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

Lab Screening and Field Testing

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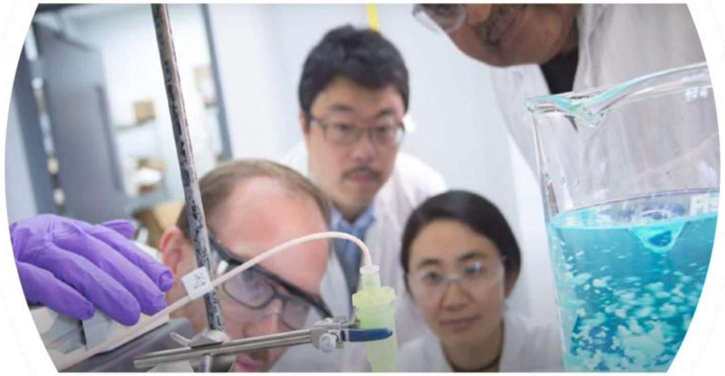
Team and Achievements

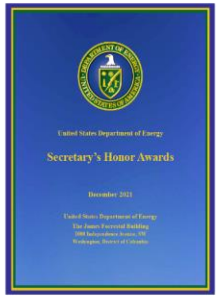
The Team



(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

Industrial Partners

Dow

dep – environmental protection – driven by employee pride

SES – SOMERSET ENVIRONMENTAL SOLUTIONS

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hedinenvironmental

Critical Metal (CM) Background

- **Critical mineral definition**: "…a non-fuel mineral or mineral material essential to the economic or national security of the U.S. and which has a supply chain vulnerable to disruption." – *Energy Act of 2020.*
- ***Acid mine drainage (AMD) has a bounty of un-tapped CMs:***
  - Millions of gallons/day; thousands of miles of streams
  - Mg (259 ppm surveyed max.) – steelmaking, batteries
  - Al (189 ppm max.) – ubiquitous, found in nearly all sectors
  - Zn (30 ppm max.) – metallurgy for producing galvanized steel
  - Mn (20 ppm max.) – alloying, and for reducing metals
  - Ni (1 ppm max.) – hydrocarbon production

Bauxite (Al)

Pyrolucite (Mn)

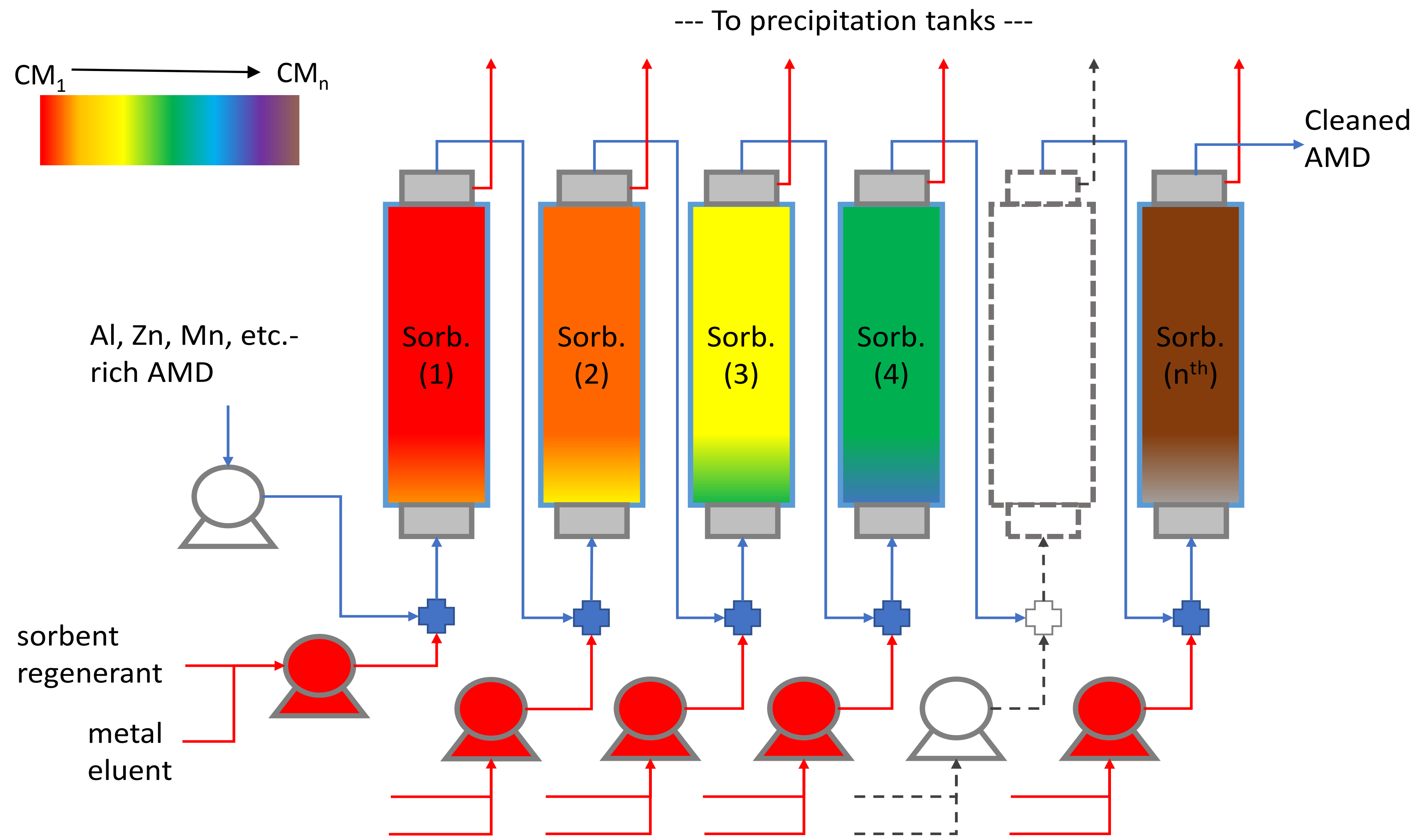
Sphalerite (Zn)

https://www.usgs.gov/news/national-news-release/us-geological-survey-releases-2022-list-critical-minerals

W.C. Wilfong, T. Ji, Y. Duan, F. Shi, Q. Wang, M.L. Gray, Critical review of functionalized silica sorbent strategies for selective extraction of rare earth elements from acid mine drainage, J. Hazard. Mater., 424 (2022) 127625.

