Treating a mixture of cVOCs contaminated groundwater using nano zerovalent iron

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Outline

• Introduction
  - Chlorinated Volatile Organic Compounds
  - Zerivalent Iron Technology
  - Reaction Mechanisms

• Research Focus
  - Groundwater Samples
    - Sample A (cVOCs < 200 ppm)
    - Sample B (some cVOCs >200 ppm)
  - Treatments
    - High dose of nZVI (5 g L\(^{-1}\))
    - Low dose of nZVI (2.5 g L\(^{-1}\))
    - Pd-nZVI

• Results

• Summary
Chlorinated Volatile Organic Compounds (cVOCs)

- Hydrocarbons containing at least one chlorine atom.

- Used as degreasers, cleaning solutions, paint thinners, in adhesives, refrigerants, plastic wraps and PVC pipes.
Chlorinated Volatile Organic Compounds (cVOCs)

- Denser than water and sink through saturated zone when released into subsurface
Approaches to Treat Contaminated Groundwater

- **BIOREMEDIATION**
  - Natural Attenuation
  - Stimulate Native Microorganisms

- **CHEMICAL TREATMENT**
  - Chemical oxidation/reduction

Chemical Injection into Groundwater
Chemical Reduction

**Reduction** – a process involving gain of electrons, where electrons are transferred from an electron donor (reductant) to an electron acceptor (oxidant)

Why chemical reduction as a treatment for cVOCs?

Cl is an e⁻ withdrawing group

Cl⁻ add e⁻

![Chemical Reduction Diagram](attachment:image.png)

PCE \[\text{Perchloroethylene}\] → TCE \[\text{Trichloroethylene}\]
Zerovalent Iron (Fe⁰) Technology

Fe⁰ → Fe²⁺ + 2e⁻  \[ E^0 = -0.44V \]

“An Avid Electron Donor”

How Does Iron Work?

\[
\begin{align*}
\text{Cl} & \text{C} = \text{C} & \text{Cl} & \quad E^0 = 0.57V \\
\text{Cl} & \text{C} = \text{C} & \text{Cl} & \quad \text{PCE} \\
\text{Cl} & \text{C} = \text{C} & \text{Cl} & \quad \text{TCE} \\
\text{H} & \text{C} = \text{C} & \text{H} & \quad E^0 = 0.45V \\
\text{H} & \text{C} = \text{C} & \text{H} & \quad \text{Ethylene} \\
\text{H} & \text{C} = \text{C} & \text{Cl} & \quad E^0 = 0.42V \\
\text{H} & \text{C} = \text{C} & \text{Cl} & \quad \text{VC} \\
\text{Cl} & \text{C} = \text{C} & \text{H} & \quad \text{DCE} \\
\text{Cl} & \text{C} = \text{C} & \text{Cl} & \quad \text{TCE} \\
\end{align*}
\]
Micro/Macro Zerovalent Iron (mZVI)

1993: Granular zerovalent iron was patented by University of Waterloo.

Shortcomings:
- Depth limitations
- Needs extensive changes at the site.
Nano Zerovalent Iron (nZVI)

1997: Wang & Zhang published reduction of TCE & PCBs by bare nZVI.

Bare nZVI < 50 nm

- Large surface area & greater reactivity
- Potential for rapid subsurface injection
- Low subsurface mobility

Aggregation due to magnetic interactions result in rapid settling

Photos – Courtesy of N. Sakulchaicharoen
Enhancement of nZVI Stability & Mobility

Coating with a stabilizer - Carboxymethyl cellulose (CMC)

CMC-nZVI

No aggregation

Photos – Courtesy of N. Sakulchaicharoen
Nano Zerovalent Iron (Injection & Mobility)

- nZVI Injection Well
- Unsaturated zone
- Saturated zone
- Leaky Underground Storage Tank
- DNAPL
- Impervious Layer
How does the e\textsuperscript{-} transfer occur at Fe\textsuperscript{0} surface?

