Metals Got You Down? A Look at Effective Mining-Influenced Water Treatments

CARUS®

ONE COMPANY, ENDLESS SOLUTIONS

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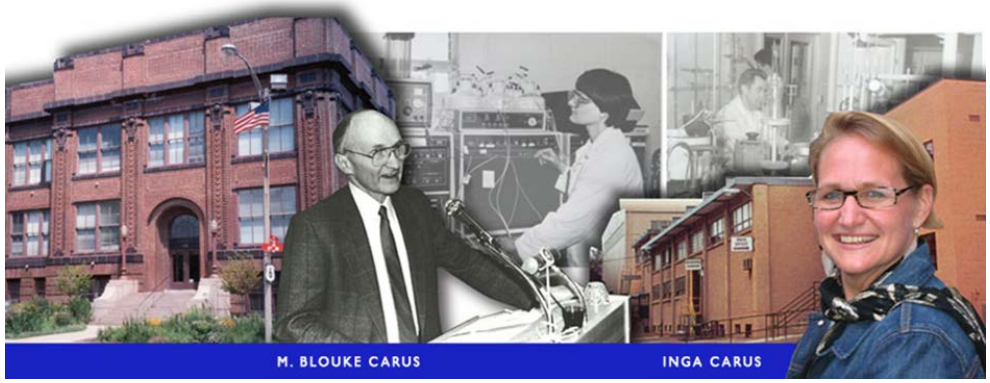
Today's Talking Points

- About Us
- Mn Treatment Challenges
- Product Development
  - ➢Permanganate Tablets and Alkaline Permanganate
- Field Trials: PA and KY
- Reactive Capping for Remediation, Reclamation and Slope Stabilization
- New Developments:
  - ➢As, Se, Hg and B Treatments

About Us

- Privately Held; Founded in 1915
  - About 400 Employees



- Five Manufacturing Sites in the United States
  - Warehouses in Europe
- International Sales and Distribution Organization
- Key Markets:
  - Water Treatment, Air Purification and Remediation

Mn Treatment Challenges

1. Effluent geochemistry (e.g., pH and Eh) are unfavorable for Mn precipitation
2. Complex effluent chemistries and competing ions

- Chemical-neutralizing reagents to precipitate manganese are problematic
  - ➢ High pH increases costs due to chemical consumption *(nuisance reactions)* leads to untreated water
  - ➢ Traditional processes generate large amounts of sludge

- *Permanganates are very effective for Mn (and Fe) removal*

Permanganates for *Rapid* Removal of Mn and Fe

- Widely used in drinking water, wastewater, and remediation (inorganics and organics)
  - Oxidizes Fe and Mn to convert ferrous (2+) iron into the ferric (3+) state and manganese (2+) to the 4+ state

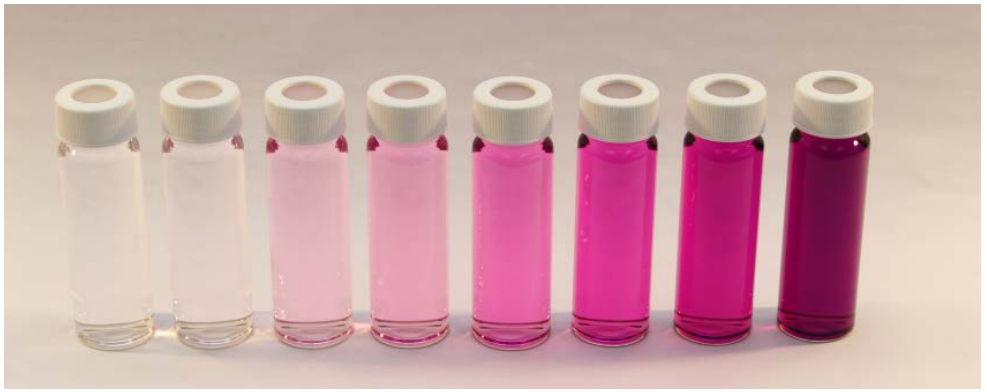
- *Permanganate dose*
- *0.94 mg/mg iron*
- *1.92 mg/mg manganese*

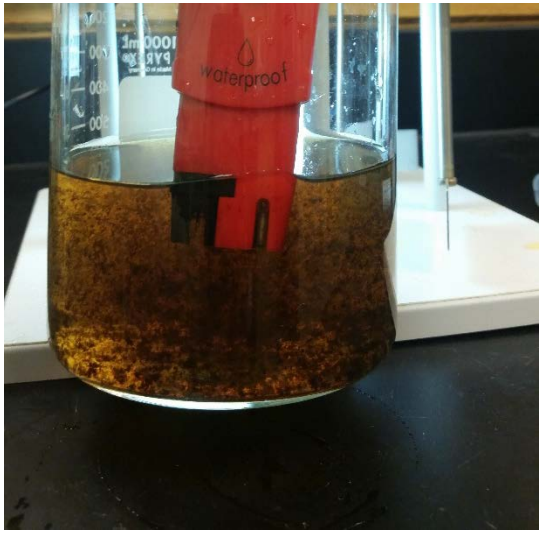
$$3Fe^{2+} + KMnO_4 + 7H_2O \rightarrow 3Fe(OH)_{3(s)} + MnO_{2(s)} + K^+ + 5H^+$$

$$3Mn^{2+} + 2KMnO_4 + 2H_2O \rightarrow 5MnO_{2(s)} + 2K^+ + 4H^+$$

- CARUSOL®
  - Liquid sodium permanganate $NaMnO_4$ (20% and 40%)
- CAIROX®
  - Solid potassium permanganate $KMnO_4$(solubility ~3%)

