Chemical Reduction processes for In Situ Soluble Metals Remediation and Immobilization in Groundwater

2014 RPIC Federal Contaminated Sites National Workshop
Ottawa 2014

Prepared by

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Presentation Outline

• Problem Description and Common Metals
• Technology Review and Performance
• Using ISCR for Toxicity and/or Mobility Control
• Design Parameters
• Case Study Presentation
Problem Description

• Source of Metals Contaminant
  • Contaminated Wastewater discharges
  • Direct contact with impacted soil from
    • Sludges
    • Mining Wastes
    • Spills
    • Airbone Emissions
Common Metal Impacts

Superfund Sites (soil and groundwater)

Source: Remediation of Metals - Contaminated Soils and Groundwater, GRWTAC
# Technology Review and Performance

## Table 1. Remediation Technologies Matrix for Metals in Soils and Ground-Water

<table>
<thead>
<tr>
<th>Remediation Technology</th>
<th>Metals Treated</th>
<th>Cost</th>
<th>Long-term Effectiveness/Permanence</th>
<th>Commercial Availability</th>
<th>General Acceptance</th>
<th>Applicability to High Metals Concentrations</th>
<th>Applicability to Mixed Waste (metals &amp; organics)</th>
<th>Toxicity Reduction</th>
<th>Mobility Reduction</th>
<th>Volume Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capping</td>
<td>1-3</td>
<td>+</td>
<td>«</td>
<td>+</td>
<td>+</td>
<td>«</td>
<td>+</td>
<td>«</td>
<td>+</td>
<td>«</td>
</tr>
<tr>
<td>Subsurface Barriers</td>
<td>1-3,5</td>
<td>+</td>
<td>«</td>
<td>+</td>
<td>+</td>
<td>«</td>
<td>+</td>
<td>«</td>
<td>+</td>
<td>«</td>
</tr>
<tr>
<td>Solidification/Stabilization Ex situ</td>
<td>1-3,5</td>
<td>•</td>
<td>•</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>«</td>
<td>+</td>
<td>«</td>
</tr>
<tr>
<td>Solidification/Stabilization In situ</td>
<td>1,2,4,6</td>
<td>+</td>
<td>•</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>«</td>
<td>+</td>
<td>«</td>
</tr>
<tr>
<td>Vitrification Ex situ</td>
<td>1-3,5</td>
<td>«</td>
<td>+</td>
<td>•</td>
<td>•</td>
<td>+</td>
<td>+</td>
<td>«</td>
<td>+</td>
<td>«</td>
</tr>
<tr>
<td>Vitrification In situ</td>
<td>1-3,7</td>
<td>«</td>
<td>+</td>
<td>•</td>
<td>•</td>
<td>+</td>
<td>+</td>
<td>«</td>
<td>+</td>
<td>«</td>
</tr>
<tr>
<td>Chemical Treatment</td>
<td>2</td>
<td>-</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Permeable Treatment Walls</td>
<td>2</td>
<td>-</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>«</td>
</tr>
<tr>
<td>Biological Treatment</td>
<td>1-5</td>
<td>+</td>
<td>«</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>«</td>
</tr>
<tr>
<td>Physical Separation</td>
<td>1-6</td>
<td>•</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>«</td>
<td>«</td>
<td>+</td>
</tr>
<tr>
<td>Soil Washing</td>
<td>1-3,5,7</td>
<td>•</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>•</td>
<td>«</td>
<td>«</td>
</tr>
<tr>
<td>Pyrometallurgical Extraction</td>
<td>1-5,7</td>
<td>«</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>«</td>
<td>«</td>
<td>«</td>
</tr>
<tr>
<td>In situ Soil Flushing</td>
<td>1,2,7</td>
<td>+</td>
<td>«</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>«</td>
</tr>
<tr>
<td>Electrokinetic Treatment</td>
<td>1-6</td>
<td>•</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>«</td>
<td>«</td>
<td>+</td>
</tr>
</tbody>
</table>

