In Situ Monitoring of the Ten-Year Old PRB at CFB Borden, Ontario

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PRB Uncertainty

• long-term effectiveness due to corrosion and precipitates
• precipitates
  - reduce porosity
  - coat iron surface reducing transfer of electrons
• predictive methods, mainly laboratory columns
• limited empirical evidence!
Waterloo Permeable Reactive Wall
Field Trial 1991

- CFB Borden, Ontario, Canada
- unconfined sand aquifer
- groundwater flow velocity: 9 cm/day (0.3 ft/day)
- wall 4-6 m (13-20 ft) bgs, ∨ 2.5 m (8.2 ft) bgs
- contaminants: TCE - 253 mg/L
  PCE - 43 mg/L
- reactive wall (20 m³, 706 ft³)
  - 22% Kanmet iron (local Ontario foundry)
  - 78% coarse sand

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Proof of Concept
(Borden Field Trial, 1991)
Performance

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O’Hannesin & Gillham, 1998
Waterloo Permeable Reactive Wall

5 Year Field Trial Results

- 5 years of consistent performance
- 90% TCE and 86% PCE removal
- breakdown products degraded
- complete remediation possible with increased iron
- trace amounts of calcium / iron carbonates and iron oxides
- very low microbial activity
Is the Waterloo PRB Still Effective After 10+ Years? (1991-2001)

- assessment of iron reactivity by comparing TCE half lives in both lab and field
- evaluation of core material
  - K, biological activity and precipitates
- 1996 source removed by permanganate
  - effects on iron in PRB
Plan View

Former Source

Groundwater Flow Direction

IST 5

West Side

PRB

IST 4

East Side

0.5 m 1.0 m

Front Interface

Vertical Cores

Angled Cores

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Cores - Vertical and Angled

- iron %, K, microbial activity and precipitates
- laboratory column testing

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Laboratory Column Testing using Core Material

- 10-20 cm h, 3.8 cm ID
- V = 15 to 25 cm/day, Temp = 10°C
- TCE 10 mg/L, >30 pv
- 1 control column original material
- 4 columns with angled core samples
- 3 columns with vertical core samples
In-Situ Tester (IST) Device
Developed at Waterloo (1990)

- allows field comparison with laboratory columns and with field results from 5 years ago
- isolates 5L aquifer
- allows for in-situ solute loading and sampling to characterize chemical reactions
Operation of In-Situ Tester

- installed with hollow stem drill rig
- groundwater is withdrawn using a pump into a Teflon bag
- groundwater is amended with chemicals of interest
- solution pumped back into device
- samples collected over time
Field Testing

- testers installed 0.5 and 1.0 m distance at 5.2 m bgs
- bromide 50 mg/L
- TCE 10 and 250 mg/L
- samples collected over 17 days
- material also used in column testing
Kanmet Iron Source

- waste foundry material
- no commercially available source available in 1991
- only contained 30% iron
- non-magnetic material silica sand
- SA = 0.37 m²/g
- pptes – magnetite and hematite
Core Precipitates Results

- carbonate analyses indicated a 19.4% total porosity loss within the wall
- reduced from the original 33% to 27% over 10 yrs
- pptes: Fe(OH)₃, calcite, dolomite and sulphide minerals
- bottom 20 cm of wall influenced by permanganate evidence of MnO₂, MnOOH and MnFeCO₃

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## Core Results

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Years</th>
<th>Aquifer</th>
<th>PRB</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hydraulic Conductivity</strong></td>
<td>10 yr</td>
<td>$2 \times 10^{-3}$ cm/sec</td>
<td>$2 \times 10^{-3}$ to $1 \times 10^{-2}$ cm/sec</td>
</tr>
<tr>
<td></td>
<td>5 yr</td>
<td>$7.2 \times 10^{-3}$ cm/sec</td>
<td>$4.4 \times 10^{-2}$ cm/sec</td>
</tr>
<tr>
<td><strong>Lipid Biomass</strong></td>
<td></td>
<td>$10^5$ cells/g</td>
<td>$10^6$ cells/g</td>
</tr>
<tr>
<td><strong>Anaerobic Microbial Counts</strong></td>
<td></td>
<td>3 – 70 CFU/g</td>
<td>$10^2$ – $10^3$ CFU/g</td>
</tr>
</tbody>
</table>
7 Lab Columns: Core Material
TCE 10 mg/L (10°C)

