Sustained-Release Plus (SR+): Reactive Synergies with Permanganate and Persulfate

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Agenda

- Sustained-Release (SR) Technology Motivation (permanganate, unactivated persulfate, mixtures)
- Environmental Security Technology Certification Program (ESTCP) - Experimental Approach/Results
- Engineering Design Tool
- Q&A
What is the Problem?

- Chlorinated solvents in groundwater
- Dense non-aqueous phase liquids (DNAPL) sources and large, back-diffusing plumes of chlorinated solvents
  - Common to many sites
  - Technological challenges
  - Significant remediation costs
- Emerging contaminants
  - 1,4-Dioxane
  - PFOS/PFOA
  - NDMA
  - EDB
- Current Approach
  - Biological, chemical, and physical remediation
  - Separate technologies
  - Low level of integration
  - Unrealized potential for synergy
  - Sometimes pump and treat
Sustained-Release Chemical Oxidants are a Solution

- RemOx® SR ISCO Reagent: $\text{KMnO}_4$-based product dispersed in a solid matrix, (~80% w/w)
- Persulfate SR: $\text{NaS}_2\text{O}_8$-based product dispersed in a solid matrix (~73% w/w)
- 18 inches long (1.35 and 2.5 inch diameter)
- Deployed via DPT or in wells
Sustained-Release Chemical Oxidants for Long-Term Plume Management

Slow Release Chemical Oxidant Cylinders

GW Flow

Oxidant

“Candle” Wells

1,4-Dioxane Plume

Physical

Biological

Chemical

SYNERGY
Oxidant Release Mechanism
Passive Treatment with *In Situ* Reactive Zones/Barriers

- Contaminated Groundwater
- Treated Groundwater
- GW Flow
- Water Table
- Bedrock
- Receptor Well
SR Technology – Direct Push Installation

- 2.25 and 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 – Well Installation
Minimizes Site Disruption

• Traditional Footprint

• Reduced Site Impact

Christenson - 2010
SR Deployment Strategies

• Possible Configurations:
  ➢ Permeable reactive barrier (PRB)
  ➢ Permeable reactive zone/grid (PRZ)
  ➢ Flow-focusing
  ➢ Funnel and gate
  ➢ Horizontal wells
Application of SR with Emerging Contaminants

- 1,4-Dioxane
  - Solvent stabilizer (e.g. TCE)
  - Carcinogen
  - High miscibility creates long/dilute plume
  - Not biodegradable
  - ESTCP ER-201324 (Evans, Dugan, Crimi 2013)
Dioxane Destruction with Permanganate and *Unactivated* Persulfate

Both permanganate and unactivated persulfate oxidize dioxane and TCE at various sites.

Courtesy of CDM Smith
Experimental Approach

1. Evaluate oxidant release characteristics
2. Contaminant degradation/kinetics
   - Batch studies, 1-D column and 2-D tanks
Oxidant Release Characteristics - Permanganate

Permanganate Release from 3 Diameters RemOx SR Cylinders
0.27, 1.35 and 2.5 inch
Length 1-inch, Flow rate 0.7 mL/min

Increasing Diameter

Permanganate Mini-Cylinder (80% w/w) running for ~6 months

Measured permanganate concentrations match model!

\[ Q' = \pi hA(r_0^2 - r^2) \]

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

Lee and Schwartz (2007)
Oxidant Release Characteristics - Persulfate

Release data was fit to simple Gaussian Distribution Model

\[ f(t) = A \frac{1}{\sigma \sqrt{2\pi}} e^{-\frac{(t-t_{\text{max}})^2}{2\sigma^2}} \]
New product opportunity?

Permanganate

Permanganate Release from 3 Diameters RemOx SR Cylinders 0.27, 1.35 and 2.5 inch Length 1-inch, Flow rate 0.7 mL/min

Persulfate

2.5" Persulfate SR, 1-inch piece - 0.5 mL/min
Mixed Oxidant Release Characteristics – RemOx SR+

RemOx SR+ Control Column (DI Influent):
Permanganate + Persulfate, 2.5 inch OD, 3 inch long
Flow rate = 0.05 mL/min

Max permanganate = 12,000 mg/L
Max persulfate = 23,000 mg/L
3-inch piece of cylinder > 12.5 months

Oxidant Release Conclusions

• Permanganate release is characterized by high initial concentration, followed by long-term and sustained release
  ➢ Release rates can be *modeled using an analytical solution*
  ➢ Release rates can be *scaled and quantified*

• Persulfate exhibits a different oxidant release profile than permanganate
  ➢ Particle size differences?
  ➢ Crystalline packing differences?
  ➢ Solubility

