Evaluation of ISCR PRB Longevity under High Sulfate and High Flux

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SMART Remediation
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Presented by Jean Paré, P. Eng.
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Presentation Outline

• About us
• Chemical Reduction – Technology Review
• New Geobiochemical process
• Field Application Example
About us

• Canadian Company founded in 1988
• Production and warehouses throughout Canada
  • Quebec
  • Ontario
  • Alberta
  • British Columbia
• Sectors of activity:
  • Industrial and Municipal Potable & Waste Water
  • Contaminated Soil and Groundwater
  • Air, Odours and Atmospheric Emissions (Activated Carbon, filtering medias)
  • Process Water & Thermal Exchange Fluids (Glycols)
  • Drilling Fluids (Oil and Gas & Diamond exploration)
  • Aircraft De-icing Fluids

Our product and services

- Expert Technical Team
- Field-Proven Technologies
- Training & Education
- R&D and Treatability Laboratories
- Mixing and Handling Equipment
- Field Support
- Technical and Design Support
- Chemical Oxidation
- Chemical Reduction
- Co solvent-Surfactant soil Washing
- Enhanced Bioremediation
What is Chemical Reduction?

- Transfer of electrons to contaminants from reduced metals (ZVI, ferrous iron) or reduced minerals (magnetite, pyrite)

- Major dechlorination pathway is $\beta$-elimination = dechlorination of TCE & PCE with less accumulation of metabolites (cis-DCE, VC) than enzymatic systems

- Secondary dechlorination pathway is biological (hydrogenolysis, hydrogenation)
β elimination (abiotic) pathway

Tetrachloroethene  Trichloroethene  Dichloroethylene

Redox Potential in Soil during Reductive Phase
Fermentable Carbon + ZVI Synergies Generate Multiple Dechlorination Mechanisms: ISCR

3. Biostimulation:
- Serve as electron donor and nutrient source for microbial activity
- VFAs reduce precipitate formation on ZVI surfaces to increase reactivity
- Facilitate consumption of competing electron acceptors such as O₂, NO₃, SO₄
- Increase rate of iron corrosion/H₂ generation

4. Enhanced Thermodynamics:
- Very low redox reached by addition of fermentable carbon and ZVI (-500 mV)
- Two processes simultaneously reduce Eh
- Enhances kinetics of dechlorination reactions via higher electron/H⁺ pressure

1. Direct Iron Effects:

2. Indirect Iron Effects: Dissolved iron precipitates to reactive minerals

Hydrocarbon generation:

ISCR ZVI + Fermentable Carbon Treatment Mechanisms

Direct Chemical Reduction

Indirect Chemical Reduction

Stimulated Biological Reduction

Enhanced Thermodynamic Decomposition
**Biotic and Abiotic Reductive Pathways**

**Biotic**

- PCE → TCE
- Cis 1,2-DCE → Trans 1,2-DCE
- VC → Ethene → Ethane
- \( \text{CO}_2, \text{CH}_4, \text{H}_2\text{O} \)

**Abiotic**

- PCE → Dichloroacetylene
- TCE → 1,1-DCE, trans 1,2-DCE, cis 1,2-DCE
- VC → Ethene → Ethane
- \( \text{CO}_2, \text{CH}_4, \text{H}_2\text{O} \)

**In Situ Chemical Reduction (ISCR) Groundwater Remediation Technology**

**ZVI + FOC**
ZVI + FOC Reagent Composition

- Product is delivered as a dry powder and includes:
  - Micro-scale zero valent iron (standard ~40%)
  - Controlled-release, food grade, complex carbon (plant fibers) (standard ~60%)
  - Major, minor, and micronutrients
  - Food grade organic binding agent
  - Sustainable Solution
    - By-product ZVI
    - Food production by-products

PRB Type Field Application

- PRB amendment longevity dictates reapplication frequency
- High substrate longevity prevents rebound.
- Traditional trenches PRBs containing granular ZVI with or without solid carbon sources (sawdust, woodchips) have very long life.