Permanganates for *Rapid* Removal of Mn and Fe





Permanganate-Based MIW Product Development

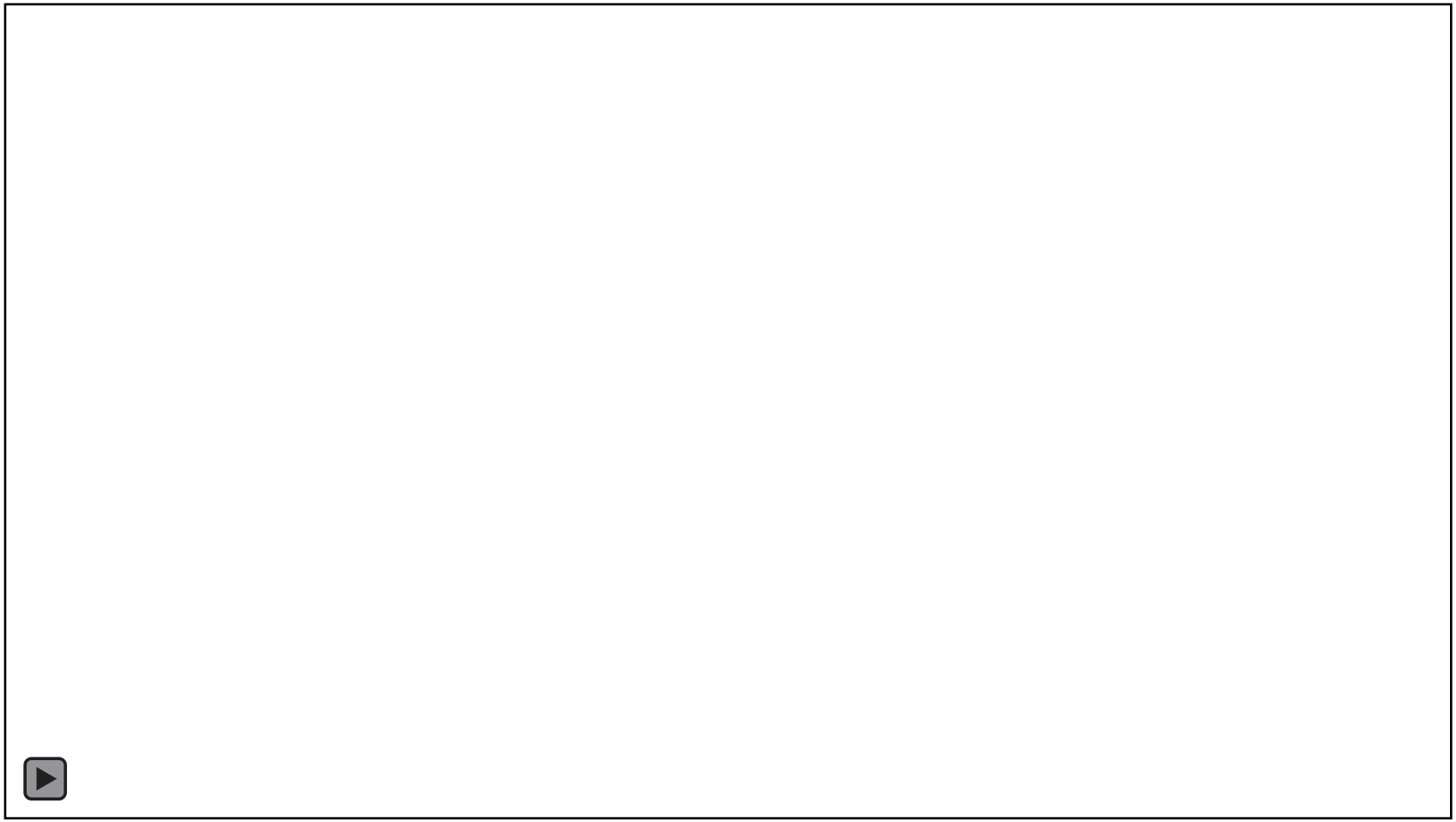
- CAIROX® CR Permanganate Tablets (80% $KMnO_4$ with inert binder)
  - Slow-release permanganate for many days to weeks (depends on flow rate)
  - Passive treatment for Mn/Fe removal
  - Excellent for remote locations

- Alkaline CARUSOL® (liquid $NaMnO_4$):
  - Stable permanganate/caustic blend for Mn/Fe removal and pH adjustment
- Spreadsheet calculators assist with dosing

Initial Field Trials: Permanganate Tablet Deployment

Lessons Learned:
Tablet Dispenser for Field Trials (PA)

