Multi-Bed Adsorption Study for the Fractionation of Critical Metals from Acid Mine Drainage

Project Number 2.018

Chris Wilfong (support contractor, presenter)

McMahan Gray (NETL, PI)

U.S. Department of Energy

National Energy Technology Laboratory

Resource Sustainability Project Review Meeting

October 25 - 27, 2022

Disclaimer

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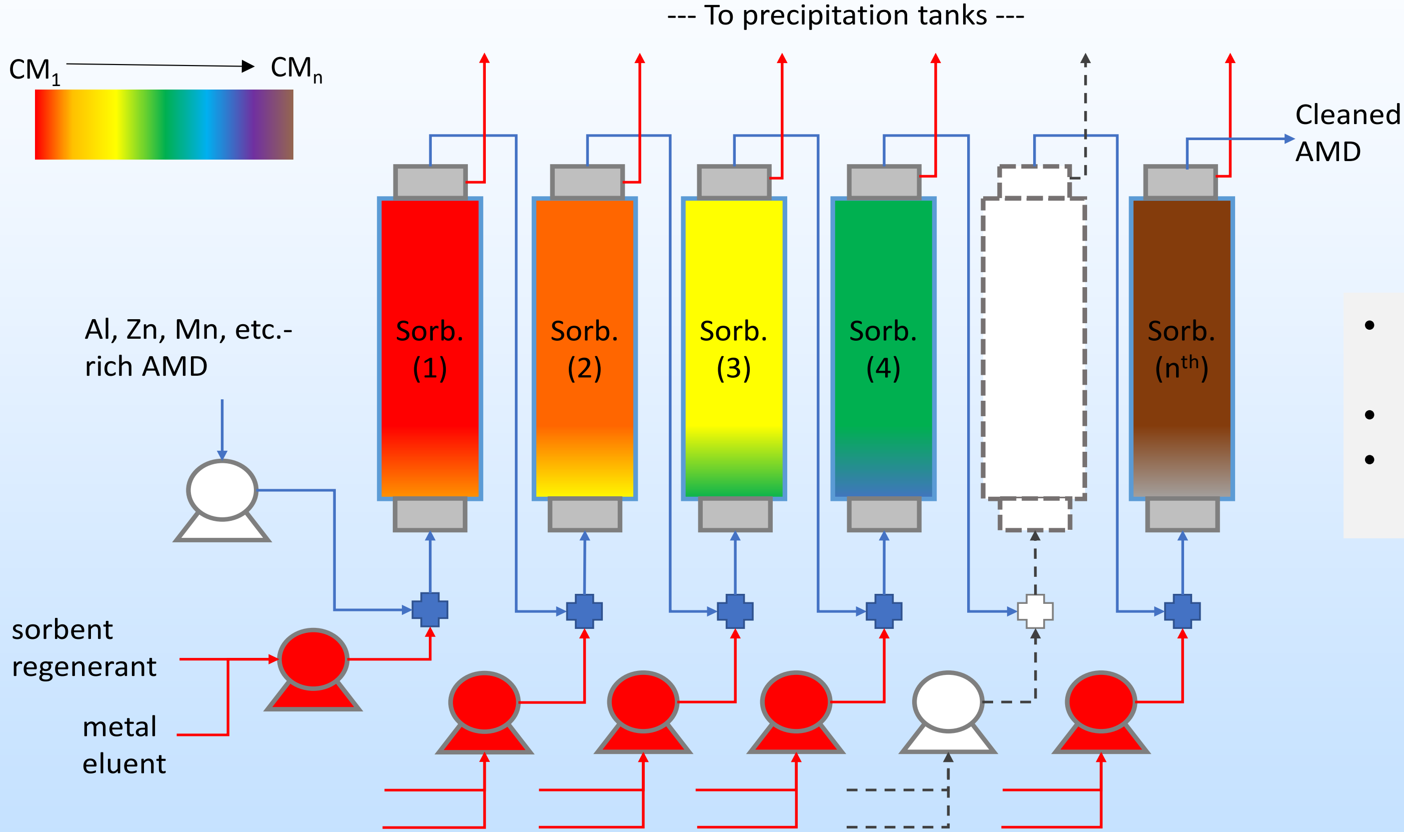
Project Overview

- Funding (DOE and Cost Share)
  - EY22 – $180k, EY23 – $196k
- Overall Project Performance Dates
  - Oct.1, 2021 – Sept. 30, 2022
- Project Participants
  - McMahan (Mac) Gray – PI; Chris Wilfong, Qiuming Wang, Fan Shi
- Overall Project Objectives
  - Use regenerable, multi-functional sorbent technology (MUST) sorbents to recover CM from coal waste waters: AMD, produced water, etc.
  - Separate and enrich CM into individual or group metals demonstrating the commercial feasibility of an adsorption-based process.

