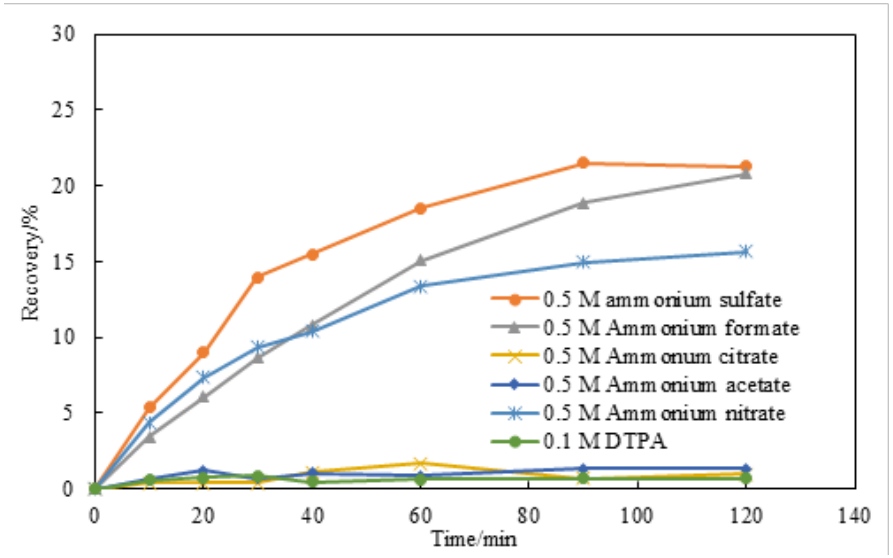




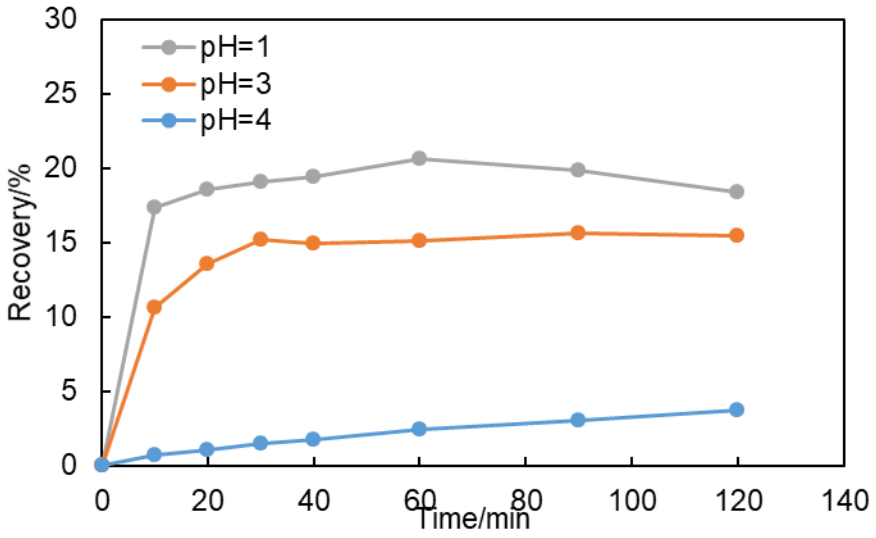
Ion-Exchange vs. Acid Leaching

Kinetics

- Ion-Exchange Leaching



- Acid Leaching



A US Rare Earth Resources Map

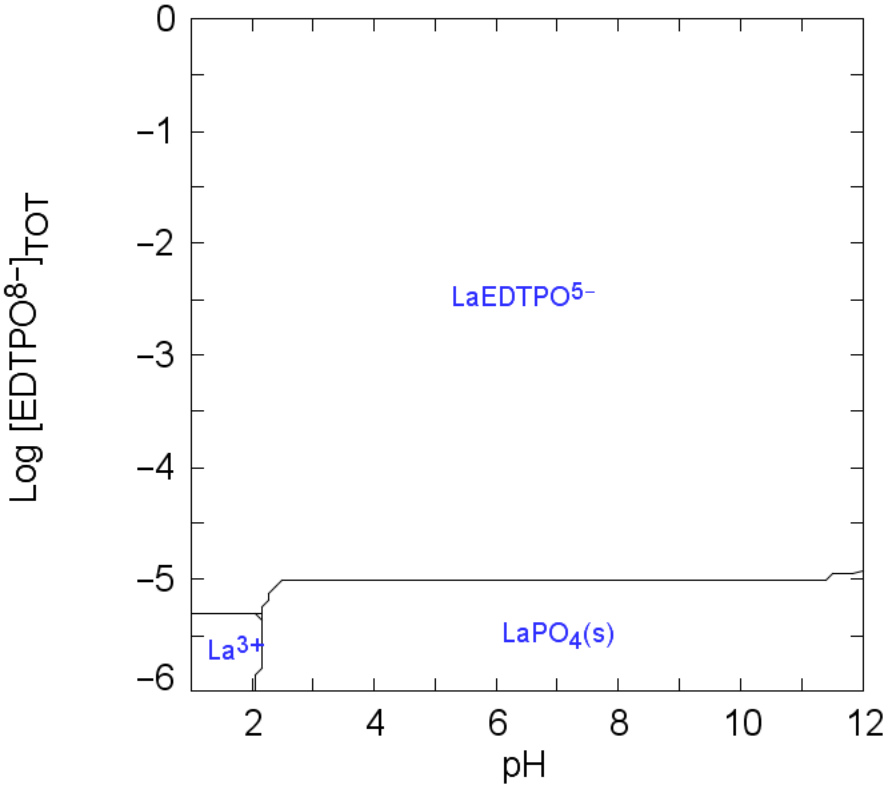
USGS Circular 1454, April 2019

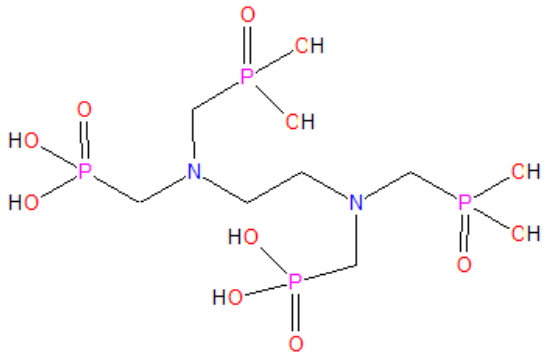
8. Clay deposit in Stewartsville, VA
10. (yellow) Atlantic coastal plain, monazite from beach sands