Prototype Tablet Dispenser



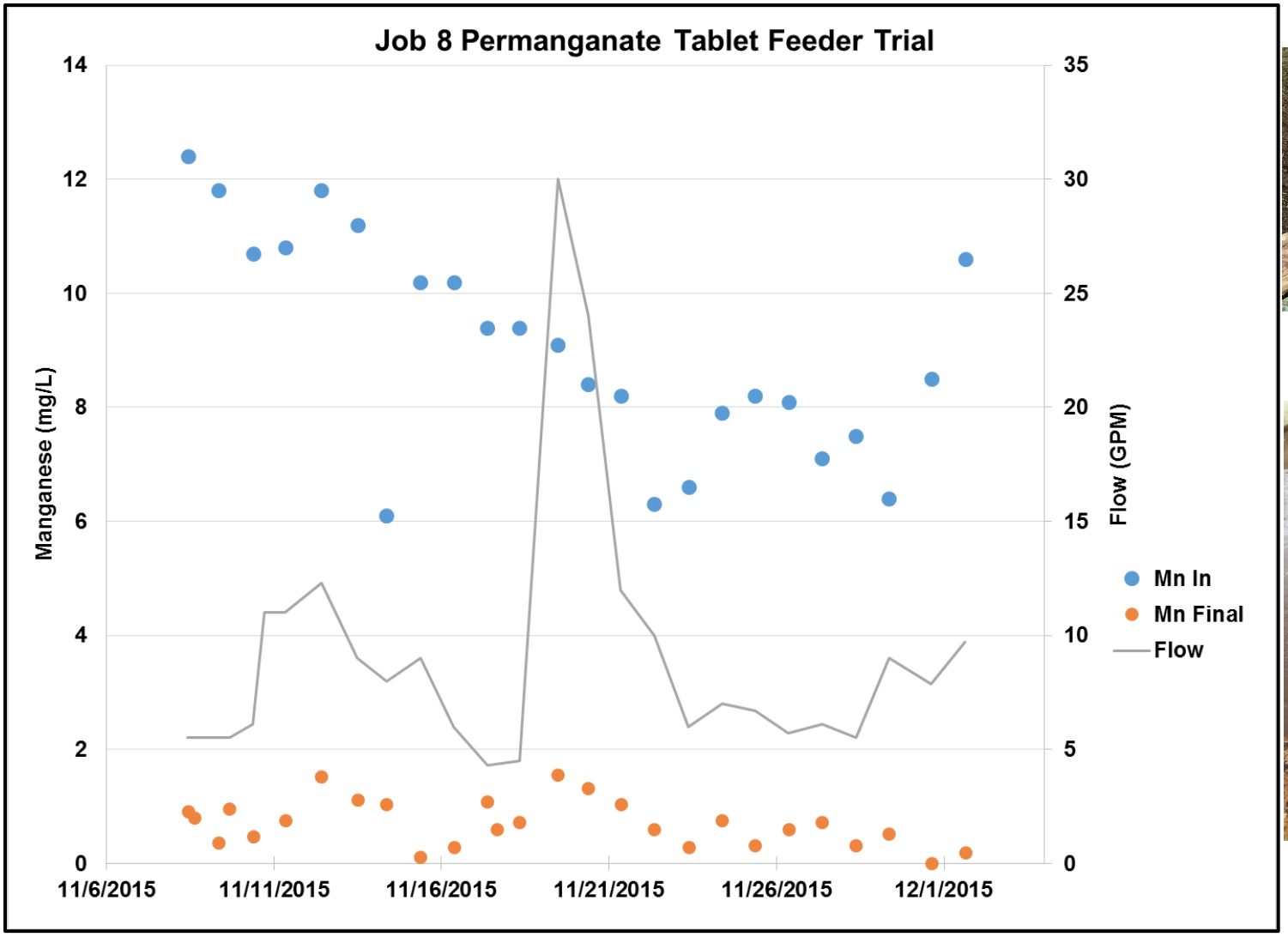
Penn Coal Tablet Trial

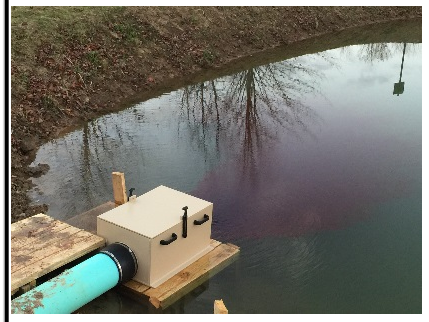
- Lower flow pond 5 – 30 GPM
- Bio-bed pretreatment
- 6 – 13 ppm Mn, pH 6-7

Prototype Tablet Dispenser Learnings

- Weir plates and tablet holders are adjustable based on flow
- Adjustable Design allows Passive Treatment of Variable Flows (Up to 50 GPM)

PA Permanganate Tablet Trial





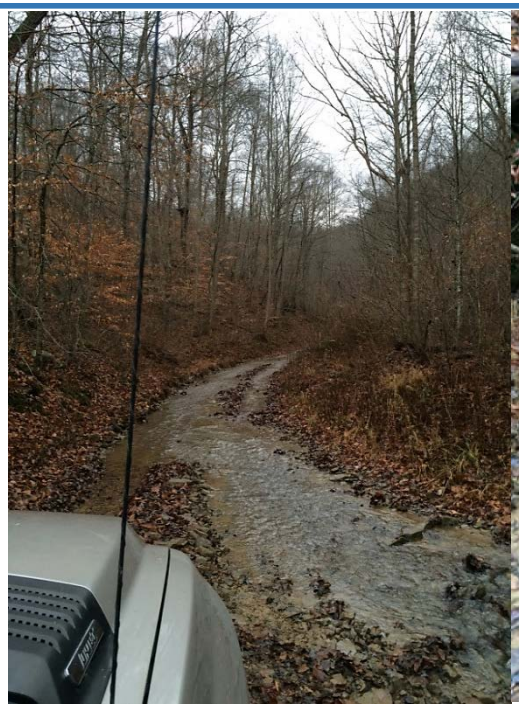
Month-Long Final Discharge Mn Concentration < 2 mg/L

Tablet Trial Highlights

- Final Mn discharge compliance achieved at PA sites (<2 mg/L)
- Dispenser compensates for variable flow
- Effective for treating Mn in the presence of Al

Alkaline CARUSOL: KY Field Trial

- Remote pond with acidic waste stream Fe and Mn above discharge limits
- Sodium permanganate & caustic were being applied separately
- Alkaline CARUSOL: Custom-blended product to adjust pH + treat metals
- Bench-scale jar tests determine baseline geochemistry to develop appropriate blend
- Average pH = 4.7
  - Fe = 2.3 mg/L
  - Mn = 21 mg/L
- Flow 40-80 GPM



Alkaline CARUSOL: Tote Deployment




Pre- and Post-Treatment (December 2014)	Mn/Fe Concentrations (mg/L)	Mn/Fe Removal (%)
Fe Pre-Treatment	11	86%
Fe Post-Treatment ~15 min reaction	1.7	
Mn Pre-Treatment	22	97%
Mn Post-Treatment ~15 min reaction	0.04	