Experimental – Adsorption-Based CM Recovery

Multi-Bed Approach

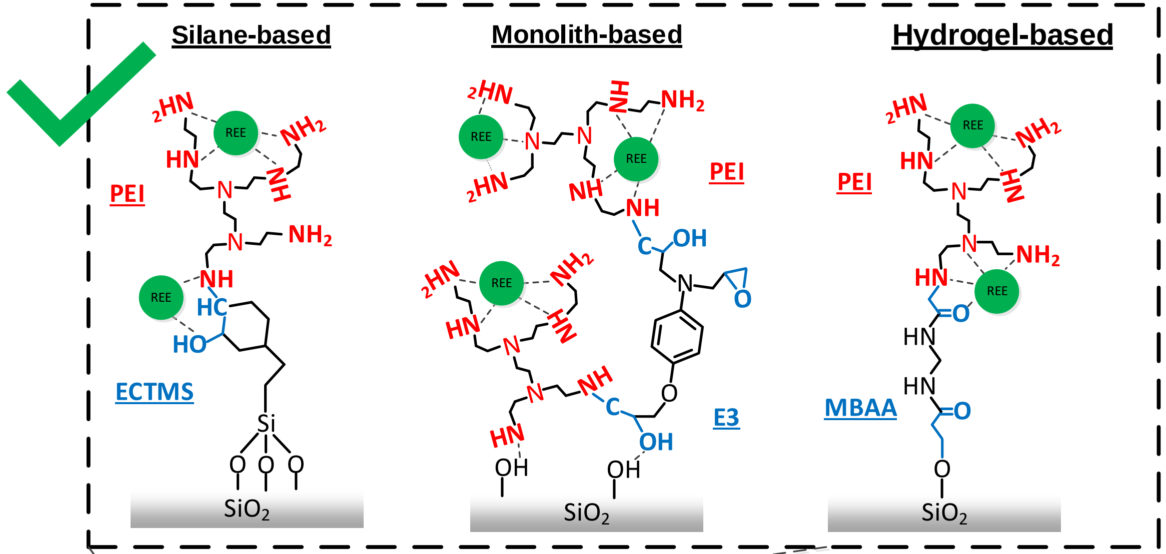


- Multi-bed fractionation to separate CM by selectivity.
- Separate bed elution to purify CM.
- Precipitation to achieve solid CM species.

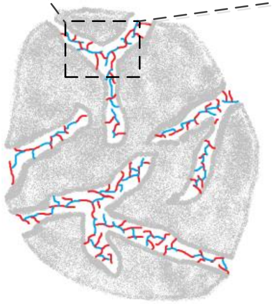
NETL Multi-Functional Sorbent Technology (MUST) for CM Recovery

Preparation and Structure

Sorbent Preparation



Functionalized SiO_2



18 Kg BIAS

Licensed by PQ Corporation!

(19) **United States**
(12) **Patent Application Publication** (10) **Pub. No.: US 2018/0100065 A1**
Gray et al. (43) **Pub. Date: Apr. 12, 2018**

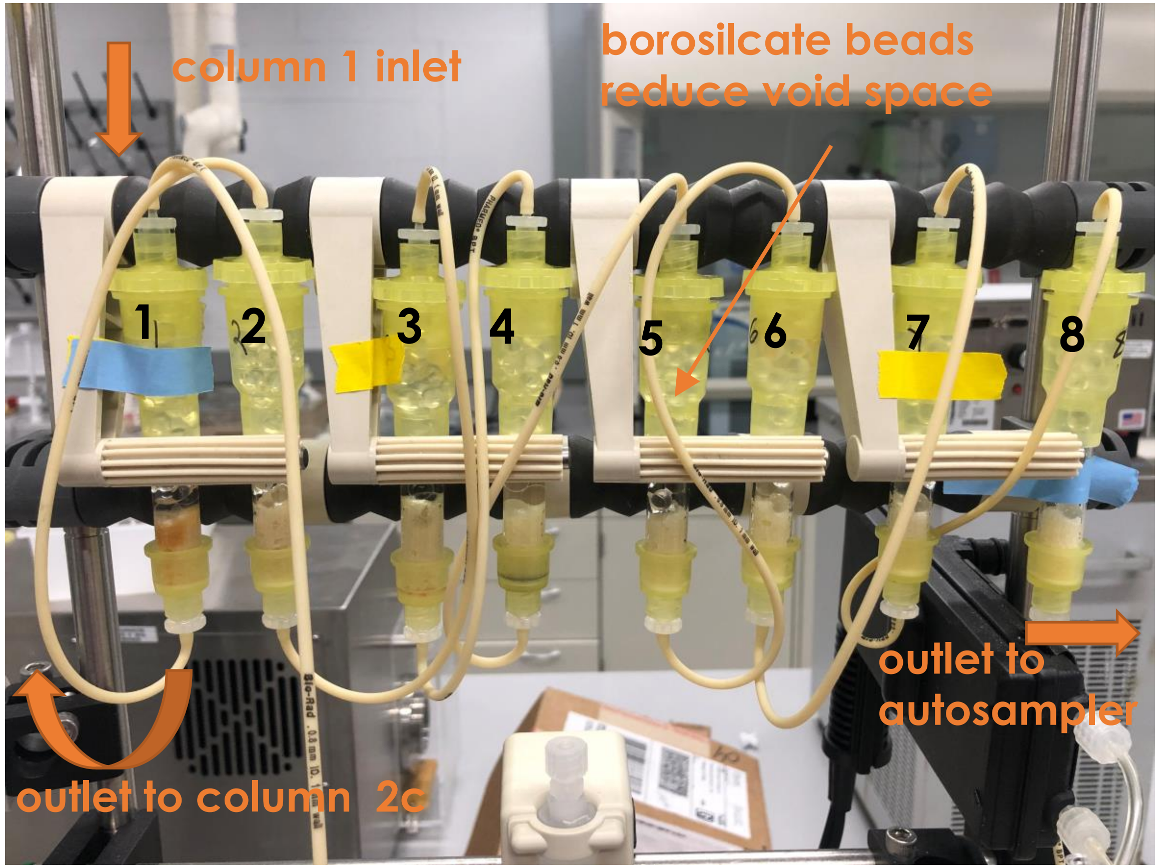
(54) STABLE IMMOBILIZED AMINE SORBENTS FOR REE AND HEAVY METAL RECOVERY FROM LIQUID SOURCES

