The Effect of Heterogeneity and Delivery Methods on In Situ Remediation

Enhanced Monitoring and Remediation Methods for Contaminated Groundwater

Solinst Symposium
October 27-28
Presentation Outline

- Remediation Trends
- Governing Factors for InSitu
- Study Methodology
- Study Results
  - Vertical Distribution
  - Lateral Distribution
  - Vertical/Lateral Distribution
  - Persistence
  - Effects of Pressure
- Wrap Up
Why This Talk?

- Growing trend towards in situ approaches
  - New kid on the block - are we a trendy industry?
  - “Traditional” technologies kind of work but not really, especially for source zones, are we desperate?
  - Is in situ being “overapplied”?
  - Is application ahead of academic research?
  - Does the chemistry work?
  - Do we know where the injectant is going?
Why This Talk?

AND OF COURSE

• Are we ignoring the limitations of the technology?
  • Geology
    • heterogeneity effects
  • Contaminant Distribution
    • Can we remediate something if we don't know where it is?
    • How do we remediate low K areas?
  • Hydrogeology
    • Are we “pushing” plumes around?
    • Can we get the volume/mass of solution into the formation?
• Natural oxidant and reductant demands
  • Often ignored
Remediation Trends

- In-Situ GW Treatment Technologies selected in 2008

<table>
<thead>
<tr>
<th>In-Situ Technology</th>
<th># Sites</th>
<th>% of total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bioremediation</td>
<td>15</td>
<td>38%</td>
</tr>
<tr>
<td>Chemical Treatment</td>
<td>14</td>
<td>36%</td>
</tr>
<tr>
<td>Multi-Phase Extraction</td>
<td>2</td>
<td>5%</td>
</tr>
<tr>
<td>Air Sparging</td>
<td>2</td>
<td>5%</td>
</tr>
<tr>
<td>Permeable Reactive Barrier</td>
<td>1</td>
<td>2%</td>
</tr>
<tr>
<td>Other</td>
<td>5</td>
<td>14%</td>
</tr>
<tr>
<td><strong>Grand Total</strong></td>
<td><strong>39</strong></td>
<td></td>
</tr>
</tbody>
</table>
InSitu Trends

- Source: Krembs et al. 2010
Factors Governing In Situ

• Geology
  • Heterogeneity (not well understood)
  • Effects of fine-grained materials
    • Distribution
    • Back diffusion (i.e. rebound)

• Contaminant

• Groundwater Chemistry
  • Electron donors/receptors

• Reagent
  • Fast acting vs slower reacting
  • High concentration vs low concentrations
Factors Governing In Situ

- Source: Krembs et al. 2010
Factors Governing In Situ

### Table 5
Summary of ISCO System Design Parameters for Projects Involving Four Common Oxidants

<table>
<thead>
<tr>
<th>Design Parameters and Median Values</th>
<th>Permanganate</th>
<th>CHP</th>
<th>Persulfate</th>
<th>Ozone</th>
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</thead>
<tbody>
<tr>
<td>Design radius of influence (feet)</td>
<td>14 (29)</td>
<td>15 (30)</td>
<td>13 (6)</td>
<td>25 (5)</td>
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<tr>
<td>Observed radius of influence (feet)</td>
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<td>15 (6)</td>
<td>20 (3)</td>
<td>38 (2)</td>
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<tr>
<td>Oxidant dose (g/kg)</td>
<td>0.4 (36)</td>
<td>1.2 (19)</td>
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<td>Number of pore volumes delivered</td>
<td>0.16 (32)</td>
<td>0.073 (26)</td>
<td>0.57 (6)</td>
<td>No data</td>
</tr>
<tr>
<td>Number of delivery events</td>
<td>2 (65)</td>
<td>2 (57)</td>
<td>1 (10)</td>
<td>1 (15)</td>
</tr>
<tr>
<td>Duration of delivery events (days)</td>
<td>4 (45)</td>
<td>6 (42)</td>
<td>4 (7)</td>
<td>210 (15)</td>
</tr>
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</table>

1For additional data on these parameters refer to Krembs (2008).
2Values in parenthesis = number of sites included in computing the median value given.