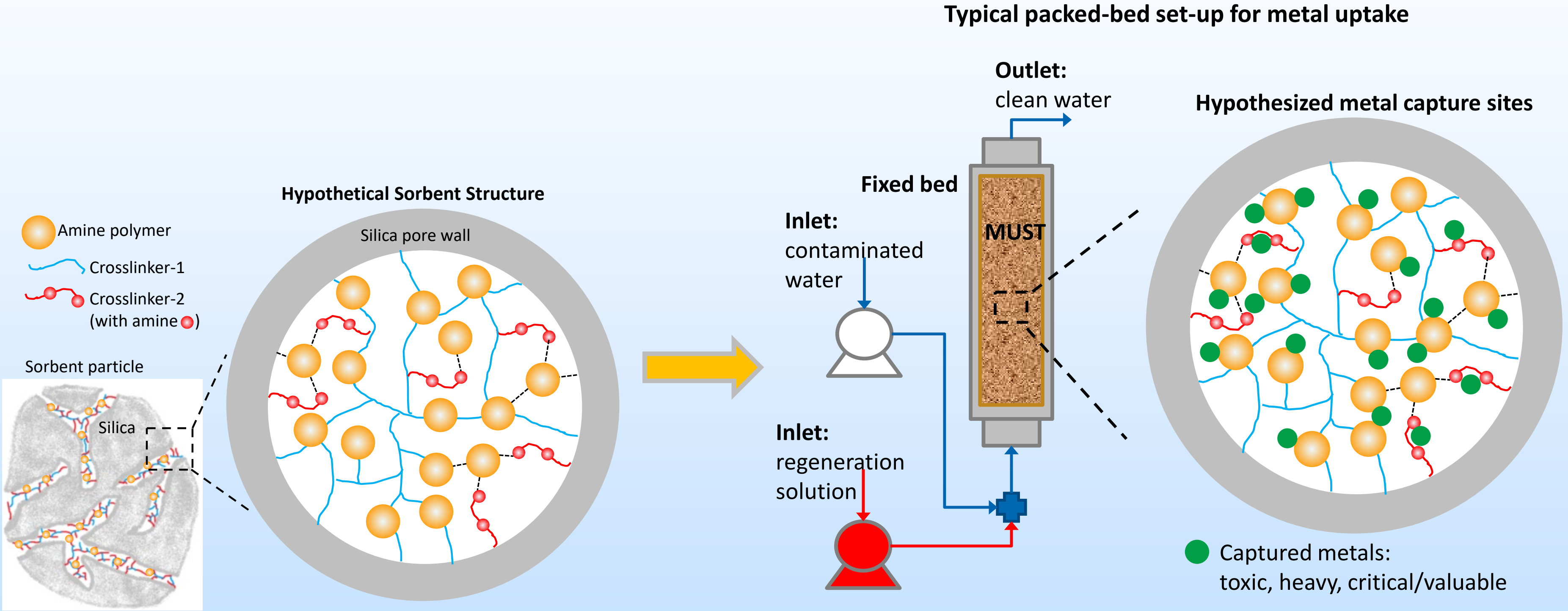
Technology Background - Process



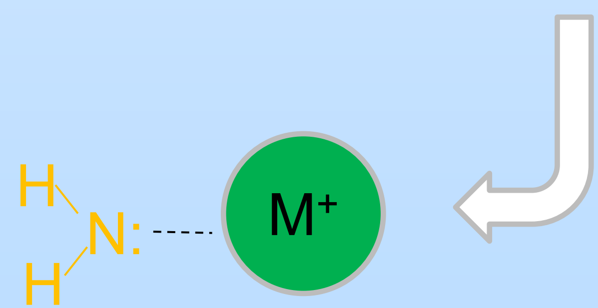
- Temperature range: 5 °C to 95 °C
- Flow rate: variable
- Pressure: up to 125 psig.

- Multi-bed fractionation to separate critical metals (CM) by selectivity.
- Separate bed elution to purify CM.
- Precipitation to achieve solid CM species.

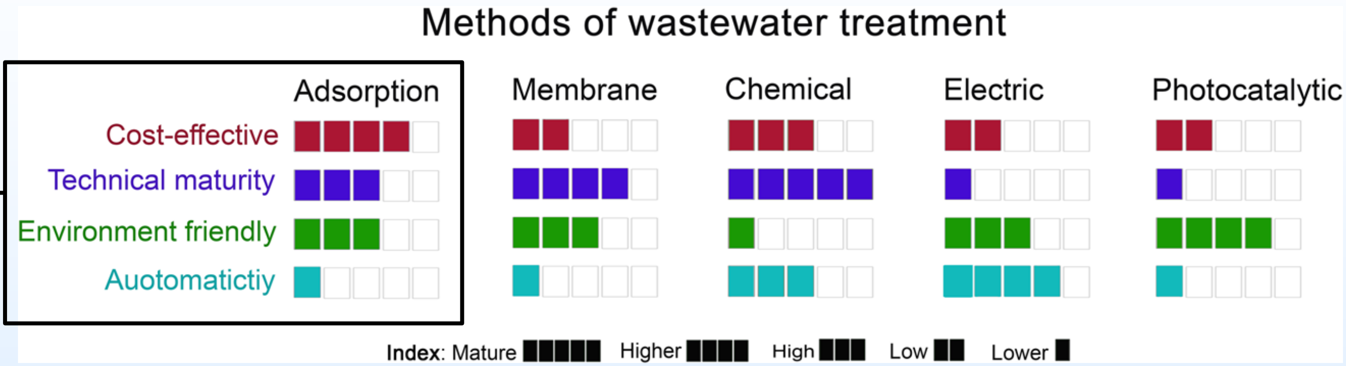
Technology Background – Sorbent



- CMs are adsorbed to the sorbent by forming dative bonds between the CM and metal capture groups - amine groups:



Technology Background – Sorbent



N.A.A. Qasem, R.H. Mohammed, D.U. Lawal, Removal of heavy metal ions from wastewater: a comprehensive and critical review, npj Clean Water, 4 (2021) 366

As-is or functionalized…

- **Carbon** (nanotubes, activated carbon) — *physisorbents*
- **Mineral** (zeolite, silica, clay) — *Ion exchange or chemisorbents if funct.*
- **Polymer** (chitosan, ion exchange resin, hydrogel) — *resin commercialized*
- **Non-carbon Bio** (algae, bacteria) — *highly condition-dependent, variable growth*

<u>Advantages</u>

- ✓ Easily prepared
- ✓ Tailored chemistry
- ✓ Easily scaled
- ✓ Low cost, $6-7/lb

<u>Challenges</u>

- ○ Capacity ←→selectivity trade-off
- ○ Optimal CM elution procedure
- ○ Long-term field study

Technology Background – Prior work

2017

Particle: BIAS (EPOXYsilane)

Gray, M.L.; Kail, B.W.; Wilfong, W.C.; Wang, Q, Stable Immobilized Amine Sorbents for REE and Heavy Metal Recovery from Liquid Sources, PCT/US17/56421. **2017** **International**

REEs, heavies

Licensed by PQ

Gray, M.L.; Kail, B.W.; Wilfong, W.C.; Wang, Q, Stable Immobilized Amine Sorbents for REE and Heavy Metal Recovery from Liquid Sources, US 2018/0100065A1. **2018**

REEs, heavies

Gray, M.L.; Kail, B.W; Wang, Q.; Wilfong, W.C.; Shi, F., A Method for Radioactive Contaminant Removal from Wastewater, U.S. Provisional Application no. 62814531, **2019**

Radioactive (patent not filed)

Previously licensed by Somerset International

Gray, M.L.; Kail, B.W.; Wilfong, W.C.; Wang, Q; Shi, F, Novel Multi-Functionalized Basic Immobilized Amine Sorbents for the Removal of Metal Contaminants from Wastewater (19N-04). Provisional Application no. 62875829, **2019**

REEs, heavies

Previously licensed by Somerset International

Gray, M.L.; Kail, B.W.; Wilfong, W.C.; Wang, Q; Shi, F, Metal-Loaded BIAS Sorbents for Improved Capture of Heavy Metals from Liquid Sources. Provisional Application no. 62875364. **2019**

CrO_4^{2-}, SeO_4^{2-}, AsO_4^{2-} etc.

