Chemical Fixation of Priority Heavy Metals in Soil, Sediment and Groundwater using MetaFix™ Reagents

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Presentation Outline

• Chemical Reduction for Metals
• Approaches to Metals Treatment
• Useful Reductants – Identity, Efficacy, Longevity
• Examples of Heavy Metal Treatment with ISCR Approaches
• Questions?
Definition of In Situ Chemical Reduction

How Does It Work?

When reducing agents are added to contaminated soil and groundwater, a chemical reaction occurs that changes contaminants into other forms. For example, a very toxic form of chromium called “hexavalent chromium,” or “chrome 6,” can be changed to chrome 3 when reducing agents are injected into contaminated groundwater. Chrome 3 is a much less toxic form of the metal. Chrome 3 is also less mobile because it does not dissolve as easily in water.

Common reducing agents include zero valent metals, which are metals in their pure form. The most common metal used in ISCR is zero valent iron, or “ZVI.” ZVI must be ground up into small granules for use in ISCR. In some cases, micro- or nano-scale (extremely small)

Illustration of the treatment of contaminated water with a PRB made of ZVI.

EPA 542-F-12-012

......transfer of e⁻ from reducing agent to contaminant

...... as well as sulfides, iron sulfides, and other minerals activated with ferrous iron.
Recognized Treatment Mechanisms for Heavy Metals in Soil and Groundwater

<table>
<thead>
<tr>
<th>Metal</th>
<th>Precipitation as Metal Hydroxides or Iron Metal Hydroxides</th>
<th>Precipitation as Metal sulfides/Iron Metal Sulfides</th>
<th>Adsorption on or Co-precipitation with Iron Corrosion Products</th>
<th>Precipitation as Metal Carbonates</th>
<th>Adsorption of organo-metal species PAC/GAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>As (III, V)</td>
<td>●</td>
<td>○</td>
<td>●</td>
<td>•</td>
<td>●</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>●</td>
<td></td>
<td>●</td>
<td>•</td>
<td></td>
</tr>
<tr>
<td>Pb, Cd, Ni</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
</tr>
<tr>
<td>Cu, Zn</td>
<td>●</td>
<td></td>
<td>●</td>
<td>•</td>
<td></td>
</tr>
<tr>
<td>Se</td>
<td>●</td>
<td></td>
<td>●</td>
<td>•</td>
<td></td>
</tr>
<tr>
<td>Hg</td>
<td>●</td>
<td></td>
<td>●</td>
<td>•</td>
<td>●</td>
</tr>
</tbody>
</table>

Ammonium and cyanide can interfere with precipitation of copper
Cyanide can interfere with precipitation of cadmium
Mercury and nickel organic complexes can be resistant to reductive precipitation
Abiotic reductants that have been studied very thoroughly include:

1. Elemental iron (ZVI), most commonly and usefully in micro-scale form.

2. Minerals (or their amorphous analogs) that derive reducing properties from \( \text{Fe}^{II} \). These include magnetite, green rust, ferruginous clays (i.e., nontronite), iron oxides with adsorbed \( \text{Fe}^{II} \), and possibly minerals commonly associated with basalt.

3. Minerals (or their amorphous analogs) deriving their reducing properties from \( \text{S}^{-II} \) (or \( \text{S}^{-I} \)) as well as \( \text{Fe}^{II} \). The most-studied such minerals are mackinawite and pyrite, but other \( \text{Fe}^{II} \) and \( \text{S}^{-II/-I} \) phases of possible significance include greigite, marcasite, and amorphous \text{FeS}.

4. Organic matter with redox-active functional groups (e.g., quinones): example is Cr(VI) reduction in aerobic soils with substantial organic matter.
Materials that Mediate Abiotic Reduction, Adsorption, and Precipitation of Heavy Metals

Heavy metals can be reduced by ZVI and a variety of reactive minerals

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

Pyrite (FeS$_2$)  Magnetite(Fe$_3$O$_4$)  Mackinawite (Fe$_{(1+x)}$S)
Do reactive minerals really work as reductants?
Chromium Reduction by Iron Sulfide

Table 2
Cr(VI) reduction by iron sulfide with initial Cr(VI) concentrations of 10 mM and 0.5 g FeS

<table>
<thead>
<tr>
<th>pH</th>
<th>Cr(VI)$_{o}$ (mM)</th>
<th>Cr(VI)$_{f}$ (mM)</th>
<th>Cr(III)$_{f}$ (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>10.0</td>
<td>0.780</td>
<td>9.22</td>
</tr>
<tr>
<td>5</td>
<td>10.0</td>
<td>0.920</td>
<td>9.08</td>
</tr>
<tr>
<td>7</td>
<td>10.0</td>
<td>0.931</td>
<td>9.07</td>
</tr>
</tbody>
</table>

0.5 g FeS/50 mL solution; 4 h incubation; >90% reduction over a broad pH range
How long will reactive minerals last?
Influence of pH on Fe$^{+2}$ release from FeS

Upflow columns packed with FeS coated sand. Effluent Fe$^{+2}$ between 1 µg/L and 5 µg/L. Indicates that thin layers of FeS will last for 16 years under the pH 5.5 condition and 15 cm/day GW velocity. About 2% Fe released over 60 PV.