- Injected PRBs using fine-grained ZVI and carbon substrates have gained popularity, allowing for more efficient delivery and installation into more complex geologies, but potentially offer a more limited PRB life.
ISCR + Biogeochemical Reduction

Geobiochemical process

Biogeochemical Degradation

GeoForm™
Improved Distribution Properties

Direct Chemical Reduction Requires Contact with ZVI Particle

Advection and Dispersion of Soluble Components

Extended Zone with Biological Reduction and Reactive Mineral Formation

- VFAs
- H₂
- Nutrients
- SO₄⁻ Fe²⁺

Diffusion Between Reagent Seams

Direct Push Injection Point

FeS Minerals Formed on Soil Particles

Iron Sulfide Minerals May Serve as a Reservoir of Electrons

- Fe²⁺ will be oxidized to Fe³⁺ during reaction with chlorinated contaminants
Regeneration of Reactive Minerals – Iron Redox Cycle

- Remaining smaller concentrations of organic carbon and/or natural background TOC (~2 mg/L) may be sufficient to continuously restore Fe$^{3+}$ to Fe$^{2+}$

Biogeochemical Transformation

Processes where contaminants are degraded by abiotic reactions with naturally occurring and biogenically-formed minerals in the subsurface.

Reactive minerals include iron sulfides (e.g. pyrite, mackinawite, greigite) and oxides (e.g. magnetite)

β-Elimination does not generate stable toxic daughter products
• All-In-One BioGeoChemical Reagent

• Provides All Building Blocks Needed for Reactive Mineral Formation

• Combines Sulfate, Ferrous Iron, Electron Donors, pH Buffer, and Nutrients (ZVI in Geoform Extended Release)

• Effective for Chlorinated Organics and Many Heavy Metals

• Promotes ISCR, ERD and reactive mineral formation

• Composition has been optimized to maximize generation of reactive iron sulfide minerals

• Reagents will migrate with groundwater and form an expanded treatment zone

• Increased reactive surface area for abiotic dehalogenation
**Engineering Reactive Iron Sulfide Minerals In Situ**

Injection of GeoForm

**REAcTIONS PROMOTED**

- Organic Substrate Fermentation → Reduced RedOX Conditions
- Sulfate reduction by SRBs:
  \[ 2\text{CH}_2\text{O}(s) + \text{SO}_4^{2-} + 2\text{H}^+\text{(aq)} \rightarrow \text{H}_2\text{S} + 2\text{CO}_2\text{(aq)} + \text{H}_2\text{O} \]
- Precipitation of Ferrous Iron with Sulfide:
  \[ \text{Fe}^{2+}(\text{aq}) + \text{H}_2\text{S}(\text{aq}) \rightarrow \text{FeS}_2(s) + 2\text{H}^+(\text{aq}) \]

**Expanded Surface Area for Abiotic Pathway**

Electron microprobe analyses performed on iron sulfide precipitation products estimated that 4.7 ft² of very reactive surface area was generated per liter of groundwater with 3,000 mg/L sulfate reduced to an estimated 3 µm thick FeS precipitate (Leigh et al.).

<table>
<thead>
<tr>
<th>Particle Size (µm)</th>
<th>Surface Area (m²/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micro-Scale ZVI</td>
<td>50-250</td>
</tr>
<tr>
<td>Framboidal Pyrite</td>
<td>20</td>
</tr>
<tr>
<td>FeS Coatings</td>
<td>3</td>
</tr>
<tr>
<td>Euhedral Pyrite</td>
<td>1</td>
</tr>
</tbody>
</table>
**GeoForm Formulations**

<table>
<thead>
<tr>
<th>GeoForm™ Formulation</th>
<th>Treatment Mechanisms</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Biotic Reduction</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>GeoForm™ Soluble</td>
<td>•</td>
</tr>
<tr>
<td>GeoForm™ Extended Release</td>
<td>•</td>
</tr>
</tbody>
</table>

- Provides a longer lasting source of electron donors for continued rejuvenation of reactive minerals.
- Extended Release Organic Carbon, Micro-Scale ZVI, Sulfate, Ferrous Iron, pH buffers and nutrients
- Longevity of 5-10 years

**GeoForm Application**

Geoform Soluble

Geoform Extended Release
Case Study - Introduction

- One of the first full-scale ISCR reagent injection PRBs was installed in 2005 for treatment of carbon tetrachloride (CT).