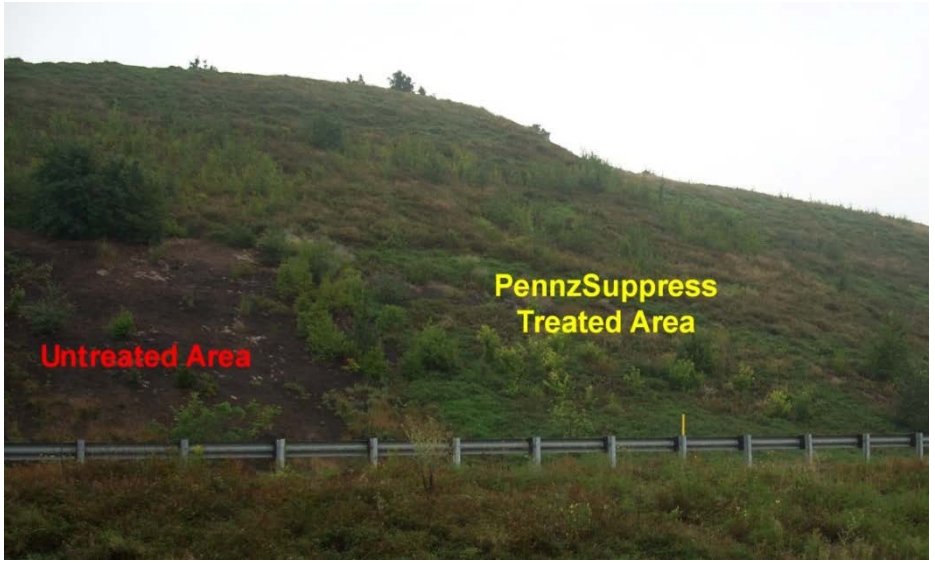
Alkaline CARUSOL: KY Field Trial

Outfall Sampling	Outfall Fe (ppm)	Outfall Mn (ppm)	Outfall pH
Pre-Alkaline Carusol tote September 2014	**0.744**	**1.12**	**7.1**
Post-Alkaline Carusol tote December 2014	**0.134**	**0.818**	**7.3**
Post-Alkaline Carusol tote January 2015	**0.137**	**0.28**	**7.1**

PennzSuppress™ Reactive Capping Overview

- I-99 road construction through Central PA resulted in exposure of pyritic material
- Acid Rock Drainage by pyrite weathering required remediation
- Reactive barrier prevents wash-off of neutralizer
- Mulch and seed applied with hydroseeder creating a reactive barrier for revegetation and slope stabilization
- Neutral pH, healthy revegetation, and slope stabilization remains 10+ years after emplacement

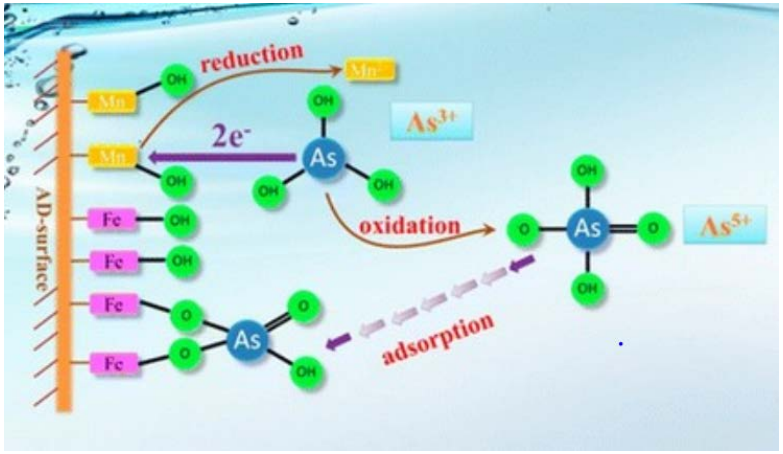
Reactive Capping: Remediation, Reclamation and Slope Stabilization



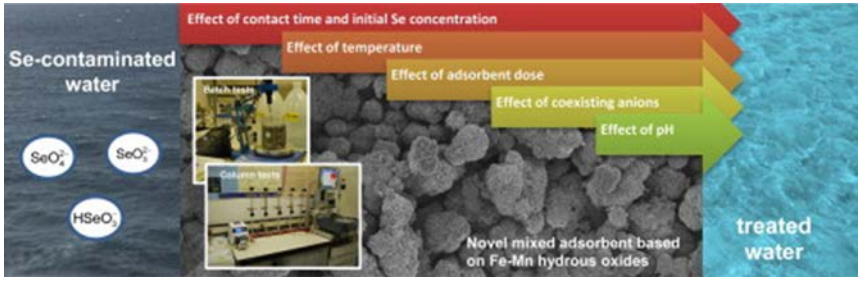
Reactive Capping: Remediation, Reclamation and Slope Stabilization

New Developments: Treatment Approaches for As, Se, Hg and B

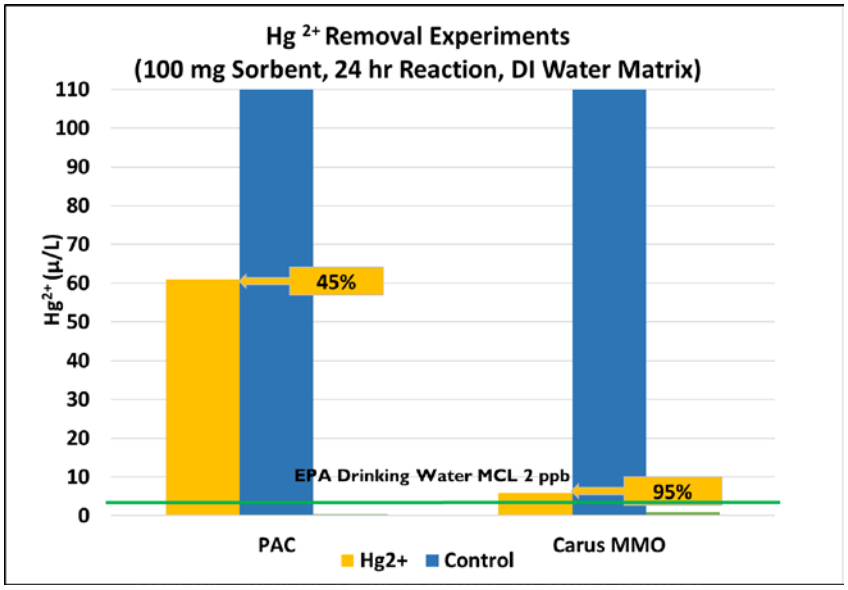
- Oxidation/Reduction
- Adsorption
- Co-precipitation