• The combination of persulfate and permanganate in SR+ results in both:
  ➢ Improved oxidant release characteristics and,
  ➢ Provides *multiple oxidants for mixed plume degradation*
### ESTCP North Island Site

**Primary Contaminants**

<table>
<thead>
<tr>
<th>COC</th>
<th>OU11-SMU-05A (35 to 40 ft bgs)</th>
<th>OU11-SMU-07A (33-38 ft bgs)</th>
<th>Average Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,4-DIOXANE</td>
<td>6,500</td>
<td>6,000</td>
<td>6,250</td>
</tr>
<tr>
<td>1,1-DCA</td>
<td>3,200</td>
<td>1,600</td>
<td>2,400</td>
</tr>
<tr>
<td>1,1-DCE</td>
<td>6,300</td>
<td>6,400</td>
<td>6,350</td>
</tr>
<tr>
<td>CIS-1,2-DCE</td>
<td>3,900</td>
<td>6,000</td>
<td>4,950</td>
</tr>
<tr>
<td>TCE</td>
<td>9,200</td>
<td>3,500</td>
<td>6,350</td>
</tr>
</tbody>
</table>

**Historical Data (µg/L)**

- Used for Treatability (µg/L)
ESTCP Column Tests
Contaminant Destruction

Permanganate front - 18" oxidant transport distance

Permanganate Cylinder Piece - 4" from the bottom

Persulfate Cylinder Piece - 4" from the bottom
ESTCP Column Tests – Permanganate SR or Persulfate SR

Site Soil and Spiked-Site Groundwater
### ESTCP Column Tests – Reactor Rate Constants

**Oxidant** | **2° Rate Constant** | **Oxidant Concentration** | **Overall Rate**
--- | --- | --- | ---
Permanganate | High | Very Low | Low
Persulfate | Low | High | High
ESTCP Treated Column Tests – Effluent Oxidant Concentrations

Site Soil and Spiked-Site Groundwater
ESTCP Column Tests – MnO$_2$ Deposition
Incomplete Permanganate Release at "Lower" Mass Loading

~70% KMnO₄ was released over 170 days...
Persulfate and RemOx SR+:
Batch and 1-D Column Results
BTEX Batch Kinetic Oxidation Results

Unactivated Persulfate Oxidation

RemOx SR+ Oxidation

Second Order Oxidation Rate Constants (M⁻¹s⁻¹)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Permanganate</th>
<th>Persulfate</th>
<th>MultiOx</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>Negligible</td>
<td>5.72E-5²</td>
<td>1.1E-4²</td>
</tr>
<tr>
<td>Toluene</td>
<td>5.74E-4¹</td>
<td>5.63E-5²</td>
<td>3.2E-4²</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>7.07E-3¹</td>
<td>5.91E-5²</td>
<td>1.9E-3²</td>
</tr>
<tr>
<td>Xylene(s)</td>
<td>2.22E-3¹</td>
<td>4.81E-5²</td>
<td>4.0E-3²</td>
</tr>
<tr>
<td>MTBE</td>
<td>8.82E-5¹</td>
<td>Negligible</td>
<td>7.6E-5²</td>
</tr>
</tbody>
</table>

¹ISCO-kin Database  
²This study
Persulfate SR & SR+:
1-D Column Results – BTEX Removal

Removal Efficiencies:
- **Benzene**: 85.3%-98.3%, **Toluene**: 84.6%-96.6%,
- **Ethylbenzene**: 88.5%-98.3%, **Xylene**: 94.6%-99.3% over the 40-day experiment
SR+ Treated Column - Dioxane & VOC Removal

> 99.9% Removal of 1,4 Dioxane and Chlorinated Ethenes ~ 7 months
SR+ Treated Column -
1,1 DCA Removal

1-D Column: RemOx SR+, Flow Rate = 0.05 mL/min
1,1 DCA Removal Efficiency

Oxidant Concentration (mg/L)

DCA % Removal

Time (days)

Persulfate
Permanganate
DCA % Removal

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Mn-Activated Persulfate?

\[ 2\text{HSO}_5^- + 2\text{MnO}_2 \rightarrow 2\text{SO}_5^{2-} + \text{H}_2\text{O} + \text{Mn}_2\text{O}_3 \]

\[ 2\text{HSO}_5^- + \text{Mn}_2\text{O}_3 \rightarrow 2\text{SO}_4^{2-} + \text{H}_2\text{O} + 2\text{MnO}_2 \]

\[ \text{Org} + \text{SO}_4^{2-} \rightarrow ... \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{SO}_4^{2-} \]
Engineering Design Tool

- Spreadsheet Design Tool estimates
  - Oxidant release and reactive transport
  - Contaminant destruction
- In order to determine
  - Number of cylinders for site treatment
  - Cylinder spacing
  - Distance and time treatment goals are met
  - Cost
- Valuable in understanding conditions that drive oxidant transport along flow path
- Separate evaluations needed to manage oxidant distribution
## Cost