1-Lead, 2-Chromium, 3-Arsenic, 4-Zinc, 5-Cadmium, 6-Copper, 7-Mercury
+ Good, • Average, « Marginal, - Inadequate Information

Source: Remediation of Metals - Contaminated Soils and Groundwater, GRWTAC
Technology Review and Performance

Pemeable Reactive Barrier (PRB) Applications (2000)
In Situ/Ex Situ Chemical Reduction - Principles

• Introduction of a reducing material or generating reducing species to help degrade toxic organic compounds or immobilize metals in the desired area
• The most commonly used reductant is zero valent iron (ZVI)
• Possible introduction of organic substrates to produce enhanced conditions to conduct microbial reduction
• Degradation / Immobilization of contaminants by abiotic or biotic processes

Source: EPA
Chemical Reduction Advantages

• Low Cost and Efficient. Sustainable Technology.
• Uses existing natural processes and groundwater flow.
• Easy to implement and using non dangerous material.
• Can be used by itself and with other treatment technology to remediate soils and groundwater.
Dissolved Metal Fate (Remediation) Controls

- Depending on their aqueous form, the mobility of trace metals in groundwater is affected by various chemical reactions, including:
  - dissolution-precipitation,
  - oxidation-reduction,
  - adsorption-desorption and complexation.

- Precipitation, sorption, and ion exchange reactions can retard the movement of metals in groundwater and at the same time serve as remediation (stabilization) mechanisms.
Chemical Reduction
Cr precipitation using ZVI

\[
\begin{align*}
\text{CrO}_4^{2-} (aq) + \text{Fe}^0 + 8\text{H}^+ (aq) & \rightarrow \text{Fe}^{3+} + \text{Cr}^{3+} (aq) + 4\text{H}_2\text{O} \\
(\alpha)\text{Cr}^{3+} (aq) + (1-\alpha)\text{Fe}^{3+} (aq) + 2\text{H}_2\text{O} & \rightarrow \text{Cr}_\alpha\text{Fe}_{1-\alpha}\text{OOH}_\alpha (aq) + 3\text{H}^+ (aq)
\end{align*}
\]
Adsorption-Desorption: Divalent metals

Important adsorptive solids:
- Hydrous oxides of iron or manganese
- Clay minerals
- Organic matter

Graph showing adsorption-desorption of Pb, Cu, Zn, and Cd at different pH levels.

- Metal Concentration = 0.125 mM
- I = 1.0M NaNO₃
- Fe gel = 0.093M Fe
Co-precipitation/adsorption of Arsenic in the presence of dissolved Fe and S

