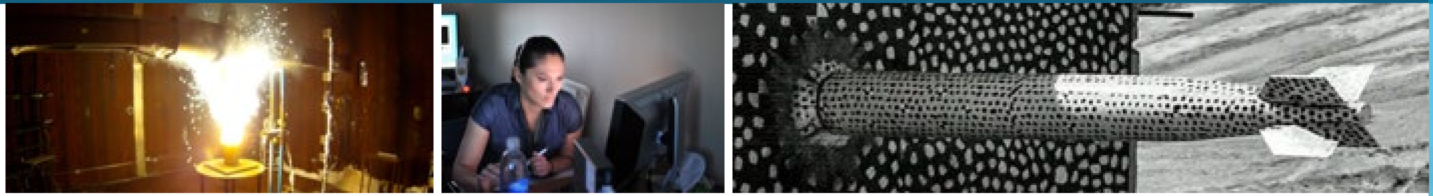
Recent Advancements in Critical Minerals Recovery at Sandia



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DOE Alaska Workshop on Critical Materials

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Controlled by: Sandia
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Recovery from Critical Minerals from Coal Ash

Balance of Recovery Efficiency vs. Cost ($ + environmental burden)

(685 ppm total w/ 70% recovery)

0.480 Kg REE +

0.8 ton coal ash in 2 ton H_2SO_4 acid solution

What will you do with the waste?

It is NOT economic viable!

When working with solid waste:

- High recovery efficiency is not always cost effective
- Waste picking strategy (i.e., recover as much as you can with minimum effort and minimum environmental burden)

Lower yield but time efficient and min mess

Max yield but creating mess

An analogue: How can the waste picker recover the most value with minimum effort AND has the permit from owner of the waste?

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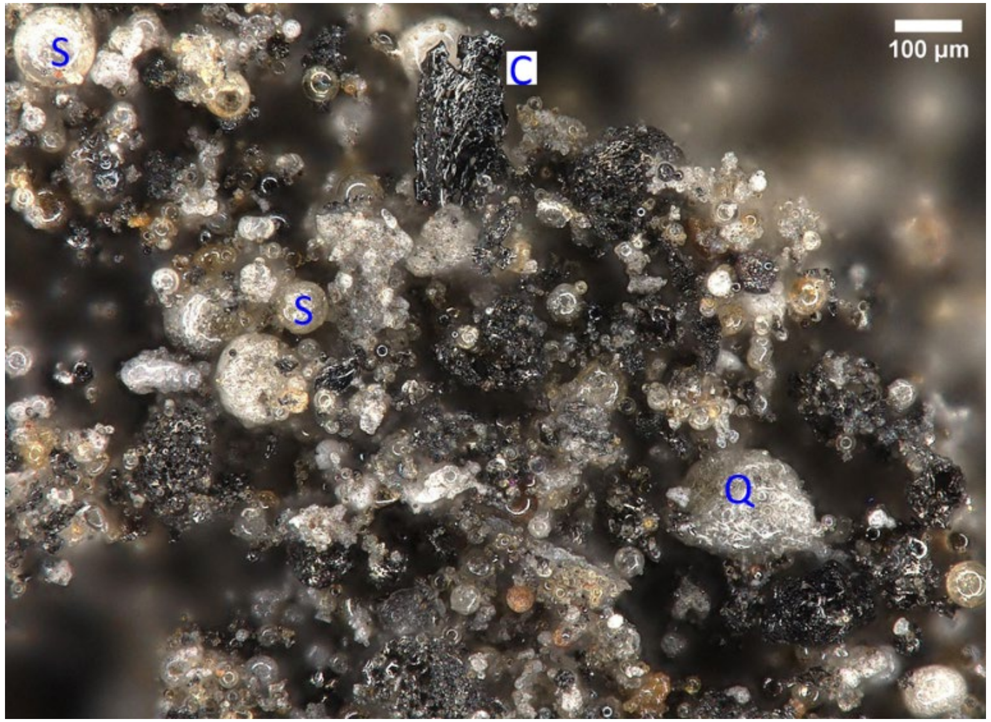
Recovery from Critical Minerals from Coal Ash

Environmentally benign is a priority!