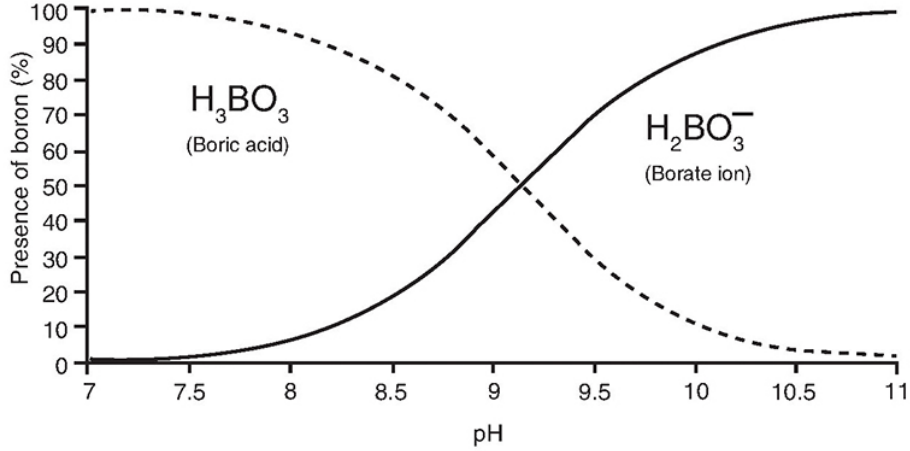


Source: Zhang et al., (2014). Respective Role of Fe and Mn Oxide Content for Arsenic Sorption in Fe and Mn Binary Oxide: An X-Ray Adsorption Spectroscopy Investigation Environ Sci Technol. 2014 Sep 2;48(17):10316-22



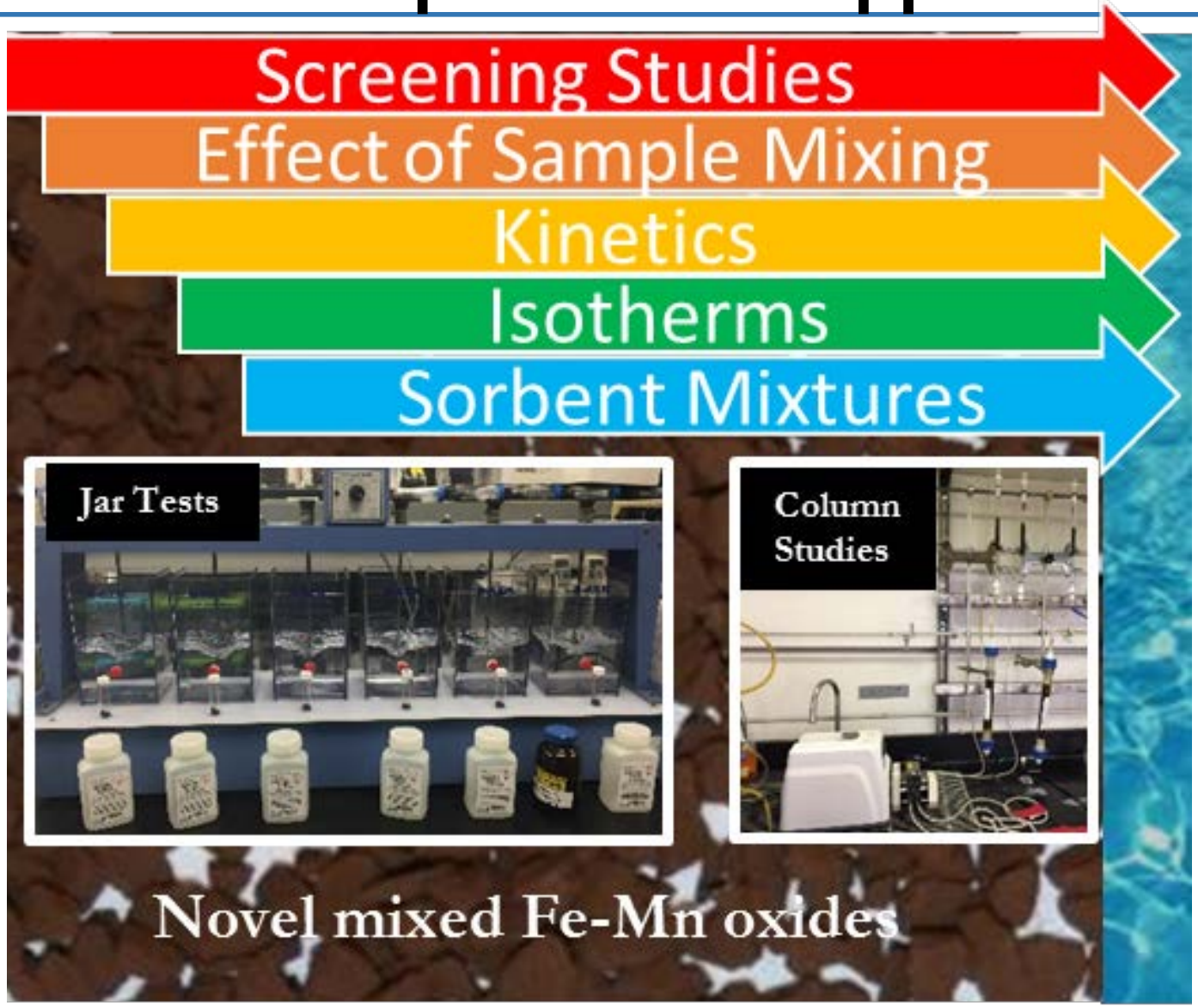
Source: Szlachta and Chubar. (2013).The application of Fe–Mn hydrous oxides based adsorbent for removing selenium species from water. Chem. Eng, Jour.