Kail, B.W; Gray, M.L.; Wang, Q; Wilfong, W.C., Stable Immobilized Amine Sorbents for Removal of an Organic Contaminant from Wastewater. US.10,836,654. **2020**

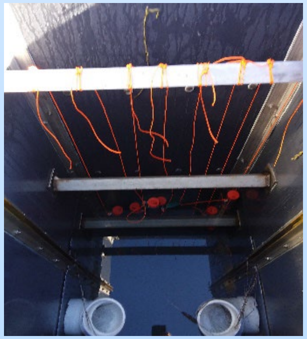
Organics

Leidos interest-PFAS

2021

18 kg pre-pilot scale-up

AMD field test



Technical Approach/Project Scope

Identifyer	Type	Date	Key Milestone
3.BB	Go/No-Go	21-Sep	Determine if enrichment work into individual REE elements and/or high purity "baskets" should be continued.
3.6.D	Project	Mar-22	Remove at least one critical metal at ≥75% purity from an authentic acid mine drainage source, using the scaled-up BIAS separations process.
12.A	Project	Dec-22	Identify at least 1 eluent that optimizes CM release and minimizes silica leaching from MUST
12.C	Project	Mar-23	Identify and characterize at least one other authentic AMD or other produced water source.
12.D	Project	Dec-23	Obtain a solid portion of at least one or a mixture of CM derived from elution of CMs originating from a multi-bed adsorption field test.

Pivot to CM recovery

Lab-scale: AMD CM capture-release; parameter evaluation

Pre-pilot: AMD filed site CM capture test; bed elution

Lab-scale: test sorbent for versatility in CM capture

Pre-pilot: AMD filed site CM capture test; bed elution

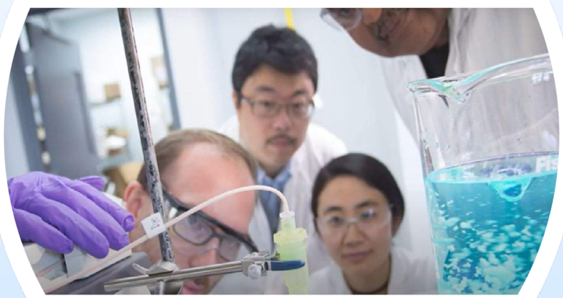
Technical Approach/Project Scope

- Project success criteria
  a. Recover and release CM from an authentic coal wastewater field site test, using a multi-bed adsorption system.
  b. Produce single or mixed solid critical metal compounds.

Risks	Mitigation strategies
Unpredictable water composition	Versatile sorbent portfolio
Sorbent longevity during field test	Rigorous lab evaluation
Partner follow through	Detailed screening process

Progress and Current Status of Project - Accomplishments

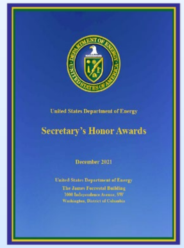
The Team



(From Left to Right)

Chris Wilfong
Fan Shi
Qiuming Wang
McMahan Gray

Achievements



2021 Secretary of Energy's Achievment Award

2021 R&D 100 WINNER

2021 R&D 100 Award

2022 Edison Award, Bronze

Review paper: IF=14.2

Contents lists available at ScienceDirect
Journal of Hazardous Materials
journal homepage: www.elsevier.com/locate/jhazmat
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Review

Critical review of functionalized silica sorbent strategies for selective extraction of rare earth elements from acid mine drainage

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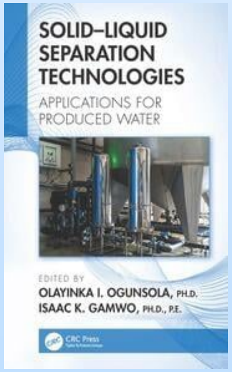
Book chapters

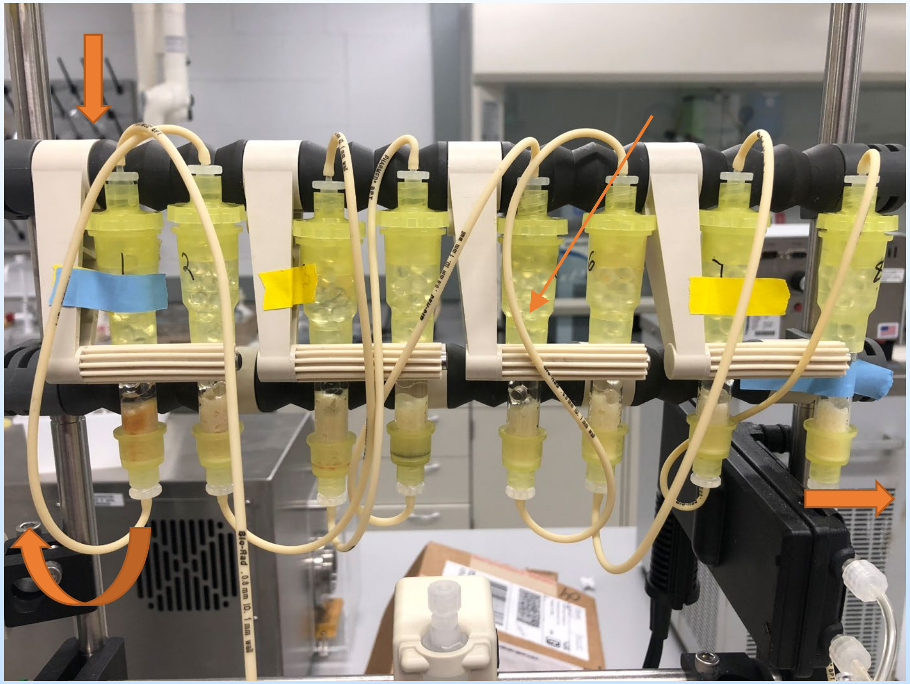
CH.6 Membrane Technologies and Applications for Produced Water Treatment