Environmentally benign chemicals: Citric acid



Total 685 ppm REE-Y-Sc

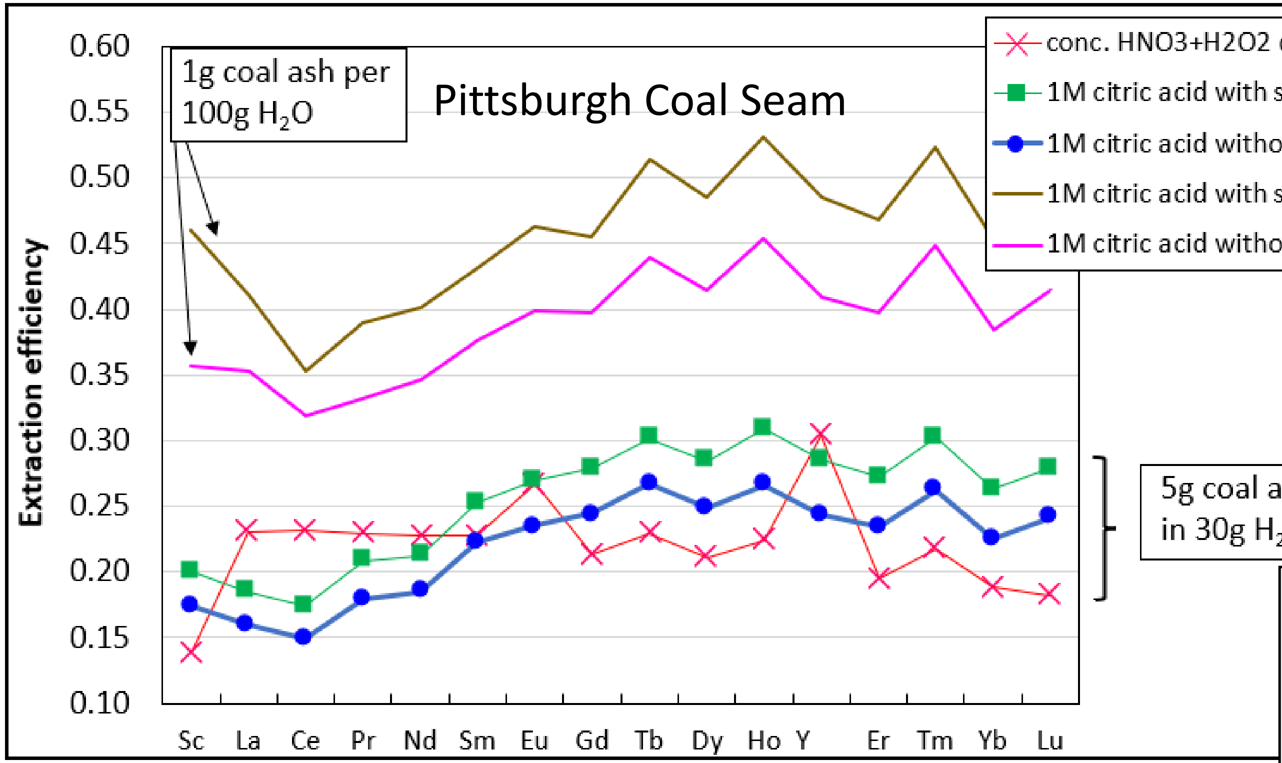
Pittsburgh Coal Seam

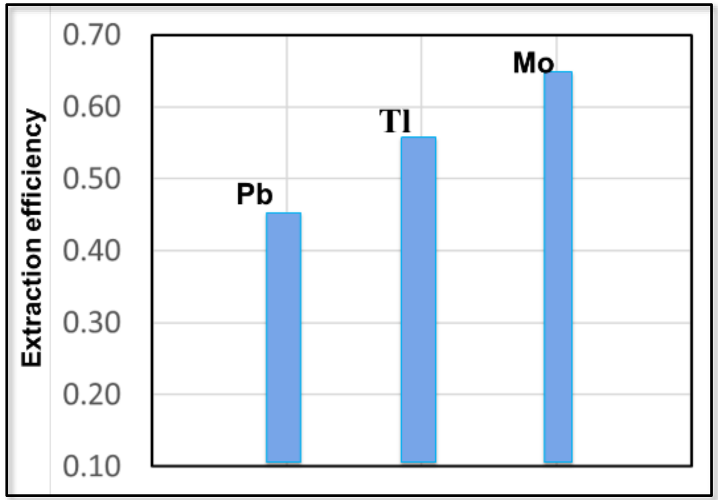
Total ~400 ppm REE-Y-Sc

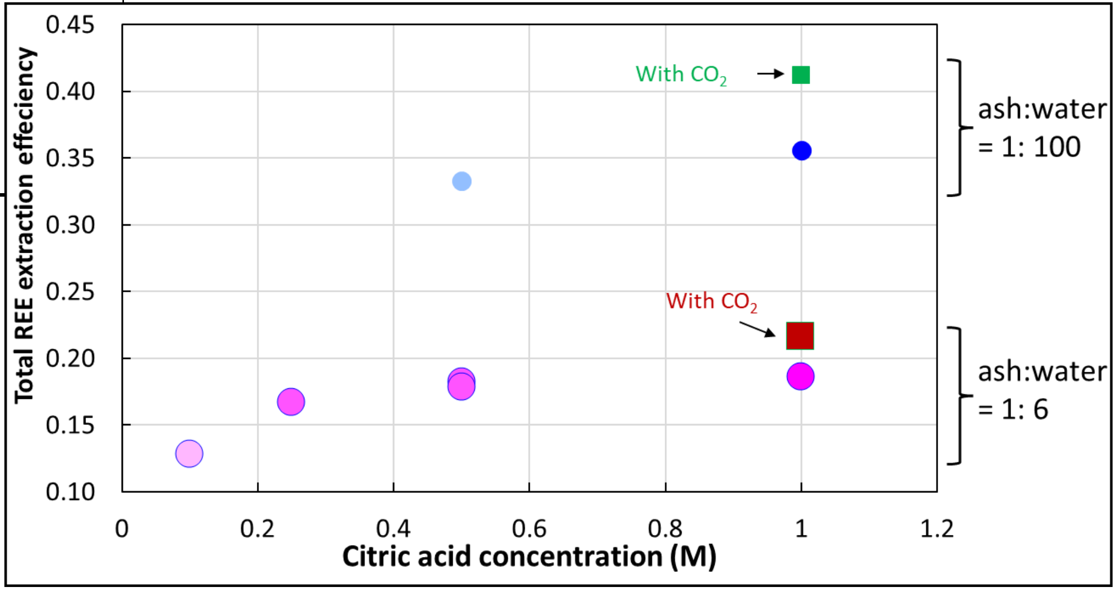
Originated from Powder River Basin (PRB) Coal

