REE-Critical Minerals (NETL FWP) Waste Stream: Ion Exchangeable REE Extraction

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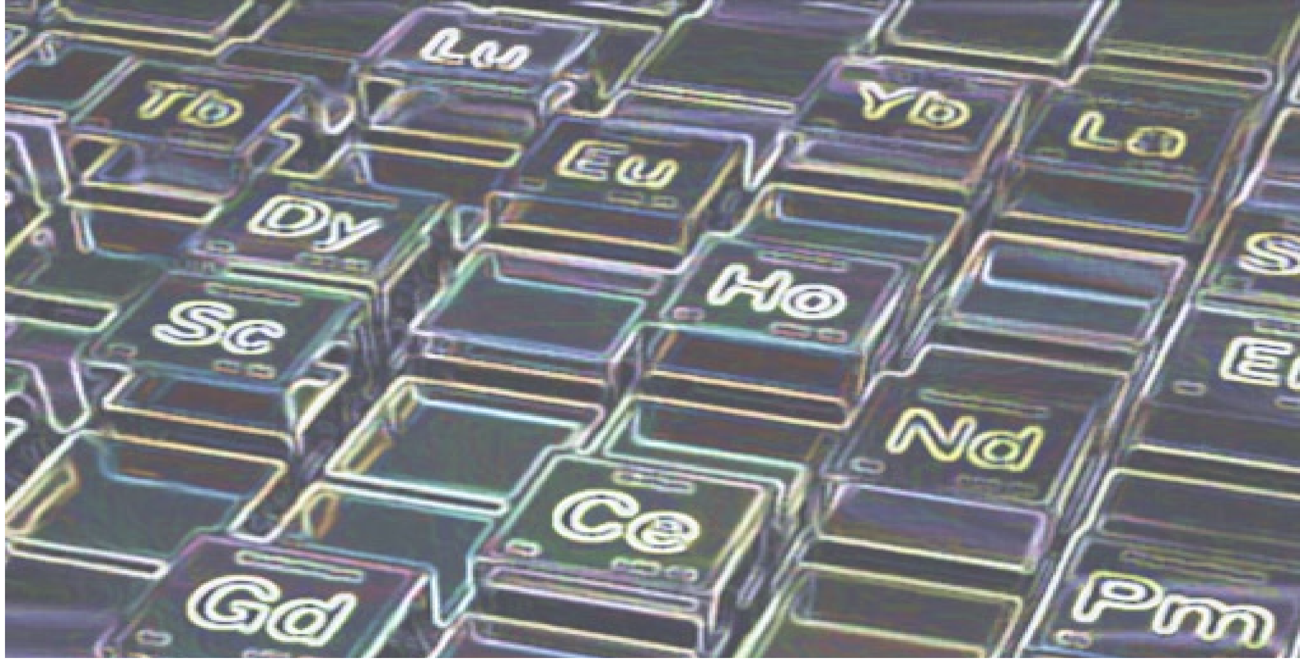


Project Current Status

NETL - RIC Separation Chemistry (Task 3)

Results compared to benchmark:

- **Reduce** in reagent consumption
- Reduction in process steps/complexity: e.g. **no pre-treatment (grinding, floatation) or reduction of solvent separations**
- Reduction in process intensity: **ambient temperature and pressure**

How have project goals changed?:

- Increased focus on maturing technologies:
  - Rapid move to larger scale experiments
  - Validation on representative feedstocks provided from industrial partners
  - Extended engagement with industry for partnership

Industry input/validation:

- Regular communication with industry partners
- Field work and test projects are underway/development with industry partners, and more are planned

Current Mines Targeting Middle Kittanning

- In 2019 44 mines targeting the Middle Kittanning coal seam produced coal
  - 34 mines in Pennsylvania
  - 3 mines in West Virginia
  - 7 mines in Ohio
- Production at each mine ranged from 601 tons to 4,274,748 tons
  - 32 mines produced more than 10,000 tons
  - 10 mines produced more than 100,000 tons
  - 2 mines produced more than 1,000,000 tons

Mine Name	State	Production (Tons)
Leer Mine	WV	4,274,748
Sentinel Mine/Leer South Mine	WV	110,6710
Mine Complex #6 Mine/Buckingham Mine No. 6	OH	829,737
Acosta Deep Mine	PA	401,848
North Fork	PA	363,971

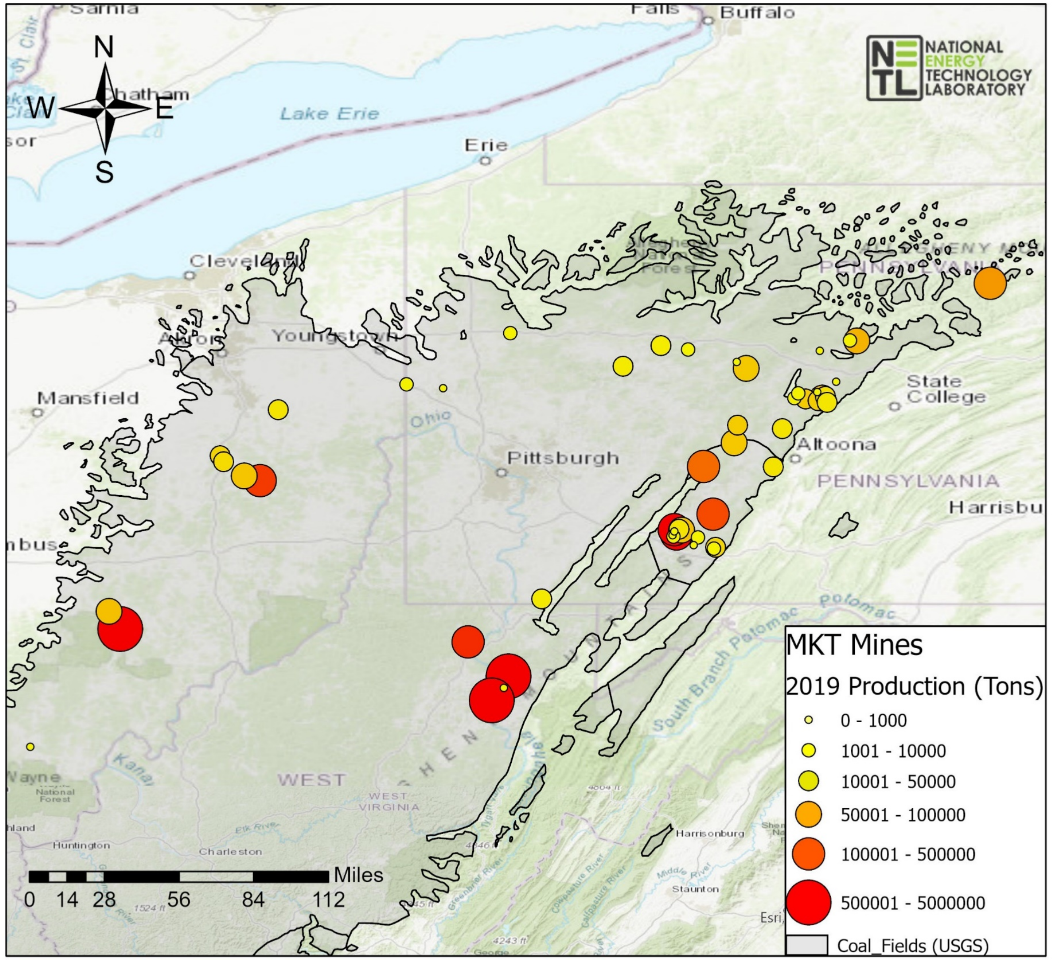
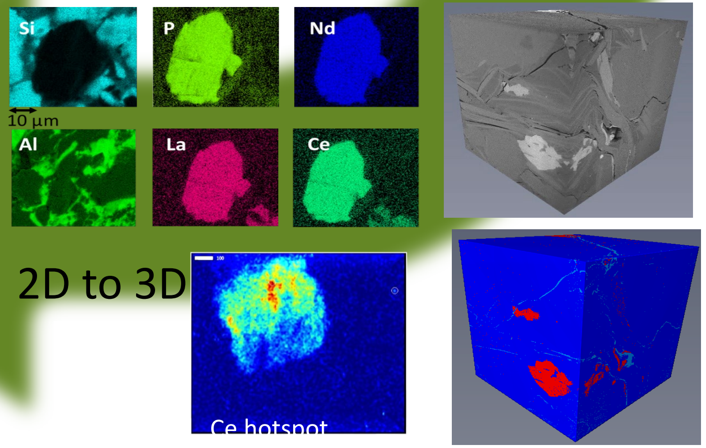


Figure : Map of permitted and active coal mines targeting the Middle Kittanning coal seam. Varying data sources for mine production.