1. Direct Reduction at the Metal Surface
   \[ \text{Fe}^3+ + \text{RCl} + \text{H}^+ \rightarrow \text{Fe}^2+ + \text{RH} + \text{Cl}^- + \text{H}^+ \]

2. Reduction by Adsorbed Ferrous Iron
   \[ \text{RH} + \text{Cl}^- \rightarrow \text{RH} + \text{Cl}^- + \text{H}^+ \]

3. Reduction by Hydrogen with Catalyst
   \[ \text{RH} + \text{Cl}^- + \text{H}^+ \rightarrow \text{RH} + \text{Cl}^- + \text{H}^+ \]

Adapted from Matheson & Tratnyek (1994)
Bimetallic (Fe-Pd) Nanoparticles

\[
\begin{align*}
Fe^0 & \rightarrow Fe^{2+} + 2e^- \quad E^0 = -0.44V \\
Pd^{2+} & + 2e^- \rightarrow Pd^0 \quad E^0 = 0.92V
\end{align*}
\]

\[Pd^{2+} + Fe^0 \rightarrow Pd^0 + Fe^{2+}\]
Reductive Dehalogenation of cVOCs with nZVI

1) Dihaloelimination

**β-elimination:** Two Cl atoms released from adjacent Carbons
Formation of an additional C-C bond

\[
\begin{align*}
\text{Cl} & \text{C} \text{C} \text{Cl} \\
\text{Cl} & \text{Cl} \text{Cl}
\end{align*}
\xrightarrow{\text{H}}
\begin{align*}
\text{H} & \text{C} \equiv \text{C} \text{H} \\
\text{Cl} & \text{C} \equiv \text{C} \text{Cl}
\end{align*}
\]

1,1,2,2-TeCA \quad \text{Cis 1,2-DCE} \quad \text{Trans 1,2-DCE}

**α-elimination:** Two Cl atoms released from same C atom
Forms an additional C-C bond

\[
\begin{align*}
\text{Cl} & \text{C} \text{C} \text{Cl} \\
\text{Cl} & \text{Cl} \text{Cl}
\end{align*}
\xrightarrow{\text{H}}
\begin{align*}
\text{H} & \text{C} \equiv \text{C} \text{H} \\
\text{H} & \text{C} \equiv \text{C} \text{Cl}
\end{align*}
\]

1,1,2,2-TeCA \quad \text{1,1-DCE}
Reductive Dehalogenation of cVOCs with nZVI

2) Hydrogenolysis
- Replacement of Cl atom by H atom
- Requires an e⁻ donor and a H⁺ donor

\[
\text{Cl-C-Cl} \quad \rightarrow \quad \text{Cl-C-H}
\]

1,1,2,2-TeCA → 1,1,2-TCA

3) Hydrogenation
- Addition of hydrogen across = or ≡ C-C bond.

\[
\text{H-C=H} \quad \rightarrow \quad \text{H-C-C-H}
\]

Ethylene → Ethane
Pathways for Transformation of Chlorinated Ethenes

A – Hydrogenolysis
B – β-elimination
C – α-elimination
D – Hydrogenation

Modified from: Arnold and Roberts (2000)
Pathways for Transformation of Chlorinated Ethanes

- **A** = Hydrogenolysis
- **B** = $\beta$-elimination
- **C** = $\alpha$-elimination
- **D** = Hydrogenation

Modified from: Chen et al. (1996)
### cVOCs Concentrations (mg L\(^{-1}\)) in Groundwater Samples

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Sample A</th>
<th>Sample B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trichloromethane (Chloroform)</td>
<td>9.51</td>
<td>1.33</td>
</tr>
<tr>
<td>Dichloromethane (DCM)</td>
<td>0.20</td>
<td>nd</td>
</tr>
<tr>
<td>1,1,2,2-Tetrachloroethane (1,1,2,2-TeCA)</td>
<td>nd</td>
<td>39.8</td>
</tr>
<tr>
<td>1,1,2-Trichloroethane (1,1,2-TCA)</td>
<td>162.1</td>
<td>1513</td>
</tr>
<tr>
<td>1,2-Dichloroethane (1,2-DCA)</td>
<td>105.7</td>
<td>565</td>
</tr>
<tr>
<td>Tetrachloroethene (PCE)</td>
<td>4.39</td>
<td>1.70</td>
</tr>
<tr>
<td>Trichloroethene (TCE)</td>
<td>32.3</td>
<td>40.3</td>
</tr>
<tr>
<td>1,1-Dichloroethene (1,1-DCE)</td>
<td>2.16</td>
<td>6.74</td>
</tr>
<tr>
<td>(t) 1,2-Dichloroethene (trans 1,2-DCE)</td>
<td>0.17</td>
<td>0.69</td>
</tr>
<tr>
<td>(c) 1,2-Dichloroethene (cis 1,2-DCE)</td>
<td>0.31</td>
<td>2.34</td>
</tr>
<tr>
<td>Vinyl chloride (Chloroethene)</td>
<td>49.5</td>
<td>14.2</td>
</tr>
</tbody>
</table>
Motivation

High concentrations of cVOCs in groundwater are toxic to microorganisms and result in limited or no biodegradation.

CMC-nZVI, which can effectively degrade most of the cVOCs, seems to be a proper choice for treating a multi-contaminant system.