Recovery from Critical Minerals from Coal Ash

Citric acid + supercritical CO_2 leaching



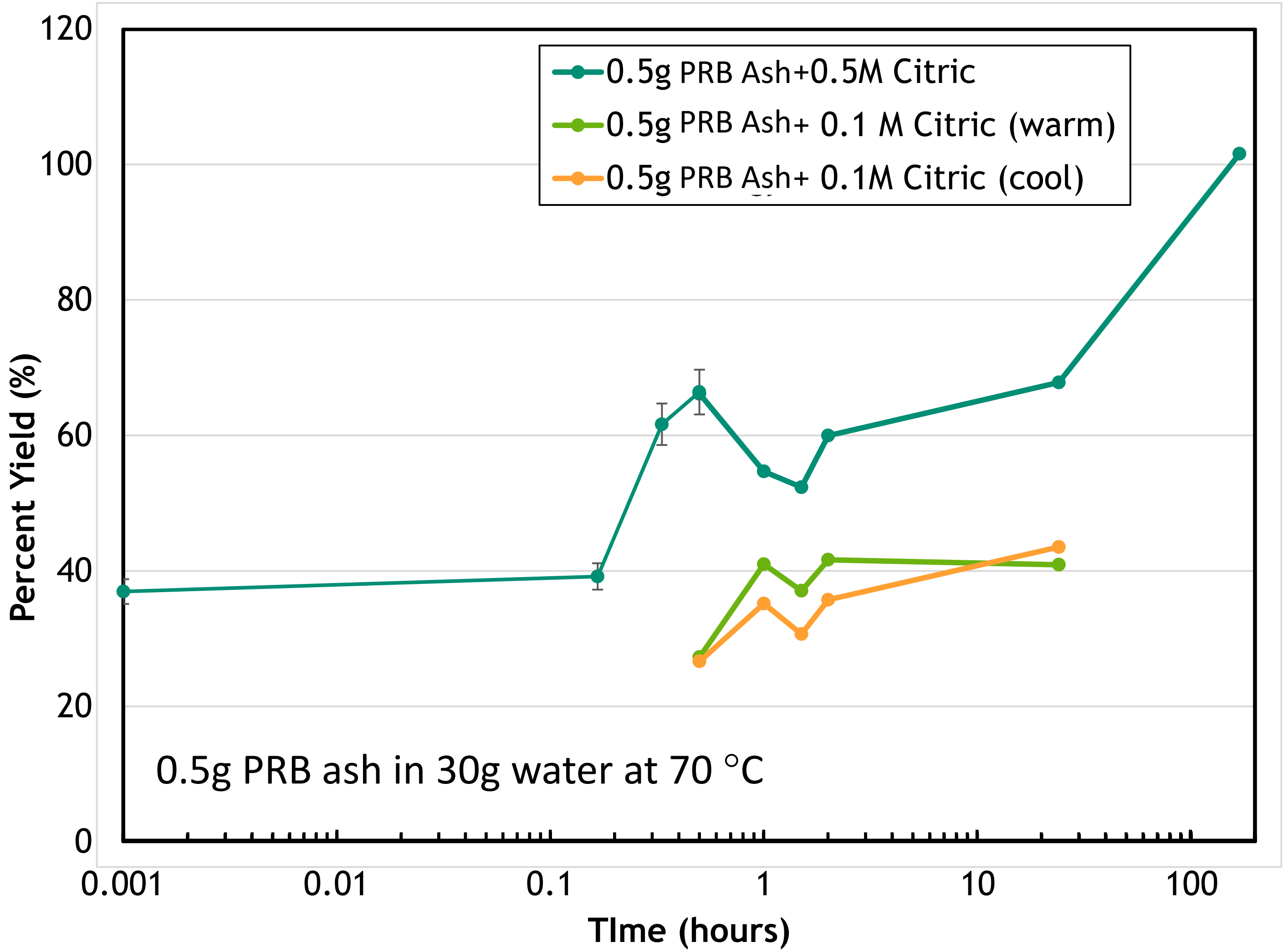




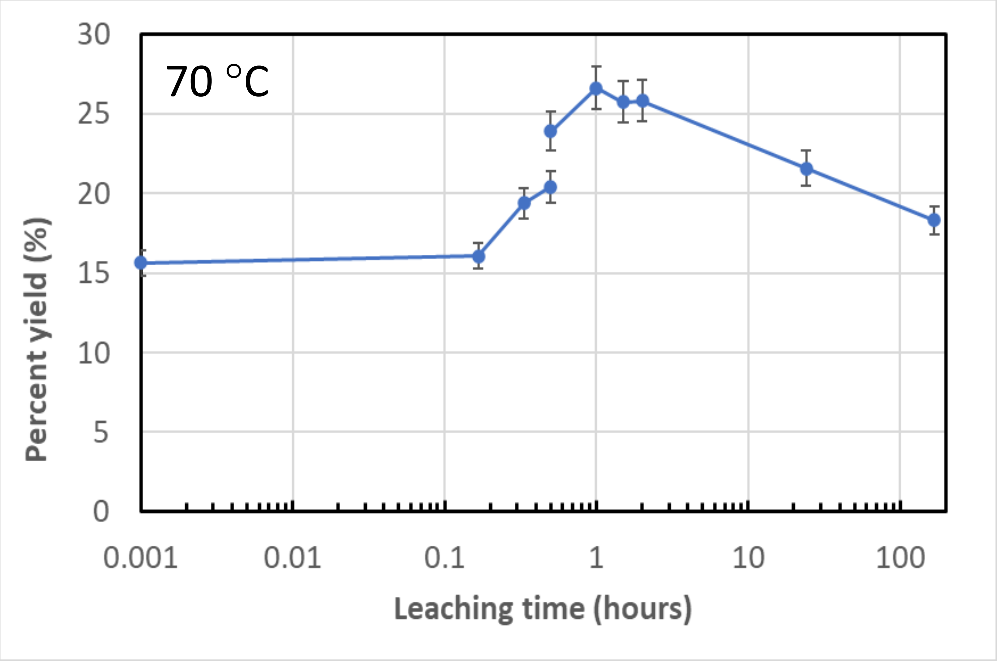
- Up to 50% heavy rare earths extracted without using strong acids/base; >82% for coal ash originated from Powder River Basin
- > 90% coal ash recovered after extraction
- 45 – 65% toxic/heavy metals were also removed, resulting in cleaner coal / coal ash for reuse (reduce liability)

Recovery from Critical Minerals from Coal Ash

Three Practical Issues in Applications: Pressure tank cost, citric acid cost, gel formation