Publication Classification

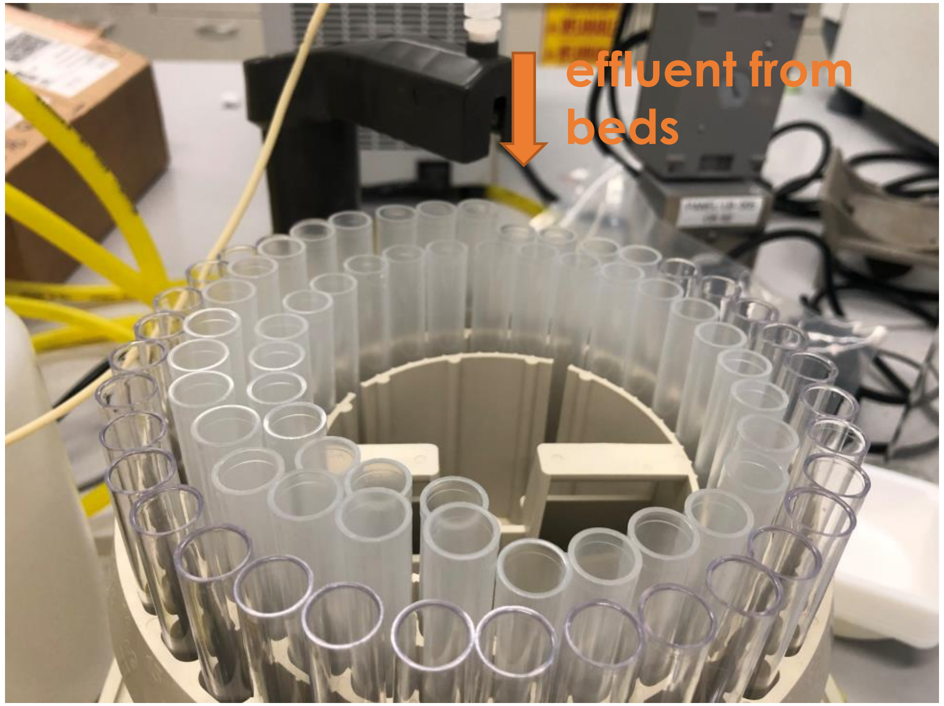
(51) Int. Cl.
C08L 79/02 (2006.01)
C08K 5/5419 (2006.01)

Multi-Bed Set-Up for Lab-Scale CM Fractionation

Beds in Series



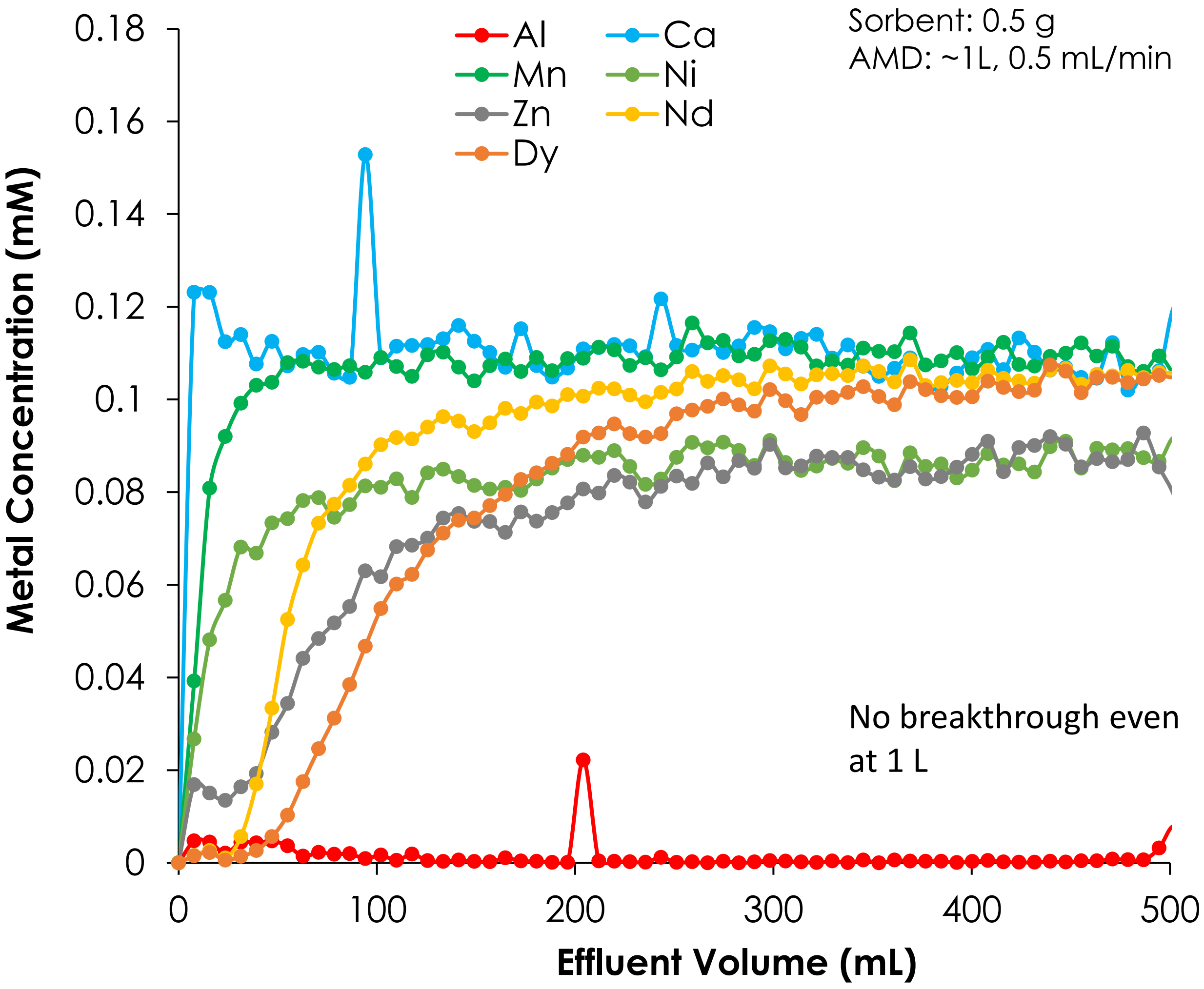
Autosampler (up to 7 mL/sample)



