Passive Groundwater Plume Treatment using Sustained-Release Oxidants

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Agenda

• Background
  – *In situ* Reactive Barriers/Zones
  – Sustained-Release (SR) Oxidants (Permanganate/Persulfate)

• Experimental Work

• Pilot-Scale Field Studies (UNL, SES)

• SR Design Tool

• Take Home Message/Questions
The Challenge...

• All remedial technologies have an impact...
  – Electricity/fossil fuel to power equipment
  – Aboveground treatment of extracted fluids
  – Site disruption/landfill disposal

• Reactive materials used successfully to remove contaminants in soil and groundwater
  – Do not require continued supply of electrical/fossil fuel energies
  – Serve as long-term, low-cost passive treatment

http://www.murraydemolition.com/
• Promising slow-release permanganate and persulfate modeling, lab, pilot-scale field studies (e.g., Ohio State University, Clemson, University of Nebraska, Colorado School of Mines)

• 2003 Specialty Earth Sciences-patented methods of encapsulation for sustained-release of reactants

• Variety of reactive materials are possible
  – Oxidants, bio-amendments, oxygen release compounds, activators, chelating agents
Technology Development – SR Oxidants

- Sustained-release permanganate is a KMnO$_4$-based product dispersed in a solid paraffin wax matrix (~80% w/w)

- Sustained-release persulfate is a NaS$_2$O$_8$-based product dispersed in a solid paraffin wax matrix (70-80% w/w)
• Solid product formed as cylinder, chipped for trench/barrier applications or small pellets (1-2 mm) for hydro-fracturing into low permeability media/fractured bedrock
  • 1.35 or 2.5 inch diameter
  • 3.4 cm/6.4 cm diameter
  • 18 inches long (46 cm)
  • DPT emplacement or well installation
SR Technology – Direct Push Installation

• 2.25 or 3.25 inch tooling and disposable tip

• Lowering cylinders within inner space of rods provides confirmation that cylinder placed at desired depth

• Rods retracted with cylinders remaining in place
SR Technology – In-Well SR Cylinder Holders

- Cylinders within stainless steel or plastic mesh cylinder holders secured to flush mount cover with stainless steel wire and clamp

- Cylinders can be removed and weighed for relative comparison against baseline measurements
SR Technology – Versatility in Application

• Configurations
  – Permeable reactive barrier (PRB)
  – Permeable reactive zone/grid (PRZ)
  – Trench
  – Funnel and gate

![Diagram of ground flow and oxidation process with oxidant wells and 1,4-Dioxane plume]
Applicable to contaminants oxidized by:

- Permanganate (chlorinated ethenes) (Lee and Schwartz, 2007; Christenson et al., 2012)
- Persulfate (BTEX, petroleum hydrocarbons) (Kambhu et al., 2012)
- Emerging contaminants (e.g., 1,4-dioxane) (Crimi, Dugan and Evans, 2012)

Can be applied in tandem or following ISCO (or other remedial treatments) to mitigate rebound and back-diffusion
1,4 Dioxane is a challenging emerging contaminant (ESTCP SON 2012)

- Navy – Dioxane has been detected at over 200 sites
- Air Force - Observed in 17.4% of wells co-mingles with TCE/TCA

Sustained-release oxidant cylinders are a solution:
- Permanganate or unactivated persulfate oxidize 1,4 dioxane
- Applicable to co-contaminants & large/dilute plumes
MnO$_4^-$ Release from Wax

- As permanganate solids dissolve void spaces are created
MnO$_4^-$ Release from Wax

- Newly created void spaces expose permanganate solids for dissolution and diffusion
- Process occurs radially from the exterior of the cylinder to the inner core
MnO$_4^-$ Release from Wax

- As permanganate releases/reacts, porosity develops inward to the core of the cylinder
- Diffuses across a greater distance
This is why we see and initial spike of permanganate in early time...
MnO$_4^-$ Release from Wax

- And a significantly slower and lower release of permanganate at later times
Experimental Approach – 1-D Columns and 2-D Mini-Tanks