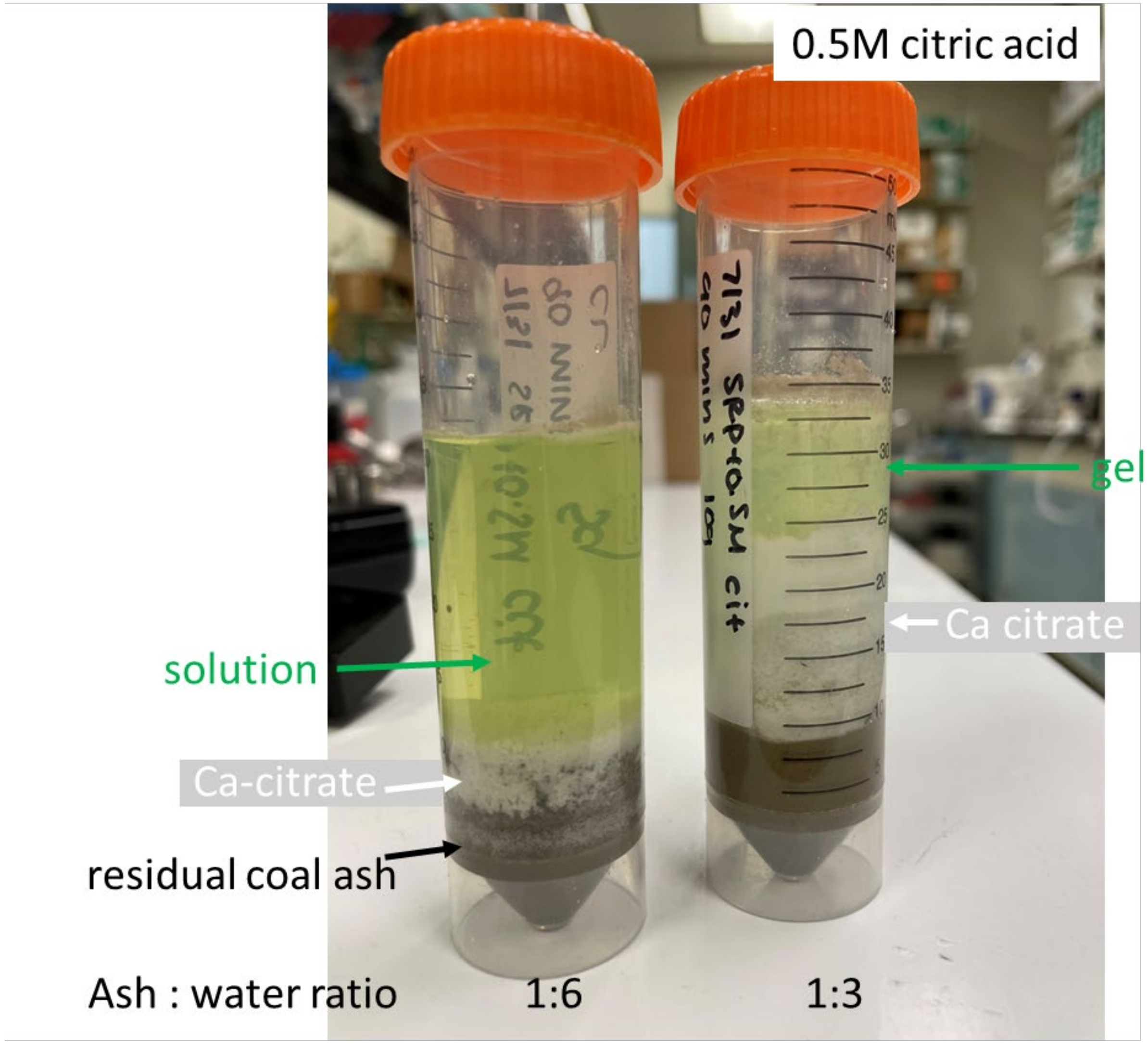
PRB 5g ash in 30g H_2O with 2.88g citric acid (0.5M)



- 26% leaching efficiency within one hour.
- **Challenges**: At high ash-water ratio, Ca citrate precipitation and gel formation limits extraction efficiency

Recovery from Critical Minerals from Coal Ash

Three Practical Issues in Applications: Pressure tank cost, citric acid cost, gel formation



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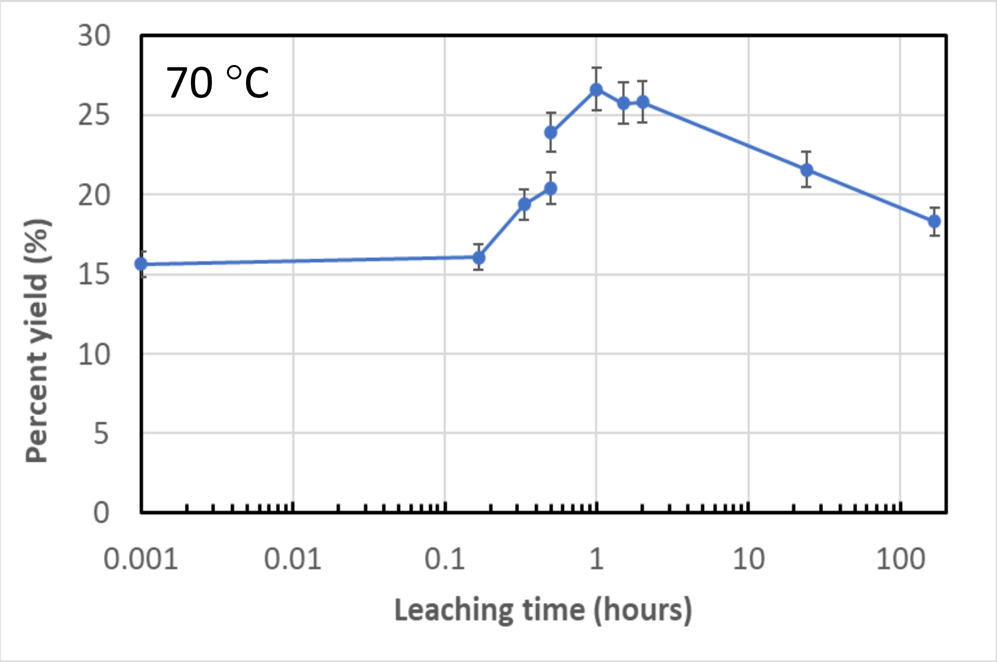

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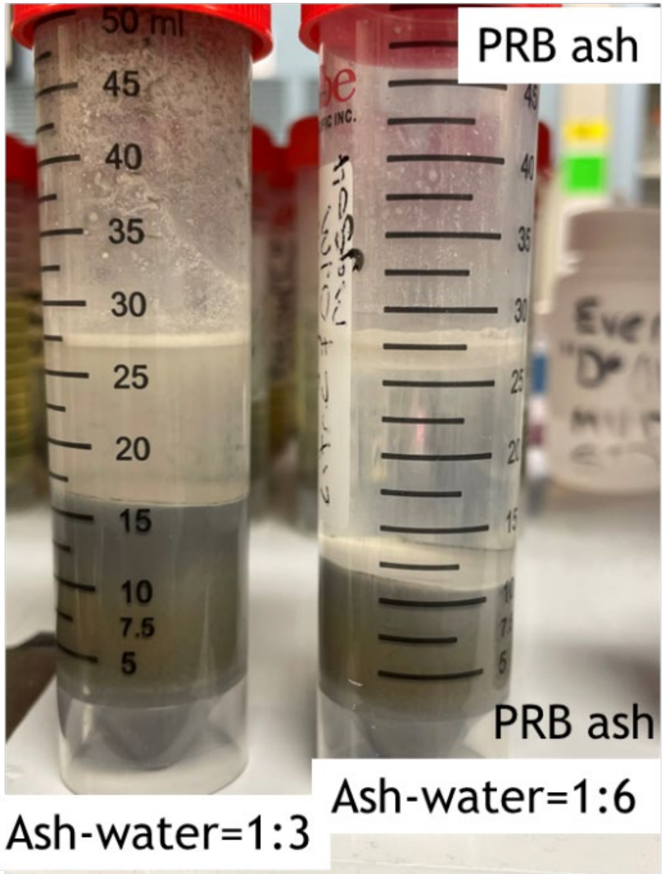
Recovery from Critical Minerals from Coal Ash