- 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

Results – Breakthrough Testing of Different AMD Metals

Simulated AMD mix ~0.1mM each of Al, Mn, Ni, Zn, Nd, Dy, Ca, Mg, Na, K



Sorbent metal affinity: Al >> Dy > Nd > Zn > Ni, Mn > Ca, K, Mg, Na

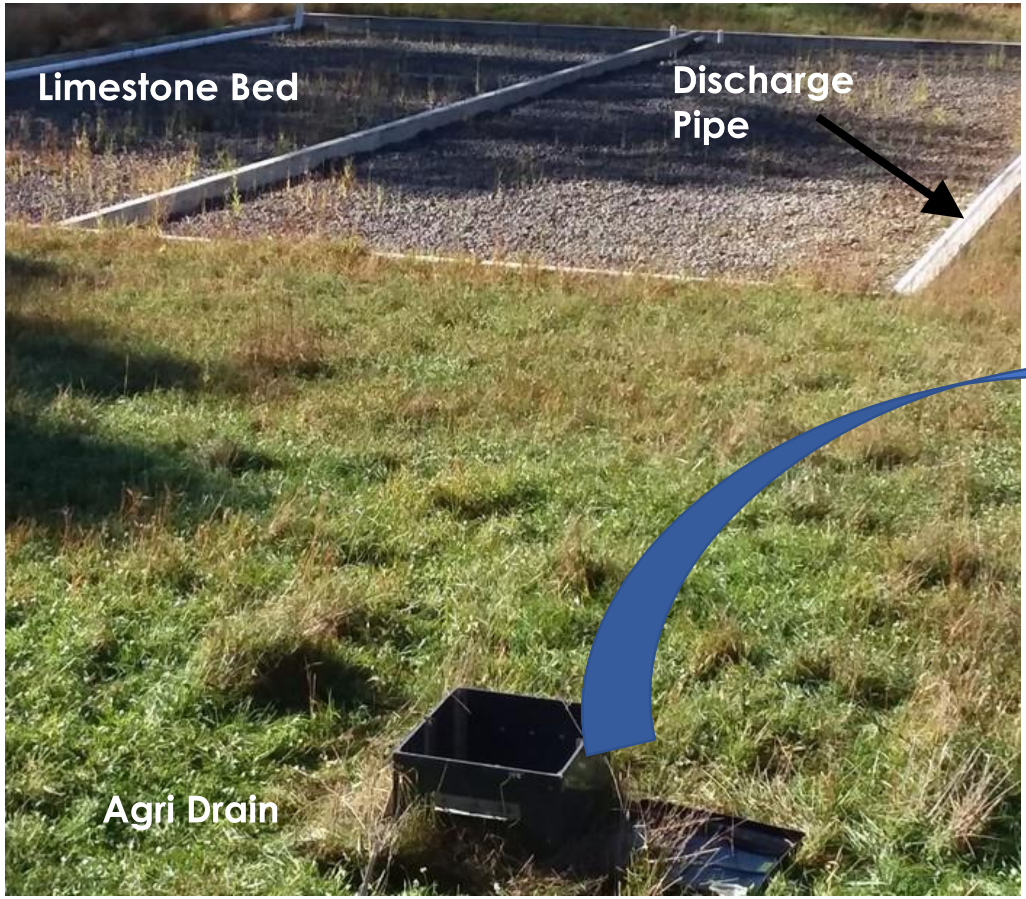
Strong covalent and ionic bonding contributions for Al and Dy > Ca to amine groups → stable metal-ligand bond

R.D. Hancock, A.E. Martell, Hard and Soft Acid-Base Behavior in Aqueous Solution: Steric Effects Make Some Metal Ions Hard: A Quantitative Scale of Hardness-Softness for Acids and Bases, J. Chem. Educ., 73 (1996) 654.

AMD Field Sampling – Pittsburgh Botanic Garden

Site Water Analysis

"Kentucky Hollow – Hedin Environmental"



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 (Al)

secondary (Mn)

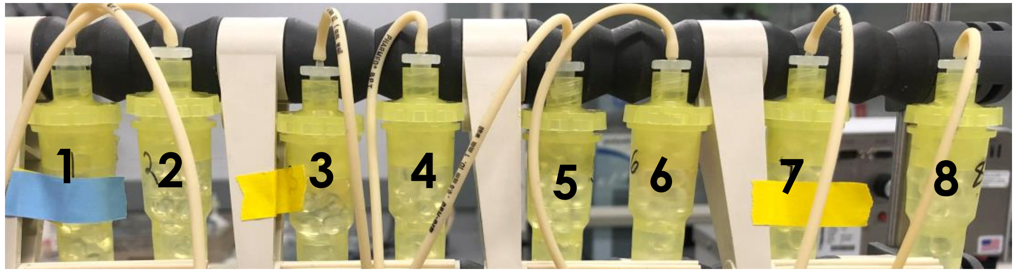
heavies

rare earth elements (REEs)

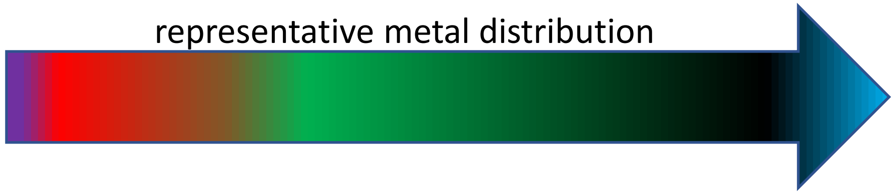
toxic (EPA)

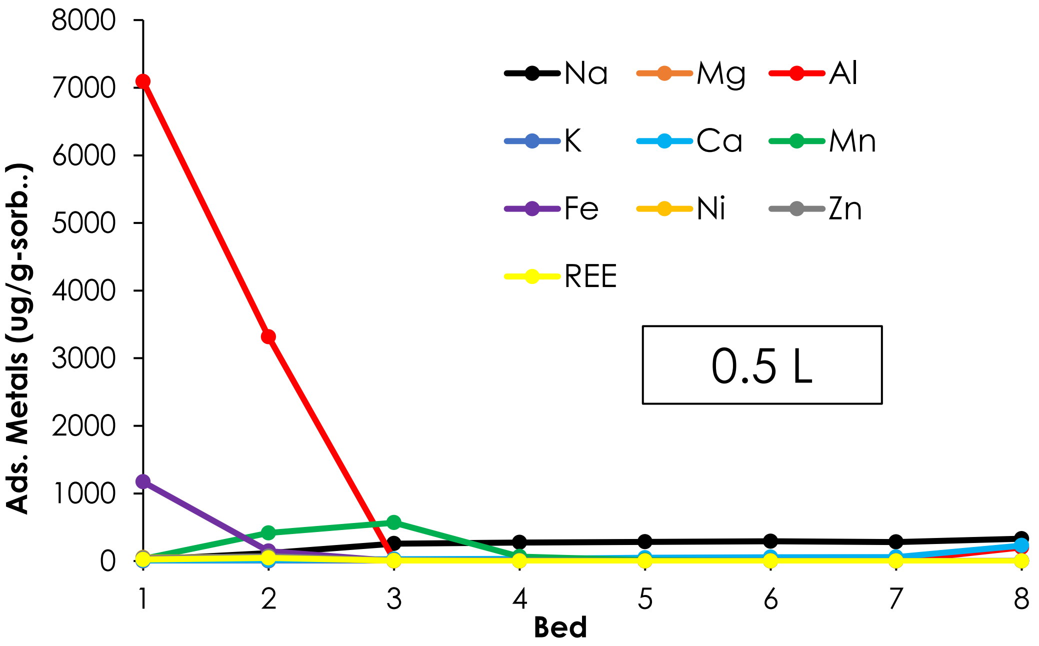
Lab-Scale Multi-Bed Fractionation Test, Using AUTHENTIC AMD