- Decreases overall contaminant loading
- Removes ‘inhibitory’ compounds
- Transforms parent compounds to easily biodegradable intermediates
- Produces hydrogen and other electron donors
- Creates reducing conditions for anaerobic biodegradation
- Provides carbon source
Objective

To assess the degradation potential of

(a) CMC-nZVI

and

(b) palladized CMC-nZVI

for treating multi-cVOCs contaminated groundwater samples.
Groundwater Sample A

**Treatment 1: Lower Dose of Nano Iron**

1. nZVI : Freshly synthesized 7.5 g L\(^{-1}\) nZVI with 1.5 weight% CMC
2. Pd-nZVI : nZVI + 0.05% Pd (w/w of Fe)
3. Control : 1.5 weight% CMC

30 mL nZVI/Pd-nZVI + 60 mL groundwater sample in a 120 mL reactor bottle. The sample was diluted 1.5 times and the final nZVI dose was 2.5 g L\(^{-1}\).
Experimental Setup

Glove Box

Shaker

GC-FID

GC-ECD
Transformation of Trichloromethane

Groundwater Sample A
nZVI dose = 2.5 g L\(^{-1}\)
Transformation of Dichloromethane

Trichloromethane $\rightarrow$ Dichloromethane $\rightarrow$ Chloromethane $\rightarrow$ Methane

Hydrogenolysis

Boparai & O’Carroll
Transformation of 1,1,2-Trichloroethane

1,1,2-TCA Conc. (mg L$^{-1}$) vs. Time (h)

- Control
- nZVI
- Pd-nZVI

Complete nZVI utilization

Groundwater Sample A
nZVI dose = 2.5 g L$^{-1}$
Transformation of 1,2-Dichloroethane

Groundwater Sample A
nZVI dose = 2.5 g L\(^{-1}\)
Transformation of Trichloroethene

Groundwater Sample A
nZVI dose = 2.5 g L⁻¹
Transformation of Chloroethenes

Groundwater Sample A

nZVI dose = 2.5 g L⁻¹
Transformation of (trans)1,2-Dichloroethene

PCE

\[
\text{Cl} = \text{C} = \text{C} = \text{Cl} \quad \text{Hydrogenolysis} \quad \rightarrow \quad \text{Cl} = \text{C} = \text{C} = \text{Cl}
\]

TCE

\[
\text{Cl} = \text{C} = \text{C} = \text{Cl} \quad \text{Hydrogenolysis} \quad \rightarrow \quad \text{H} = \text{C} = \text{C} = \text{H}
\]

(t) 1,2-DCE

\[
\text{Cl} = \text{C} = \text{C} = \text{Cl} \quad \text{Hydrogenolysis} \quad \rightarrow \quad \text{H} = \text{C} = \text{C} = \text{H}
\]
Transformation of (cis)1,2-Dichloroethene

- **nZVI**
  - Control
  - Pd-nZVI

- **Pd-nZVI**
  - Control
  - Pd-nZVI

Conversion reactions:
- PCE → Hydrogenolysis → TCE → Hydrogenolysis → (c) 1,2-DCE
Transformation of Vinyl Chloride

Groundwater Sample A
nZVI dose = 2.5 g L\(^{-1}\)
cVOCs (mg L\(^{-1}\)) in Groundwater Sample A at 1000h (2.5 g L\(^{-1}\) nZVI)

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Initial</th>
<th>nZVI</th>
<th>Pd-nZVI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trichloromethane (Chloroform)</td>
<td>5.68</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Dichloromethane (DCM)</td>
<td>0.13</td>
<td>0.45</td>
<td>0.38</td>
</tr>
<tr>
<td>1,1,2-Trichloroethane (1,1,2-TCA)</td>
<td>101.5</td>
<td>49.7</td>
<td>12.9</td>
</tr>
<tr>
<td>1,2-Dichloroethane (1,2-DCA)</td>
<td>69.9</td>
<td>68.7</td>
<td>68.7</td>
</tr>
<tr>
<td>Tetrachloroethene (PCE)</td>
<td>2.19</td>
<td>1.02</td>
<td>0.06</td>
</tr>
<tr>
<td>Trichloroethene (TCE)</td>
<td>18.5</td>
<td>1.14</td>
<td>ND</td>
</tr>
<tr>
<td>1,1-Dichloroethene (1,1-DCE)</td>
<td>1.08</td>
<td>0.30</td>
<td>0.22</td>
</tr>
<tr>
<td>(t) 1,2-Dichloroethene (Trans 1,2-DCE)</td>
<td>0.13</td>
<td>0.17</td>
<td>0.15</td>
</tr>
<tr>
<td>(c) 1,2-Dichloroethene (Cis 1,2-DCE)</td>
<td>0.20</td>
<td>0.22</td>
<td>ND</td>
</tr>
<tr>
<td>Vinyl chloride (Chloroethene)</td>
<td>26.3</td>
<td>18.4</td>
<td>0.78</td>
</tr>
</tbody>
</table>
(A) nZVI & (B) Pd-nZVI (2.5 g L$^{-1}$) after treating Groundwater Sample A for 45d