Rare Earth Elements: Understanding the resource



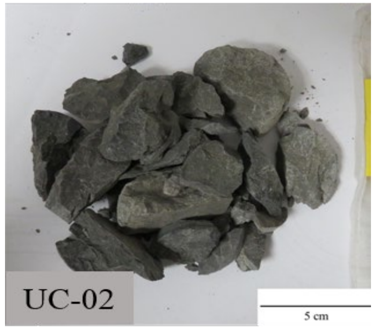
- Characterize underclay
- Quantification & benchtop/lab scale to inform future REE extraction techniques & optimal candidate feedstocks with salable REE concentrations
- Goal: upscale to the field/commercialization

REEs in Coal-Associated (Middle Kittanning) Clays

Sample Designation	Coal Seam	General Locale	Total C (ppm)	Total S (ppm)
UC-02	Middle Kittanning	WV, 1460 ft depth	22,767	1,293
UC-12	Middle Kittanning	WV, underground mine	9,765	36,450
UC-14	Lower Kittanning	PA, surface pit mine	1,370	224
UC-15	Middle Kittanning	PA, surface pit mine	17,600	12,300

Mineral composition from semi-quantitative XRD: Major (Ma) (>50%)-Intermediate (In) (25–50%) Minor (Mn) (5–25%)-Trace (Tr) (<5%).

Mineral	UC-2	UC-12	UC-14	UC-15
NON-CLAYS				
Quartz	Mn	In	Ma	Mn
Pyrite		Tr		
Marcasite		Tr		
Fluorapatite				In
Plag	Tr			
Carbonate (calcite/siderite)	In			
K-spar	Tr			
Ilmenite	Tr			
CLAYS				
Halloysite	Mn			
Kaolinite	Mn	In	Mn	Mn
Smectite	Mn			
Muscovite		In	Mn	Ma
Illite	Mn		In	
Total clays	57.3	65.6	57.7	72.5



REE in Sedimentary Deposits

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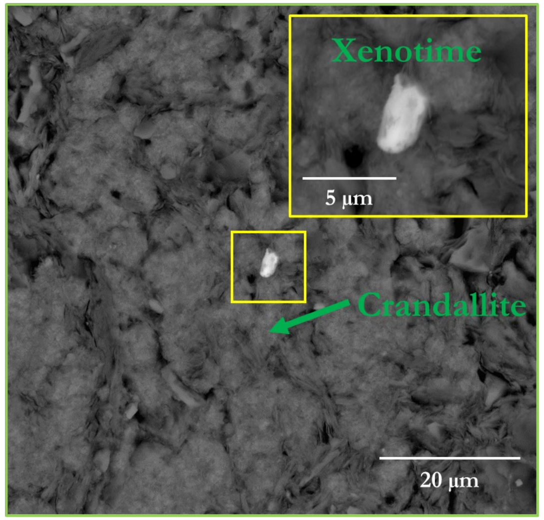
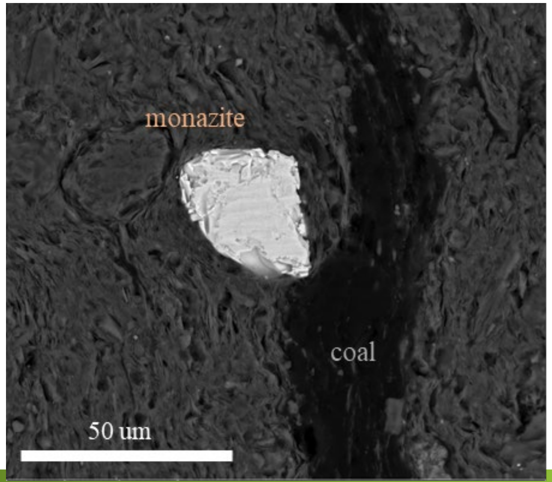
Primary REE minerals

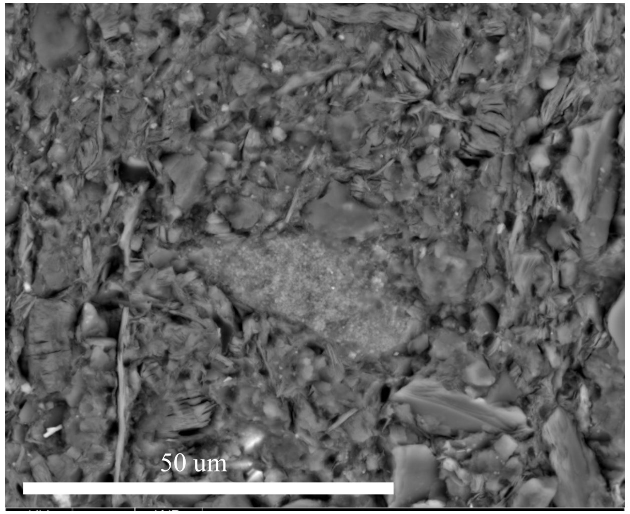




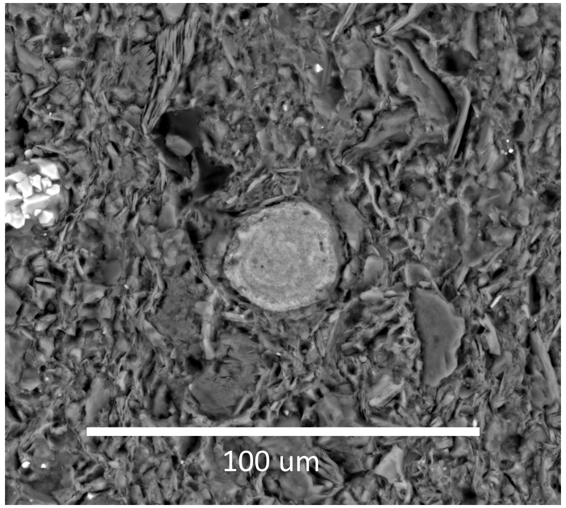
Trace minerals in underclays
Pyrite (La, Ho, Dy, Lu, Yb, Er)
Chalcopyrite (La, Nd)
Ti-oxide (Lu, Er, Nb)*
Zircon (Lu, Sc)*
Siderite
Galena
Fe-oxide (Er)
Monazite/ rhabdophane (La, Ce, Nd, Gd)
Xenotime/ churchite (Y, Sm, Eu, Gd, Dy, Er, Tm, Yb)

Our Process Targets:

Secondary minerals/colloids/adsorbed components



crandallite

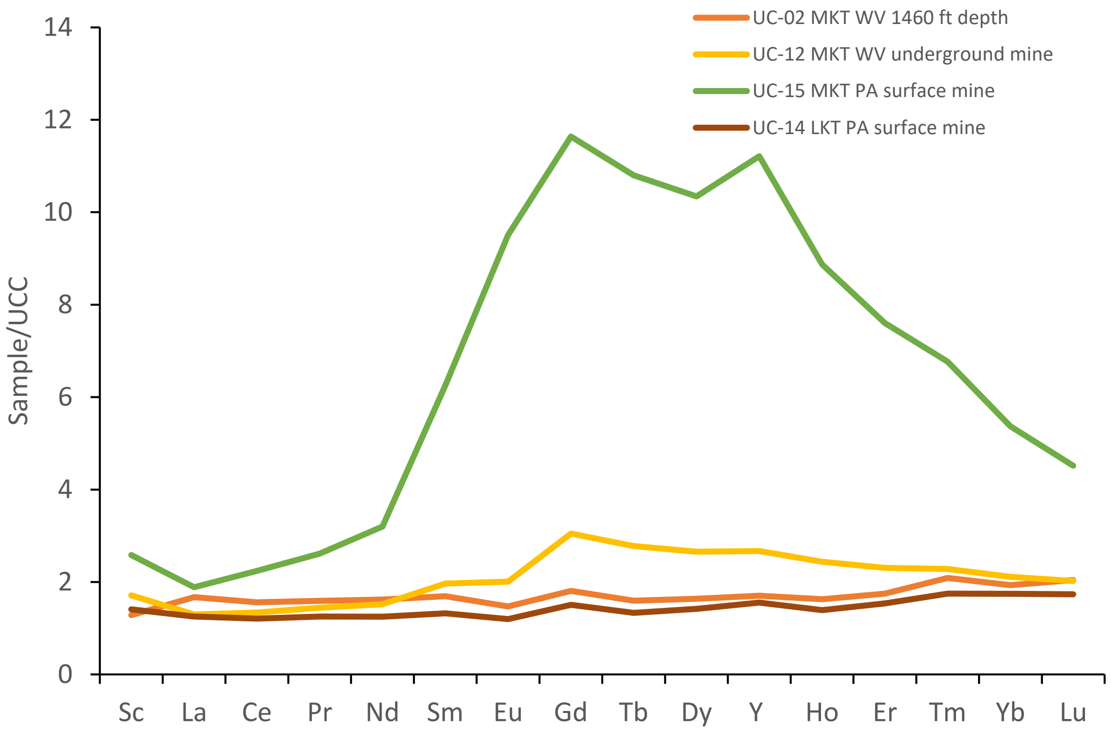


apatitic minerals

REEs in Coal-Associated (Middle Kittanning) Clays

Sample Designation	REY	Sc	Co	Ni	Cu		GdN/LaN	YbN/LaN	Y*
	ppm	ppm	ppm	ppm	ppm				
UC-02	276	18	20	24	20		1.1	1.2	1.04
UC-12	281	24	44	107	107		2.3	1.6	1.05
UC-15	713	36	21	68	65		6.2	2.8	1.17
UC-14	219	20	8	28	18		1.2	1.4	1.11

- Middle Kittanning clay materials from directly below the coal seam show a strong middle-REE enrichment
- In the case of UC-15 MKT Central PA surface mine sample, middle-REE enrichment can account for a total REE content of 713 ppm



MKT = Middle Kittanning
LKT = Lower Kittanning

*Samples normalized to Upper Continental Crust

Coal waste & underclay as a feedstock

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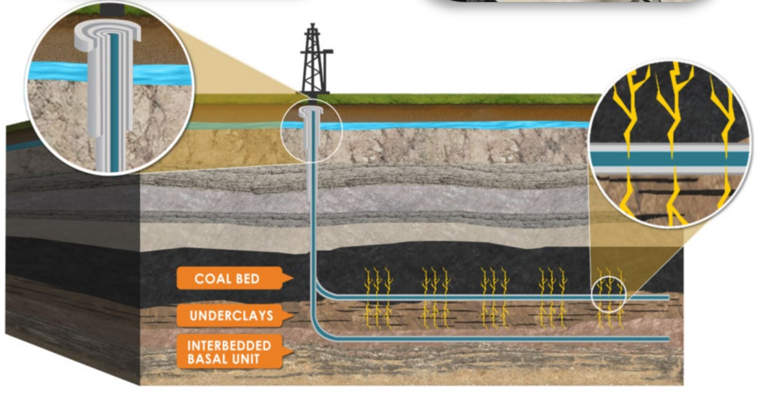
- **Mild organic acid**: less hazardous chemicals than conventional approaches
- Targets accessible ion-exchangeable REE species & mineral surfaces at ambient pressure/temperature
- **Up to 30% of REE** without extracting other gangue materials, reducing chemical costs and downstream processing requirements

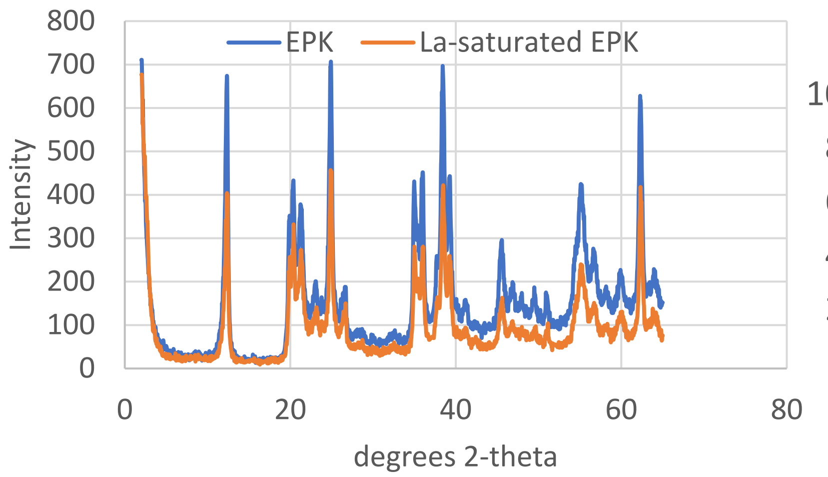
- <u>Multiple Potential Applications</u>:
  - ***Ex situ* heap leach recovery & plant processing** from coal mining waste and co-mined materials
  - ***In situ* recovery** from undisturbed sedimentary rock layers, open pits, or underground mines

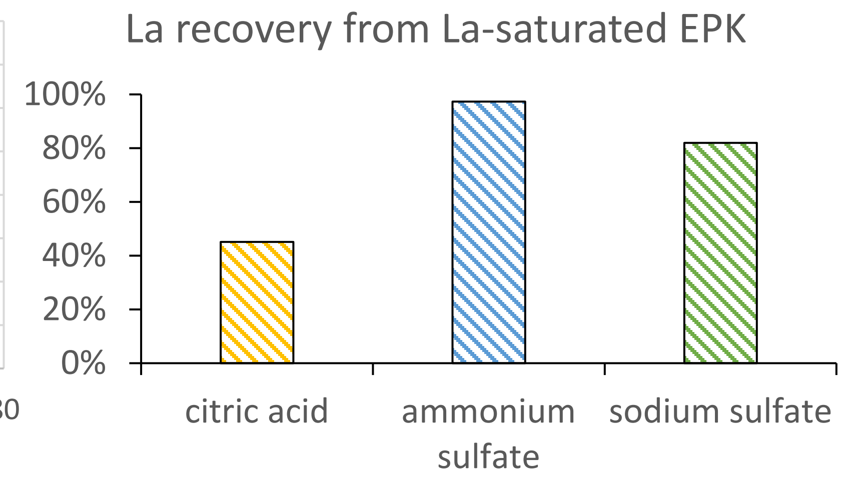


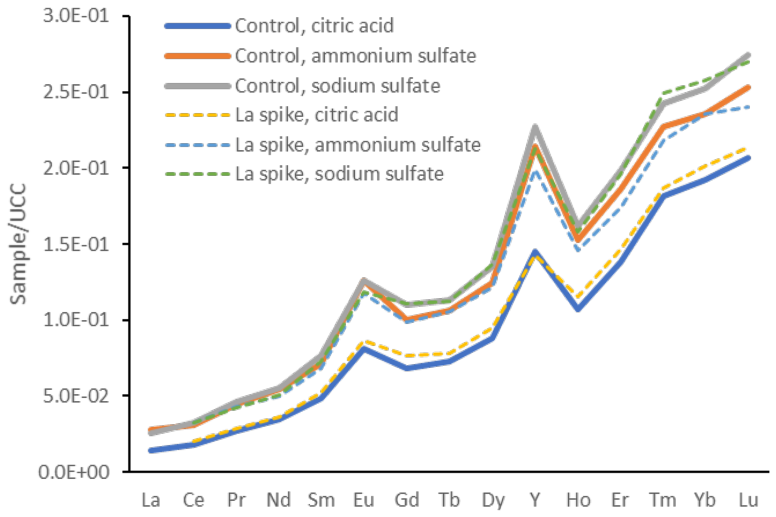
Non-Provisional Application filed, S-150,861, September 2020.
C. Verba, M. McKoy, T. Tarka, S. Montross, J. Yang, "Process for Extraction of Recoverable Rare Earth Elements (REE) Using Organic Acids and Chelating Compounds,"

Edgar Plastic Kaolinite (EPK) La-sorption/desorption

- Determine efficacy of citrate solutions in extracting sorbed lanthanides on clay surfaces, using a synthetically prepared La-sorbed clay
- Isolate the effect of ligand-promoted extraction from ion exchange
- Isolate effect of citrate speciation (with NaOH buffer)
- Compare efficacy of citrate solutions to $(NH_4)_2SO_4$ and Na_2SO_4