From Craw et al. (2003)
Precipitate Stability using hydroxide or sulfide

Reference
EPA 625/8-80-003
# Precipitate Stability

## Theoretical Solubilities of Selected Metals in Pure Water at 25 °C (mg/L)

<table>
<thead>
<tr>
<th>Metal</th>
<th>As Hydroxide</th>
<th>As Sulfide</th>
<th>As Carbonate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium (Cd(^{2+}))</td>
<td>$2.3 \times 10^{-5}$</td>
<td>$6.7 \times 10^{-10}$</td>
<td>$1.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>Chromium (Cr(^{3+}))</td>
<td>$8.4 \times 10^{-4}$</td>
<td>No precipitate</td>
<td>—</td>
</tr>
<tr>
<td>Cobalt (Co(^{2+}))</td>
<td>$2.2 \times 10^{-1}$</td>
<td>$1.0 \times 10^{-8}$</td>
<td>—</td>
</tr>
<tr>
<td>Copper (Cu(^{2+}))</td>
<td>$2.2 \times 10^{-2}$</td>
<td>$5.8 \times 10^{-18}$</td>
<td>—</td>
</tr>
<tr>
<td>Iron (Fe(^{2+}))</td>
<td>$8.9 \times 10^{-1}$</td>
<td>$3.4 \times 10^{-5}$</td>
<td>—</td>
</tr>
<tr>
<td>Lead (Pb(^{2+}))</td>
<td>2.1</td>
<td>$3.8 \times 10^{-9}$</td>
<td>$7.0 \times 10^{-3}$</td>
</tr>
<tr>
<td>Manganese (Mn(^{2+}))</td>
<td>1.2</td>
<td>$2.1 \times 10^{-3}$</td>
<td>—</td>
</tr>
<tr>
<td>Mercury (Hg(^{2+}))</td>
<td>$3.9 \times 10^{-4}$</td>
<td>$9.0 \times 10^{-20}$</td>
<td>$3.9 \times 10^{-2}$</td>
</tr>
<tr>
<td>Nickel (Ni(^{2+}))</td>
<td>$6.9 \times 10^{-3}$</td>
<td>$6.9 \times 10^{-8}$</td>
<td>$1.9 \times 10^{-1}$</td>
</tr>
<tr>
<td>Silver (Ag(^{+}))</td>
<td>13.3</td>
<td>$7.4 \times 10^{-12}$</td>
<td>$2.1 \times 10^{-1}$</td>
</tr>
<tr>
<td>Tin (Sn(^{2+}))</td>
<td>$1.1 \times 10^{-4}$</td>
<td>$3.8 \times 10^{-8}$</td>
<td>—</td>
</tr>
<tr>
<td>Zinc (Zn(^{2+}))</td>
<td>1.1</td>
<td>$2.3 \times 10^{-7}$</td>
<td>$7.0 \times 10^{-4}$</td>
</tr>
</tbody>
</table>
# ZVI and Carbon Substrates Metals Treated and Mechanisms

<table>
<thead>
<tr>
<th>Contaminant, metals and metalloids</th>
<th>Treatment Mechanisms in the ZVI-Carbon ISCR zone</th>
</tr>
</thead>
</table>
| As (III, V)                       | • Reductive precipitation with oxidized iron minerals  
                                         • Precipitation as As sulfide and mixed Fe-As sulfide |
| Cr(VI), Mo(VI), Se (IV,VI), U(VI) | • Reductive precipitation with oxidized iron minerals  
                                         • Adsorption to iron oxides |
| Me^{2+} (Cu, Zn, Pb, Cd, Ni)      | • Metal cations precipitate as sulfides, following stimulated heterotrophic microbial sulfate reduction to sulfide  
                                         • Adsorption to iron corrosion products (e.g.; iron oxides and oxyhydroxides) |
## Summary of Treatment Efficiencies Observed in Internal Lab Tests

<table>
<thead>
<tr>
<th>Compound</th>
<th>Influent Concentration Range (ug/L)</th>
<th>Observed Removal Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antimony</td>
<td>24,500</td>
<td>&gt;99</td>
</tr>
<tr>
<td>Arsenic</td>
<td>500</td>
<td>98</td>
</tr>
<tr>
<td>Cadmium</td>
<td>11</td>
<td>&gt;99</td>
</tr>
<tr>
<td>Chromium</td>
<td>200</td>
<td>&gt;99</td>
</tr>
<tr>
<td>Cobalt</td>
<td>210</td>
<td>&gt;99</td>
</tr>
<tr>
<td>Copper</td>
<td>86</td>
<td>&gt;99</td>
</tr>
<tr>
<td>Lead</td>
<td>64,000</td>
<td>&gt;99</td>
</tr>
<tr>
<td>Nickel</td>
<td>350</td>
<td>&gt;99</td>
</tr>
<tr>
<td>Zinc</td>
<td>50,400</td>
<td>92</td>
</tr>
</tbody>
</table>
## Summary of Removal Efficiencies Observed in the Field