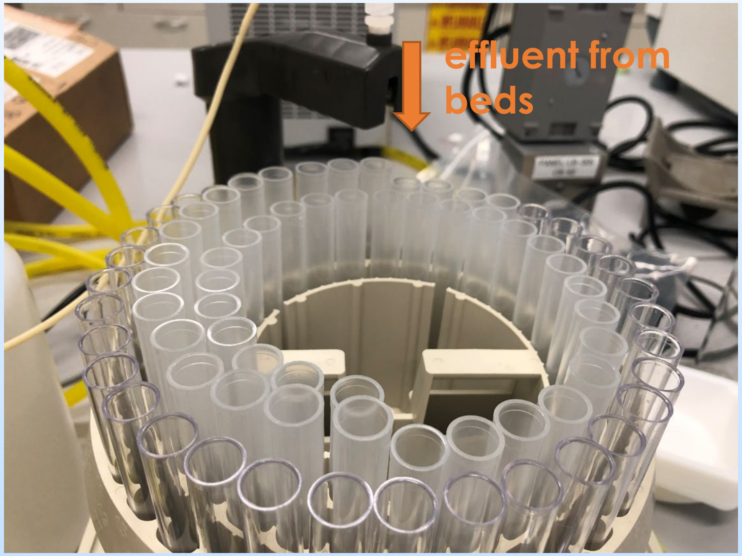
CH.8 Enrichment of Rare Earth Elements (REEs) Minerals from Different Sources in the Coal Value Chain by froth flotation



Progress and Current Status of Project – Multi-bed Testing

Beds in Series

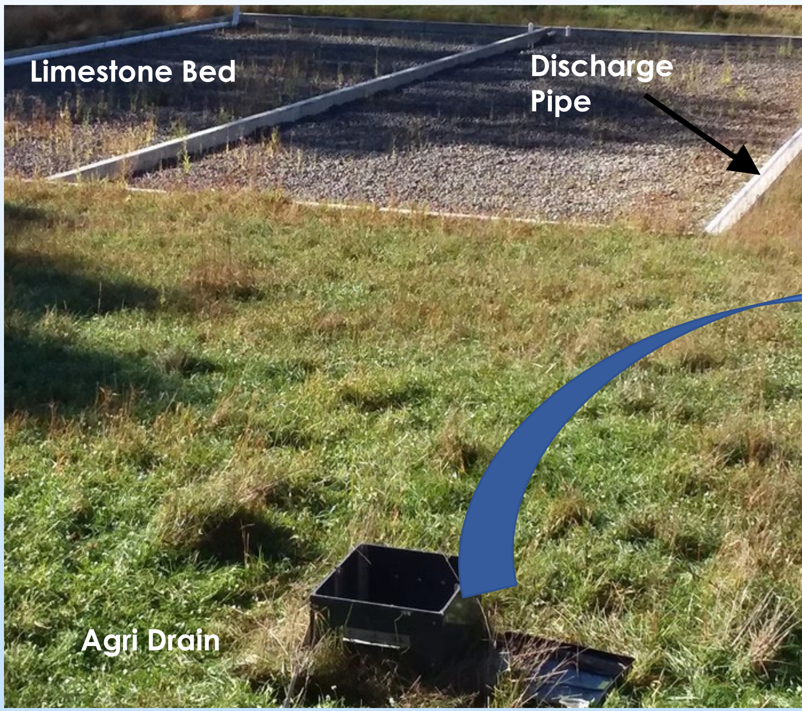




- Sorbent = 4 g 181D, 0.5 g/bed
- Volume=0.25 to 3.0 L of authentic Pittsburgh Botanic Garden (PBG)-AMD; ~0.4 mL/min to 8 mL/min top-to-bottom

Progress and Current Status of Project – AMD field site

Pittsburgh Botanic Garden (PBG)



Analysis

Metal	ug/L
Ca	117,483
Na	96,138
Mg	45,227
K	1,952
Si	11,655
Al	11,602
Fe	1,851
Mn	1,318
Zn	172
Ni	131
Co	54.1
Cu	18.3
Sr	836
Sc	1.08
REE, Y	112
Cd	0.96
As	0.53
Pb	1.46
Ba	5.06
Cr	2.36

non-heavies

primary

secondary

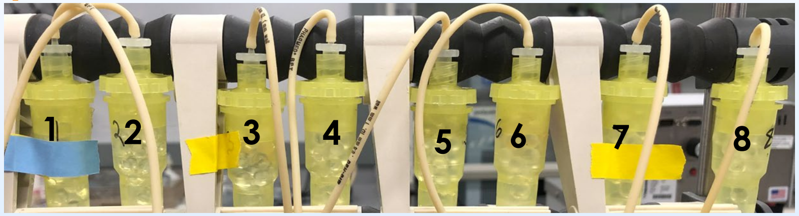
heavies

rare earth elements (REEs)

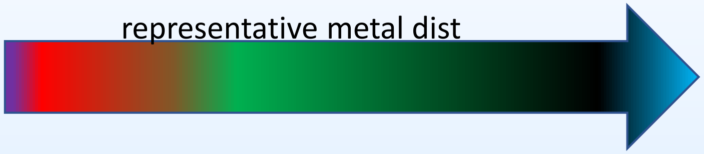
toxic (EPA)