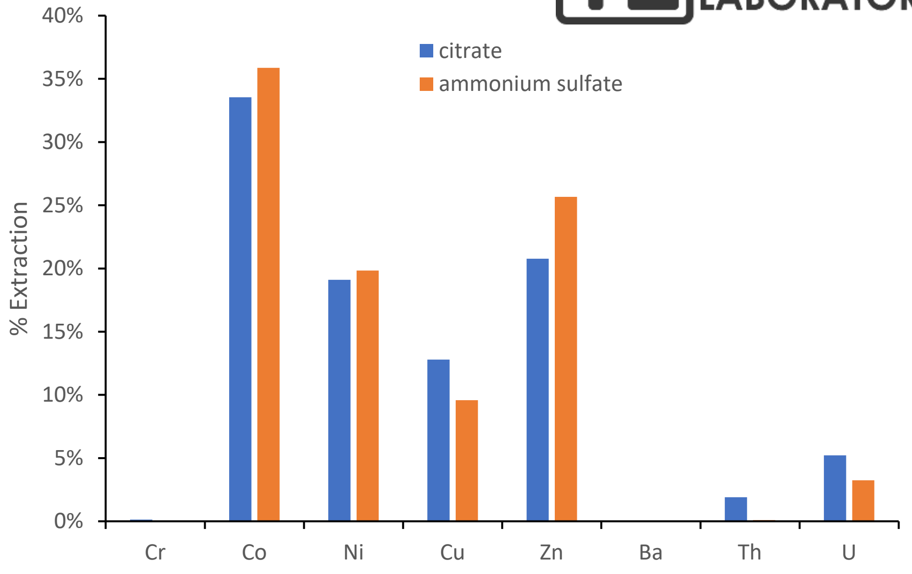


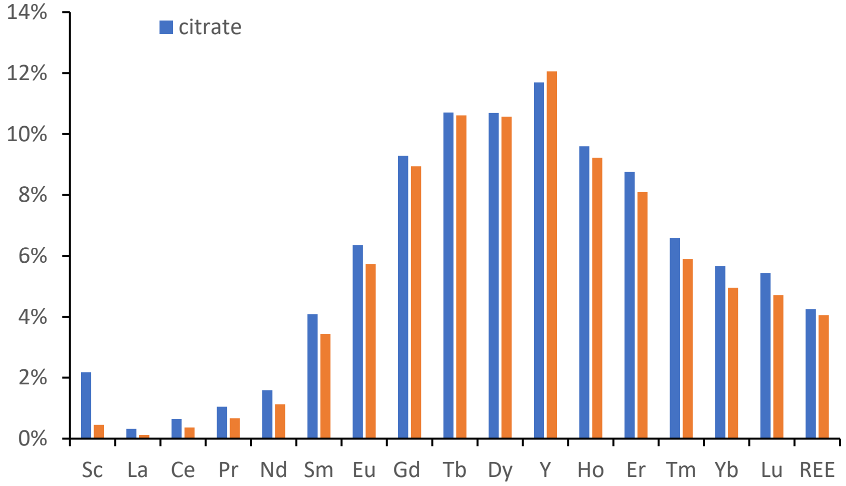


Waste Coal heap leaching applications

Upscaled (~10kg) column experiments

- Packed columns with Middle Kittanning (UC-12) underclay with a 0.1 M citric acid/sodium citrate solution buffered at pH 5 (1:1.2 leach ratio)
- **~4% TREY**
- Similar extractions levels obtained using ammonium sulfate solution
- 30-35% Co; 20% Ni; 10-13% Cu extracted in both the citrate and ammonium sulfate
- Sharp drop in pH → pyrite oxidation or other Fe sulfide phase.

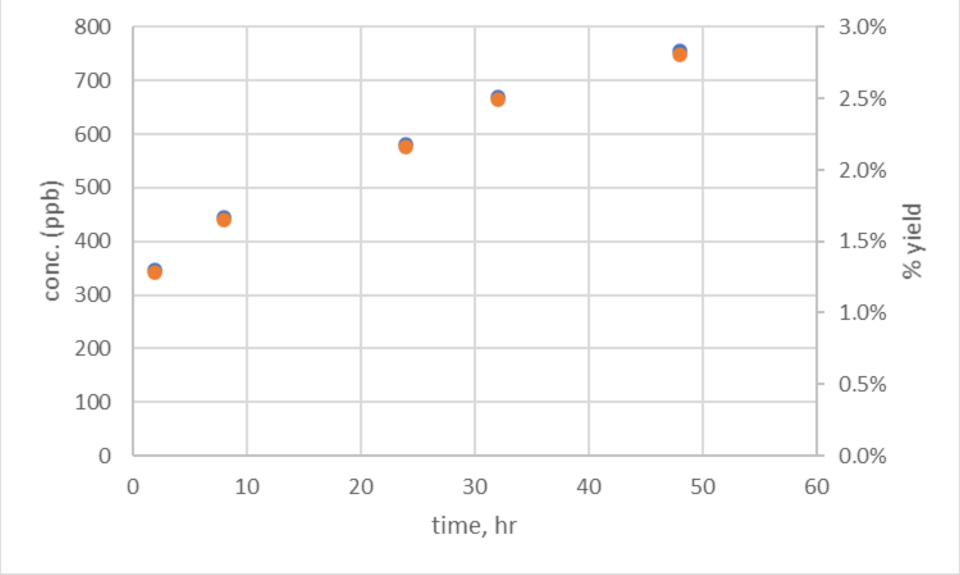


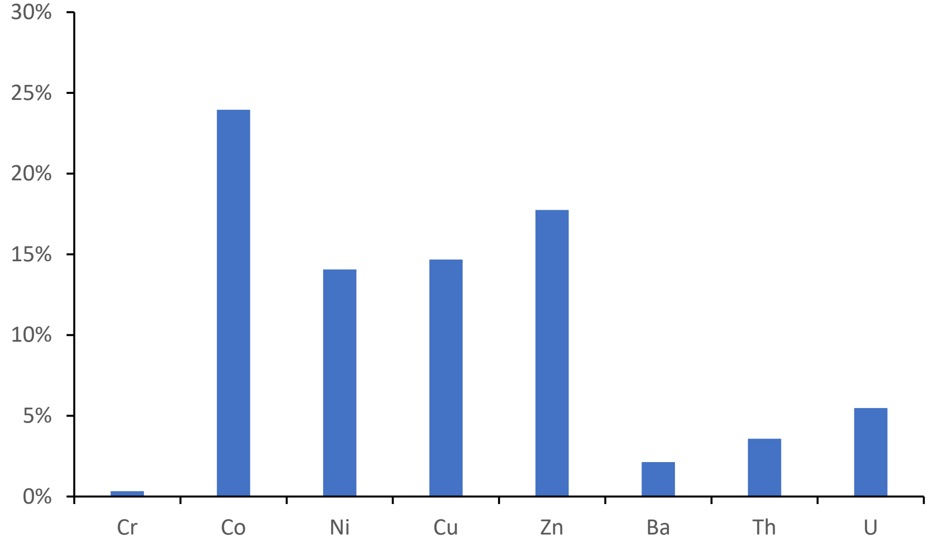


Batch processing

Upscaled experiments: 55-gal drum

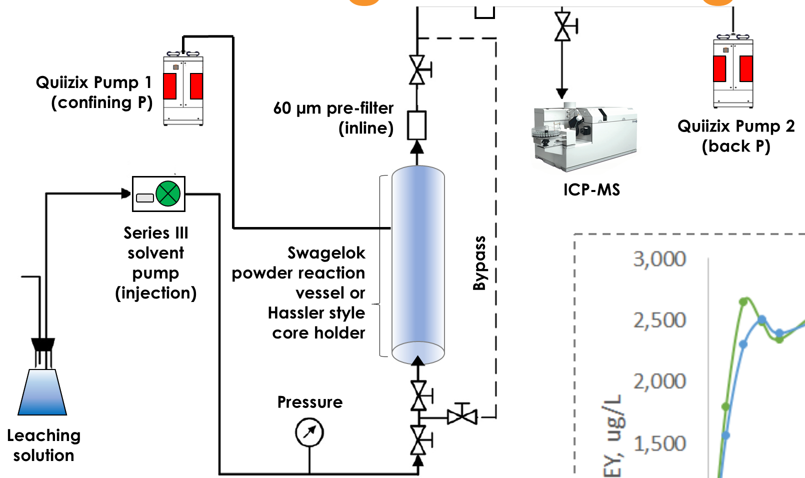
- 0.1M sodium citrate solution (pH 5) will be continually mixed with pulverized underclay for up to 48 hours
- 10 kg underclay – 100 L solution (1:10)
- **3% TREY**
- ~ 8% Gd and Tb <2% La, Ce, Pr, and Nd
- 24% Co; 14% Ni; 15% Cu; 18% Zn
- Low recovery, but may need longer residence time or different water amount
    - Experiment being repeated for longer duration (May 2021)