<table>
<thead>
<tr>
<th>Location</th>
<th>Compounds Treated</th>
<th>Baseline Conc. (µg/L)</th>
<th>Post Treatment Conc. (µg/L)</th>
<th>Removal Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Washington, USA</td>
<td>Chromium(VI)</td>
<td>165</td>
<td>&lt;5</td>
<td>&gt;97%</td>
</tr>
<tr>
<td></td>
<td>TCE</td>
<td>6.1</td>
<td>&lt;0.5</td>
<td>&gt;92%</td>
</tr>
<tr>
<td>Ontario, Canada</td>
<td>Copper</td>
<td>120</td>
<td>10</td>
<td>92%</td>
</tr>
<tr>
<td></td>
<td>Cobalt</td>
<td>260</td>
<td>40</td>
<td>85%</td>
</tr>
<tr>
<td></td>
<td>Nickel</td>
<td>320</td>
<td>70</td>
<td>78%</td>
</tr>
<tr>
<td>Sao Paulo, Brazil</td>
<td>Lead</td>
<td>306</td>
<td>&lt;10</td>
<td>&gt;97%</td>
</tr>
<tr>
<td>Florida, USA</td>
<td>Arsenic</td>
<td>550</td>
<td>&lt;10</td>
<td>&gt;98%</td>
</tr>
</tbody>
</table>
Using In Situ Chemical Reduction (ISCR) for Metals Toxicity and/or Mobility Reduction in Groundwater

Zero Valent Iron (ZVI (40%) + Solid Organic Carbon (50%) + Soluble Organic Carbon (10%) for In-situ integrated biological and chemical reduction (ISCR)

- Major, minor, and micro nutrients are provided
- Balances acidity (Volatile Fatty Acids -VFAs) and alkalinity (ZVI) to prevent acidification of groundwater
- Formulated for injectability
- Product adds sulfate salts and sulfide sources (K and Mg sulfate)
- Very long life from 36 to 72 months
Synergy Carbon + ZVI

US Patents W.R. Grace & Company / ADVENTUS
ISCR ZVI + Carbon Treatment Mechanisms

- Direct Chemical Reduction
  - Water table
  - Injection layers
  - Groundwater flow

- Indirect Chemical Reduction

- Stimulated Biological Reduction

- Enhanced Thermodynamic Decomposition
In Situ Strategy Intervention

**Source Area/Hotspot Treatment**

Dosing: 0.15 to 1% wt/wt
Spacing: 5 to 15 ft (DPT)

**Injection PRB for Plume Control**

Dosing: 0.4 to 1% wt/wt
Spacing: 5 to 10 ft (DPT)

**Plume Treatment**

Dosing: 0.05 to 0.2% wt/wt
Line Spacing: based on 1 year g.w. travel distance
Influence of ZVI + Carbon Substrates on Aquifer Eh Conditions

60 ft (18 m) injection zone

- Upgradient of Injection Zone
- 10 ft (3 m) Into Injection Zone
- Centre of Injection Zone (30 ft; 9 m)
- 10 ft (3 m) Downgradient of Injection Zone

Eh (mV)

Flow Direction

Source: URS
Installation Methods

- **Direct Placement:**
  - Trenching
  - Excavations
  - Deep soil mixing

- **Injection Methods:**
  - Direct injection
  - Well injections (EHC-A)
  - Hydraulic fracturing
  - Pneumatic fracturing
  - Jetting
Design and Field Measurements Requirement

- Total concentration in soil and groundwater of targeted metals
- Dissolved (field filtered) metals concentrations
- pH, Redox Potential (Eh), Dissolved Oxygen
- Cation scan (calcium, sodium, magnesium, silicon)
- Anion Scan (chloride, sulfate, nitrate)
- Total Organic Carbon (TOC), Dissolved Organic Carbon (DOC)
- Alkalinity

These parameters are used to assess the applicability of an ISCR approach and for optimizing the application rate. The same parameters are also recommended monitoring parameters.
Design Considerations ZVI + CS

Are metal levels/mass fluxes and general chemistry amenable to ISCR treatment?