- Source: Krembs et al. 2010
# Factors Governing In Situ

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Factors Governing In Situ

- Radius of Influence vs Area of Influence

We like to Believe
Factors Governing In Situ

- Radius of Influence vs Area of Influence

We like to Believe

Reality
Factors Governing In Situ

- Radius of Influence vs Area of Influence
Factors Governing In Situ

- Radius of Influence vs Area of Influence
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Factors Governing In Situ

• Soil Chemistry/Mineralogy/Texture
  • SOD/NOD
    • Oxidant specific
    • Effect of time and concentration

• Injection Method
  • Vertical/horizontal wells vs Direct Push
  • High vs low pressure
  • Hydraulic vs pneumatic fracturing
  • Vaporization vs solution
  • Soil mixing
  • Low volume vs high volume
Factors Governing In Situ

### Table 4
Summary of Oxidant Delivery Methods Used at Sites Where ISCO Has Been Applied

<table>
<thead>
<tr>
<th>Oxidant Delivery Method</th>
<th>Percent of Sites, ( n = 181 ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injection wells</td>
<td>40</td>
</tr>
<tr>
<td>Direct push</td>
<td>23</td>
</tr>
<tr>
<td>Sparge points</td>
<td>14</td>
</tr>
<tr>
<td>Infiltration</td>
<td>10</td>
</tr>
<tr>
<td>Injectors</td>
<td>7</td>
</tr>
<tr>
<td>Recirculation</td>
<td>7</td>
</tr>
<tr>
<td>Fracturing</td>
<td>6</td>
</tr>
<tr>
<td>Mechanical mixing</td>
<td>2</td>
</tr>
<tr>
<td>Horizontal wells</td>
<td>1</td>
</tr>
</tbody>
</table>

1Percentages sum to greater than 100% because multiple delivery techniques were used at some sites. “Injectors” refers to permanent well points that are designed to mix activators and oxidants at the well point so that they may be delivered simultaneously. “Infiltration” refers to trenches, galleries, or vertical well points installed in the vadose zone designed so that the oxidant will migrate vertically through the treatment zone.

- Source: Krembs et al. 2010
Factors Governing In Situ Limitations

- NAPL
  - Mass balance
  - Effective porosity
- High SOD/foc
  - Mass balance
- Vadoze Zone
  - Delivery
  - Moisture
- High K contrast zones
  - Fractures
  - Sand seams
- Back diffusion
Back Diffusion

- Source age
- Aquitard thickness
- Organic carbon content
- Upgradient sources
- Groundwater velocity
- Diffusion coefficient
- Treatment objectives
Back Diffusion

Can We Engineer For It?

• Delivery
  • Oxidant to area of concern
Back Diffusion

Can We Engineer For It?

- Delivery
  - Oxidant to area of concern
- Persistence
  - Increase diffusion rate
Back Diffusion

Can We Engineer For It?

• Delivery
  • Oxidant to area of concern
• Persistence
  • Increase diffusion rate
• Concentration
  • Increase diffusion rates
Back Diffusion

Can We Engineer For It?

- Delivery
  - Oxidant to area of concern
- Persistence
  - Increase diffusion rate
- Concentration
  - Increase diffusion rates
- Sequential Applications
  - e.g. ISCO/ISCR followed by enhanced bioremediation
Study Methodology

- **Comparison field studies**
- **Oxidants**
  - Permanganate
  - Percarbonate (RegenOx)
  - Persulfate (Klozur)
  - Hydrogen Peroxide
- **Injection Method**
  - Vertical Wells
  - Direct Push - Bottom Up
  - Direct Push - Side Injection
- **Pressure**
Results

Vertical Distribution
Vertical Distribution - Direct Push

Metres Below Ground Surface

C/Co

0.0 0.2 0.4 0.6 0.8 1.0

24 hours

Fine Sand

Silty Sand

Target Zone

Oxidant - Permanganate
Vertical Distribution - Well

Metres Below Ground Surface vs C/Co

- 24 hours

Target Zone

Fine Sand

Silty Sand

Oxidant - Permanganate
Vertical Distribution Summary

**Direct Push**
- 83% of permanganate into target zone
- 71% of persulphate into target zone

**Wells**
- 49% of oxidant into target zone
- ~12% of screen length used
Results

Lateral Distribution
Lateral Distribution
Lateral Distribution - Direct Push

Flow Direction
Transverse to Flow

Persulfate
Permanganate

\[ \frac{C}{C_0} \]

Distance from Injection Point (m)

Flow Direction
Transverse To Flow

Distance from Injection Point (m)
Lateral Distribution - Wells

Persulfate

Permanganate
Lateral Distribution Summary

Radius of Influence
- Did not look at vertical distribution, just furthest extent