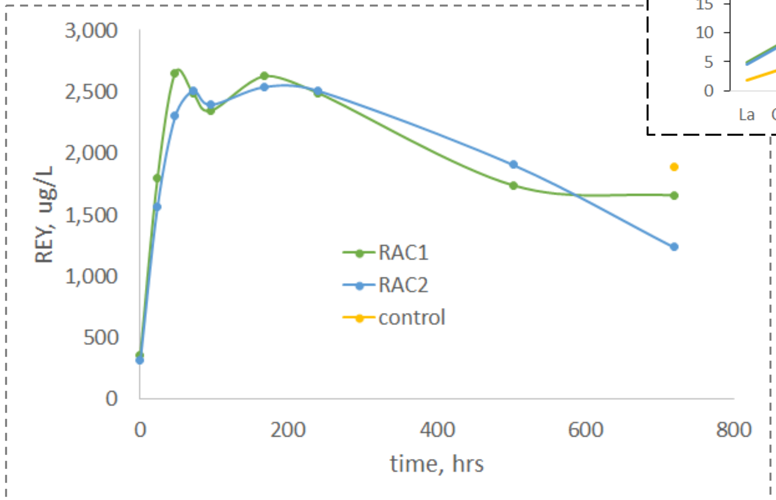


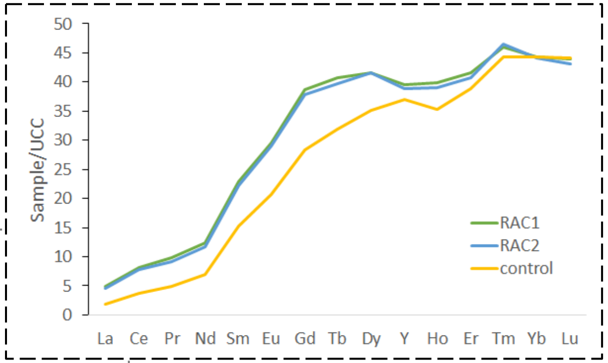


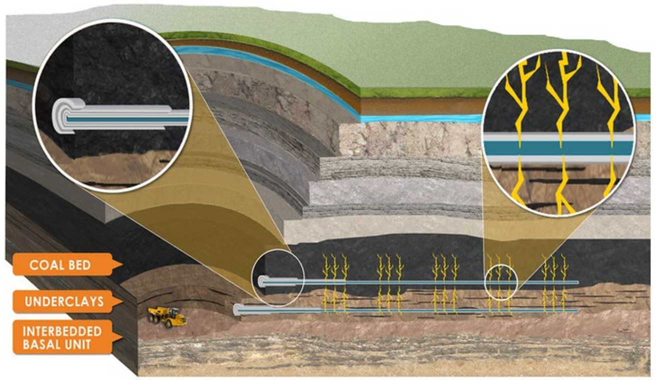
In-situ applications: underclay-coal partings

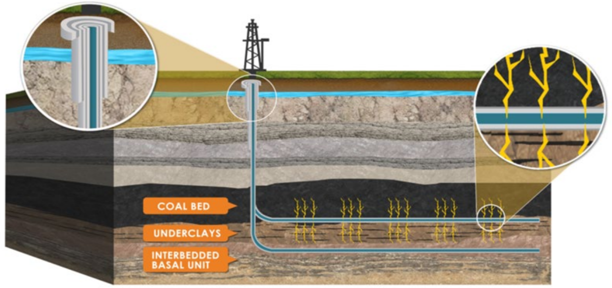
Flow-through & rocking autoclave experiments









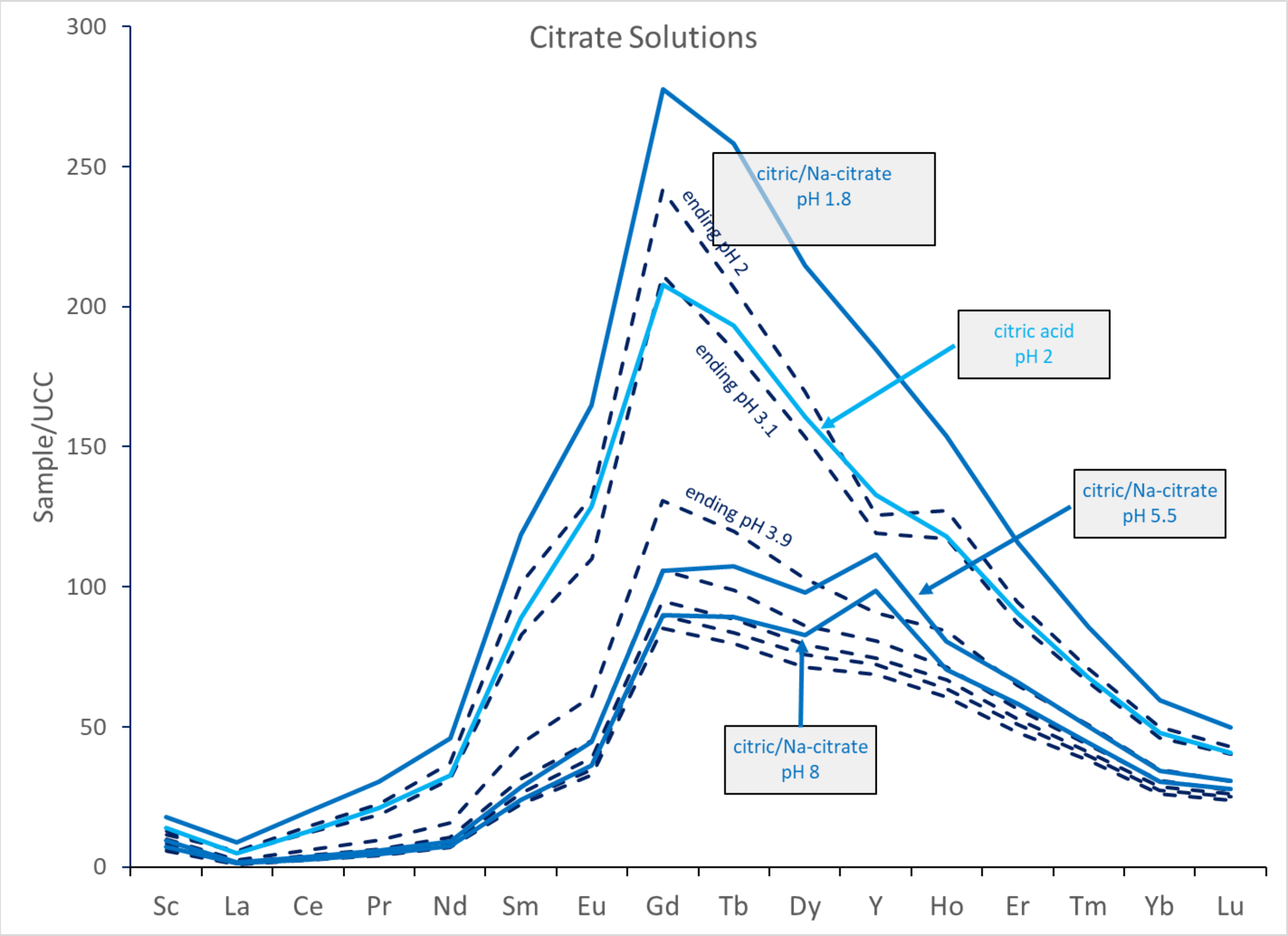


- Simulated downhole testing ranging from 20 min to 30 days; limited extraction <2.5%
  - 2-7 days for maximum REY extraction (lithology dependent)
- Citrate solutions show tendency towards **heavy REE recovery** relative to light REE
- Recycling solution will play a role to improve recovery