Hayes et al., 2009. SERDP ER-1375
Approaches to Metals Treatment

- Alkaline treatment approaches that rely on formation of heavy metal hydroxides are well-understood, well-proven, and can be relatively inexpensive.

- In general, heavy metal hydroxides are stable under alkaline to neutral conditions, however, they have higher solubility than metal sulfides or heavy metal iron sulfides.

- ISCR treatment approaches based on iron, iron sulfides, and other iron-bearing minerals have not been as widely-applied, and are less established.

- Treatment mechanisms based on iron, iron sulfides, and other iron-bearing minerals have advantages due to lower solubility and greater stability of iron-bearing, and iron-sulfide bearing heavy metal mineral precipitates over a range of pH.

- When selecting the treatment chemistry for heavy metals, one should consider (a) the remedial goals, (b) the oxidation state, and (c) the pH of the environment to be treated. Consider both present and potential future conditions – when determining whether treatments that form heavy metal oxides or heavy metal sulfides/iron sulfides are more appropriate.
Background: ZVI + Carbon + Sulfate Approach

- The established PeroxyChem reagent for metals treatment is EHC® Metals.
- It is composed of micro-scale ZVI (30%), sulfate salts (30%), slow-release solid organic carbon (30%), and soluble organic carbon (10%).
- Promotes reduction, precipitation, and adsorption of heavy metals.
- The efficacy of EHC Metals is based on: (a) creation of strong reducing conditions through iron corrosion and microbial oxygen consumption, (b) fermentation of provided organic carbon, (c) release of ferrous iron from ZVI, and (d) microbial sulfate reduction to produce iron sulfide mineral precipitates.
- Provides the “building blocks” needed to ensure that that Fe\(^{+2}\), sulfide, pH, and redox state are adequate.
- Activate indigenous non-reactive minerals (even clays) into reactive minerals and create new reactive minerals.
- Proven to be very effective on many metals including Cr(VI), As, Cu, Zn, Pb, and Ni.
## Metals Treated and Mechanisms for EHC-M

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Treatment Mechanisms in the ZVI-Carbon zone</th>
</tr>
</thead>
<tbody>
<tr>
<td>As (III, V)</td>
<td>Reductive precipitation with oxidized iron minerals. Precipitation as As sulfide and mixed Fe-As sulfide</td>
</tr>
<tr>
<td>Cr(VI), Mo(VI), Se(IV,VI), U(VI)</td>
<td>Reductive precipitation with iron minerals and adsorption to iron oxides.</td>
</tr>
<tr>
<td>Me$^{2+}$ (Cu, Zn, Pb, Cd, Ni)</td>
<td>Metal cations precipitate as sulfides, following stimulated heterotrophic microbial sulfate reduction to sulfide. Adsorption to iron corrosion products (e. g.; iron oxides and oxyhydroxides).</td>
</tr>
</tbody>
</table>
Field Applications of EHC®-M

- Over 30 world-wide (pilot and full-scale)
- Target concentrations met for various metals including Cr(VI), divalent metals, arsenic
- VOCs present simultaneously treated
- Case study: Illinois (Cr, Ni)
# Case Study
## EHC-M for Cr(VI) and Ni Immobilization

### Case Description

<table>
<thead>
<tr>
<th>Location</th>
<th>Midwest US</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of Site</td>
<td>Active industrial</td>
</tr>
<tr>
<td>Description of Impacts</td>
<td>Dissolved metal plume measuring 250 ft long x 150 ft wide x 10 ft deep (from 13 to 23 ft bgs.)</td>
</tr>
<tr>
<td>Objective and Approach</td>
<td>Pilot test followed by full-scale injection of EHC-M.</td>
</tr>
</tbody>
</table>
Results - Pilot test

CR-1 Concentrations of Metals in Groundwater versus Time

- Total Chromium
- Hexavalent Chromium
- Nickel

EHC-M injection

[Graph showing concentration changes over time for different metals]
Full-scale Injection design

- 450 lb of EHC-M injected at each location (0.5% to soil mass).
- Spacing of 8 to 10 ft between injection points.
- Monitoring at two wells: PMW-9 and PMW-10.
Results - Full-scale

PMW-9 Concentrations of Metals in Groundwater versus Time

EHC-M injection
Results - Full-scale

PMW-10 Concentrations of Metals in Groundwater versus Time

- EHC-M injection

Comparison of dissolved chromium, hexavalent chromium, and dissolved nickel concentrations over time.
More Background: Acute Toxicity

- The building blocks approach (ZVI + carbon + sulfate) has proven to be effective, but………..