Leaching using Citric acid and $MgSO_4$ Mixture to Save Cost and Avoid Gel Formation

- $MgSO_4$ is food supplement & inexpensive
  - Citric acid: $0.65 /Kg; magnesium sulfate: $0.10/Kg
- Mg^{2+} in solution (higher ionic strength) preventing gel formation
- $MgSO_4$ release heat in water (0.1M → 2.4°C; 1M →16°C in 30g H_2O)
- Lower citric acid decreases Ca-citrate precipitation
- Patent pending (SD16672)

	Total REE-Y-Sc (ppm)	Leach effciency
PRB coal ash at 70 °C for one week (0.5g in 30g H_2O)		
0.1M $MgSO_4$	0.0	0%
0.1M citric acid	164.4	42%
0.1M citric acid + 0.1M $MgSO_4$	329.7	85%
1M $MgSO_4$	0.0	0%
0.1M citric acid + 1M $MgSO_4$	334.7	86%
0.1M ascorbic acid	73.1	19%
0.1M ascorbic acid + 0.1M $MgSO_4$	98.4	25%

0.1M citric acid + 0.1M MgSO4



No precipitation and gel formation!

Recovery from Critical Minerals from Coal Ash

Deployment strategy: onsite trailer for coal ash pond vs. onsite at cement company

On-site operation at coal ash pond

+

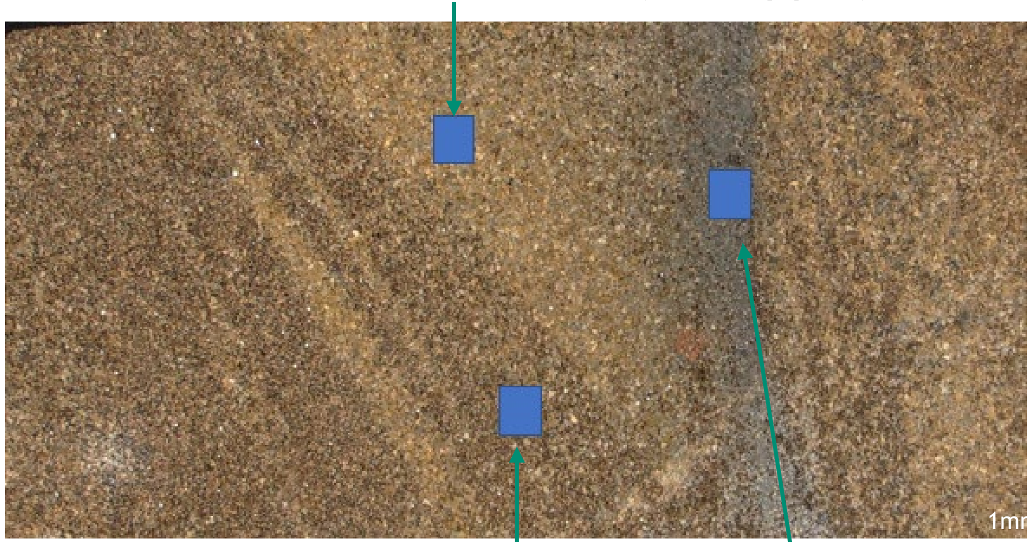
- Clean coal ash pond (liability)
- Provide critical minerals

On-site operation at cement company

- ☐ Coal ash yet to be regulated as hazardous waste
- ☐ Duke Energy agreed to pay $1.1B North Carolina coal ash cost before 2030
- ☐ The total clean-up cost for 8 coal ash ponds projected at between $8 billion and $9.5 billion. The rest of the expenses will occur after 2030
- ☐ Venture Capital licensed technology – Critical Materials LLC
- ☐ The goal is to achieve continuous leaching

Recovery from Critical Minerals from Beach Placer Deposits

Citric acid and $MgSO_4$ Mixture is effective to recover >50% REE in ore deposit



Quartz + zircon (1984 ppm)

3820 ppm

(ilmenite, rutile, Fe oxides, zircon, monazite, 28507ppm)

	Total REE-Y-Sc (ppm)	Leach effciency
Sandstone bleach placer at 70 °C for one week (0.5g in 30g H_2O)		
0.1M $MgSO_4$	286.2	4%
0.1M citric acid	2822.1	38%
0.1M citric acid + 0.05M $MgSO_4$	4032.4	55%
0.1M citric acid + 0.1M $MgSO_4$	4125.1	56%
0.1M citric acid + 0.2M $MgSO_4$	4584.6	62%
0.1M ascorbic acid	876.7	12%
0.1M ascorbic acid + 0.1M $MgSO_4$	1602.9	22%

The citric acid + sulfate mixture can **recover >50% REE** from ore grade heavy mineral beach placer deposit

Recovery from Critical Minerals from Lithium Clay Deposit

Application in lithium ore deposit

Li-Mn clay deposit	**REE-Y-Sc**		**Li**		**Mn**	
	ppm	%	ppm	%	ppm	%
0.1M $MgSO_4$	0.0		143	7.9%	47.9	2.9%
0.2M $MgSO_4$	0.0		133	7.3%	63.6	3.9%
0.1M citric acid	79.3	32%	898	49.6%	1092	66.2%
0.1M citric + 0.05M $MgSO_4$	125.1	50%	780	43.1%	1332	80.7%
0.1M citric + 0.1M $MgSO_4$	149.4	60%	792	43.8%	1573	95.3%
0.1M citric + 0.2M $MgSO_4$	150.5	60%	804	44.4%	1632	98.9%