Waste Coal optimization

Organic acid by pH

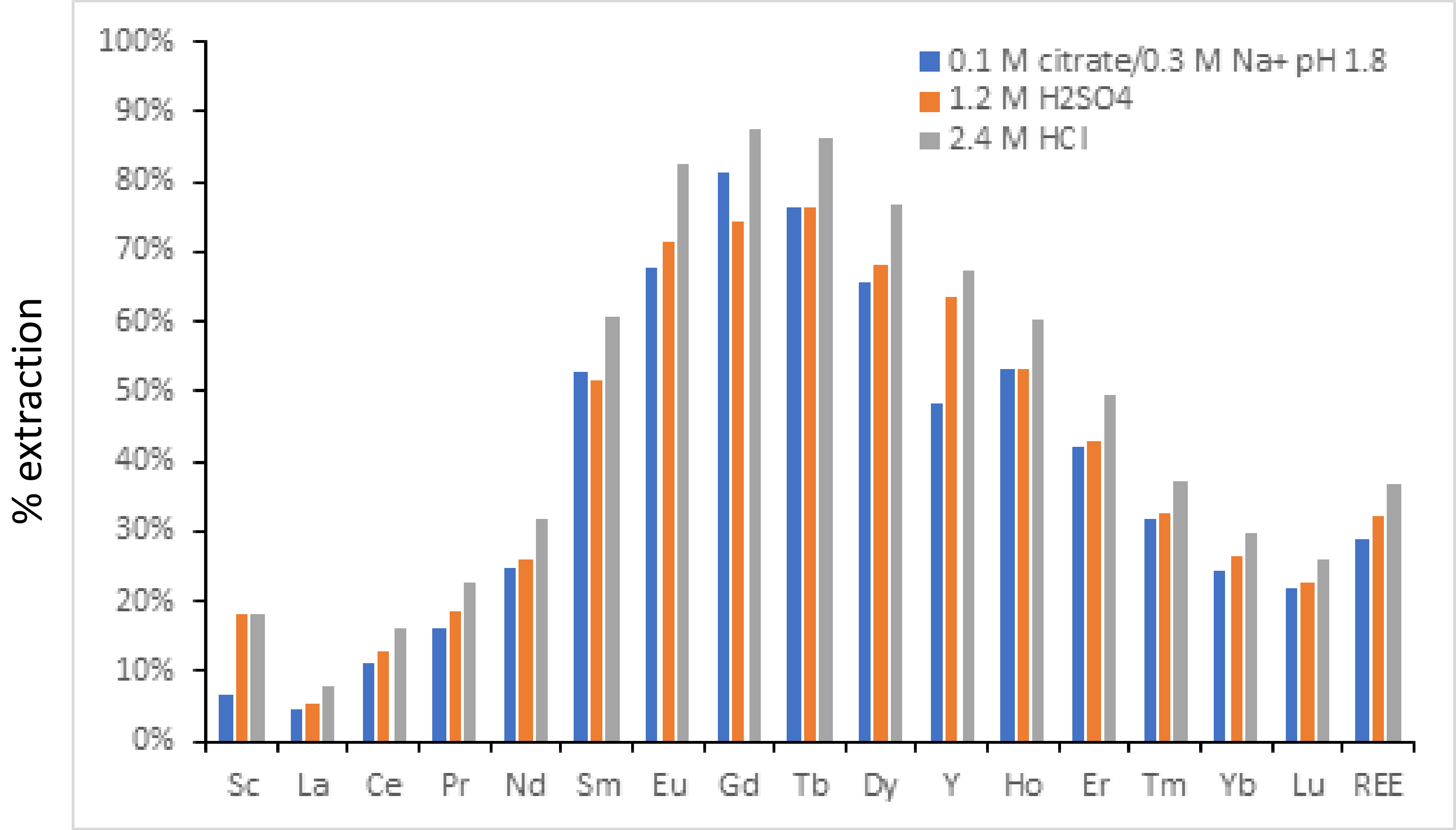
- Scoping tests were conducted on a Middle Kittanning underclay sample (West Virginia) to isolate a mechanism of REE (and other critical metal) extraction
- Maximum REE extraction of **~30%** at pH 2



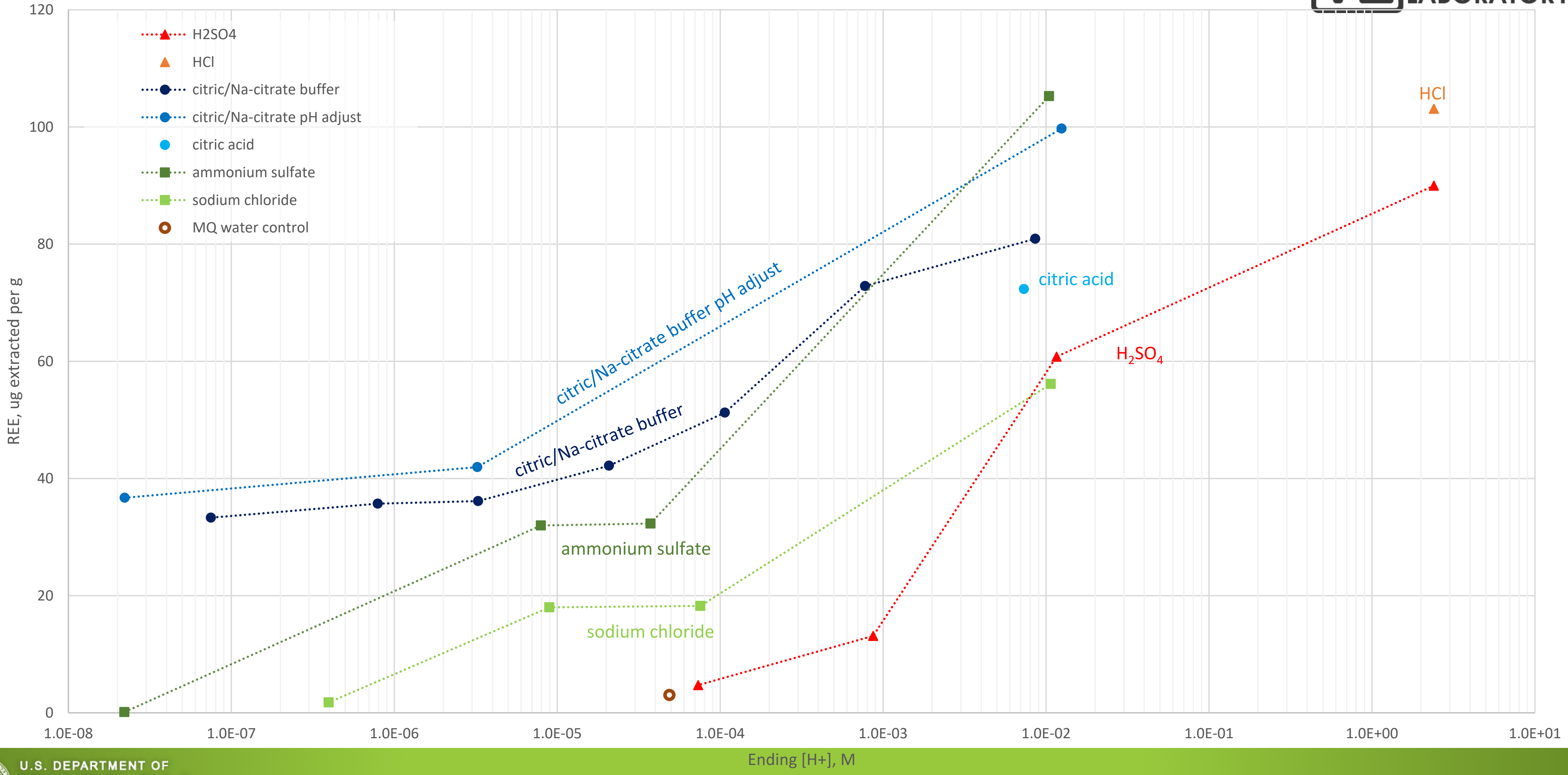
Waste Coal Optimization

Organic acid by pH

- Extraction liquids were relatively more enriched in MREE/HREEs
- 70-80% extraction for Gd and Tb at pH ~2
- Co-extraction of ~70% Co, ~40% Ni, ~25% Cu