- Some sites/soils/wastes that need treatment for heavy metals have high acute microbial toxicity.

- Treatment approaches that rely on microbial processes, including EHC® Metals, may not function well in an acutely toxic matrix because carbon fermentation, oxygen consumption, and sulfate reduction can be slowed or inhibited.

- Thus, a metals treatment reagent approach that does not depend on microbial activity could be advantageous.

- Treatment mechanisms based on iron, iron sulfides, and other iron-bearing minerals have significant advantages due to lower solubility and greater stability of iron-bearing, and iron-sulfide bearing heavy metal mineral precipitates.

- Could we treat heavy by providing already-formed reductants and adsorbents?
A New ISCR Approach to Treatment of Heavy Metals

• New reagents based on mixtures of ZVI, iron sulfides, iron oxides, pH regulators, adsorbents, and ion exchangers.

• Create a robust multi-mechanism environment for reduction, adsorption, precipitation, and sequestration of heavy metals.

• Applicable to treatment of soil, groundwater, and industrial wastes.

• Effective in acutely toxic environments including those created by high concentrations of heavy metals, organics, and salts.

• Applied in low dosages – typically between 0.5% to 4% w/w.
Approach: ISCR (Abiotic Iron-Sulfide)

- Does not rely on microbial processes
- Provide source of ferrous iron
- Provide iron sulfides and iron oxides
- Solid formulation so requires direct push
- Easy Handling, Neutral pH, minimal health & safety issues
- Longevity: high (years+)
Independent Evaluation of ISCR for Heavy Metals
MetaFix™ Reagent

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Independent Evaluation of ISCR for Metals
MetaFix™ Reagent

- Bench-scale treatability studies on soil and groundwater impacted with chromium VI (Cr\(^{+6}\), commonly referred to as “hexavalent Cr”) and nickel (Ni) associated with historical plating operations at a site located in Michigan. The treatability study was completed in two phases.

- The first phase of the study consisted of a series of batch reactors with the reagents to test their effectiveness in reducing groundwater concentrations of the metals and reducing future leaching of the metals. The purpose of the batch studies was to determine amendments and amendment doses that might be suitable for treatment of the source area. The “leachability” of Cr\(^{+6}\) and Ni in soil samples was measured using the Synthetic Precipitation Leaching Procedure (SPLP).

- The second phase of the study tested a subset of the amendments using flow-through column reactors, selected based on their performance in the batch tests. The purpose of the column reactors was to evaluate selected amendments for their potential to be used in a permeable reactive barrier (PRB) near the Site boundary, designed to reduce dissolved phase Cr\(^{+6}\) and Ni groundwater impacts at the Site.
Phase 1: Batch Reactor Study Procedure

• The set-up of each of the reactors consisted of the adding approximately 1 kg (~500 mL) of soil and 200 mL of groundwater in 1 L glass vessels.

• These relative amounts of soil and groundwater are intended to allow the pores of the soil to be saturated without leaving a layer of standing water on top.

• The doses of amendments were then added and mixed into the soil by hand.

• The vessels were covered during the 20-day reaction period to minimize evaporation of the pore water.

• All of the various amendments and dosages were allowed to react for 20 days before analyzing the soils.
Independent Evaluation of MetaFix™
Phase I Chromium Results

Bench-scale Reactor Study Results
Meta-Fix® and Control
Former Plating Site

Day 20 Results: 79.3 mg/L, 11.4 mg/L and 3.3 mg/L
Independent Evaluation of MetaFix™
Phase I Chromium Results

Bench-scale Reactor Study Results
Calcium Polysulfide (CaPS) and Control
Former Plating Site

Day 20 Results: 79.3 mg/L, 13.4 mg/L and 4.1 mg/L
Independent Evaluation of MetaFix™
Phase I Nickel Results

Bench-scale Reactor Study Results
Meta-Fix® and Control
Former Plating Site

Day 20 Results: 31.9 mg/L, 6.4 mg/L and 2.1 mg/L
Day 20 Results: 31.9 mg/L, 12.1 mg/L and 8.4 mg/L
## Independent Evaluation of MetaFix™
### Phase I ORP and pH Results