Fresh nZVI

A

B

Pd-nZVI (2.5 g L$^{-1}$)
The uncatalyzed ZVI treatment could not successfully degrade 1,1,2-TCA; 1,2-DCA and VC, an experiment was conducted at higher dose of nZVI.

**Treatment 2: Higher Dose of Nano Iron**

1. **CMC-nZVI** : Freshly synthesized 7.5 g L$^{-1}$ nZVI with 1.5 weight% CMC
2. **Control** : 1.5 weight% CMC

60 mL CMC-nZVI + 30 mL water sample in a 120 mL reactor bottle. The sample was diluted 3 times and the final nZVI dose was 5.0 g L$^{-1}$. 
<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Initial</th>
<th>At 1000h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trichloromethane (Chloroform)</td>
<td>2.73</td>
<td>ND</td>
</tr>
<tr>
<td>Dichloromethane (DCM)</td>
<td>0.09</td>
<td>0.14</td>
</tr>
<tr>
<td>1,1,2-Trichloroethane (1,1,2-TCA)</td>
<td>55.1</td>
<td>ND</td>
</tr>
<tr>
<td>1,2-Dichloroethane (1,2-DCA)</td>
<td>36.9</td>
<td>34.3</td>
</tr>
<tr>
<td>Tetrachloroethene (PCE)</td>
<td>1.18</td>
<td>0.01</td>
</tr>
<tr>
<td>Trichloroethene (TCE)</td>
<td>10.3</td>
<td>ND</td>
</tr>
<tr>
<td>1,1-Dichloroethene (1,1-DCE)</td>
<td>0.57</td>
<td>0.15</td>
</tr>
<tr>
<td>(t) 1,2-Dichloroethene (Trans 1,2-DCE)</td>
<td>0.07</td>
<td>ND</td>
</tr>
<tr>
<td>(c) 1,2-Dichloroethene (Cis 1,2-DCE)</td>
<td>0.11</td>
<td>ND</td>
</tr>
<tr>
<td>Vinyl chloride (Chloroethene)</td>
<td>13.0</td>
<td>0.21</td>
</tr>
</tbody>
</table>
Contaminant                      | Initial | nZVI | Pd-nZVI |
---------------------------------|---------|------|---------|
Trichloromethane (Chloroform)    | 0.12    | ND   | ND      |
1,1,2,2-Tetrachloroethane (1,1,2,2-TeCA) | 17.9    | ND   | ND      |
1,1,2-Trichloroethane (1,1,2-TCA) | 453.3   | ND   | ND      |
1,2-Dichloroethane (1,2-DCA)     | 183.1   | 174.8| 173.3   |
Tetrachloroethene (PCE)          | 1.04    | ND   | ND      |
Trichloroethene (TCE)            | 15.2    | ND   | ND      |
1,1-Dichloroethene (1,1-DCE)     | 2.12    | ND   | ND      |
(t) 1,2-Dichloroethene (Trans 1,2-DCE) | 0.22    | ND   | ND      |
(c) 1,2-Dichloroethene (Cis 1,2-DCE) | 0.60    | 0.05 | 0.03    |
Chloroethene (Vinyl chloride)    | 4.15    | 0.17 | ND      |
Summary

- nZVI is an effective remediation approach.
- Both nZVI and Pd-nZVI successfully degraded cVOCs (except 1,2-DCA & dichloromethane) in multi-contaminant groundwater samples.
- The degradation of cVOCs was faster and greater with Pd-nZVI.
- Increasing the dose of uncatalyzed nZVI enhanced the rate and extent of cVOCs degradation.
- There was complete utilization of Fe$^0$ in transforming the cVOCs.
CMC-nZVI subsurface injection alters environment in the aquifer by creating strongly reducing conditions and providing hydrogen and carbon source. This may result in enhanced biodegradation of even the most recalcitrant cVOCs such as 1,2-DCA.


Application of Nanoscale Zero Valant Iron for Contaminant Site Remediation: Results from Two Field Trials – D.M. O’Carroll et al.

Stream G1 – Remediation Case Studies
Acknowledgements

-Nataphan Sakulchaicharoen
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Questions ?