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Lab Column: Core Material
TCE 10 mg/L (10°C)

- half lives normalized ($t_{1/2N}$) to 1 m²/mL to compare on equal iron content
- control column (fresh iron), $t_{1/2N} = 3$ h
- 7 core columns $t_{1/2N}$ ranged: 2.2 to 5.6 h
- not a significant decline in reactivity over 10 years
IST Field Results
TCE 10 mg/L (10°C)

$\ln(C/Co)$ vs. Residence Time (hours)

- $t_{1/2N} = 40$ h (ISM 5)
- $t_{1/2N} = 27$ h (ISM 4)

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Lab Column: IST Material
TCE 10 mg/L (10°C)

Residence Time (hours)

TCE (Ln C/C₀)

t₁/₂N = 9 h

t₁/₂N = 5 h

t₁/₂N = 3 h

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## Comparison of TCE Reactivity
### 10 mg/L

<table>
<thead>
<tr>
<th></th>
<th>0 - 10 cm distance in PRB</th>
<th>30 - 50 cm distance in PRB</th>
<th>100 cm distance in PRB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lab Core Material</td>
<td>1.6 x lower</td>
<td>1.1 x lower</td>
<td>1.0</td>
</tr>
<tr>
<td>Lab IST Material</td>
<td>--</td>
<td>2.9 x lower</td>
<td>1.6 x lower</td>
</tr>
</tbody>
</table>

Relative to control column
Comparison: TCE 10 mg/L

- factor 5 difference between IST and laboratory results at each location
- maybe due to role of mass transport limitations in IST with low iron contents and low concentrations
- lab column controlled by advective flow
- IST by diffusion due to concentration gradients
IST Field Results
TCE 250 mg/L (10°C)

\[ t_{1/2N} = 71 \text{ h} \]

\[ t_{1/2N} = 39 \text{ h} \]
Lab Column: IST Material
TCE 250 mg/L (10°C)

\[ t_{1/2N} = 38 \text{ h} \]
\[ t_{1/2N} = 22 \text{ h} \]
\[ t_{1/2N} = 23 \text{ h} \]

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# Comparison of TCE Reactivity 250 mg/L

<table>
<thead>
<tr>
<th></th>
<th>30 - 50 cm distance in PRB</th>
<th>100 cm distance in PRB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lab IST Material</td>
<td>1.8 x lower</td>
<td>1.1 x lower</td>
</tr>
<tr>
<td>Field IST Results</td>
<td>1.8 x lower (t1/2N=71 h)</td>
<td>--- (t1/2N=39 h)</td>
</tr>
</tbody>
</table>
## Comparison of Half Lives For TCE 250 mg/L

<table>
<thead>
<tr>
<th></th>
<th>10 Years IST</th>
<th>5 Years Field</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 x higher than lab column</td>
<td>138 hours (average IST)</td>
<td>142 hours</td>
</tr>
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<td>2 x higher than lab column</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Field:
  - 10 Years IST: 138 hours (average IST)
  - 5 Years Field: 142 hours
IST Conclusions

- promising approach for reactivity in PRBs
- may be used at different locations/depths
- deviation from 1st order kinetics at low concentrations may be due to mass transfer limitations with low iron content but may be less dominant in 100% iron PRBs
- IST may give more accurate results than laboratory columns
Conclusions

- 0 – 30 cm evidence of precipitates
- precipitates mainly CaCO$_3$ and Fe(OH)$_3$
- reduction in reactivity
  - 0 to 30 cm: 1.7 x less reactivity
  - 50 to 100 cm: 1.1 x less reactivity
- $K$ is equal or one order of magnitude greater than aquifer
Conclusions

• microbial activity only slightly elevated
• no indication of biofouling
• after 10 yrs wall is still reactive suggesting it could last for several more years
• provides encouraging indicator of long-term performance