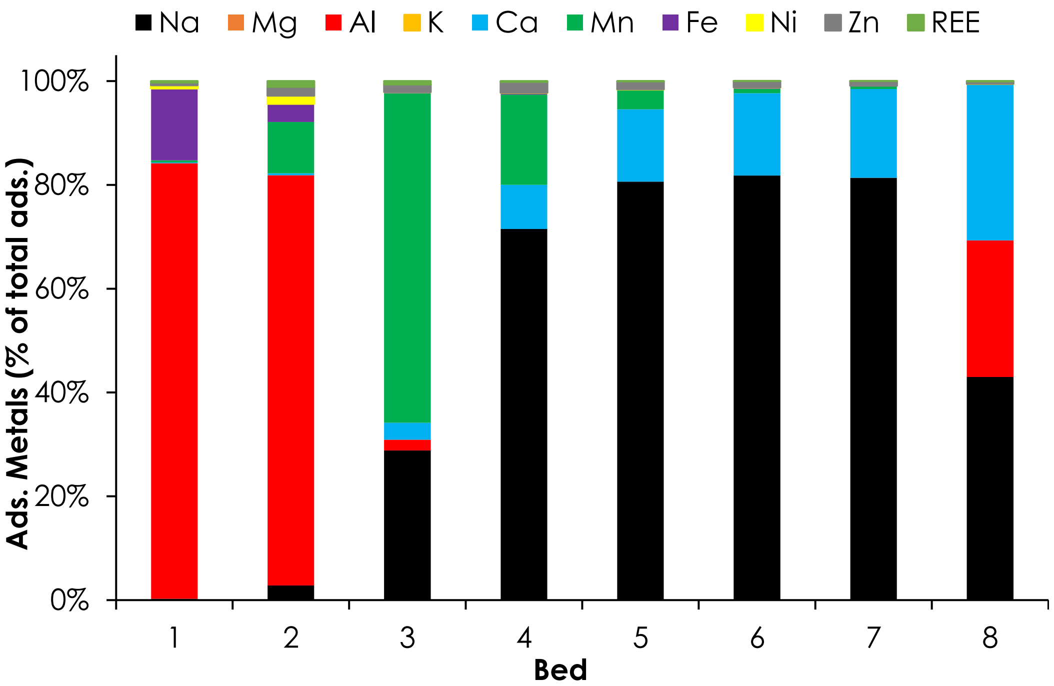
Separate 8–Bed Tests: 0.5 mL/min



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

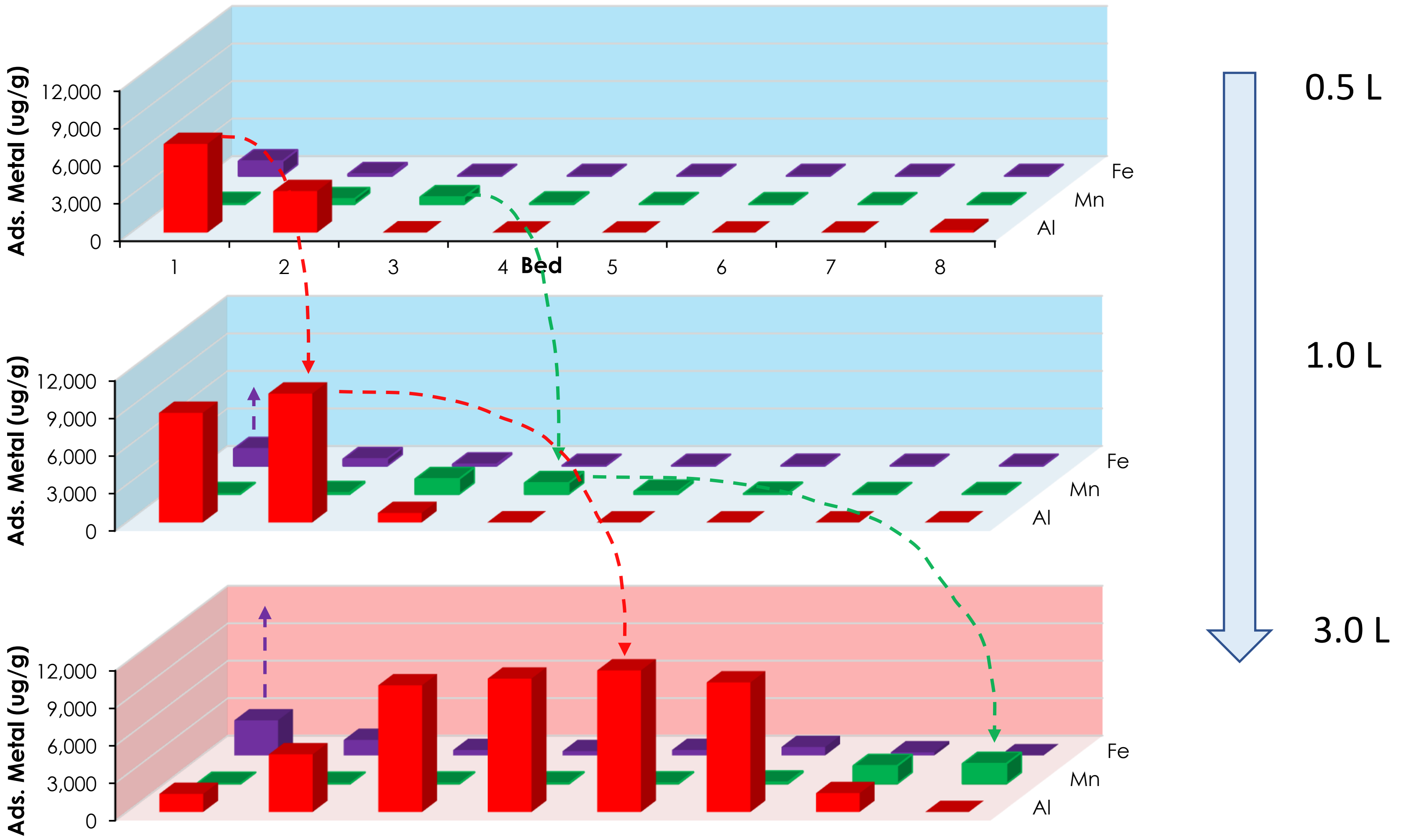






Effect of Treated AMD Volume on Metal Distribution

Separate 8–Bed Tests: 0.5 mL/min



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.

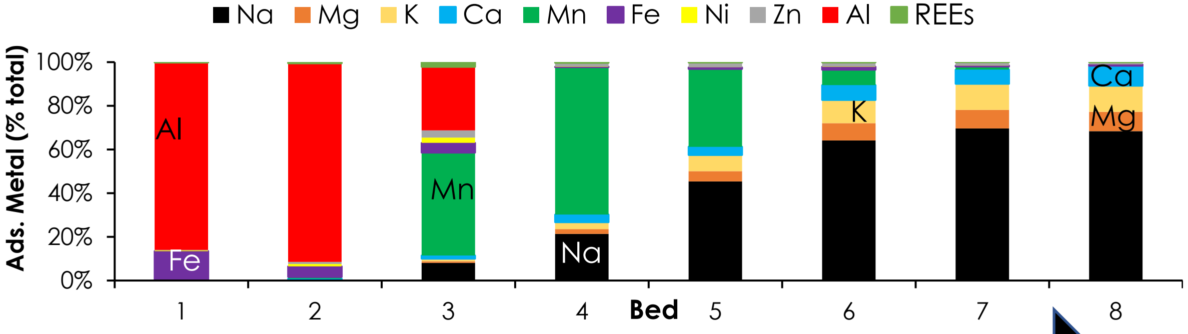
Fractionation achieved:

Beds 1, 2:
~1.1 wt% Al; ≥ 90% pure

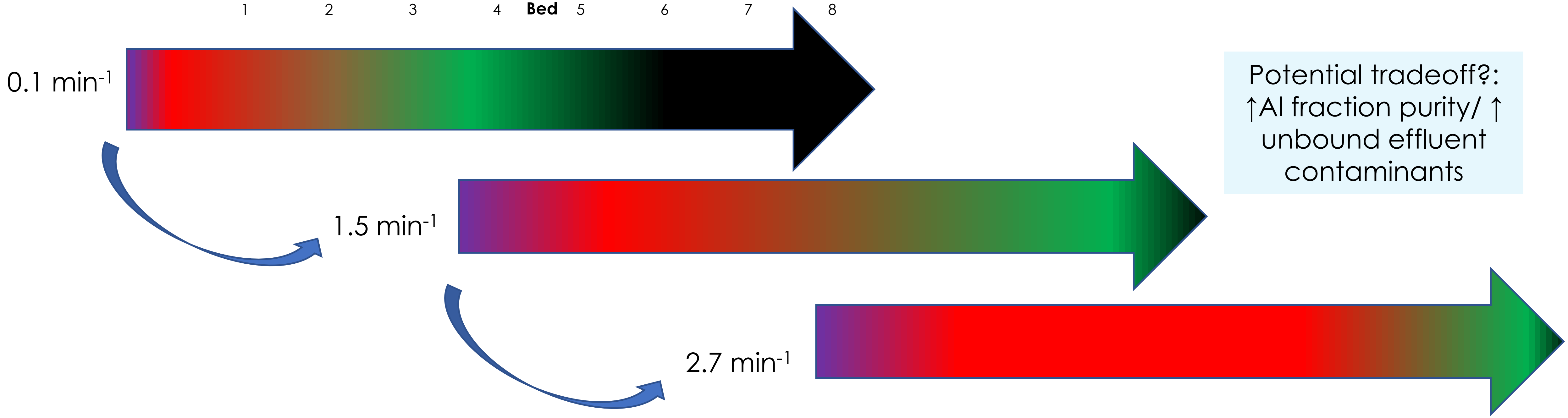
Bed 8:
0.16 wt% Mn, ~84% pure

Effect of Weighted Hourly Space Velocity (WHSV) Ratio on Metal Distribution

Separate 8–Bed Tests: 1L AMD



Higher WHSV preferentially distributed metals according to uptake kinetics - f(*c*, *k*): Al > Mn > Na, Ca



Potential tradeoff?: ↑Al fraction purity/ ↑ unbound effluent contaminants

PBG AMD Field Site Set-Up for Recovery of Critical Metals

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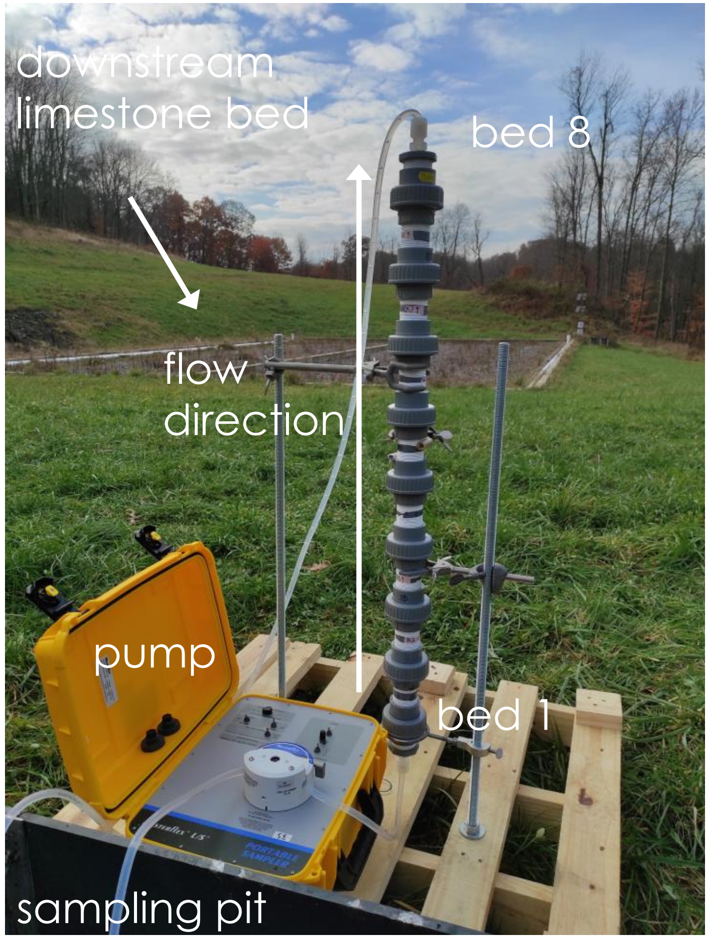
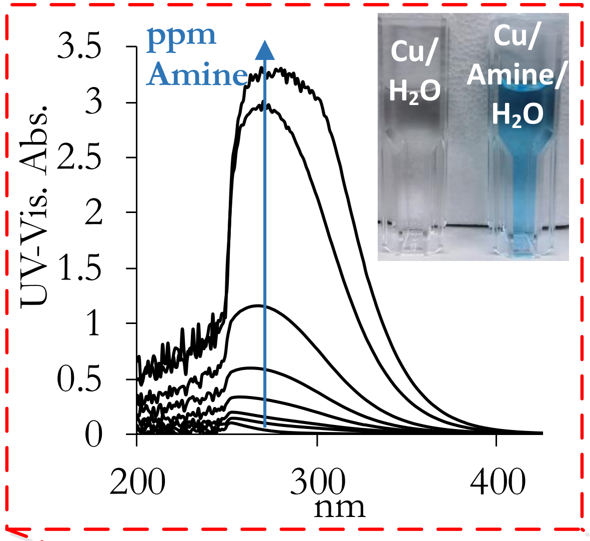
8-Bed Scale-Up

