Optimization of ZVI Technology for *In-Situ* Remediation of Chlorinated Contaminants

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Chlorinated Solvent Contamination - Background

- **Dry cleaners**
  - PCE used as cleaning agent
  - Many dry cleaning facilities had leaks, spills, improper disposal

- **Former and current industrial facilities**
  - PCE, TCE, VC, 1,1,1-TCA, etc.
  - Degreasing, cleaning, surface preparation
  - Remanufacturing, metalworking, etc.
  - Electronics manufacturing

- **Aerospace / defense installations**
  - Cleaning agents for planes, weapons, etc.
  - PCE, TCE, VC, 1,1,1-TCA, etc.

Primary contaminants and daughter products have varying levels of toxicity.
Chlorinated Solvent Contamination - Remedial Options

**Physical Methods:**
- Excavation
- Soil Mixing
- Soil Vapor Extraction

**In-Situ Methods:**
- Chemical Reduction
- Bioremediation
- Chemical Oxidation

Source: NC DEQ
Source: OnMaterials
Source: Terra Systems
Source: Geo-Solutions
Source: NRC

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Why use Zero Valent Iron?

• If used properly, ZVI can address chlorinated contamination through either chemical reduction and/or enhanced bioremediation pathways.

• It is possible to use ZVI in a manner which satisfies all of the requirements for successful in situ remediation...

• In-Situ remediation technologies are attractive because they don’t involve excavation or permanent system installation (O&M costs)
Requirements for Successful In-Situ Remediation

Reactivity

Ease of Use

Success!

Persistence

Distribution

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AMZVI: S 2 g/L TCE degradation

TCE (mg/L)

Day

0 1 2 3 4 5 6 7 8

TCE (mg/L)

Persistence Distribution

Success!
Chemical Reduction (Abiotic): Zero Valent Iron and TCE

$$4\text{Fe}^0 + \text{C}_2\text{HCl}_3 + 5 \text{H}^+ \rightarrow 4 \text{Fe}^{+2} + \text{C}_2\text{H}_6 + 3 \text{Cl}^-$$

Reaction pathway can bypass toxic daughter products
Reactivity: Commodity Iron Vs. Engineered Iron

Comparison of the following against 36 mg/L TCE:

- **10 g/L** Carbonyl iron powder (commodity product)
- **2 g/L** Z-Loy™ AquaMetal ZVI (engineered product)

Z-Loy™ AquaMetal ZVI exhibits a 27x faster degradation rate.

- Particle size reduction
- Increased reactive surface area
- Surface preparation & catalysis

![TCE Degradation Kinetics](chart)

**TCE Degradation Kinetics**

- Carbonyl Iron Powder (10 g/L)
- AquaMetal ZVI (2 g/L)
ZVI – Passivity and the Importance of Optimized Material

**Reaction with water**

Fe(s) + 2 H₂O(l) → Fe(OH)₂(s) + H₂(aq)
3 Fe(OH)₂(s) → Fe₃O₄(s) + H₂(aq) + 2H₂O(l) → Passivating oxide/hydroxide

**Reaction with DO**

2 Fe(s) + 1.5 O₂(aq) → Fe₂O₃(s) → Passivating oxide

**Reaction with Carbonate**

Fe(s) + 2 H₂O(l) + CO₃⁻²(aq) → FeCO₃(s) + H₂(g) + 2 OH⁻(aq) → Passivating carbonate

**Reaction with Sulfate**

4 Fe(s) + SO₄⁻²(aq) + 4 H₂O(l) → FeS(s) + 3 Fe(OH)₂(s) + 2 OH⁻(aq) → Reactive iron sulfide

Optimization of ZVI Technology for *In-Situ* Remediation of Chlorinated Hydrocarbons
Case Study – Abiotic Dechlorination at Active Mfg. Facility

- Prior bioremediation efforts / cis-1,2 DCE was primary remaining contaminant
- 2 phase treatment – No access to source under active building
  - 1st phase was 26 DPT points (Z-Loy™ MicroMetal and pH modifier)
  - 2nd phase was 32 DPT points (Z-Loy™ MicroMetal and pH modifier)
- No daughter product formation means abiotic system

![Graph showing reduction in contaminants over time](image)
Case Study – Abiotic Dechlorination at Active Mfg. Facility
Metal-Assisted Bioremediation: Biotic Degradation

PCE \rightarrow TCE \rightarrow c-1,2-DCE \rightarrow VC \rightarrow Ethene

Hydrogenolysis: 2 e^-

Co-application of:

Dechlorinating Microbes

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Photos: OnMaterials
Case Study: Metal-Assisted Bioremediation

**Source:** Texas industrial site had a degreaser which ruptured spilling 100+ gal of TCE. Residual TCE DNAPL with little natural attenuation.