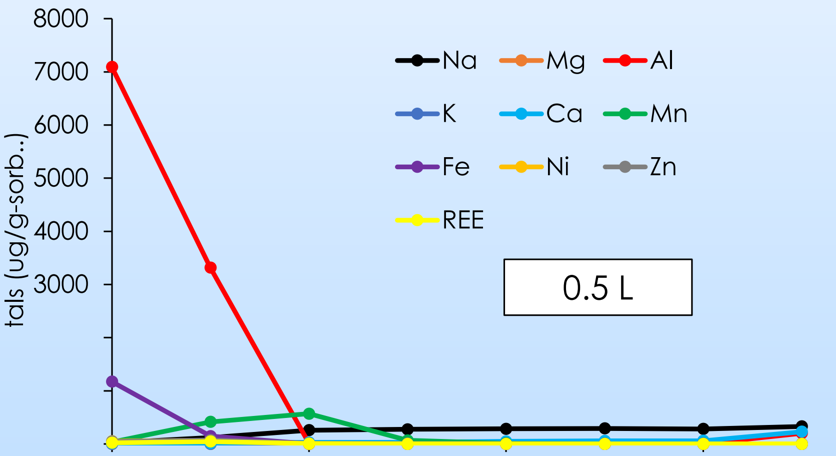
Progress and Current Status of Project: Lab-scale Multi-bed Test

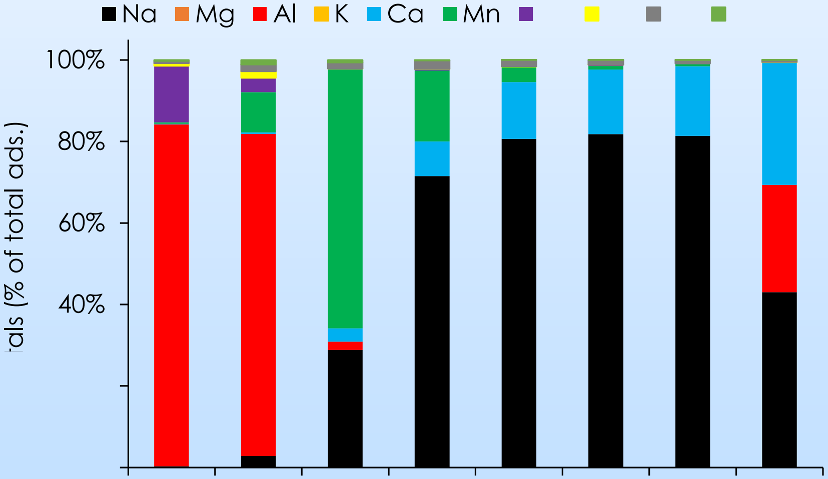
Separate 8–Bed Tests: 0.5 mL/min



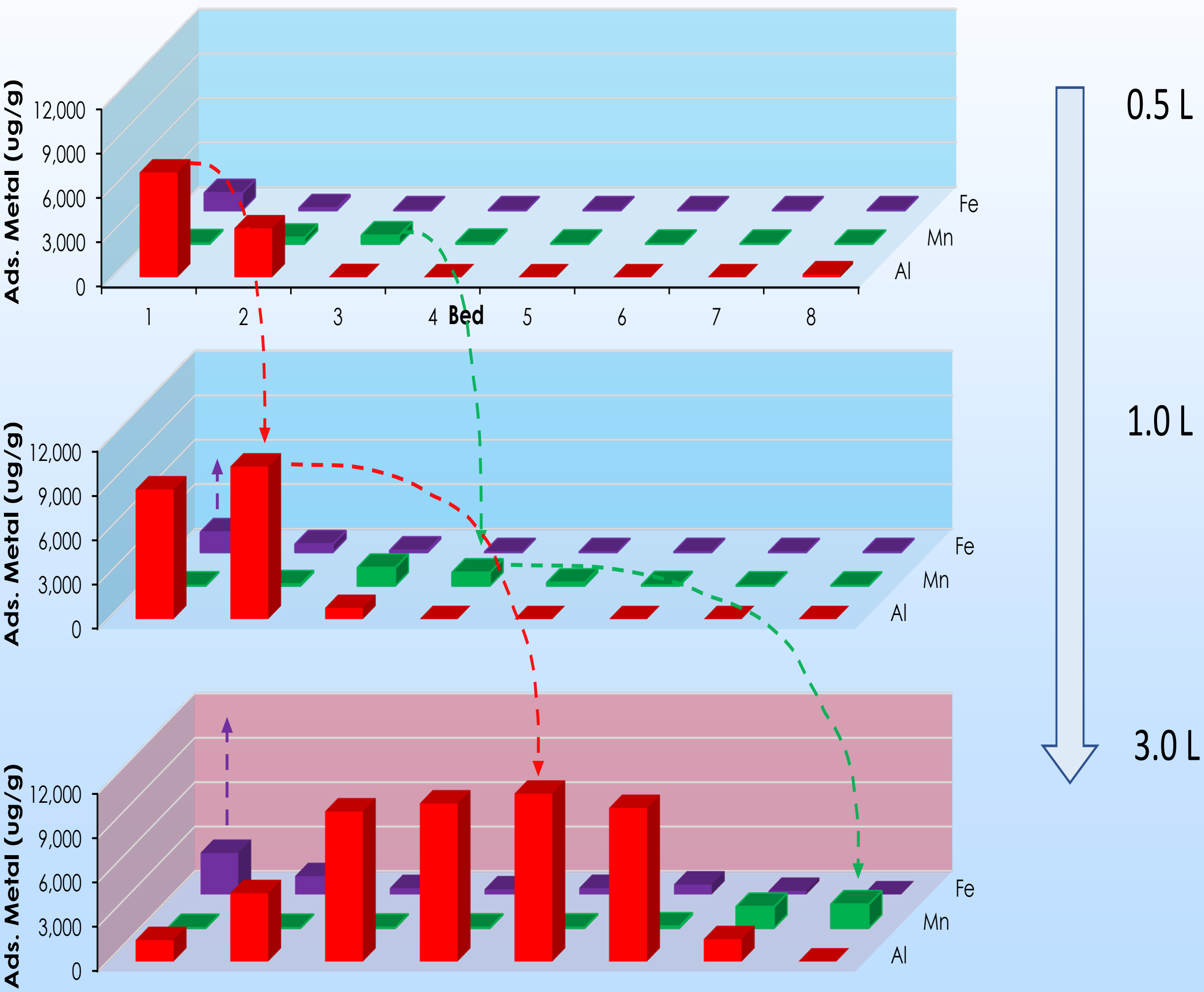
Sorbent: 0.5 g/bed
AMD: 0.5 L, 0.5 mL/min