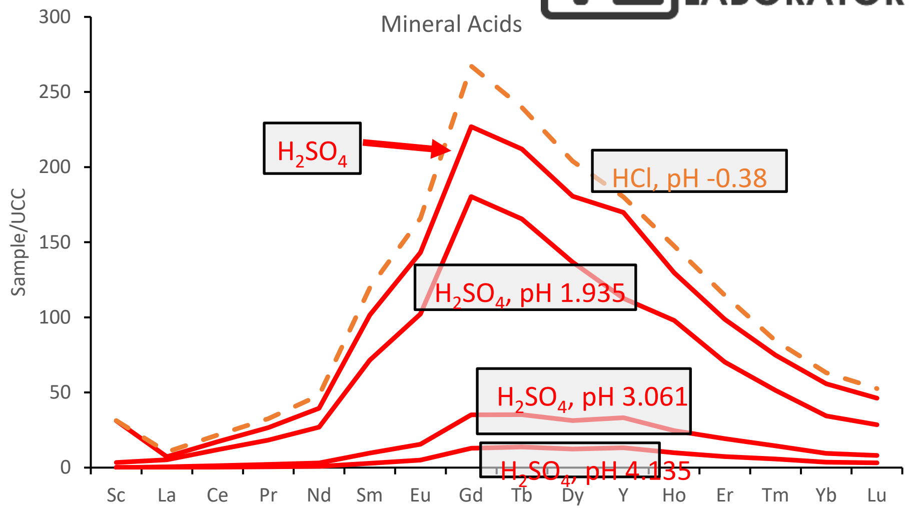
Organic vs conventional acid

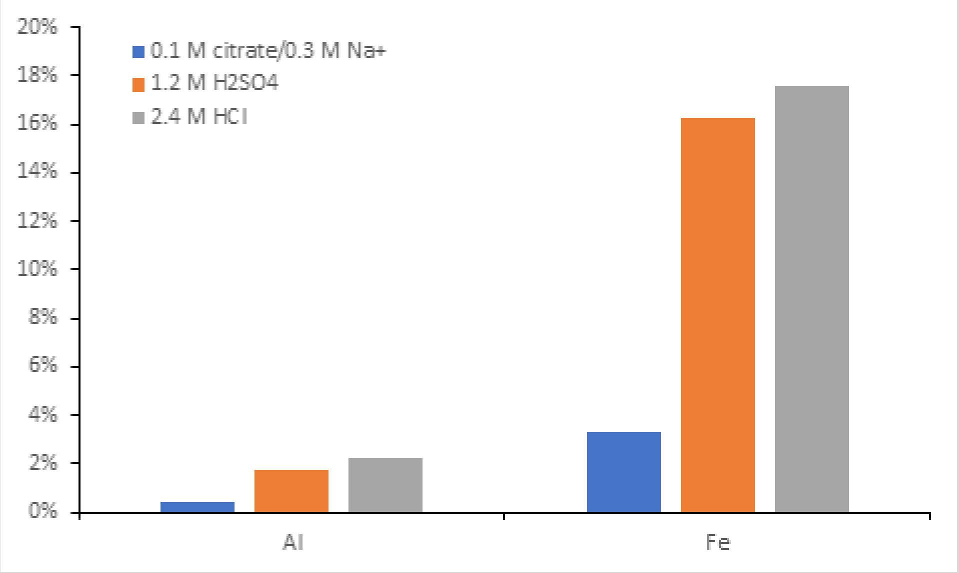


Waste Coal optimization

Conventional mineral acid recovery

- Optimal solution composition (i.e., REE and critical metal extraction against gangue element). Mildly acidic solutions (pH 2-3) were found to have comparable performance in REE compared to concentrated acids (Middle Kittanning)
- H_2SO_4 or HCl extracted **32% and 37%** of the REEs
- 100%* Co, ~65% Ni, ~50% Cu
- Nearly 4-5x amount of Al and Fe in concentrated acids compared to mildly acidic solutions

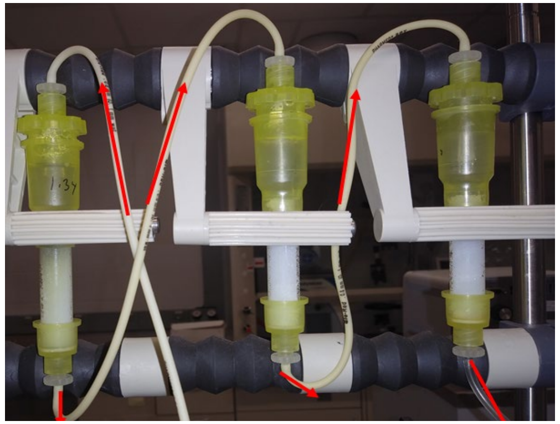


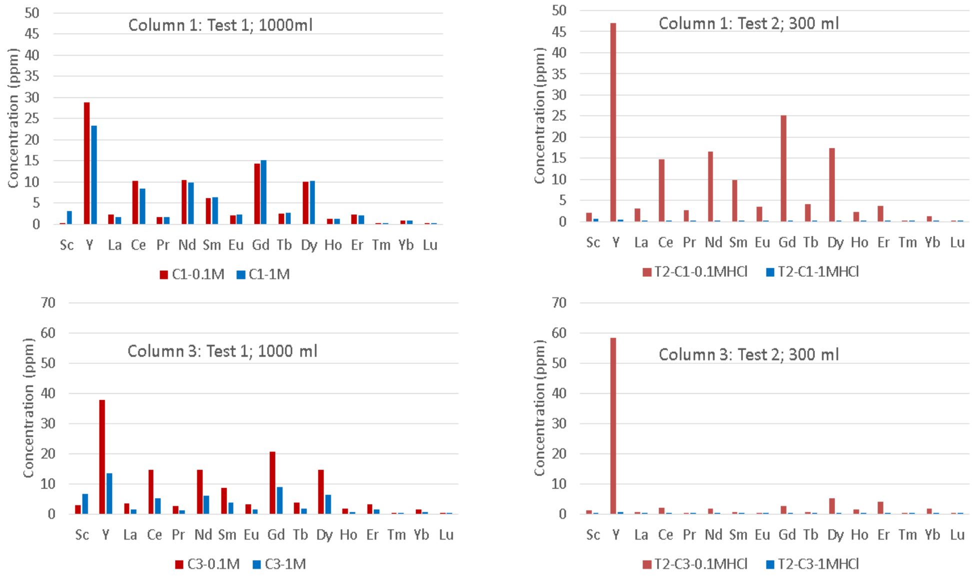


Citrate recycling: Sorbent

Synergistic effort BIAS Sorbent to Enable Solution Recycling

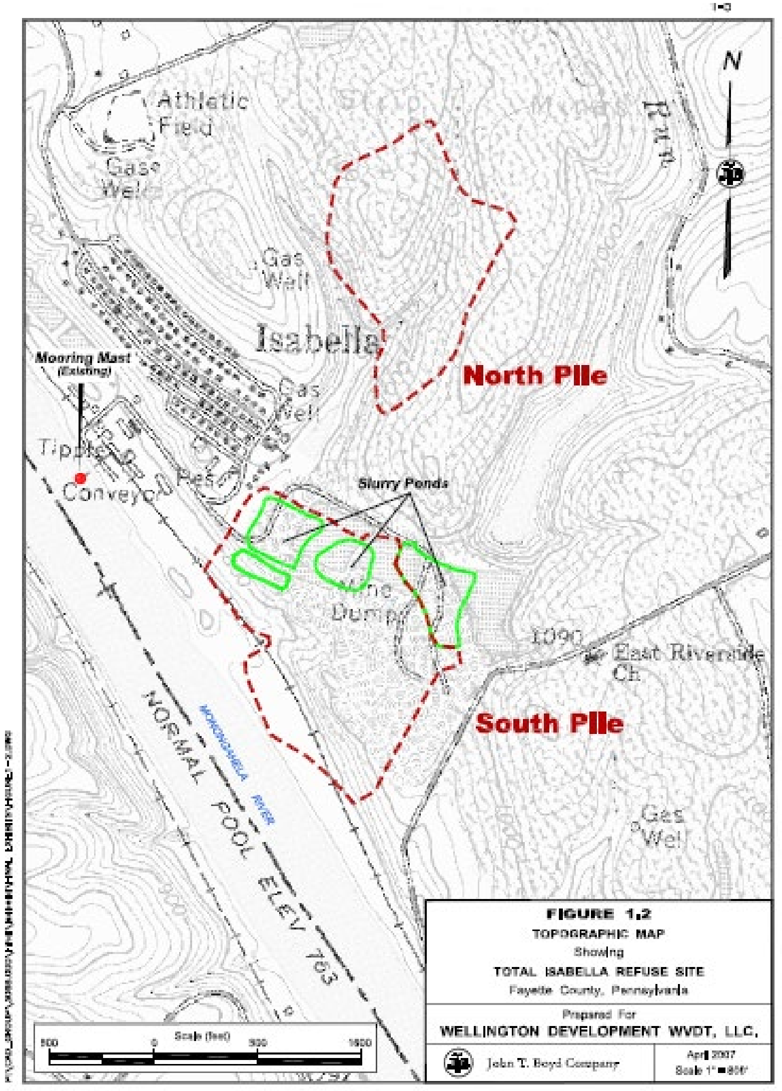
- REE concentrates of **3.6 wt% (~70% REE)** from 300 ml and **<1.4 wt% (<30% REE)** from 1 L citrate-underclay PLS feedstock from BIAS 181D packed beds
  - Citrate concentration issue (ion-exchange/sorbent pairing)
- Successful coupling of these technologies will allow acid recycling, dramatically reducing operating costs
- 30 g of 181D per L of leachate may be required (10x more)
- Additional testing required





