Evaluation of Sustained Release Permanganate Treatment of Residual Solvents in Fractured Bedrock

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Background

- RemOx® SR (Carus)
  - Sustained-Release Form of Potassium Permanganate
  - Dispersed in Solid, Parrafin Wax Cylinder (1.35” or 2.5”)
  - Dissolves Passively in Groundwater

- Potential Uses
  - Reactive Barrier
  - Residual Source Treatment

Photo courtesy of Carus Corporation
Deployment Methods

- Direct Push Placement
- Or Simply Hang in Wells
  - 300 lb. test nylon string – broke
  - 65 lb. test braided microfilament fishing line – broke
- Stainless steel harness
  - 175 lb. test, 49-strand 7x7 stainless steel fishing leader wire
  - double barrel crimp sleeves
  - 270 lb. stainless steel snap swivels
Deployment and Retrieval Methods

- All deployment methods failed
- Retrieved with wire hook at end of tremie pipe
Why So Much Interest?

- **Liquid Injection is a Pain**
  - Can be labor & equipment intensive (e.g. mixing infrastructure)
  - Permitting and site access can be onerous
  - Multiple injection rounds needed = multiple mobilizations

- **Long-Term, Passive Treatment is Desirable**
  - Minimal O&M, cylinders can last for years
  - Reduces concentrations over the long-term
  - Can provide plume containment without pump & treat
  - Potentially effective in diffusion-limited situations
Conceptual Site Model (CSM)

- Site Use
  - Commercial property – Northwest New Jersey
  - Very limited access to impacted area in rear fire lane

- Hydrogeology
  - Fractured Bedrock
  - Radial Flow Component
  - Relatively Limited Available Data

- Contaminant Fate and Transport
  - Tetrachloroethene is Primary COC
  - Fractured Rock is Complicating Factor
Rationale for Remox® SR Pilot Test

- Evaluate Residual Source Treatment
  - Potential for remediation of moderate residual concentrations of PCE

- Evaluate Plume Containment
  - Prevent further migration
  - Evaluate PRB potential

- Improve CSM
  - Ancillary Benefit: Tracer Test
  - Potential for Back-Calculating GW Flux
  - New Wells = New Discoveries
Pilot Test Design

- Deploy 13 Cylinders in 3 Source Area Wells
- Goal to Have Coverage Over Shallow - Deep Intervals
  - 1 vertical line in well cluster
  - From water table ~ 7’ bgs
  - To 51’ bgs
- Monitoring Program
  - Permanganate field kit (Hach DR 890 Colorimeter supplied and calibrated by Carus)
  - Sampling at 1 month, 4 months, and 6 months from deployment
- Test Conducted Over 6 Months Per Permit-by-Rule authorization
- **Total Cost to Procure & Install Candles $5,000 – 6,000 (Excludes Drilling)**
- Drilling Cost ~5 Times Cost of Media
Pilot Test Implementation

- Twelve Weeks Prior to Cylinder Deployment –
  - Sampled monitoring well network
- Cylinders Deployed
- 1 Month After Cylinder Deployment
  - Sampled monitoring well network
  - Removed, weighed, re-deployed cylinders
- 4 Months After Cylinder Deployment
  - Sampled monitoring well network
  - Removed, weighed, re-deployed cylinders
- 6 months after cylinder deployment
  - Sampled monitoring well network
  - Permanently removed all cylinders
Pilot Test Results: Permanganate Dissolution

MW-1 Permanganate and ORP

CW-3 Permanganate and ORP

MW-11 Permanganate and ORP

CW-4 Permanganate and ORP
Pilot Test Results: Permanganate Dissolution

Legend
- Permanganate (PPM)
- Permanganate Contours
- Parcels

Woodard & Curran
Pilot Test Results: Permanganate as a Tracer

- Clear Preferential Pathways Exist in Fractured Rock
  - Permanganate observed 270 feet away from deployment location after only 172 days (1.6 feet/day)
  - Apparent delayed dissolution – 6 months until concentrations reached > 100 mg/L at any location
- Radial Flow Component
Pilot Test Results: PCE Treatment

- Effective treatment observed at some locations
  - Additional time needed to evaluate down-gradient impacts
  - More widespread source-level concentrations found during drilling may be consuming permanganate
  - Additional time needed to determine what constitutes a “viable” permanganate concentration (e.g. 100 mg/L)
Modeling Permanganate Dissolution

- Carus Decision Support Tool
  - 1D Analytical Model (Wolf, 2013)
  - Input Groundwater Hydraulic Parameters & Cylinder Characteristics
  - Natural Oxidant Demand Rate (NOD) is a Key Parameter
  - Combined Permanganate Release Model & 1D Transport
    - Advection Only with 1\textsuperscript{st} Order NOD-Mediated Decay
    - \textbf{Does Not Simulate Contaminant Reactions}
Modeling Process