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Reactor Description</th>
<th>Dose</th>
<th>pH-Day 20</th>
<th>ORP-day 20 (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1 (Control)</td>
<td>Control (nothing added)</td>
<td>nothing</td>
<td>6.4</td>
<td>147</td>
</tr>
<tr>
<td>R2 (1% Meta-Fix™)</td>
<td>Low dose of MetaFix™</td>
<td>1.0% (0.5% on day 0, 0.5% on Day 10)</td>
<td>6.6</td>
<td>139</td>
</tr>
<tr>
<td>R3 (5% Meta-Fix™)</td>
<td>High dose of MetaFix™</td>
<td>5.0% (2.5% on day 0, 2.5% on Day 10)</td>
<td>6.5</td>
<td>163</td>
</tr>
<tr>
<td>R8 (50mL CaPS)</td>
<td>Low dose of Calcium Polysulfide</td>
<td>50 mL/kg</td>
<td>8.2</td>
<td>-169</td>
</tr>
<tr>
<td>R9 (250mL CaPS)</td>
<td>High dose of Calcium Polysulfide</td>
<td>250 mL/kg</td>
<td>9.4</td>
<td>-241</td>
</tr>
</tbody>
</table>
Independent Evaluation of MetaFix™
Phase II

Phase 2: Flow-Through Column Study Procedure

• Each of the columns was 1 foot (ft.) in length and 1-inch (in.) in diameter made of PVC pipe. The columns were equipped with sampling ports at mid-column and effluent locations (i.e., 0, 6, and 12 in., respectively.

• Low-flow pumps were fitted to each of the columns and the flow rate of water through the columns was established at an initial rate of 0.19 liter (L)/day. The initial column flow rate is equivalent to an assumed groundwater flow velocity of 1.2 ft./day, which is representative of groundwater flow velocities historically reported at the Site.

• After calibrating the pumps, five (5) x 155 mL aliquots of homogenized soil (site-specific) were placed in clean 500 mL beakers and mixed with groundwater and the required amount of the reagents. For the control column only mixed soil was added, with no reagent.

• Each of the flow-through columns contained approximately 300 grams (g) of soil. The columns were carefully packed from the bottom up by placing approximately 2 in. of soil into the column at a time and gently tamping down the soil to provide for a consistent flow field through the column.

• As soon as each of the flow-through columns were charged, the groundwater pumps were turned on and replacement of pore waters in the columns began using site-specific groundwater, which was collected from an existing groundwater monitoring well at the Site.
Phase II Flow-through Columns
Independent Evaluation of MetaFix™
Phase II Chromium Results: Control

Bench-scale Column Study Results Summary
Control Column Cr⁺⁶ Concentration [µg/L]

Column Flow Rate Reduced 50% on Day 20
Independent Evaluation of MetaFix™
Phase II Chromium Results: MetaFix™

Bench-scale Column Study Results Summary
MetaFix™ Column Cr⁺⁶ Concentration [µg/L]

Column Flow Rate Reduced 50% on Day 20
Extended to 70 Days
Independent Evaluation of MetaFix™
Phase II Chromium Results: Control

Bench-scale Column Study Results Summary
Control Column Ni Concentration [µg/L]

Column Flow Rate Reduced 50% on Day 20

Days: Day1, Day3, Day6, Day9, Day12, Day16, Day19, Day20, Day21, Day22, Day23, Day24, Day25, Day28, Day32, Day40, Day50, Day60, Day70
Independent Evaluation of MetaFix™
Phase II Chromium Results: MetaFix™

Bench-scale Column Study Results Summary
MetaFix™ Column Ni Concentration [µg/L]

Column Flow Rate Reduced 50% on Day 20
Ex-situ treatment of Lead-impacted industrial process waste in United States

TCLP lead reduced from 11.7 mg/L to 0.22 mg/L

- Direct soil mixing with excavator
- MetaFix dosage at 2% w/w
- Soil water content set to 80% of WHC (wet, not saturated)
- 7 day treatment time
Selection of Treatment Approach

- Remedial Objectives (solubility of heavy metal precipitates)
- Site Type (plume, source, both)
- Site Conditions (pH, Eh, now, expected)
- COI Present (arsenic, mixed metals and organics?)
- Acute microbial toxicity
- Concern with rebound? (solubility and stability of precipitates)
- Treatment time vs. Treatment longevity
Cost Information

• Dosages between 0.5% and 4% (w/w) are expected to be adequate for most applications to soil, sediment, and other solid materials where the remedial goals are based on TCLP.

• This means that reagent costs will be between $10 and $80/ton of treated soil.

• Dosages between 0.1% and 1% (w/w) are expected for most *in situ* groundwater treatment applications.

• This means that reagent cost will be between $4 and $40 cubic yard of *in situ* reactive zone.
Next Steps

• Low cost bench-scale treatability studies on soil, groundwater, sediment samples from sites.

• $2,000 per sample for evaluation of three MetaFix reagents at two doses along with an untreated control.

• TCLP, SPLP, or groundwater leachate at the discretion of the client.

• Pilot-scale demonstrations will be supported by PeroxyChem.
Chemical Fixation of Priority Heavy Metals

Comments and Questions are Welcome!

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