Ion-exchange Leaching of IAC

(Chelating Agents to Solubilize at Neutral pH)

$[La^{3+}]_{TOT}$ = 10.00 µM $[PO_4^{3-}]_{TOT}$ = 10.00 µM





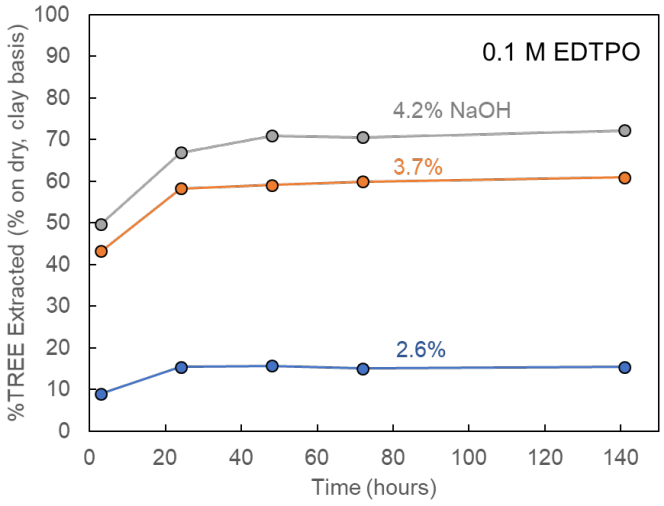
Ethylenediaminetetra(methylenephosphonic acid) (EDTPO)

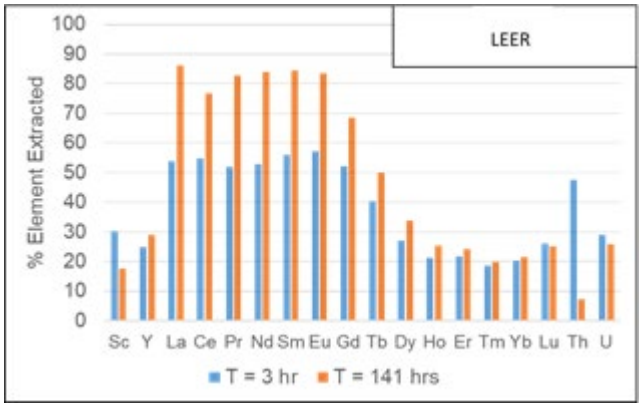
t= 25°C

- Dissolution of La(PO_4)(s), *e.g.*, monazite and apatite, is thermodynamically possible at neutral pH.