Total lithium ~1800 ppm

The leaching technology is very effective (nearly 100%) in Mn recovery from clay deposit though not helping with lithium

Recovery from Critical Minerals from Shale

Metalliferous shales – target for *in-situ* extraction

Red – 2023 Critical mineral

- The US has huge amount of shale resources, ranking top 5 in the world
- The US leads in oil production, with nearly two-thirds from shale
- The US has ~1 million production wells
- Many shale deposits have high metal content
- The *in-situ* leaching concept can be directly integrated into the existing oil/gas production and field facilities to mine CMs

Shale	As	Co	Cr	Cu	Mo	Ni	Pb	U	V	Y	Zn
Alum Shale[1]	-	-	-	-	207	316		155	1519	-	431
Gibellini Facies[2]	47	-	-	-	191	436	-	45.5	3074	-	5613
Talvivaara Shale[3]	-	200	-	1300	-	2200	-	17	-	-	5000
Antrim Shale (A)[4]	18	19	-	43	41	82	-	13	227	-	282
Antrim Shale (M)[4]	50	48	-	100	261	235	-	36	1060	-	1720
Bakken Shale[5]	-	-	-	99	-	344	43	42.7	4402	36	1223
Barnett Shale (M)[6]	-	-	295	83.5	13	168	-	11.4	165	62	387
Chattanooga (A)[7]	56	55	-	116	78	210	-	44	325	-	358
Chattanooga (M)[7]	110	143	-	185	207	595	-	91	696	-	1292
Heath (A)[8]	-	17	190	43	103	115	24	14	387	33	598
Heath (M)[8]	-	80.7	700	163	1590	509	162	67	1980	89	5140
Monterey (A)[9]	-	6	139	45	20	104	6	11	265	16	148
Monterey (M)[9]	-	11	300	130	66	260	10	32	600	29	320
New Albany (A)[10]	75	16	79	135	81	155	29	26	255	-	225
New Albany (M)[10]	2570	44	190	1230	495	495	430	110	870	-	3550
Utica (A)[11]	-	135	250	-	-	103	-	13	98	21	-
Utica (M)[11]	-	298	433	-	-	157	-	65	200	45	-
Woodford OK (A)[12]	-	-	-	96	117	90	-	292	542	-	-
Woodford OK (M)[12]	-	-	-	203	330	379	-	634	2006	-	-
Woodford TX (M)[6]	-	-	260	485	166	302	-	66	1720	52.7	1220

Modified from Rigali and Krumhansl 2019 AGU Monograph Series (https://doi.org/10.1002/9781119066699.ch4)

Recovery from Critical Minerals from Shale

Metalliferous shales – target for *in-situ* extraction

> 6.5 ft thick core with V and Zn > 2200 ppm in Bakken shale!

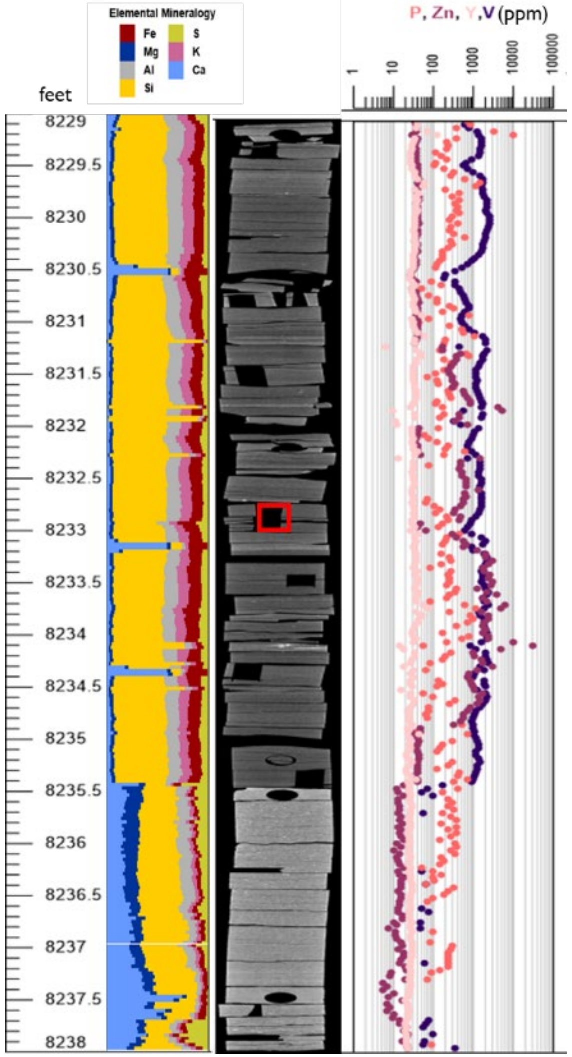
	REE-Y-Sc (ppm)	Ni (ppm)	V (ppm)	Zn (ppm)	Cu (ppm)	Mn (ppm)	Mo (ppm)
Total contents	193.4	805	2272	2372	135.2	139.4	505
leached by 0.1M citric acid + 0.1M $MgSO_4$	44	144	168	529	58	45	49
	23%	18%	7%	22%	43%	32%	10%
leached by 0.5M citric acid	65.4	189	359	917.9	93.6	68.6	62.7
	34%	23%	16%	39%	69%	49%	12%

Bakken upper shale has high contents of V, Zn, Ni

22 - 69% of REE, Ni, V, Zn, Cu can be leached out with citric acid

Note that unconventional oil and gas recovery rate is 5% - 10%!