**Approach:** Amendments were applied via screened wells at 5-20 psi.

**Amendments:**
- Z-Loy™ MicroMetal
- EVO
- pH modifier, nutrients
- Dechlorinating microbes
Case Study: Metal-Assisted Bioremediation

Implementation: Injection was done in two phases based on baseline and monitoring data.

Results: 5 year monitoring data tells an interesting story. A large spike in ethene shows complete biotic degradation after 2011 injection event.
Examples of Commercial Products

Zero Valent Iron Injection Methodology

- Soluble
- NZVI (~200 nm)
- Z-Loy™ Products (1-3 μm)
  - OnMaterials
- Commodity Iron (3-10 μm)
  - Several vendors
- Commodity Iron (44-100 μm)
  - Several vendors
- Cast / Scrap Iron (1 mm)

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### Characteristics as a Function of Particle Size

<table>
<thead>
<tr>
<th>Soluble</th>
<th>Nano</th>
<th>Near-Microscale</th>
<th>Far- Microscale</th>
<th>Scrap Iron</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(^{+2}), Bicarb</td>
<td>NZVI</td>
<td>Z-Loy™ products, EVO</td>
<td>Powdered ZVI</td>
<td></td>
</tr>
</tbody>
</table>

#### Particle Size:
- 0 \(\mu\)m
- 0.2 \(\mu\)m
- 1-4 \(\mu\)m
- 50 \(\mu\)m
- 1 mm

#### Persistence
- **Most Powerful**
- **Long Acting**
- **Less Powerful**

#### Difficulties:
- **Easy**
- **Agglomeration issues**
- **Requires mixing/recirculation**
- **High pressure/fracturing**
- **Soil Mixing/trenching**
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**Characteristics as a Function of Particle Size**

**Small particle size**
- Better suspension aids in injectability and distribution
- Uniformity can be helped by adding dispersants

**Large particle size**
- Difficult to suspend
- Thickening with gaur, etc.
- Aggressive mixing must be done

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2-3 micron Z-Loy™ AquaMetal ZVI in water

40 micron ZVI in water
Dosing Considerations

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Physical</th>
</tr>
</thead>
<tbody>
<tr>
<td>ORP</td>
<td>Porosity</td>
</tr>
<tr>
<td>pH</td>
<td>Groundwater flow/flux</td>
</tr>
<tr>
<td>Sulfate, DO, nitrate</td>
<td>Saturation / Pore replacement</td>
</tr>
<tr>
<td>Contaminant &amp; Concentration</td>
<td>Geology/ Lithology</td>
</tr>
</tbody>
</table>

- Soluble and small particle size amendments are often dosed in terms of in-situ concentration between 4 g/L – 25 g/L.
- Water-like characteristics suggest that material will occupy pore space and displace / mix with groundwater when applied at low pressure.
- Large materials (40+ micron) are often dosed in terms of soil mass basis between 0.5%-2.0%. This is usually 5x – 10x more than small particle size.
- Higher pressures required may create fractures, therefore displacing soil/groundwater. Particle size is larger than available pore spaces.
Dosing Considerations

- Dosing for commodity and engineered iron products differs because of subsurface distribution and reactivity.
Optimization of Technology

- ZVI has been used since the 1990’s for remedial applications
- Materials and methods exist which take a ‘good’ technology and make it ‘great’
- Reductive dechlorination can be done with screened wells and with a small footprint using low pressure – Much easier at active facilities, neighborhoods, etc. where “low key” installation is a must.
- Enhanced reactivity means fast results
Thank You for Your Time!

We offer our Z-Loy™ products as well as:

• Remedial design and support
• Injection services
• Custom mixing, material handling and injection equipment
• All personnel hold at least M.S. in Chem. or Env. Engineering discipline
• Over 15 years of successful results and expertise in the industry