Progress and Current Status of Project: Effect of AMD Volume



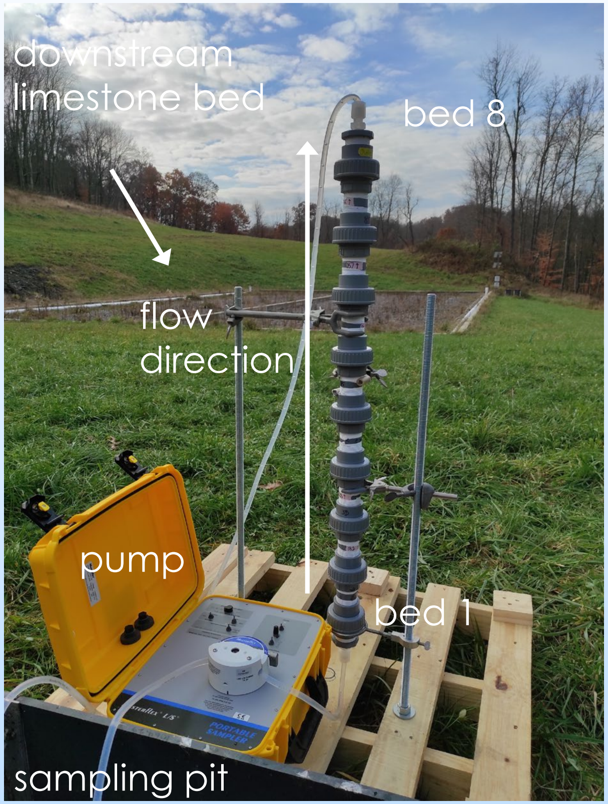
Cascading effect: higher affinity metals (Al) displace lower affinity metals (Mn) downfield.

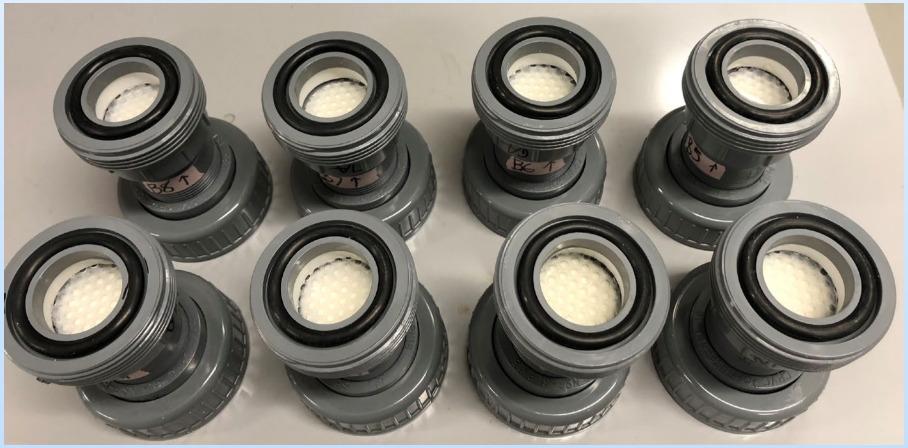
AMD/sorbent ratio can be adjusted to achieve different CM distributions and purities.

Fractionation achieved:
Beds 1, 2:
~1.1 wt% Al; ≥ 90% pure

Bed 8:
0.16 wt% Mn, ~84% pure

Progress and Current Status of Project: PBG AMD Field Test

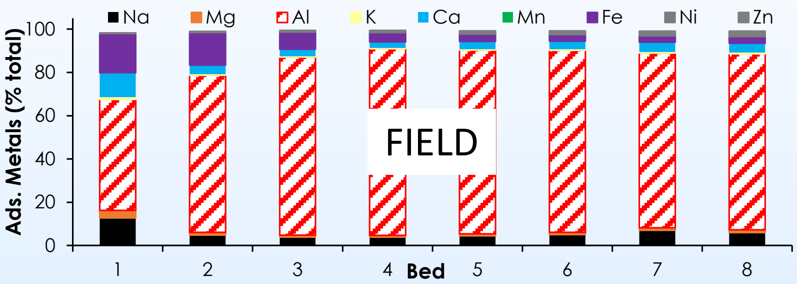




- Sorbent capacity: 160 g
- Flow rate: 0.6 – 1.1 L/min
- WHSV: 0.35 min^{1} – 7.9 min^{-1}

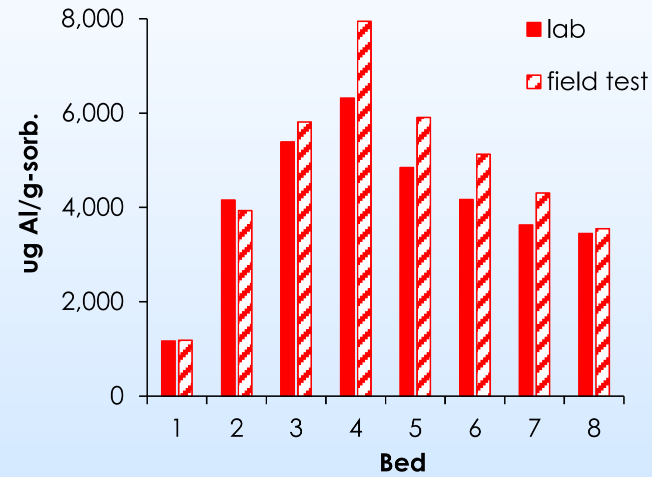
First practical application of NETL's MUST for recovering CMs from a coal waste source – AMD.