<table>
<thead>
<tr>
<th>Cost</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Direct Push</strong></td>
<td></td>
</tr>
<tr>
<td>Total installation fixed costs ($)</td>
<td></td>
</tr>
<tr>
<td>Total installation daily costs ($)</td>
<td></td>
</tr>
<tr>
<td>Number of direct push points that can be made per day</td>
<td></td>
</tr>
<tr>
<td>Number of days per installation (days)</td>
<td></td>
</tr>
<tr>
<td>Total cost per installation and per change-out ($)</td>
<td></td>
</tr>
<tr>
<td><strong>Wells</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Installation</strong></td>
<td></td>
</tr>
<tr>
<td>Well-drilling fixed costs ($)</td>
<td></td>
</tr>
<tr>
<td>Well-installation daily costs ($)</td>
<td></td>
</tr>
<tr>
<td>Number of wells that can be installed per day</td>
<td></td>
</tr>
<tr>
<td>Number of days per installation (days)</td>
<td></td>
</tr>
<tr>
<td>Total cost to install wells ($)</td>
<td></td>
</tr>
<tr>
<td><strong>Change-out</strong></td>
<td></td>
</tr>
<tr>
<td>Number of wells that can be changed-out per day</td>
<td></td>
</tr>
<tr>
<td>Number of days per change-out (days)</td>
<td></td>
</tr>
<tr>
<td>Change-out fixed costs ($)</td>
<td></td>
</tr>
<tr>
<td>Change-out daily costs($)</td>
<td></td>
</tr>
<tr>
<td>Total costs per subsequent change-out ($)</td>
<td></td>
</tr>
</tbody>
</table>
Oxidant Distribution Must Be Engineered

Contaminant by-pass

Close spacing

Funnel & Gate

Convergence/ Divergence
Graphical Scenario: Single Row of Cylinders

Each of the scenarios in the top row represent a single row of cylinders. On the left, cylinders are spaced directly side-by-side. In the middle and on the right, cylinders are offset, however flow paths don’t overlap. The spacing of cylinders perpendicular to groundwater flow is the same for each.

Each of the scenarios in the bottom row represent two rows of cylinders. In each, the flow path from one cylinder leads directly into the flow path of another cylinder.
Without inducing dispersion through engineering design, dispersion of oxidant as it moves away from and down gradient of cylinders is expected to be very limited. If cylinders are spaced apart perpendicular to groundwater flow, untreated contaminant will pass through the space between cylinders. Total contaminant flux through the treatment area will decrease. The mass of untreated contaminant passing through the treatment zone will depend on the spacing of the cylinders.

Dispersion of oxidant between cylinders can be achieved through approaches such as mixing, flow focusing, adding baffles, or funneling. The oxidant concentration available for reaction throughout the treatment zone will be lower than without dispersion, however the result will be less untreated contaminant passing through the treatment area.
Intermittent Pumping to Enhance Lateral Dispersion

- Cylinder wells spaced 1m apart
- Three downgradient wells pumped intermittently promoted oxidant mixing
- Oxidant concentration reached steady state after 7th mixing event on day 42 (Fig 6h)
ESTCP Site Cylinder Installation

• Mini “funnel and gate” concept
• Emplace 2.5-inch oxidant cylinder in 4-inch well inside an 18-inch diameter borehole backfilled with sand
• Create zone of convergence/divergence from contrast in hydraulic conductivity
  ➢ Native material \( K = 0.00608 \) cm/s
  ➢ Borehole fill \( K = 3 \) to 0.03 cm/s
• Addresses low transverse dispersion issue
SR Deployment Developments and New Geometries

Figure 1. Illustration of the horizontal reactive treatment well approach illustrating flow focusing and treatment under buildings and infrastructure at an active facility.

Average particle size 4.86 ± 0.67 mm
N = 10
Density = 1.54 g/cm³
Safety Considerations

- Carus provides detailed information on shipping and handling

  - www.caruscorporation.com

- Key considerations
  
  - Product is a mixture of an oxidizer (permanganate or persulfate) and a fuel (paraffin wax)
  
  - Product is stable under normal conditions
  
  - Do not expose to flame, sparks, or intense heat (e.g., cutting tools)
Take Home Message

• The SR Technology:
  • Effective at removing a *variety of contaminants* (e.g., 1,4 dioxane, BTEX, VOCs, phenols, PAHs)
  • Address *“rebound”, back diffusion*
  • Active industrial and commercial facilities: *passive in situ treatment without above ground equipment/infrastructure*
  • Cost savings with direct push
Acknowledgements

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Thank you!
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