EY20 Field work (PA, WV)

- Fairmont repository / waste rock facility.
  - Isabella refuse site – Fayette County, PA
  - 9 samples collected from repository and gob piles
  - Selected based on trace metal content and Y (pXRF)



- Mine wall underclay sampled (Middle and Lower Kittanning) from PA surface mine
- Goal: clarify vertical heterogeneity
  - AHA/approval was granted;
    - mine access request pending
  - Evaluating alternative feedstock sources.

Cash Flow Summary (Ex-situ Heap Leaching)

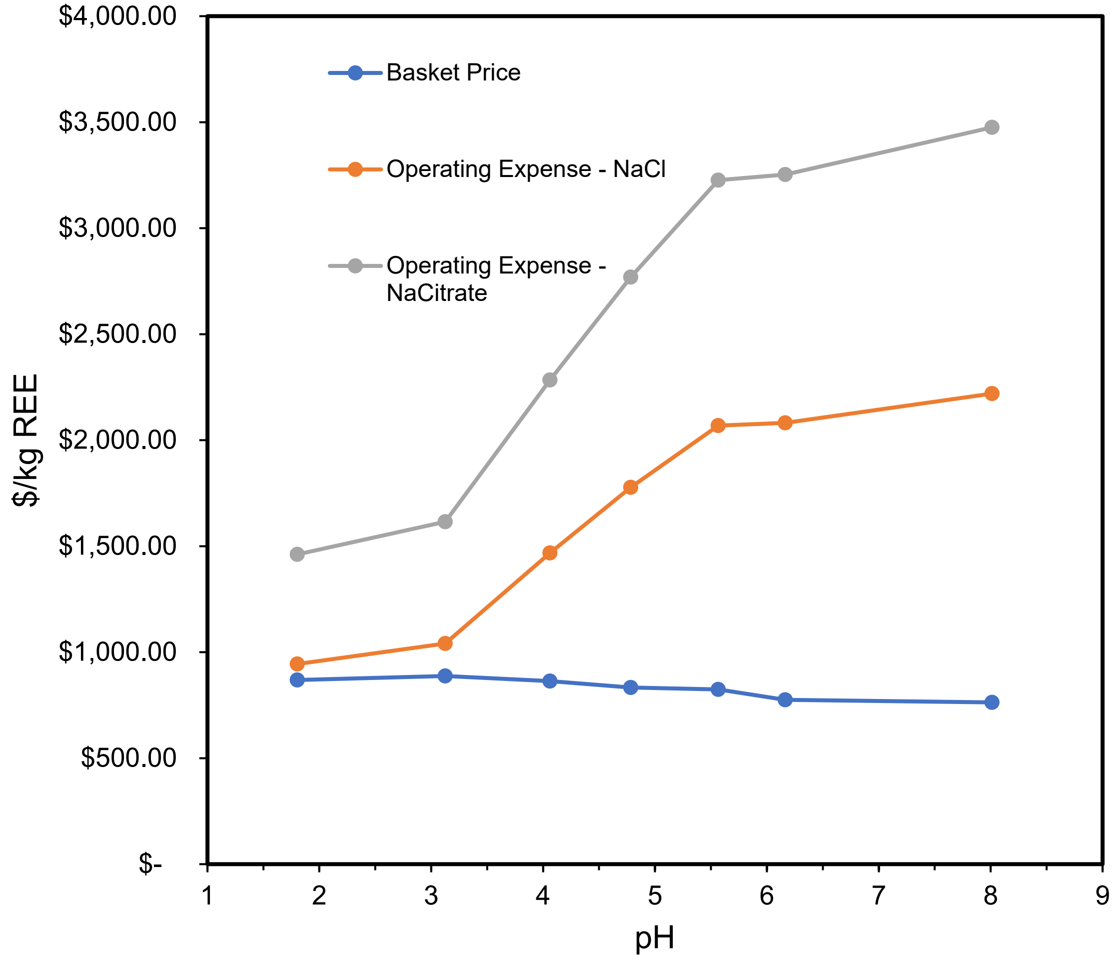
Parameter	5% Recovery	12% Recovery	35% Recovery
Variable Operating Expenses – Recycling Scenario, 10% L:S	$5,000/kg	$2100/kg	$770/kg
Fixed Costs	$190/kg	$79/kg	$27/kg
REE net revenue	-$4,100/kg	-$1,100/kg	$300/kg
REE production	33 Ton/yr	78 Ton/yr	230 Ton/yr

- Variable operating expenses are lower than the maximum basket price scenario at 35% extraction efficiency with a total expected net revenue of $66 M/year
- Facility throughput assumes Appalachian waste reserves extracted over 25-year period
- Maximum Basket Price Assumption: $1,100/kg of REE

Modeling pH Dependency of Recovery

Based on experimental Citrate and Sodium Citrate solutions

- Wastewater disposal/chemical costs increase with lower pH
- REE extraction efficiency outpaces operational costs with increasing acid consumption.
    - Basket prices are relatively constant.
- Economics will depend on further optimization



Next Steps

Coal waste & underclay

Use TEA screening results to target improvements to extraction plans to reduce operational costs

- **Maximizing extraction yields**
  - **Optimize heap depth, crush size (hydraulic conductivity)**
  - **Optimize residence time of solution, optimize the level of saturation**
- **Isolate chemical controls on extraction and identify REE phase extraction selectivity to develop feedstock criteria of future targets**
  - **i.e. water soluble, ion absorbed/exchangeable, Mn/Fe oxides, sulfides, and residual.**
- **Demonstrate REE separation from pregnant leachate via mineralization/precipitation and conversion to REE-oxides or chloride precipitates.**
- **Evaluate Critical Metal co-extraction (Cu, Co, Ni, etc.)**
- **Demonstrate feasibility of ex-situ extraction at next largest scale**

Collaboration & Future Field Work

Coal waste & underclay

Industry partnerships are crucial for scale up demonstrations of underclay targets.

- Waste coal processing/characterization of the Fairmont Repository and GOB piles
- Identify target mines with characteristics that align with necessary feedstock parameters for potential field site.

PHASE I:

- Develop industrial CRADA
- constrain real world heap leach heterogeneity etc.
    - (e.g. core drilling or LIDAR)
    - Constrain heap leach parameters on benchtop
- Preliminary site coordination and planning for operations (material supply/waste disposal)
- Go/no go: access/permitting to proceed with PHASE II

- PHASE II: Develop field test to demonstrate that NETL developed technology can work in the field and be scalable.
    - EY22 Execute preliminary testing to deploy extraction methods beyond the lab scale
    - Determine field test scale, optimize controls for environmental conditions
    - Contingent upon achieving benchmarks for extractability and industrial partnership

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- **This material is based upon work supported by the Department of Energy research under REE/Minerals Sustainability FWP.**

Sources of Mine Production Data

Coal Data Browser - List of mines for all coal, total, Appalachia Northern, all mine statuses [WWW Document], n.d. URL https://www.eia.gov/coal/data/browser/#/topic/38?agg=0,2,1&rank=g&geo=00000000000001&mntp=g&freq=A&start=2001&end=2019&ctype=map&ltype=pin&rtype=b&pin=&rse=0&maptype=0&datecode=2019

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