Bakken shale core scans

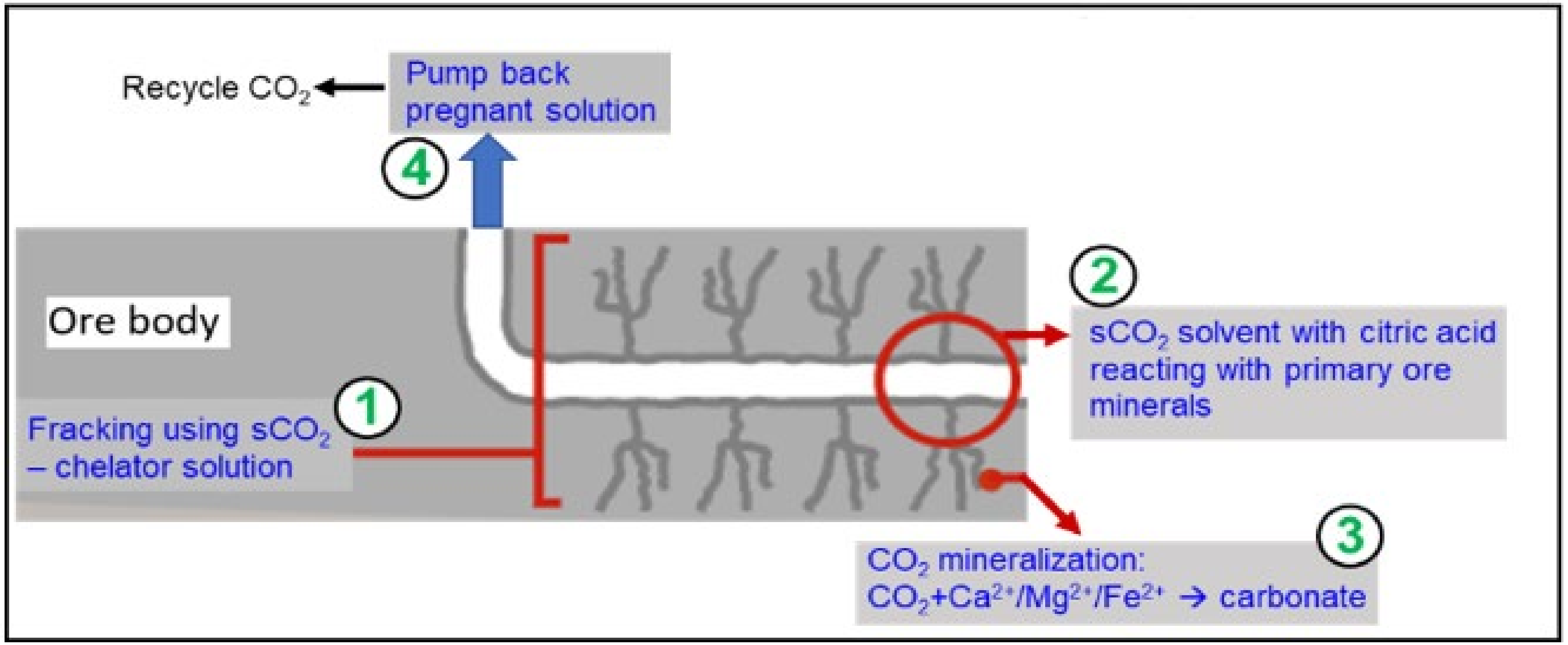


NETL pXRF

Recovery from Critical Minerals from Shale

Vision and strategy: *in-situ* extraction using existing infrastructure

In-situ mining can be deployed after oil and gas production depleted using existing well.
In-situ mining can also be deployed before oil and gas production (fracking with leachate).



Mine and slag tailings – near-term solution?

One man's trash is another man treasure!

- Typically ore grade is at least 2 order of magnitude higher than unconventional/secondary resources
- The recovery rate for many CMs in ore deposit can be much less than 50%, the missing are mostly in tailings
- Huge amount of tailings available (1 metric ton of copper produced generate 20 ton of tailings)
- Old tailings with higher concentrations
- Our partner told us that their mine tailings has 1-4ppm gold [The average recoverable gold content of U.S. gold ores mined of deposits and mines was about 1.5 ppm]

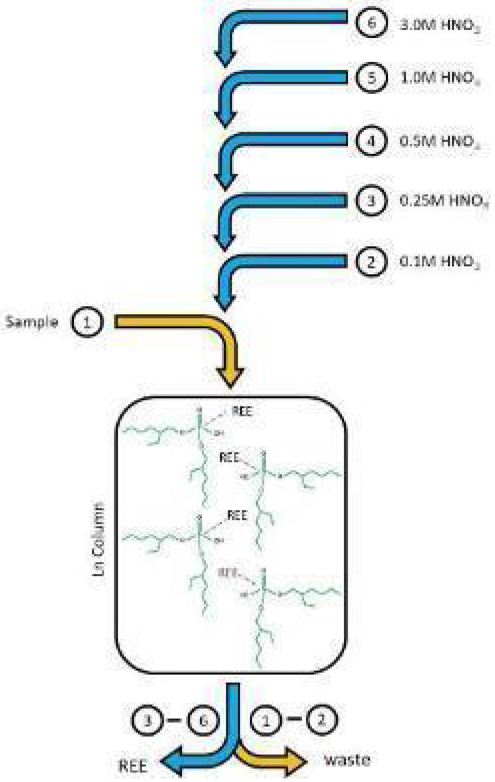
Total concentration	**REE-Y-Sc (ppm)**	**Pb (ppm)**	**Cu (ppm)**	**Mn (ppm)**	**Zn (ppm)**	
Historic tailings 1	222.9	2424	321	23682	5899	
Historic tailings 2	189.7	29550	2001	11867	64949	
Slag tailings	158	3152	2299	220	3907	
0.1M citric acid + 0.1M $MgSO_4$	46	130	594	36	467	leach 3 hrs
0.1M citric acid + 0.1M $MgSO_4$	55	210	721	83	1246	leach 24 hrs
0.1M citric acid + 0.1M $MgSO_4$	79	345	867	218	3373	leach 1 week