- PRB or Plume treatment?
  - Sufficient SO₄ present?
    - Is pH buffer needed (carbonate-based preferable for Me²⁺)?

Dose Calculation to create sulfate reducing conditions*

Dose Calculation for sufficient distribution and residence time**

* Terminal electron demand in the calculator
** Guidelines in the calculator
Bench Scale Laboratory testing

- Site groundwater and aquifer material needs to be used.
- Proper sampling and sample handling is essential to avoid sample alteration (aeration) that may result in testing artifacts.
- Flow through column tests are preferable to batch test.
- Field pilot-scale test are strongly recommended as a feasibility step, either following the lab evaluation or stand alone, for As treatment especially.
In Conclusion
Field Applications of ZVI + Carbon Substrate (CS)

• Over 50 world-wide (pilot and full-scale)
• Target concentrations met for various metals including Cr(VI), divalent metals, arsenic
• VOCs present also treated
• Case studies
  • Brazil (Pb)
  • Illinois (Cr, Ni)
  • Ontario (Cu, Ni, Zn)
ZVI + CS
ISCR Groundwater Treatment

CASE STUDY #1
Industrial Site, Rio de Janeiro, Brazil
Full-Scale Application
(March 2011)

• 11,200 kg ZVI+CS injected into a total of 73 points spaced 3 to 4 m apart.
• Application rate of 0.2% ZVI+CS by soil mass.
• Mg(OH)$_2$ added to ZVI+CS slurry to increase the pH.
Injection set-up
Betomaq grout mixer (model MV 100) ~42% Slurry

The ZVI+CS slurry was continuously prepared on site using a grout mixer, targeting approximately 42% solids.

The slurry was purposefully mixed thicker than normal (e.g., 29% solids) to limit surfacing during injection.
Gravity feed of slurry to grout pump

Injection pressures were generally below 50 psi at an injection flow rate of 20 L/min.
## Results

### Effect on Dissolved Pb and Geochemistry

<table>
<thead>
<tr>
<th></th>
<th>PM-10</th>
<th>PM-01</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Baseline Nov 2010</td>
<td>~1 year April 2012</td>
</tr>
<tr>
<td>Dissolved Pb (ug/L)</td>
<td>113</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>pH</td>
<td>4.45</td>
<td>7.15</td>
</tr>
<tr>
<td>DO (mg/L)</td>
<td>0.8</td>
<td>1.1</td>
</tr>
<tr>
<td>ORP (mV)</td>
<td>369</td>
<td>-381</td>
</tr>
</tbody>
</table>

April 29, 2014
ZVI + Carbone

Case Study 2
Industriel Site, Ontario, Canada
Case Study 2
Trace metal groundwater plume

<table>
<thead>
<tr>
<th>Case Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Location</td>
</tr>
<tr>
<td>Type of Site</td>
</tr>
<tr>
<td>Description of Impacts</td>
</tr>
<tr>
<td>Objective and Approach</td>
</tr>
</tbody>
</table>
ZVI + CS injections along site boundary cut off plume of dissolved cobalt, nickel and copper
Installation method - Ontario site

- Total of 600 kg ZVI + CS injected into area measuring 9 m L x 7 m wide x 7 m deep (0.08% to soil mass).
- ZVI + CS slurry injected via open bore holes using packers - total of 12 locations.
- Reactive gas also added to facilitate anaerobic conditions.
Field Results - Ontario site

- Sulphate reducing conditions (Eh<-250 mV) achieved in days
- Remediation objectives were met for all metals
- Regulatory approval was obtained.

(Courtesy of Vertex Environmental Solutions)
Acknowledgement

- FMC Environmental Solutions
- Vertex Environmental
- USEPA
- ITRC

Thank you for your attention!

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