- Radius of Influence Permanganate > ROI Persulphate
- ROI Direct Push > AOI Wells
- ROI for DP ~ uniform
- ROI for Wells ~ uniform
Results

Lateral/Vertical Distribution
Distribution – Direct Push

Percarbonate – Horizontal Tool Methodology

0.5 m below injection point  Injection Point  0.5 m above injection point
Distribution – Direct Push

Percarbonate Bottoms Up Methodology

0.5 m below injection point  Injection Point  0.5 m above injection point
Distribution - Percarbonate

Injection Point - Midpoint

Direct Push - Bottoms Up  Well  Direct Push - Horizontal Tool
Distribution - Direct Push

Persulphate - Bottoms Up Methodology
Distribution - Direct Push

Persulphate - Horizontal Tool Methodology

0.5 m below injection point  |
Injection Point           |
0.5 m above injection point
Distribution - Well

Persulphate

0.5 m Below Sand Seam  
Sand Seam  
0.5 m Above Sand Seam
Distribution - Persulphate

Injection Point - Midpoint

Direct Push - Bottoms Up

Well

Direct Push - Horizontal Tool
Distribution Summary

**Oxidant**
- Percarbonate > Persulphate > Hydrogen Peroxide
- Minimal vertical distribution with all methods
- Heterogeneity effects
  - Wells > Bottoms Up > Horizontal Tool

**Geologic Material**
- Percarbonate greater in coarser-grained materials
- Persulphate greater in coarser-grained materials
- Hydrogen peroxide to fast to measure
- A function of SOD or COD?
Results

Persistence
Persistence

Why important?

- Transport via advection (greater AOI)
- Diffusion into low K zones/materials
Persistence

Metres Below Ground Surface

C/Co

0.0 0.2 0.4 0.6 0.8 1.0

24 hours
168 hours

Target Zone

Fine Sand
Silty Sand

Oxidant - Permanganate
**Persistence**

- **Target Zone**: 8 - 12 metres below ground surface
- **Oxidant - Persulfate**: Silty Sand
- **C/Co**: 0.0 - 1.0
  - **168 hours**
  - **24 hours**
Persistence Summary

Oxidant
- Permanganate > Percarbonate > Persulphate > Hydrogen Peroxide

Geologic Material
- All oxidants persistence greater in coarser-grained materials
- Hydrogen peroxide to fast to measure
- A function of SOD or COD?
Oxidant Demand

- Oxidant Demand
  - Contaminant Demand from Soil (COD)
  - Contaminant Demand from Groundwater (COD)
  - Demand from “Clean” Soil (i.e. SOD)

\[ \text{TOD} = \text{COD}_{\text{soil}} + \text{COD}_{\text{H2O}} + \text{SOD} \]

- SOD varies with texture, mineralogy and oxidant
  - Fine grained materials, higher SOD
  - Organic material and clay, higher SOD
  - Higher potential, higher SOD
### Oxidant Demand

<table>
<thead>
<tr>
<th>Material</th>
<th>Permanganate</th>
<th>Persulphate</th>
<th>MFR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fine Sand - 7.5 mbgs</td>
<td>2.06</td>
<td>3.12</td>
<td>&gt;15</td>
</tr>
<tr>
<td>Find Sand - 8.2 mbgs</td>
<td>2.45</td>
<td>3.56</td>
<td>&gt;15</td>
</tr>
<tr>
<td>Silty Sand - 8.9 mbgs</td>
<td>4.47</td>
<td>5.67</td>
<td>&gt;15</td>
</tr>
<tr>
<td>Silty Sand - 9.3 mbgs</td>
<td>3.93</td>
<td>5.23</td>
<td>&gt;15</td>
</tr>
</tbody>
</table>

- Permanganate > Persulphate > MFR
- SOD increases with texture
**Oxidant Demand - SOD**

**Effect**
- 10 m³ of soil, density 2,000 kg/m³

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<tr>
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<tbody>
<tr>
<td>Fine Sand – 7.5 mbgs</td>
<td>41</td>
<td>62</td>
<td>&gt; 300</td>
</tr>
<tr>
<td>Find Sand – 8.2 mbgs</td>
<td>49</td>
<td>71</td>
<td>&gt; 300</td>
</tr>
<tr>
<td>Silty Sand – 8.9 mbgs</td>
<td>89</td>
<td>113</td>
<td>&gt; 300</td>
</tr>
<tr>
<td>Silty Sand – 9.3 mbgs</td>
<td>79</td>
<td>105</td>
<td>&gt; 300</td>
</tr>
</tbody>
</table>