- Columns (30 or 60 cm x 4.8 cm)
  - Cubed material (TCE or 1,4 Dioxane 0.7-1.5 ppm)
  - 1.35 inch diameter/1 inch long
  - 2.5 inch diameter/1 inch long
  - Flow rate (0.6 mL/min), 2 ft/day

- 2-D mini-tanks (14 x 14 x 2.5 cm)
  - Permanganate or persulfate mini-cylinders (10 grams of oxidant)
  - 0.27 inch diameter/5 inch long (DI)

- Purpose: evaluate oxidant release from SR cylinders, cubes, spatial distribution, and removal efficiencies
Approach – SR Design Tool

- Collect oxidant release rates to support modeling of releases from cylinders, cubes, pellets/pastilles
  - Model adapted after Lee and Schwartz (2007)

\[ Q = \pi h A (r_0^2 - r^2) \]

\[ \frac{r^2}{2} \ln \frac{r}{r_0} + \frac{1}{4} (r_0^2 - r^2) = \frac{C_s D_e t}{A} \]

\[ D_{et} = \frac{D_e (t-1)}{T} \]

- \( Q' \) = quantity of MnO₄⁻ released per unit time
- \( C_s \) = MnO₄⁻ solubility
- \( A \) = Amount of MnO₄⁻ available for release
- \( D_e \) = effective distribution coefficient
- \( t \) = time
- \( h \) = length of cylinder
- \( r_0 \) = radius of cylinder
- \( r \) = radius MnO₄⁻ diffusion (new porosity development)
CRT

Results – 1D Column with SR Cubes

Sustained-Release Permanganate
60% KMnO₄ - TCE influent ~ 0.7 ppm

TCE Mass Removed (%)

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>0</th>
<th>4</th>
<th>11</th>
<th>18</th>
<th>26</th>
<th>34</th>
<th>77</th>
<th>105</th>
<th>134</th>
<th>165</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCE Mass Removed (%)</td>
<td>100%</td>
<td>90%</td>
<td>80%</td>
<td>70%</td>
<td>60%</td>
<td>50%</td>
<td>40%</td>
<td>30%</td>
<td>20%</td>
<td>10%</td>
</tr>
</tbody>
</table>

TCE mass removal 86% - 100% over 170 days or > 470 PVs
Results – 2D Tank (DI Water Influent)

2D Tanks -
Sustained-Release Permanganate and Persulfate Mini-Cylinders
DI Influent ~ 0.6 mL/min, 2ft/day

Oxidant Concentration (mg/L)

Permanganate
Persulfate

Time (days)

Permanganate Mini-Cylinder (80% w/w) running for ~6 months
Persulfate Mini-Cylinder (~70% w/w) running for 2 months
Results – 2D Tank (Influent-DI Water)

Measured and Modeled Permanganate Concentration and
% Released from 0.25-in OD Mini-Cylinder

Measured permanganate concentrations from 2D tank matches model!
Proof of Concept – Persulfate for 1,4 Dioxane Removal

- SR unactivated persulfate cylinder 97% – 100%
- 1500 ppm unactivated persulfate 93% - 100%
• Developing sustained-release oxidants (2-3 mm)

• Potential to be fracked into tight clays or fractured bedrock applications

• Treat back diffusion of contaminants/address rebound
Cozad Former Solid Waste Disposal Site

University of Nebraska

Dr. Steve Comfort
• Facility closed after TCE contamination found in underlying aquifer

• Majority of TCE in a low permeable silty-clay unit near surface of water table

• TCE (100-600 ppb)

• Darcy velocity = 0.045 in/day

• UNL with NDEQ wanted to implement low-cost passive system for TCE treatment in low permeability unit
SRPC Reactive Barrier Installation

105 two inch DPT SRPCs

50 three inch injection well SRPCs

Monitoring Wells are located up gradient, inside and down gradient of treatment zones

-44 feet
Results

Contaminant Concentration in Reactive Barrier
Well MW-8, 11 ft (bgs)

- Barrier installed June 2010
- After 85 days 64%-82% TCE reduction
  (Christenson et al., 2012)
Results

8 year life expectancy for 2” SRPC

16 year life expectancy for 3” SRPC
Next Steps in Slow Release Oxidant Technology – Slow Release Persulfate