- EHC® ISCR reagent composed of:
  - ~40% micro-scale zero valent iron (50 - 200 µm)
  - ~60% fine-grained processed plant fiber particles

- This presentation assesses long-term performance and geochemical parameter changes since installation.
Site Background

- CT plume extends ~800 m from grain elevators and discharges into small creek.
- Shale bedrock rises to ~3 m above the water table at the grain mill.
- CT is believed to have transported along the bedrock surface to the downgradient aquifer.
- Access restrictions on residential properties further complicated source area clean-up.

Courtesy of Malcolm Pirnie (Arcadis)
Remedial Approach

- PRB installed April 2005 across plume width to limit migration.
- Single row of injection points installed along road right-of-way using EHC ISCR reagent.
- Remedial approach developed by Malcolm Pirnie (Arcadis)

Source Area Remediation Activities

- Organic carbon substrate applications at source area injection wells (phased pilot test):
  - Molasses – August 2011, 2012 and October 2013
  - EVO – June 2014 and 2015

Reference: 2015 Monitoring Report from Arcadis
Cross Section from Injection Area

- Saturated sand units targeted
- PRB Dimensions = 270 ft Long x 10 ft wide x 10 ft average thickness
- 24 tons of EHC ISCR Reagent injected
- Application Rate = ~1% to targeted soil mass

Field Installation

- A 30% EHC slurry injected via direct push
- Field installation completed in 12 days
Evaluation of Placement

Soil cores used to verify ROI and determine injection spacing:

- EHC slurry was found in discrete seams 5 ft away from injection locations
- Injection points spaced 10 ft apart

Performance Evaluation

- CT and degradation products
- ISCR Reagent indicator parameters (TOC)
- Geochemical parameters, including ORP, nitrate, and sulfate
- Voluntary Clean-up Plan goals minimum 95% CT reduction from baseline concentrations at compliance points located 21 m and 42 m downgradient.

(CT concentrations March 2005 in ppb)
Performance Evaluation

- **MW-105** - 21 m downgradient at plume center (~39 days travel time*).
- **MW-106** - 42 m downgradient at plume edge (~78 days travel time*).
- **MW-VCI-6** -180 m downgradient (~333 days travel time*).
- Inflowing concentrations monitored at **MW-VCI-4**

*estimated groundwater flow velocity of 0.55 m/day

(CT concentrations March 2005 in ppb)

Geochemical Data

- **Total Organic Carbon (TOC)**
- **ORP**
- **Nitrate**
- **Sulfate**

**MW-VCI4 (upgradient / inflowing)**

**MW-105 (21 m downgradient)**
Micro-scale ZVI Longevity

Theoretical estimation of micro-scale ZVI longevity:

- **ZVI oxidation** due to reduction of terminal electron acceptors; calculated based on Stoichiometric demand from:
  - Naturally occurring terminal electron acceptors such as dissolved oxygen (DO), nitrate and sulfate;
  - Chlorinated contaminant reduction.

- **Corrosion** is an important ZVI consumption process and rates are expected to be more constant over time (estimated at 1.5 mmol/kg/day for micro-scale ZVI):

  \[
  \text{Fe}^0 + 2\text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + \text{H}_2(\text{aq}) + 2\text{OH}^-
  \]

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Theoretical Calculation of ZVI Longevity

<table>
<thead>
<tr>
<th>PRB interface for gw flow (m²)</th>
<th>PRB width (m)</th>
<th>ZVI Dose Rate (mass)</th>
<th>ZVI Mass (kg)</th>
<th>GW velocity (m/day)</th>
<th>Effective porosity</th>
<th>Volume gw passing thru PRB (L/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>251</td>
<td>3</td>
<td>0.4%</td>
<td>8,709</td>
<td>0.59</td>
<td>0.2</td>
<td>100,462,501</td>
</tr>
</tbody>
</table>