Source: Kameda et a., (2016). Use of MgAl oxide for boron removal from an aqueous solution in rotation: Kinetics and equilibrium studies J. Env. Mgmt., 165, 280-285

Sorbent Experimental Approach



Properties of Carus Mn-Based Adsorbents

Micro Amorphous Manganese Oxide (AMO)

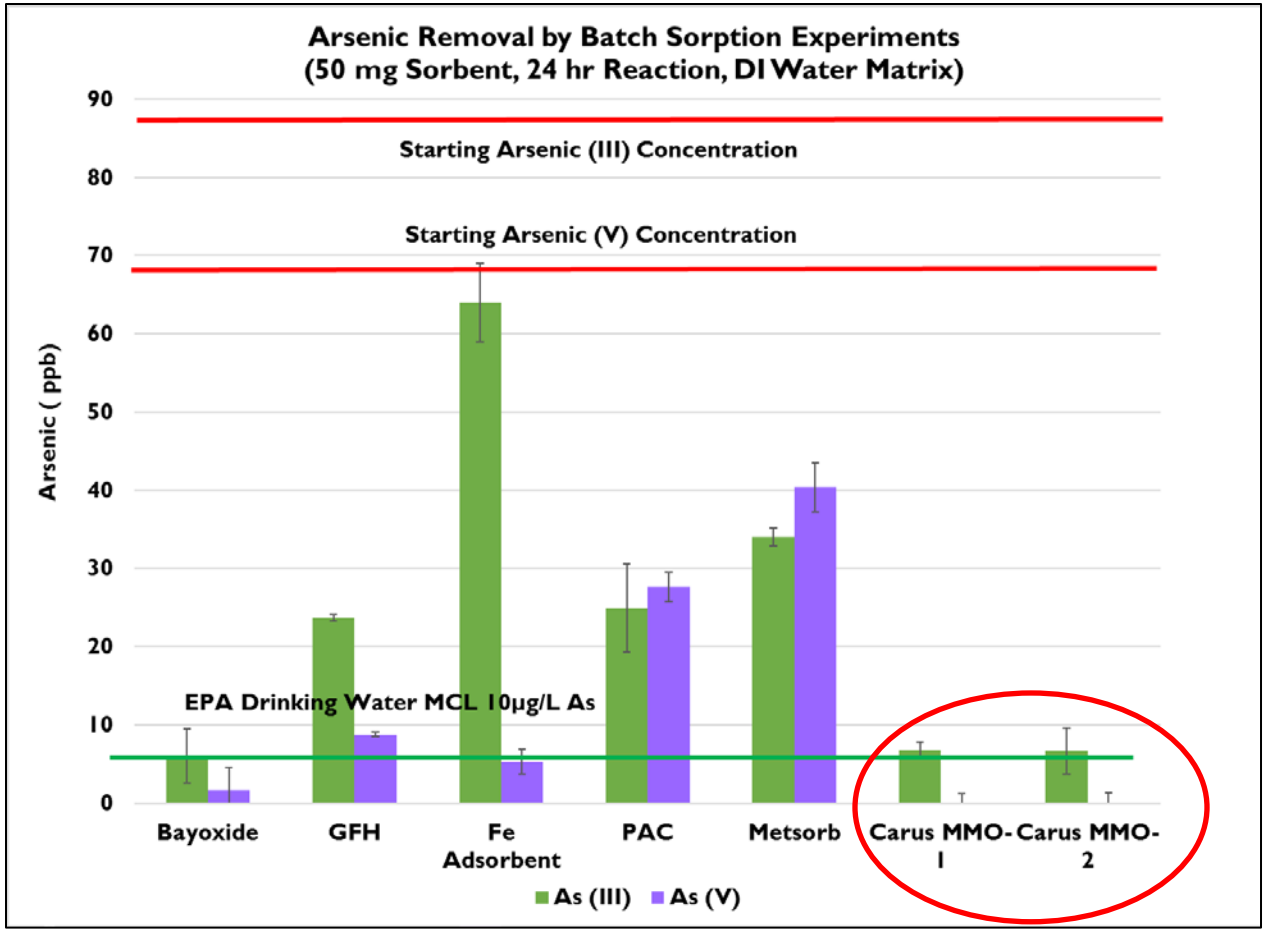
- Higher IEC than naturally occurring MnOx
- Powder, Granular, or Coating

Mixed Metal Oxide (MMO)