All units in kg
Oxidant Demand - Cost

**Effect**
- 10 m$^3$ of soil, density 2,000 kg/m$^3$

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<tr>
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<td>$247</td>
<td>$374</td>
<td>&gt; $580</td>
</tr>
<tr>
<td>Find Sand – 8.2 mbgs</td>
<td>$294</td>
<td>$427</td>
<td>&gt; $580</td>
</tr>
<tr>
<td>Silty Sand – 8.9 mbgs</td>
<td>$536</td>
<td>$680</td>
<td>&gt; $580</td>
</tr>
<tr>
<td>Silty Sand – 9.3 mbgs</td>
<td>$472</td>
<td>$628</td>
<td>&gt; $580</td>
</tr>
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</table>

All units in kg
Results

Effects of Pressure
Results - Direct Push

Distance from Injection Point (m)

C/Co

0.0 0.2 0.4 0.6 0.8 1.0

Flow Direction

Transverse to Flow

20 psi
Permanganate
Results - Direct Push

- Distance from Injection Point (m):
  - 0
  - 2
  - 4
  - 6
  - 8
  - 10

- C/Co:
  - 0.0
  - 0.2
  - 0.4
  - 0.6
  - 0.8
  - 1.0

- Flow Direction
- Transverse to Flow

- 50 psi
- Permanganate
Results - Direct Push

Flow Direction

Distance from Injection Point (m)

C/Co

20 psi
50 psi
80 psi
Results – Direct Push

Perpendicular To Flow Direction

Distance from Injection Point (m)

\( C/Co \)

- 20 psi
- 50 psi
- 80 psi

Distance from Injection Point (m)
Effect of Pressure - Wells

Oxidant - Permanganate

20 psi

Distance from Well (m)

C/Co

Flow Direction

Transverse to Flow

50 psi

Distance from Well (m)

C/Co

Flow Direction

Transverse to Flow
Effect of Pressure - DP Side Tool

Flow Direction

Perpendicular to Flow

Distance from IP (m)

Distance from Injection Point (m)

C/Co

Oxidant - Permanganate
# Results

## Effects of Pressure

<table>
<thead>
<tr>
<th></th>
<th>Direct Push - BU</th>
<th>Direct Push - HT</th>
<th>Wells</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C/Co - 100%$</td>
<td>1.5 m</td>
<td>4 m</td>
<td>0.5 m</td>
</tr>
<tr>
<td>$C/Co - 50%$</td>
<td>5 m</td>
<td>6 m</td>
<td>2 m</td>
</tr>
<tr>
<td>$C/Co - Detected$</td>
<td>9 m</td>
<td>9 m</td>
<td>4 m</td>
</tr>
<tr>
<td><strong>ROI</strong></td>
<td>Non Uniform</td>
<td>Non Uniform</td>
<td>Uniform</td>
</tr>
<tr>
<td><strong>Anisotropy</strong></td>
<td>$X\gg Y$</td>
<td>$X&gt;Y$</td>
<td>$X\sim Y$</td>
</tr>
<tr>
<td></td>
<td>Decreases with Pressure</td>
<td>Independent of Pressure</td>
<td>Independent of Pressure</td>
</tr>
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Distribution Enhancements

- Integrated Approach
- Reverse gradient
- Forced gradient
- Vacuum enhancement
- LTSBs
- Reactive zones
- Sequential treatment
Summary

- In situ approaches increasing with time
Summary

- In situ approaches increasing with time
- Limitations with approach
Summary

• In situ approaches increasing with time
• Limitations with approach
• Direct push may result in better vertical distribution than wells
Summary

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• Wells appear to be more susceptible to heterogeneity than direct push
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• Limited vertical distribution with tested delivery methods
Summary

- In situ approaches increasing with time
- Limitations with approach
- Direct push may result in better vertical distribution than wells
- Wells appear to be more susceptible to heterogeneity than direct push
- Limited vertical distribution with tested delivery methods
- SOD can vary significantly on small scale
Summary

- In situ approaches increasing with time
- Limitations with approach
- Direct push may result in better vertical distribution than wells
- Wells appear to be more susceptible to heterogeneity than direct push
- Limited vertical distribution with tested delivery methods
- SOD can vary significantly on small scale
- Increasing pressure may not result in larger AOI
Questions ?