**Oxidant Release Parameters**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Cell Type</th>
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<tbody>
<tr>
<td>Oxidant</td>
<td>KMnO₄</td>
<td></td>
<td></td>
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<tr>
<td>Cylinder Diameter (inches)</td>
<td>d</td>
<td>1.35</td>
<td>af</td>
</tr>
<tr>
<td>Cylinder Diameter (cm)</td>
<td>d</td>
<td>3.43</td>
<td>af</td>
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<tr>
<td>Initial Cylinder Radius (cm)</td>
<td>r₀</td>
<td>1.715</td>
<td>af</td>
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<tr>
<td>Oxidant solubility (g/cm³)</td>
<td>Cₛ</td>
<td>0.03</td>
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<tr>
<td>Mass of Cylinder (g)</td>
<td></td>
<td>815</td>
<td>af</td>
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<tr>
<td>Mass of MnO₄ (g)</td>
<td></td>
<td>652</td>
<td>af</td>
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<tr>
<td>% MnO₄ available</td>
<td></td>
<td>0.9</td>
<td>given</td>
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<tr>
<td>Mass of MnO₄ available (g)</td>
<td></td>
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<tr>
<td>Effective diffusion coefficient (cm²/s)</td>
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<td>4.000E-07</td>
<td>given</td>
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<tr>
<td>Amount of available oxidant (g/cm³)</td>
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<tr>
<td>Cylinder Height (cm)</td>
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<td>Cylinder Volume (cm³)</td>
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<td>af</td>
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<tr>
<td>Cylinder Density (g/cm³)</td>
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<tr>
<td>Molecular Weight of MnO₄ (g/mol or mg/mmol)</td>
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**Time and distance of Interest**

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<td>171</td>
<td>sp</td>
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<tr>
<td>Time Step (days)</td>
<td>Δt</td>
<td>2</td>
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<td>Downgradient Distance of interest (ft)</td>
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<td>20</td>
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**Site Characteristics**

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<tr>
<td>2nd order NOD rate (L/mmol-day)</td>
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<td>2nd order NOD rate (L/mg-day)</td>
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<td>Hydraulic conductivity (cm/s)</td>
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<td>sp</td>
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<td>Hydraulic conductivity (cm/d)</td>
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<td>Hydraulic gradient (dh/dl)</td>
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<td>Porosity</td>
<td>n</td>
<td>0.02</td>
<td>sp</td>
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<td>Groundwater Velocity (cm/day)</td>
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<td>15.98</td>
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<td>Cross Sectional Area of Flow (cm²)</td>
<td>CSA</td>
<td>246</td>
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<tr>
<td>Groundwater Flow (L/day)</td>
<td>Qf</td>
<td>3.9</td>
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Sensitivities

- **GW Velocity**
  - Too Fast (Flushed out)
  - Too Slow (No Dissolution)
- **NOD**
  - > 0.1 L/mmol-day likely prohibitive (Wolf, 2013)

Assumes Homogeneous/Isotropic, Porous Media

Courtesy of Carus Corporation
Modeling Results: Placement Area

Concentration vs. Time in Cylinder Placement Area (1.35" Cylinder)
Modeling Results: 20’ Down-Gradient

Concentration vs. Time 20' Down-Gradient of Cylinder (1.35" Cylinder)
Modeling Cylinder Dissolution

Model Estimate of Cylinder Mass Remaining

Time (Days)

Permanganate Mass Remaining (g)
Model Limitations

- Limitations
  - Dispersivity may be key for this Site (Account for Fractures)
  - Delayed Dissolution in Placement Wells is Hard to Simulate
    - Transient Effects
  - 3D Factors, Reactive Chemistry
  - Need a Way to Track Mass Dissolution in the Field
    - **Weighing Cylinders Does Not Work**
Pilot Test Conclusions

- CSM Updates
  - Additional source area concentrations
  - Radial flow pattern
  - High transmissivity fractures

- Treatment Prospects
  - Some evidence of treatment observed
  - Longer test required to confirm treatability

- Modeling/Bench Testing
  - How many cylinders would be needed?
  - What concentrations in ground water necessary to reduce contaminant concentrations
  - PRB containment vs. source area treatment
Future Directions

- Persulfate/Permanganate Combination
  - In development by Carus

- More Field Data Needed on Dissolution & Ground Water Flow Sweet Spot
  - Too fast (flushes out)/too slow (no dissolution)
  - Effect of NOD (site specific)

- 3D Modeling
  - Need better modeling with reactive chemistry