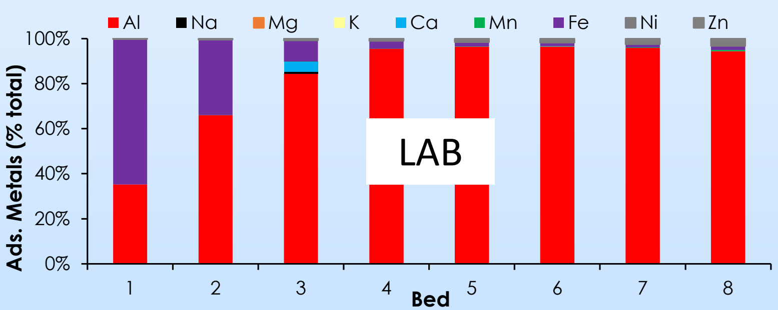
Progress and Current Status of Project: Field Site Validation



Sorb.=140 g
Flow=285 mL/min
Volume=100 L

WHSV~2.1 min^{-1}
AMD/Sorb.~750





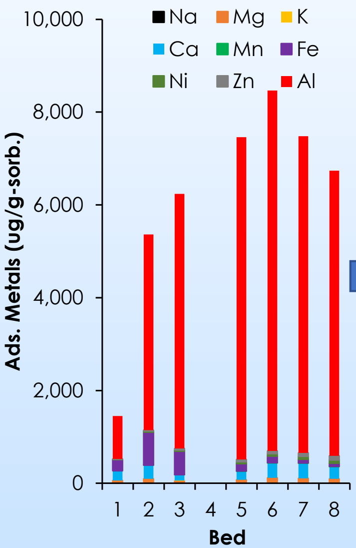
Sorb.=4 g
Flow=8.2 mL/min
Volume=3 L

Al adsorbed from field test:
- ~1 wt% Al, ≥90% pure
- 0.25 wt% Al, 80-89% pure

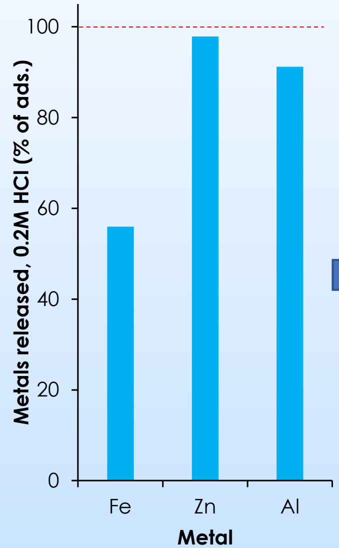
Progress and Current Status of Project: Field Test 2

Elution and Precipitation of Bed 5 CM

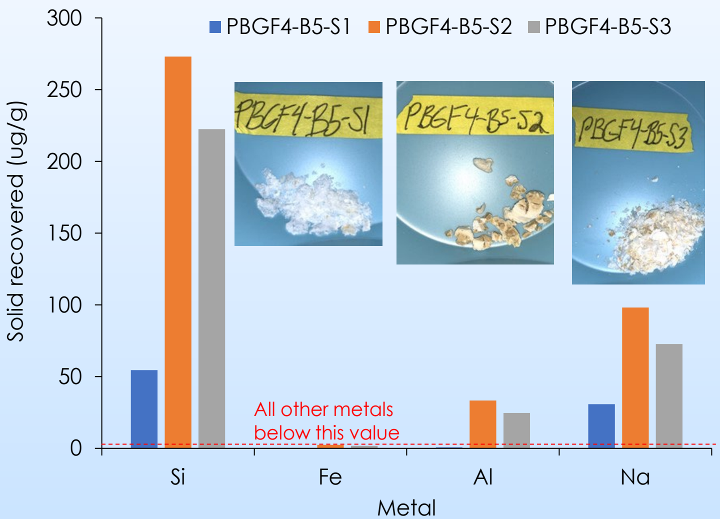
Metal-adsorbed bed 5



Bed 5 elution: 0.2M HCl, 1.5L



Eluent precipitation, pH 9.5 (NaOH) → filter → dry



- ~0.7 wt% adsorbed Al at ≥90% purity.
- ~91% elution of adsorbed Al.
- ~59 mg solid Al recovered → 41% of eluted; high precipitation pH.
- Silica co-eluted with Al → SiO_2 deterioration from high acidity?

Plans for future testing/development/ commercialization

- This project
  - ✓Improve Al % elution and % purity.
    - Elution – different types and amounts of buffers and acids.
    - Precipitation – sequential pH increase
  - ✓Evaluate produced water, other AMD, or coal ash extract.
    - Optimize adsorption and elution of other CMs.

- Next project
  - ✓ Evaluate sorbent metal uptake from coal ash leachate – partnership with Siemens (agreement in progress).

- Scale-up
  - ✓ Additional field site test at new CM water site.
  - ✓ Upcoming EYs will look at scaling partners.

Summary

✓Lab-scale fractionation: Al>90%, Mn>90%.

✓8-bed adsorption unit developed at lab-scale, then scaled for field work.

✓Appreciable, high-purity fraction of Al adsorbed from authentic AMD.

✓>90% Al elution, then recovery of Al as a low-purity solid fraction.

Take-away: MUST sorbent process was validated for solid CM recovery! Improvements will be made.