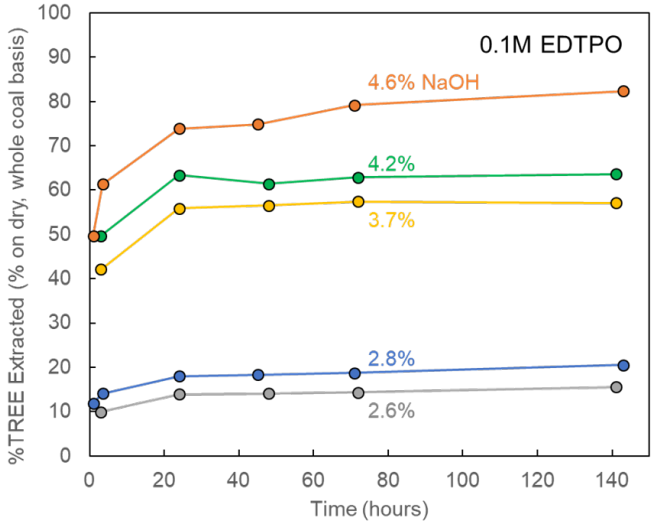
Ion-Exchange Leaching of IACs

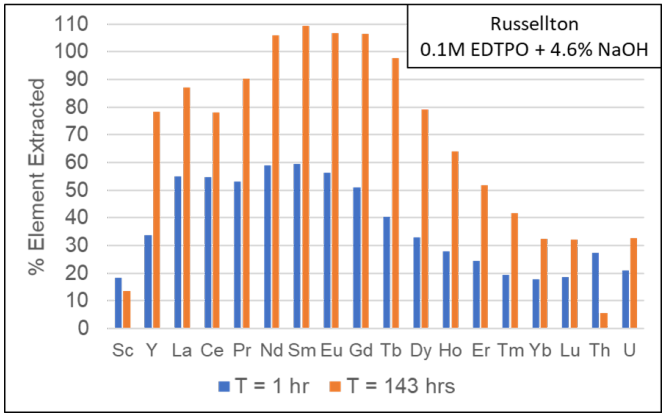
- IAC from Leer thickener underflow





- Russellton pond fines

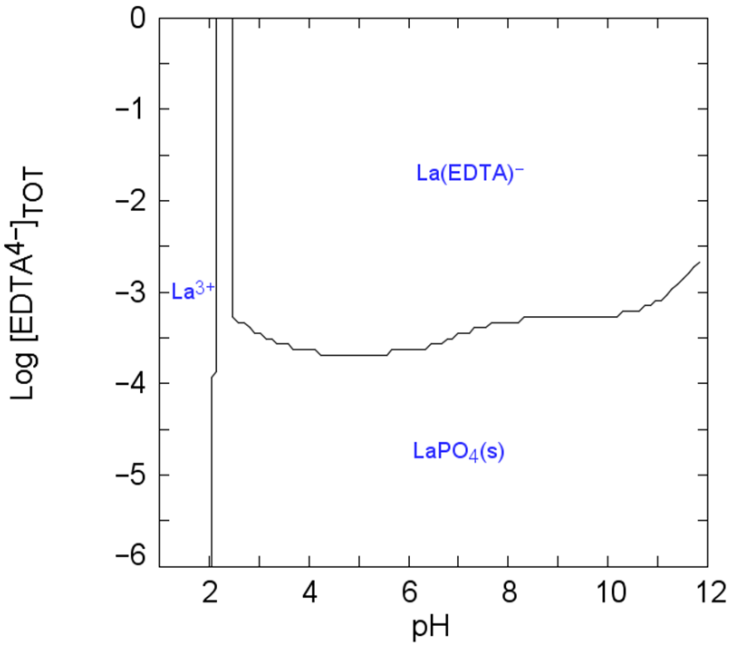


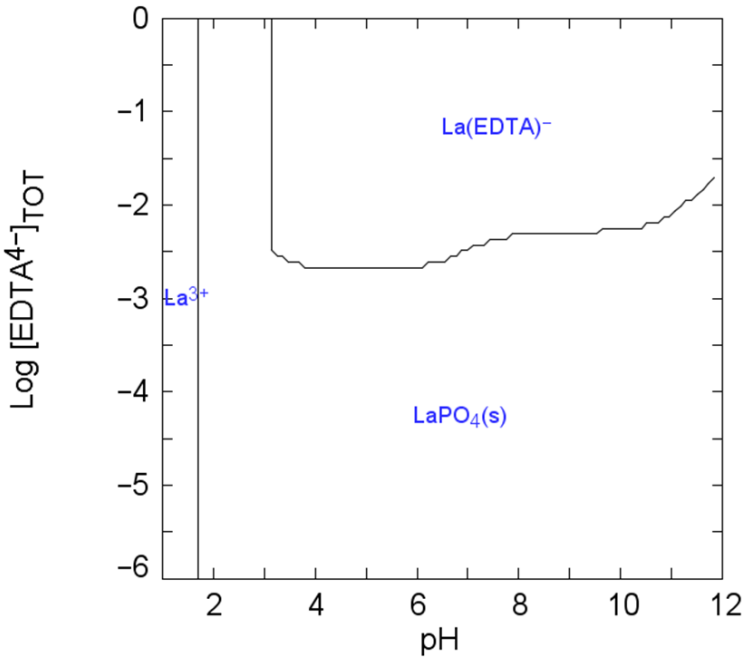


A small amount of NaOH is need due to the co-presence of monazite and passivated IACs in our sample.

Effect of Chelating Agents

- In presence of small amount of $LaPO_4(s)$
  - 10 μM La^{3+}
  - 10 μM PO_4^{3-}
- In presence of large amount of $LaPO_4(s)$
  - 10 μM La^{3+}
  - 0.1 mM PO_4^{3-}





Remove monazite prior to ion-exchange leaching of passivated IACs!

Summary

- Fine coal refuse has two REE-bearing minerals.
  - Rare earth minerals (monazite)
    - *Residual accessory minerals*
  - Ion-adsorption clays (kaolinite/halloysite)
    - *Passivated by phosphate ions from solution*
- Developed an ion-exchange leaching process for monazite.
  - Requires mild operating conditions
- HHS process may be used to increase the contained values and thereby overcome the problems associated with:
  - low REE+Y grades in coal byproducts
  - passivating effects of phosphates

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