**Estimation assuming 100% of inflowing sulfate being reduced:**

<table>
<thead>
<tr>
<th></th>
<th>Influent (mg/L)</th>
<th>Mass flux (kg/yr)</th>
<th>Mass flux (kmol/yr)</th>
<th>ZVI used (kmol/yr)</th>
<th>ZVI used (kg/yr)</th>
<th>% ZVI used per year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water corrosion</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>267.0</td>
<td>3.07%</td>
</tr>
<tr>
<td>DO</td>
<td>0.4</td>
<td>4.0</td>
<td>0.13</td>
<td>0.17</td>
<td>9.4</td>
<td>0.11%</td>
</tr>
<tr>
<td>CT</td>
<td>1</td>
<td>10.0</td>
<td>0.07</td>
<td>0.26</td>
<td>14.6</td>
<td>0.17%</td>
</tr>
<tr>
<td>CF</td>
<td>0.01</td>
<td>0.1</td>
<td>0.00</td>
<td>0.00</td>
<td>0.1</td>
<td>0.00%</td>
</tr>
<tr>
<td>NO3</td>
<td>4</td>
<td>40.2</td>
<td>0.65</td>
<td>2.59</td>
<td>145.2</td>
<td>1.67%</td>
</tr>
<tr>
<td>SO4</td>
<td><strong>120</strong></td>
<td><strong>1,205.6</strong></td>
<td><strong>12.56</strong></td>
<td><strong>50.23</strong></td>
<td><strong>2,813.0</strong></td>
<td><strong>32.30%</strong></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td><strong>37.3%</strong></td>
</tr>
<tr>
<td>Estimated ZVI Longevity (yrs)</td>
<td><strong>2.7</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Sulfate reduction over time

![Graph showing sulfate reduction over time](image)

Performance Data

- **70 ft / 21 m downgradient from PRB**
- **140 ft / 43 m downgradient from PRB (edge of plume)**

![Graph showing performance data](image)
Performance Data

**Indirect Chemical Reduction**

- Definition - processes where contaminants are degraded by abiotic reactions with naturally occurring and biogenically-formed minerals in the subsurface.
- Reactive minerals include iron sulfides (e.g. pyrite, mackinawite, greigite) and oxides (e.g. magnetite)
- **Inflowing sulfate = ~120 mg/L** → iron sulfides are likely precipitation products downgradient from PRB → indirect chemical reduction may be an important mechanism to explain reactive life
### Engineering Reactive Iron Sulfide Minerals In Situ

**Injection of GeoForm**

- Sulfate + Fe(II) + Electron donor

**REACTIONS PROMOTED**

- Organic Substrate Fermentation → Reduced RedOx Conditions
- Sulfate reduction by SRBs:
  \[ \text{Sulfate reduction by SRBs:} \quad 2\text{CH}_2\text{O}(s) + \text{SO}_4^{2-} + 2\text{H}^+ \rightarrow \text{H}_2\text{S} + 2\text{CO}_2 + 2\text{H}_2\text{O} \]
- Precipitation of Ferrous Iron with Sulfide:
  \[ \text{Precipitation of Ferrous Iron with Sulfide:} \quad \text{Fe}^{2+} + \text{H}_2\text{S} \rightarrow \text{FeS} + 2\text{H}^+ \]

**PRB Economics**

**Installation costs:**

- Amendment: 24 tons of EHC ISCR Reagent used in PRB
  - Product cost = ~$100,000
- Injection: 2 weeks of Geoprobe
  - Injection Cost = ~$50,000

Total Fixed Cost: $150,000

Operating Cost: None

**Longevity:**

A single application of EHC has remained active for a period of ~9.5 years before indications of breakthrough started to be observed, continuously supporting >95% removal of CT without the accumulation of catabolites.

PRB treated an estimated ~140,000 m³ GW over its reactive life

Product Cost = ~$0.71 /m³

*This is significantly lower than the pump and treat alternative where just the annual O&M Costs can range from $ 50K to $ 300K*
Conclusions

Combination of ZVI and FOC synergistically provides multiple biological and chemical reductive pathways

FOC provides long term source of electrons, enhances biological reduction, maintains pH and limits ZVI passivation

ZVI causes abiotic degradation, maintains pH,

Geoform enhances biological, chemical and biogeochemical degradation processes.

Acknowledgement

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