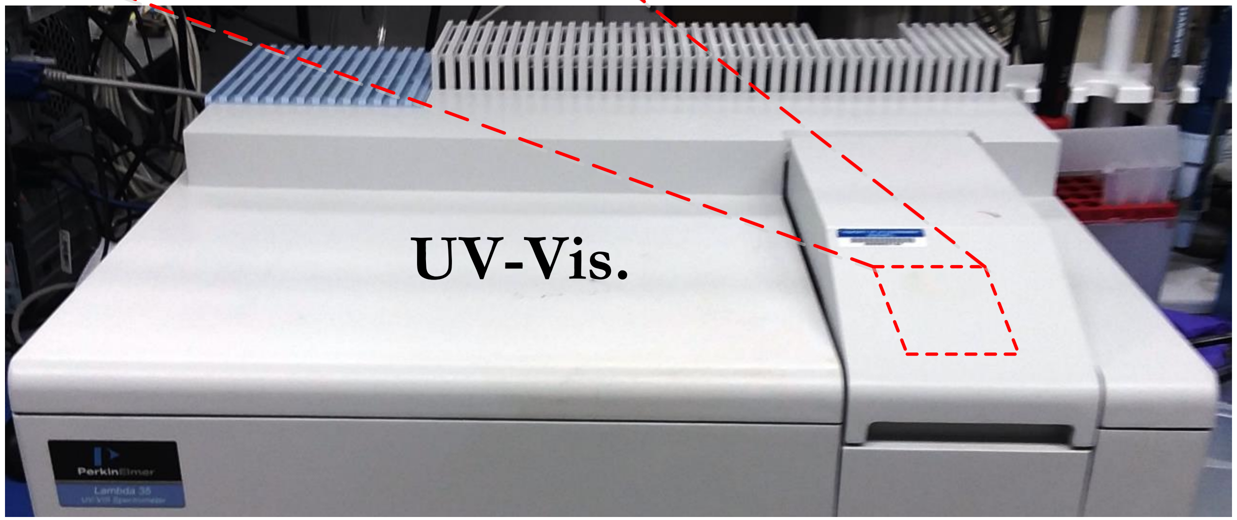


- Sorbent capacity: 160 g
- Flow rate: 0.6 – 1.1 L/min
- WHSV: 0.35 min^{1} – 7.9 min^{-1}

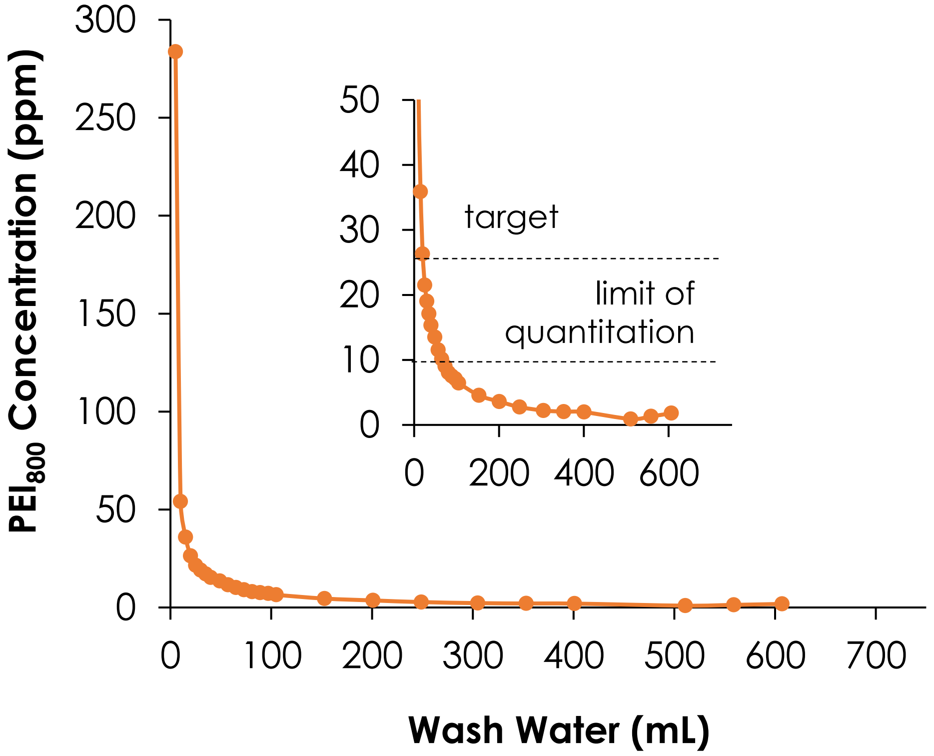
First practical application of NETL's MUST for recovering CMs from a coal waste source – AMD.

Preparation for Field Test – Sorbent Washing





- Uv-Vis/Cu^{2+} technique detects low ppm-levels of residual non-crosslinked amine.
- Quality control tool to ensure thoroughly washed sorbent keeps field site clean.



50 sorbent bed masses of H_2O needed to achieve minimum amine leach guideline.

Comparing Field Test and Lab-Scale System Performance

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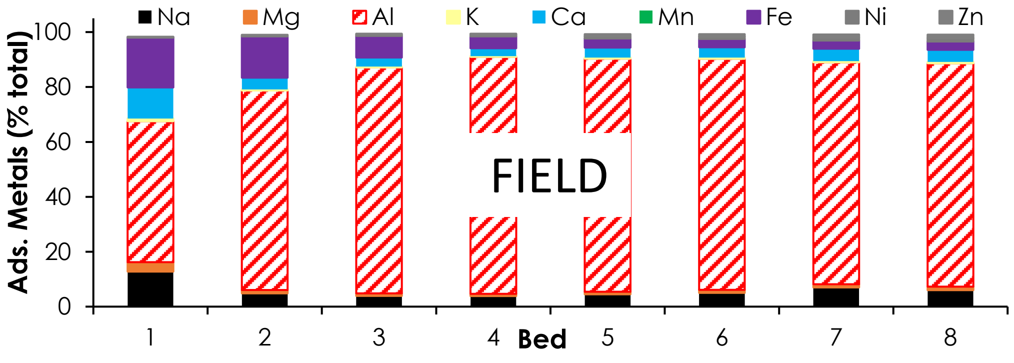
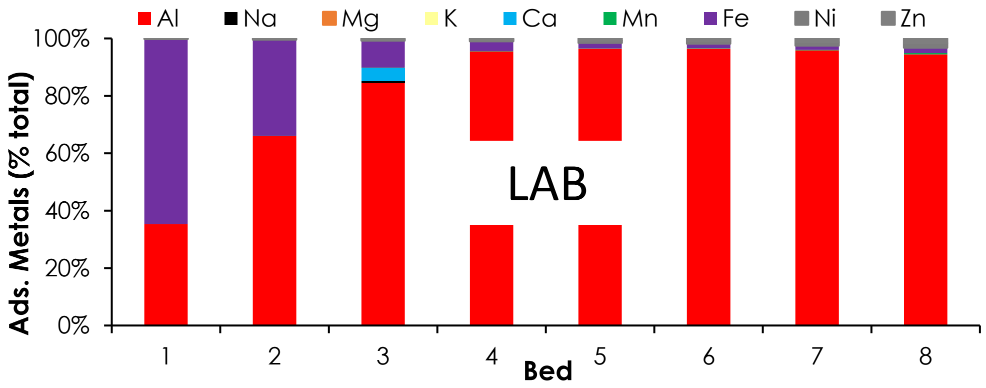
Scaled MUST Adsorption Process