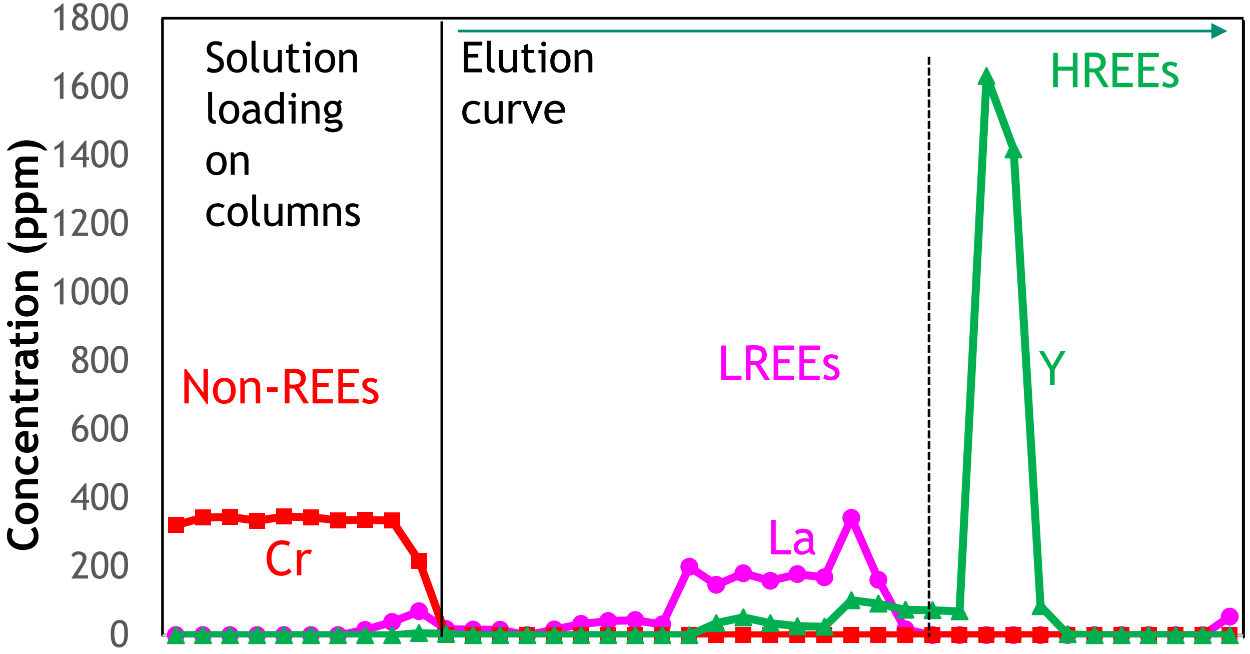
“Do you think these concentrations are high?”

Separation non-REE vs REE vs Individual REE

Vision and strategy: need low cost, environmental benign and continuous separation process

Separation using Ln resin and tested on coal ash leachate





Challenges:

1. Expensive; 2. slow; 3. not continuous

New technique is in development

Summary

- Using environmental benign leachate, such as citric acid and sulfate mixture, it is possible to recovery critical minerals from coal ash semi-continuously whereas reducing the environmental liability caused by coal ash

- There are shale intervals with thousands ppm of critical minerals, which could be mined *in-situ* using existing infrastructure

- Unconventional/secondary resources could provide CM supply, yet most with concentrations are low compared to those in mine and slag tailings, which could be the near-term target to achieve 50% domestic CM supply by 2035

Acknowledgement

Industry Partners, funding agency, and collaborators

Thanks industry partners provide samples for evaluation, proprietary information, cost share for joint proposal:

- Critical Materials LLC (Licensed leaching technology)
- Rio Tinto
- South32
- Idaho Strategic Resources
- Extractive Metallurgy Consultancy LLC
- Graphite One Inc
- Salt River Materials Group
- Seneca Engineering, LLC
- GCC Energy LLC (King II Coal Mine)
- Donaldson Engineering LLC
- Stratos Land Holdings LLC

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Fossil Energy and Carbon Management

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Solving New Mexico's Small Business Challenges

Collaborating Intuitions:

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THE UNIVERSITY OF TENNESSEE
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Sandia Collaborators:
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Current LDRD funded projects

- Sustainable Bioinspired Harvesting of Rare Earth Materials (FY22-FY24)
- Nanoconfined Interfaces for Highly Selective Separation of Critical Rare Earth Elements (FY22-FY24)
- Nano- and Earth-Science-inspired Electric Vehicle Battery Recycling to secure Battery Supply Chain (FY23-FY25)
- Electrically controlled energy efficient, low toxicity critical mineral separation (FY24-FY26)

Reclamation of Critical Minerals from Energy Extraction-Impacted Waters using Turf Algae Cultivation and Processing (PI: Ryan Davis)

R&D Challenge

Energy resource residues, such as coal ash and produced water, contain abundant critical minerals. Technology for continuous and environmentally-friendly pre-concentration and recovery of CM is required to make recovery economically viable.

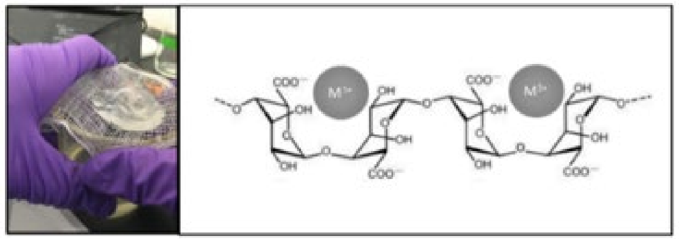
- The goal is to identify appropriate choice of algae strain (or a combination of strains) for pairing with the specific CM analytes and the associated water chemistry, to selectively concentrate a targeted group of critical minerals from complex mixtures, such as coal ash slurry or produced water.

Sandia Algae Testbed Facility

Approach

QM prediction of metal binding, experimental evaluation of alga, and ML model generation to achieve targeted pre-concentration and extraction (strategic metals, toxic metals) from coal ash and produced water using an attached algae biofilm.

- Develop ab initio models for mineral chelation by algal polysaccharide and peptide complexes.
- Test uptake of selected metals (Ni, Mn, Cr, Li) with waste-associated algae cultivars to optimize culture for targeted CM using ML



Impact & Benefit

We developed a continuous and environmentally benign technology to pre-concentrate and recover critical minerals from coal ash and produced water using attached algae cultivation and processing.

- Guided by LCA/TEA to optimize extraction and separation
- Testing metals recovery in the field using cases including, 1) water treatment (RO-concentrate, with Indian River Co, FL) and 2) environmentally-impacted locations (Salton Sea, CA)

CM Pre-concentration and Recovery
Yellow Stars: Metals hyperbioaccumulation in algae

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Fast Characterization of Critical Minerals

Streamlined Rapidly Screening and Characterization with High Precision

Sample screening and selection

NETL Portable XRF

Minerals identification & quantification

Digestion within 30 mins using multi-acid mixture

Microwave digestion

Critical Mineral quantification

ICP-MS +
ICP-OES

From sample interval selection to quantify critical mineral contents for a dozen samples within a few hours