- Cation and anion exchange functionality
- Powder, Granular, or Coating

- Mean Particle Size ~ 10 micron
- Surface Area ~ 300 m^2/g

Arsenic Removal

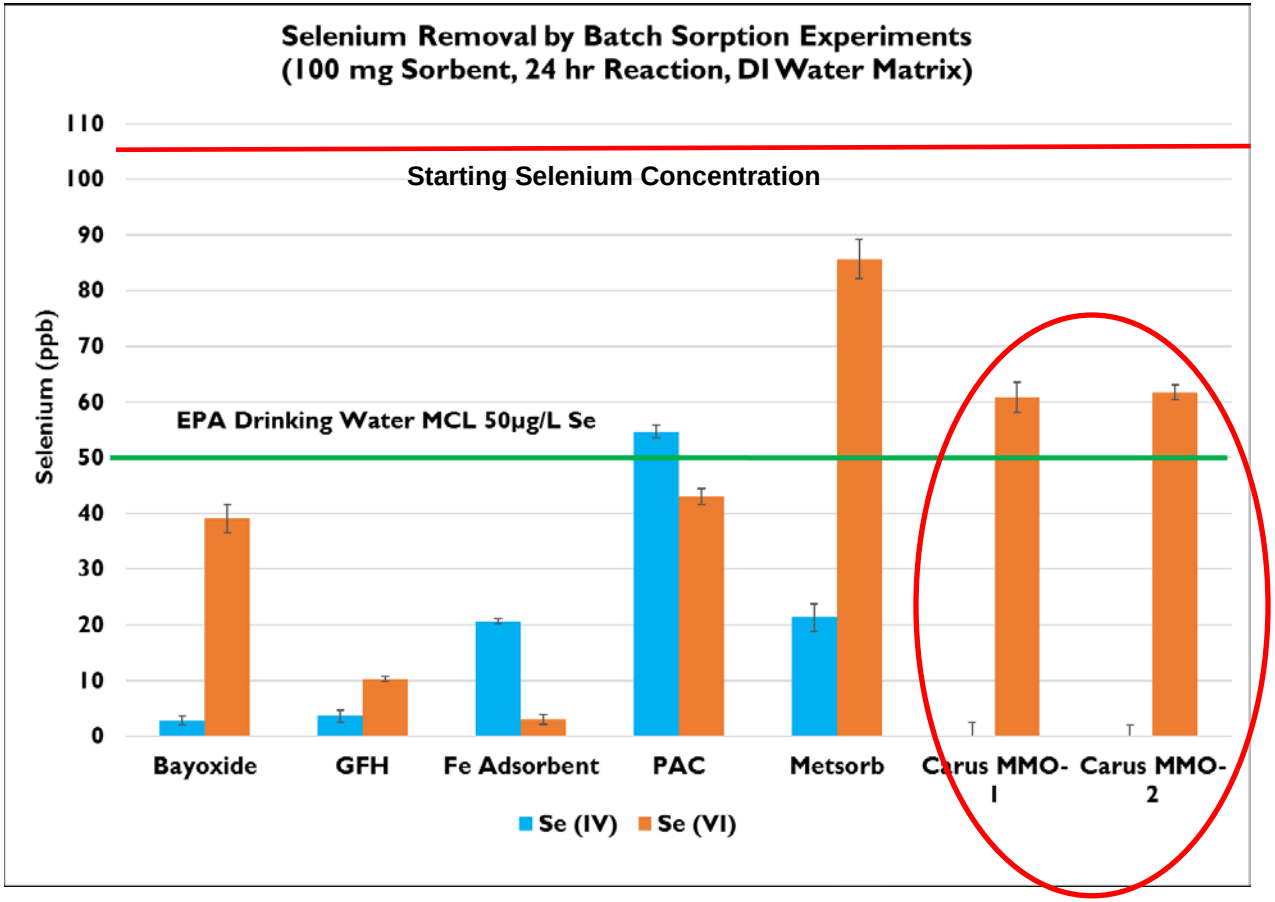


Adsorbent Loading (mg As/g Adsorbent)	
As (III)	As (V)
MMO-1, 1.6	MMO-1, 1.6
MMO-2, 1.6	MMO-2, 1.6
Metsorb, 0.9	GFH, 1.6
Bayoxide, 0.8	Bayoxide, 1.5
Iron Adsorbent, 0.7	Metsorb, 0.9
GFH, 0.7	Iron Adsorbent, 0.5
PAC, 0.7	PAC, 0.1

Arsenite: 100% Carus MMO

Arsenate: 97% Carus MMO

Selenium Removal

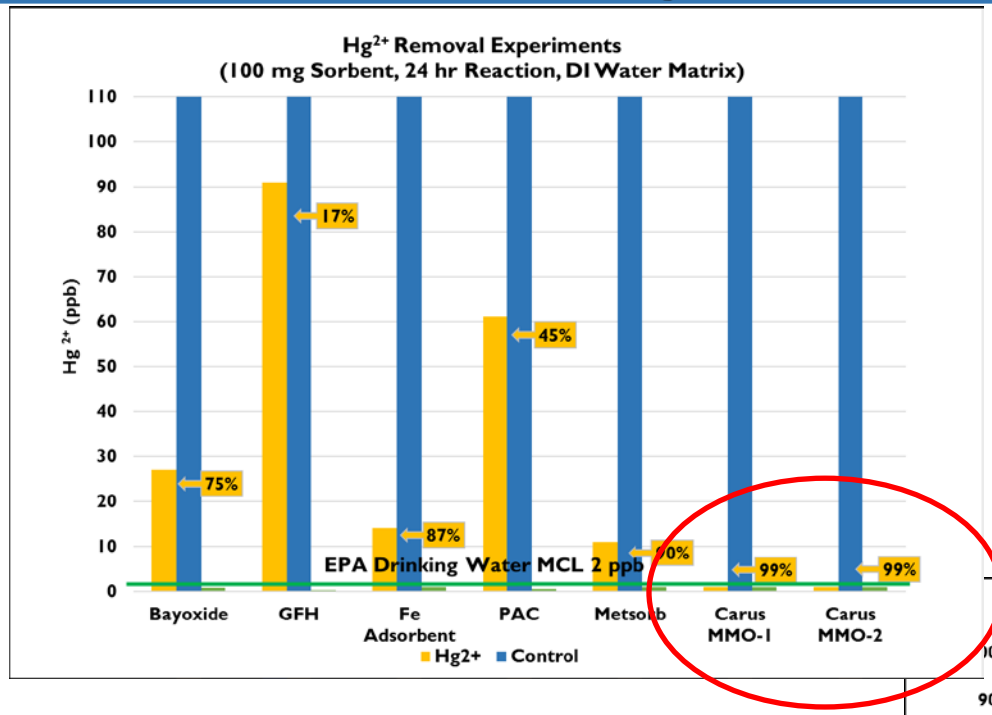


Adsorbent Loading (mg Se/g Adsorbent)	
Se (VI)	Se (IV)
Iron Adsorbent, 1.0	MMO-2, 0.92
GFH, 0.94	MMO-1, 0.91
Bayoxide, 0.65	Bayoxide, 0.91
PAC, 0.62	GFH, 0.88
MMO-1, 0.43	Iron Adsorbent, 0.70
MMO-2, 0.43	Metsorb, 0.69
Metsorb, 0.19	PAC, 0.37