NETL Resources

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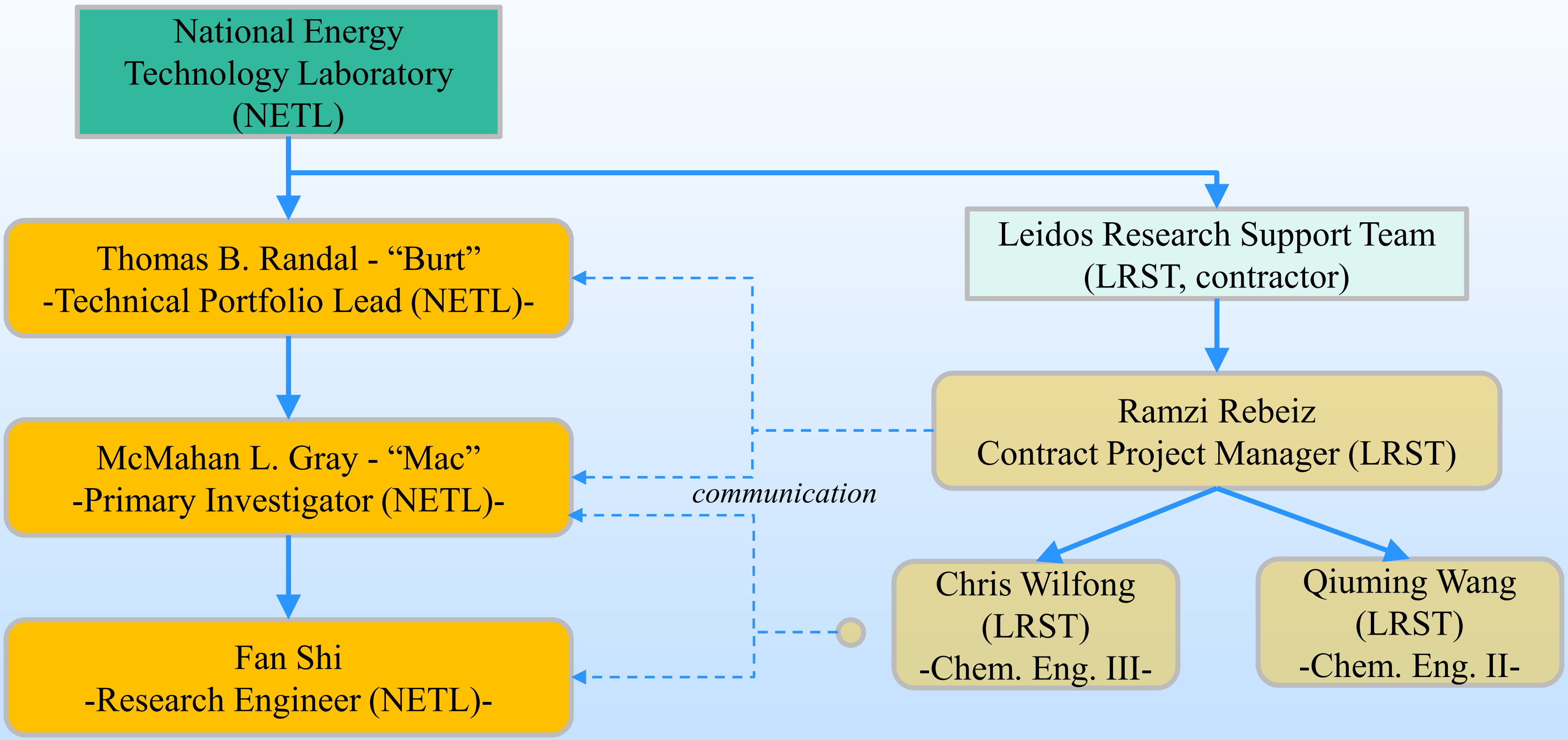
U.S. DEPARTMENT OF ENERGY

Appendix

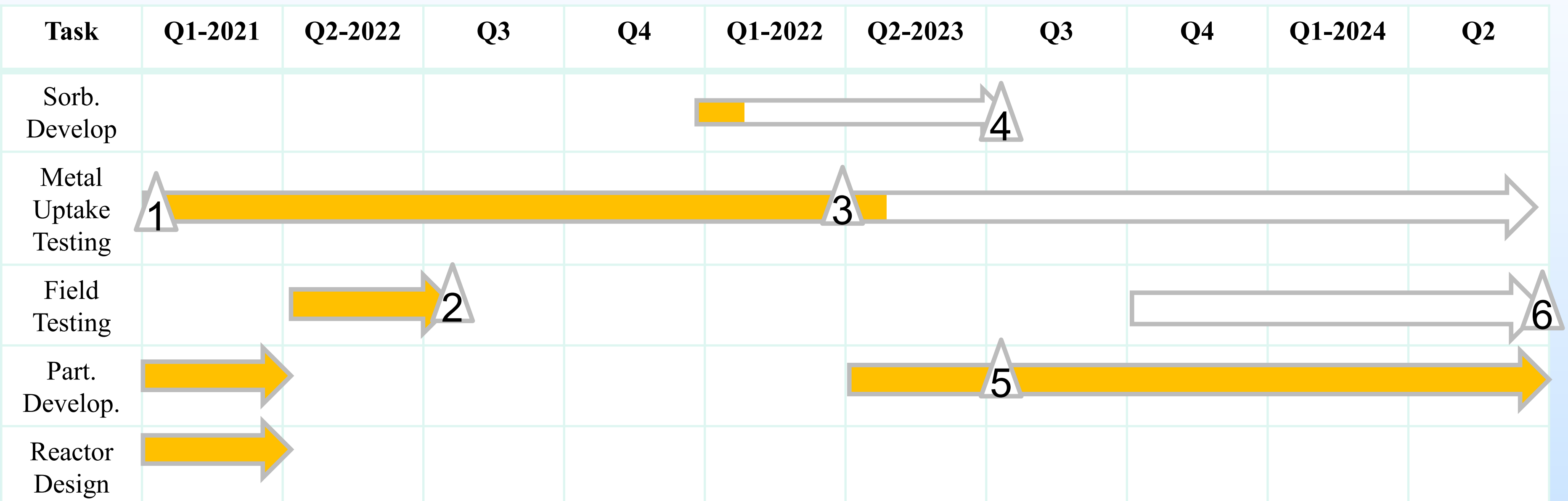
Organization Chart



- Fund acquisition, project management, and technical guidance.
- Partnership development and field site identification.
- Technology development and project expansion.

- Sorbent development, characterization, testing, analysis.
- Lab scale and field site reactor design and construction.
- Experimental protocol development.
- Writing and reporting.

Gantt Chart



Identifier	Key Milestones
1	Determine if enrichment work into individual REE elements and/or high purity "baskets" should be continued → switched broadly to CM
2	Remove at least one critical metal at ≥75% purity from an authentic acid mine drainage source, using the scaled-up BIAS separations process.
3	Identify at least 1 eluent that optimizes CM release and minimizes silica leaching from MUST
4	Develop at least one new MUST sorbent with affinity towards a CM.
5	Identify and characterize at least one other authentic AMD or other produced water source.
6	Obtain a solid portion of at least one or a mixture of CM derived from elution of CMs originating from a multi-bed adsorption field test.