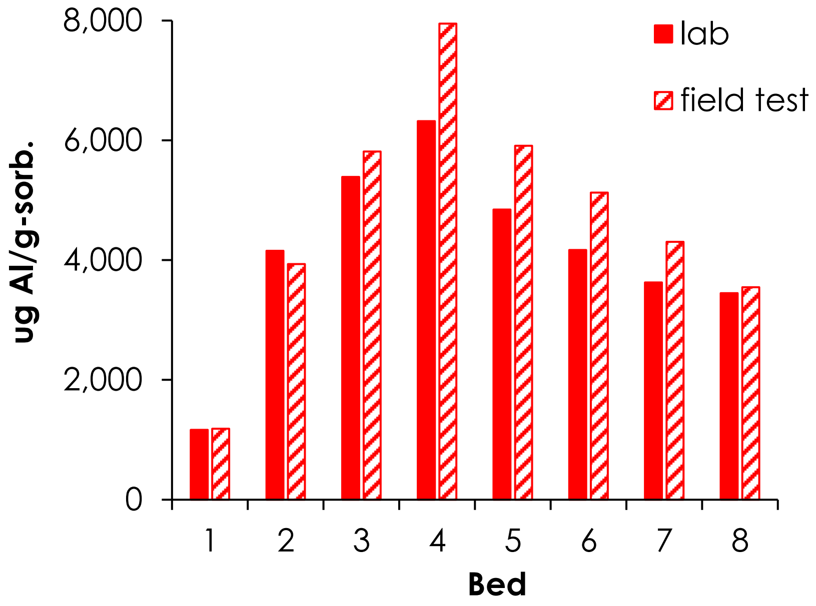


Sorb.=140 g
Flow=285 mL/min
Volume=100 L

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



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



<u>Al adsorbed from field test:</u>

- ~1 wt% Al, ≥90% pure
- 0.25 wt% Al, 80-89% pure

U.S. DEPARTMENT OF ENERGY

Recovery of Solid CM – 2nd Field Test with Modified Sorbent

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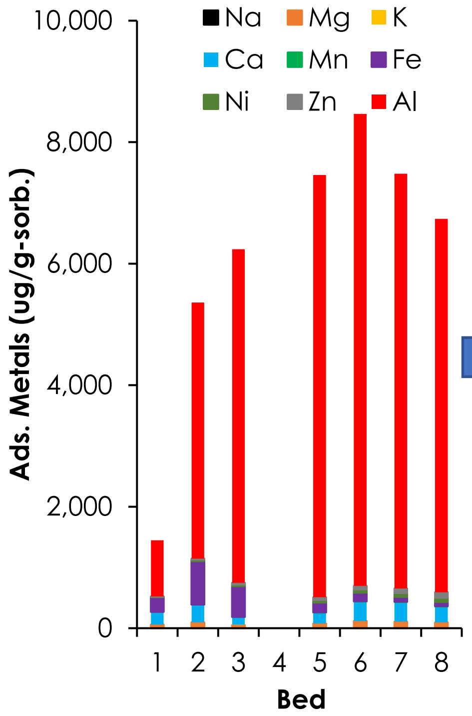
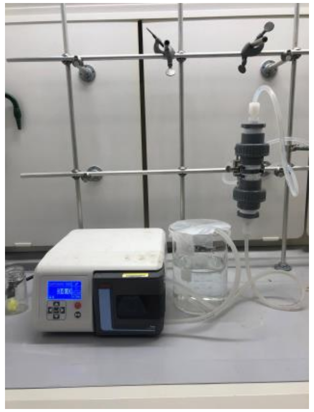
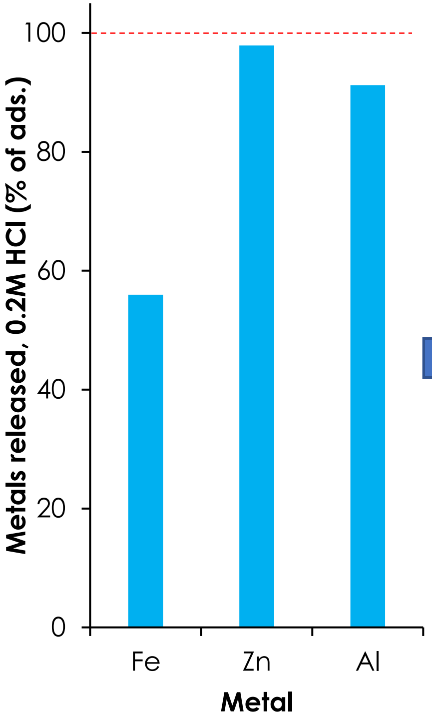
Elution and Precipitation of Bed 5 CM

Metal-adsorbed bed 5

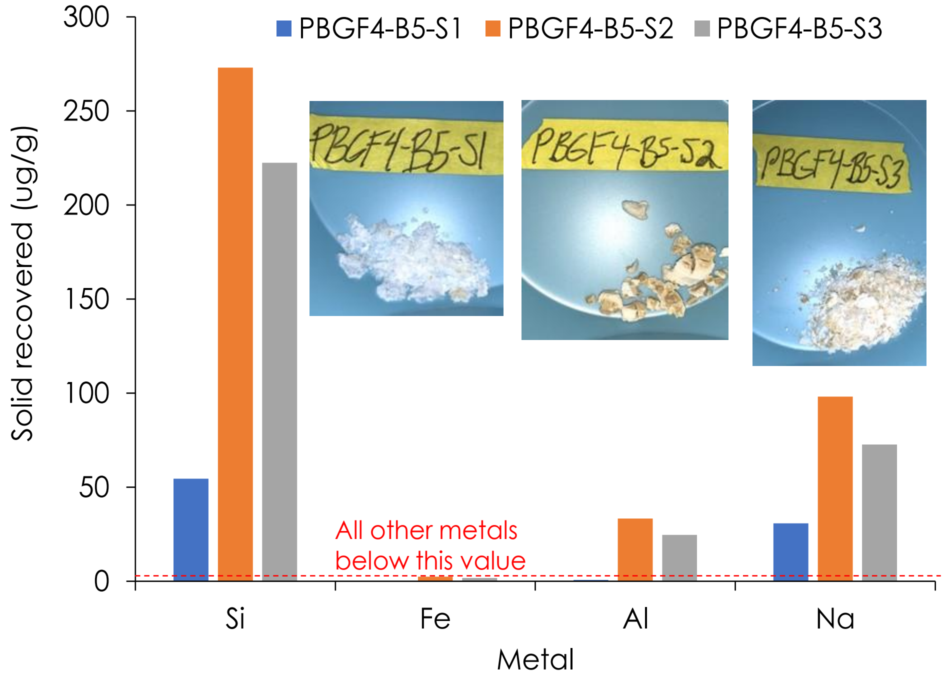




Bed 5 elution: 0.2M HCl, 1.5L



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.

Conclusions and Continuing Work

- ✓ 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.
- ✓ Additional work needed to improve % Al elution and Al purity.
  - Elution – different buffers, lower-concentration HCl.
  - Precipitation – sequential pH increase, sampling every pH 1 unit.
- ✓ Evaluate produced water or other AMD sites for CM.

NETL Resources

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