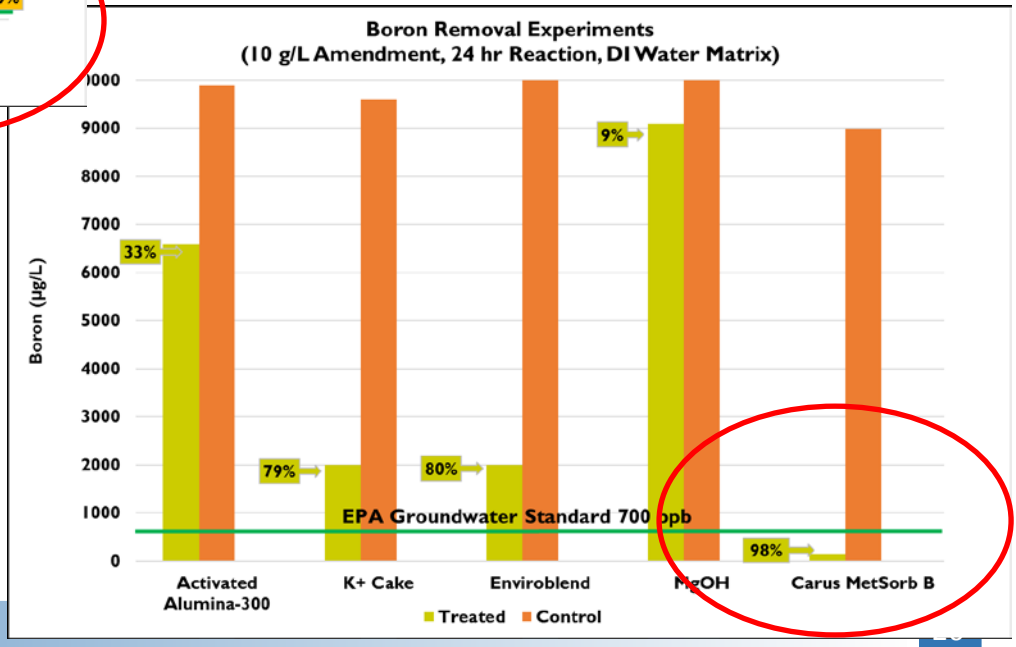
Selenite: 100% Carus MMO

Selenate: 40% Carus MMO (product optimization in progress)

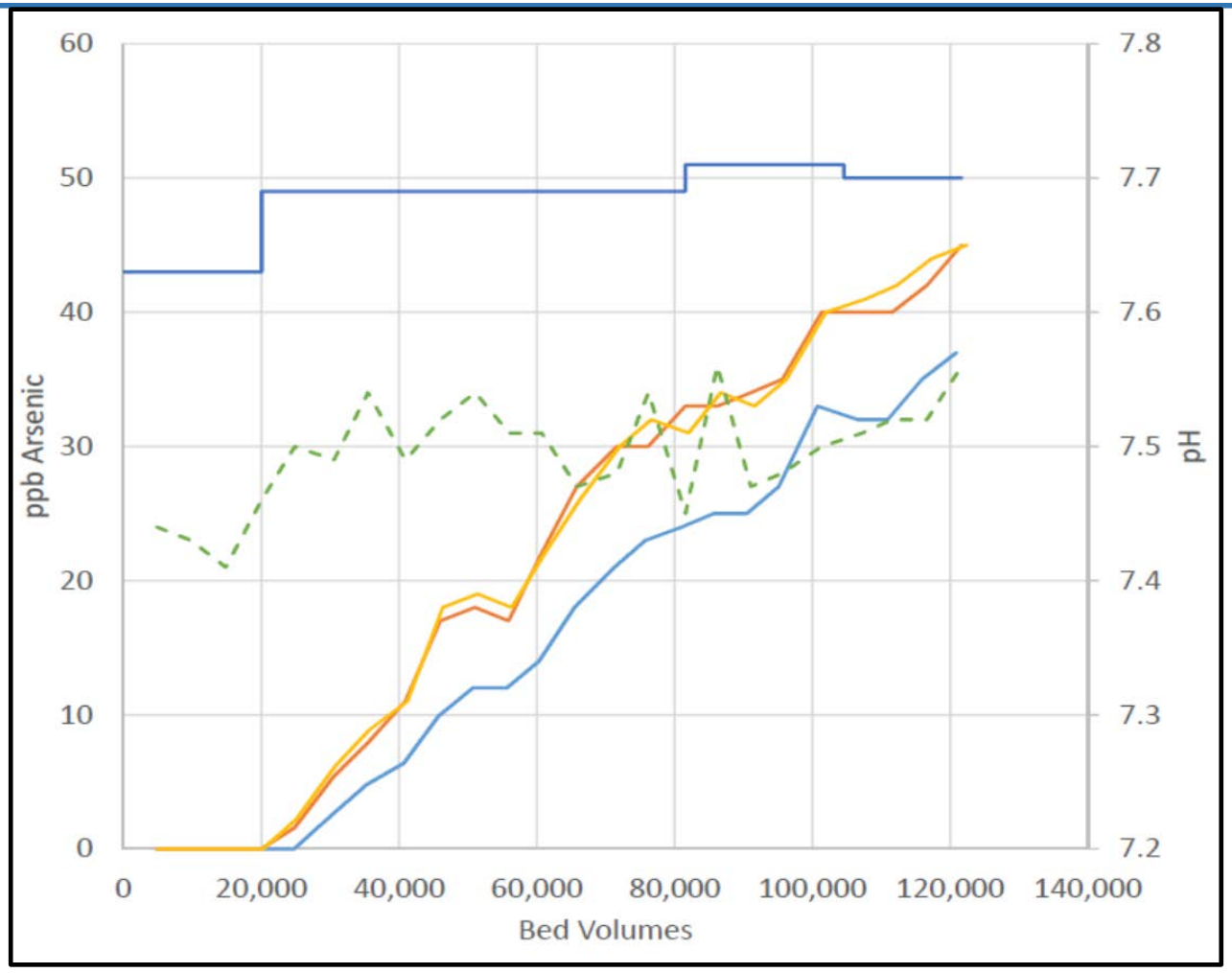
Mercury and Boron Removal



- Hg and B – 99% Removal



Results:
As Removal in Packed Bed Reactor



- 40-50 ppb As Influent
- As Breakthrough after ~ 20,000 Bed Volumes

Take Home Message

- Slow release tablet or liquid
- Solid product good for remote sites, lower flows
- Liquid product good for all flows
- Effective for Mn and Fe in the presence of Al
- MnO_2 settles quickly/serves as adsorbent for other metals
- Reactive caps remediate ***and*** reclaim mining waste piles
- Carus sorbents very effective for As, Se, Hg & B

Thanks!
Questions?

- PADEP and OSM
- Penn Coal

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