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

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Carus Corporation
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

- CARUSOL®
  - Liquid sodium permanganate NaMnO₄ (20% and 40%)

- CAIROX®
  - Solid potassium permanganate KMnO₄ (solubility ~3%)

\[
3Fe^{2+} + KMnO_4 + 7H_2O \rightarrow 3Fe(OH)_3(s) + MnO_2(s) + K^+ + 5H^+
\]

\[
3Mn^{2+} + 2KMnO_4 + 2H_2O \rightarrow 5MnO_2(s) + 2K^+ + 4H^+
\]
Permanganates for *Rapid* Removal of Mn and Fe
Permanganate-Based MIW Product Development

• CAIROX® CR Permanganate Tablets (80% KMnO₄ 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 NaMnO₄):
  ➢ 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)
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

<table>
<thead>
<tr>
<th>Pre- and Post-Treatment (December 2014)</th>
<th>Mn/Fe Concentrations (mg/L)</th>
<th>Mn/Fe Removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe Pre-Treatment</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>Fe Post-Treatment ~15 min reaction</td>
<td>1.7</td>
<td>86%</td>
</tr>
<tr>
<td>Mn Pre-Treatment</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>Mn Post-Treatment ~15 min reaction</td>
<td>0.04</td>
<td>97%</td>
</tr>
</tbody>
</table>
### Alkaline CARUSOL: KY Field Trial

<table>
<thead>
<tr>
<th>Outfall Sampling</th>
<th>Outfall Fe (ppm)</th>
<th>Outfall Mn (ppm)</th>
<th>Outfall pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-Alkaline Carusol tote</td>
<td>0.744</td>
<td>1.12</td>
<td>7.1</td>
</tr>
<tr>
<td>September 2014</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Post-Alkaline Carusol tote</td>
<td>0.134</td>
<td>0.818</td>
<td>7.3</td>
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<tr>
<td>December 2014</td>
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<td></td>
<td></td>
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<tr>
<td>Post-Alkaline Carusol tote</td>
<td>0.137</td>
<td>0.28</td>
<td>7.1</td>
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<tr>
<td>January 2015</td>
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</table>
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
New Developments: Treatment Approaches for As, Se, Hg and B

- Oxidation/Reduction
- Adsorption
- Co-precipitation

Source: Kameda et al., (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

Screening Studies
Effect of Sample Mixing
Kinetics
Isotherms
Sorbent Mixtures

Jar Tests
Column Studies

Novel mixed Fe-Mn oxides
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 m²/g
Arsenic Removal

Arsenic Removal by Batch Sorption Experiments
(50 mg Sorbent, 24 hr Reaction, DI Water Matrix)

Starting Arsenic (III) Concentration

Starting Arsenic (V) Concentration

Arsenic (ppb)

EPA Drinking Water MCL 10μg/L As

Bayoxide GFH Fe Adsorbent PAC Metsorb Carus MMO-Carus MMO-1 Carus MMO-2

Arsenite: 100% Carus MMO
Arsenate: 97% Carus MMO

Adsorbent Loading
(mg As/g Adsorbent)

<table>
<thead>
<tr>
<th></th>
<th>As (III)</th>
<th>As (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMO-1</td>
<td>1.6</td>
<td>MMO-1</td>
</tr>
<tr>
<td>MMO-2</td>
<td>1.6</td>
<td>MMO-2</td>
</tr>
<tr>
<td>Metsorb</td>
<td>0.9</td>
<td>GFH</td>
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<tr>
<td>Bayoxide</td>
<td>0.8</td>
<td>Bayoxide</td>
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<tr>
<td>Iron Adsorbent</td>
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<td>Iron Adsorbent, 0.5</td>
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<tr>
<td>GFH</td>
<td>0.7</td>
<td>GFH, 1.6</td>
</tr>
<tr>
<td>PAC</td>
<td>0.7</td>
<td>PAC, 0.1</td>
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</tbody>
</table>
Selenium Removal

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
- \( \text{MnO}_2 \) settles quickly/serves as adsorbent for other metals
- Reactive caps remediate \textit{and} reclaim mining waste piles
- Carus sorbents very effective for As, Se, Hg & B

![Image of Carus sorbents](image-url)
Thanks!
Questions?

• PADEP and OSM
• Penn Coal

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