• Sodium persulfate (60 wt%) and activator cylinders were prepared with FeSO$_4$ or zero valent iron (ZVI) for BTEX treatment

• Results showed that benzene concentrations ($C_0 = 1$ mM) decreased by $>90\%$ within 7 days (Kambhu et al., 2012)
Specialty Earth Sciences: Pilot Scale Installation for Low Permeability Media Source Zone Treatment
Pilot-Scale Sustained-Release Permanganate

- Client seeking remedial solution with potential for cost savings for site in SE US

- Difficult to remediate low permeability soils present (PCE)

- Site logistics and tenant business operations required:
  - **Rapid implementation leaving structures undisturbed**
  - **Minimized recurrent on-site events**
Pilot-Scale Sustained-Release Permanganate

- This site had two vertical zones of PCE impact (shallow and deep zones)

- Groundwater movement in the shallow zone (0-45 bgs)
  - Mississippi blue clays $10^{-9}$ cm/s

- Groundwater movement in the deeper zone clayey sands (>45 bgs)
  - ranging from $10^{-3}$ cm/s to $10^{-4}$ cm/s
- Shallow zone layout (3 ft. to 20 ft. below grade target interval)

- Rectangular grid DPT installations (5 ft. grid spacing)

- (2) product consumption monitoring wells, (3) performance monitoring wells
- Deeper transmissive zone

- 45 ft. to 60 ft. below grade target interval.

- Reactive barrier pattern direct push installations (5 ft. linear spacings)

- (3) product consumption monitoring wells (3) performance monitoring wells.
## September 2012 Monitoring Results

<table>
<thead>
<tr>
<th>Observation</th>
<th>KMnO4 concentration</th>
<th>Approx. distance</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Well ID#</strong></td>
<td></td>
<td></td>
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<tr>
<td>Shallow Zone</td>
<td></td>
<td></td>
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<tr>
<td>OW-3</td>
<td>0.0 mg/L</td>
<td>3 ft</td>
</tr>
<tr>
<td>OW-4</td>
<td>0.7 mg/L</td>
<td>12 ft</td>
</tr>
<tr>
<td>OW-5</td>
<td>1.3 mg/L</td>
<td>3 ft</td>
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<tr>
<td>Deep Zone</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IOW-1</td>
<td>1.0 mg/L</td>
<td>6 ft</td>
</tr>
<tr>
<td>IOW-2</td>
<td>0.3 mg/L</td>
<td>40 ft</td>
</tr>
<tr>
<td>IOW-3</td>
<td>1.3 mg/L</td>
<td>6 ft</td>
</tr>
</tbody>
</table>
Shallow Zone

*700 ppb KMnO4 @ 12 ft @ 10 mo
Deep Zone

*300 ppb KMnO4 @ 40 ft @ 10 mo
Evaluating Oxidant Transport and Release Kinetics
Sustained-Release Design Tool

- 1D column, 2D and 3-D tank data to develop sustained-release design tool
- Key processes
  - Oxidant release (source)
    - Oxidant type, cylinder dimensions
  - Oxidant reaction and transport
    - 2\textsuperscript{nd} order NOD
    - 1-D transport with reaction and dispersion
  - Contaminant reaction and transport
    - 2\textsuperscript{nd} order rate constants for TCE, dioxane and co-contaminant(s)
- Output: oxidant and contaminant distribution
  - Can optimize for number and spacing of cylinders
  - Conceptual design cost estimate
### Basic project information

- **Oxidant Release Parameters**
  - Oxidant:
  - Candle diameter (cm):
  - Oxidant solubility (mg/L):
  - Effective diffusion:
  - Amount of available oxidant:
  - Treatment depth:
  - Treatment width:
  - # candle delivery points (per row):
  - # candle rows:

- **Site Characteristics**
  - Primary contaminant:
    - Concentration (mg/L):
  - Secondary contaminant:
    - Concentration (mg/L):
  - Longitudinal dispersivity:
  - Transverse dispersivity:
  - Vertical dispersivity:
  - Natural oxidant demand (NOD) (mg/kg):
  - NOD rate (2nd order; M⁻¹ s⁻¹):
  - Hydraulic conductivity (cm/s):
  - Hydraulic gradient (dh/dl):
  - Porosity:

*guidance provided in ‘site characteristics guidance’ tab

### Factors affecting oxidant release rate and resulting concentration

- **Contaminant characteristics**
- **Dispersion parameters**
- **Oxidant demand – rate and extent**
- **Flow properties**

### Simulation

- **Simulation time**
- **Simulation or compliance distance downgradient**
Sustained-Release Design Tool

Oxidant concentrations vs. distance at a given time

Oxidant release from cylinders

Contaminant concentrations vs. distance at a given time

Design Tool Output
Model Results – 1-in Sections Mini-SRPC, 1.35-in, 2.5-in

Permanganate Flux from 3 diameters of SR cylinder
Flow Rate 0.6 mL/min, Length 1-in

Diameter

MnO₄⁻ flux (mg/day)

Time (days)
Model Results – Preliminary Field Data from Camp LeJeune

Site 86 Cylinders (Camp Lejeune)
1.5-in OD x 3-ft long, GW Velocity ~0.075 ft/day

![Graph showing MnO₄⁻ concentration and Permanganate utilized over time.](image-url)
## Scenario 1 - minimum required mass flux of MnO₄ required - mg/day (based on 1gTCE:1.8gMnO₄ * 10 SF)

<table>
<thead>
<tr>
<th>Vgw (feet/day)</th>
<th>0.01</th>
<th>0.05</th>
<th>0.1</th>
<th>0.5</th>
<th>1</th>
<th>5</th>
<th>10</th>
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<tr>
<td>0.01</td>
<td>0.046</td>
<td>0.229</td>
<td>0.459</td>
<td>2.294</td>
<td>4.587</td>
<td>22.937</td>
<td>45.873</td>
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<td>0.05</td>
<td>0.229</td>
<td>1.147</td>
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</table>

## Scenario 2 - minimum required mass flux of MnO₄ required - mg/day (based on 1gTCE:1.8gMnO₄ * 10 SF)

<table>
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<tr>
<th>Vgw (feet/day)</th>
<th>0.01</th>
<th>0.05</th>
<th>0.1</th>
<th>0.5</th>
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<th>5</th>
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<td>0.917</td>
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<td>45873.291</td>
<td>91746.583</td>
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</tbody>
</table>
1. Minimal aboveground infrastructure (and site disruption) so can implement quickly at an active site
   - No tanks, water needs, dust, pressurized injection
   - Favorable health & safety profile
2. Get two injections for the price of one
   • Long term treatment of residual absorbed material in clay (back diffusion)
3. No surfacing of liquids
Exploring the Possibilities...

4. Ability to approach ISCO in an active stepped manner
Take Home Message

• 5 pilot-scale sites (US), 3 pending (US, Brazil, Canada), Indiana?

• Direct push/in-well applications for treatment that may last years
  • Application in low permeability soils and fractured bedrock
  • Address “rebound” and back diffusion
  • Active industrial and commercial facilities: passive in situ treatment without above ground equipment/infrastructure
  • Boundary control
  • Plume management to break up a plume or control contaminant flow through a given x-section
  • Cost savings with direct push
  • Sustainable offering
Questions?

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Field Implementation
Cost Savings (Cylinders vs Liquid Injection)

- **SE US Site (Sustained-Release Cylinders) (shallow interval treatment):**
  - Conductivity: $10^{-9}$ cm/sec
  - Target interval: 3-20 ft bgs
  - Total pounds of permanganate: 1053 lbs
  - On-site labor: 2 field professionals + Geoprobe for 4 days (approx $12,000)
    
    $11.40 \text{ in field labor per lb of permanganate applied}$

- **Northern KY Site (Liquid Permanganate Injection):**
  - Conductivity: $10^{-6}$ to $10^{-7}$ cm/sec
  - Target interval: 2-8 ft bgs
  - Total pounds of permanganate: 440 lbs
  - On-site labor: 2 field professionals + Geo-probe for 4 days (approx $12,000)
    
    $27.27 \text{ in field labor per lb of permanganate applied}$