Subsurface Distribution of ZVI/EHC Slurry – Validating Radius of Influence

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Presentation Objective / Outline

To empirically summarize our experience from a range of EHC injection projects and provide an overview of various methods applied to verify subsurface EHC distribution, including:

• Visual observation of fractures in soil cores
• Magnetic separation of the ZVI portion of EHC from soil cores
• Electrical conductivity probing
• Monitoring of ground deformation using uplift stakes or tilt meters
• Trenching
• Groundwater Indicator Parameters
Amendment Background

EHC composition:

- *ca.* 40% micro-scale zero valent iron (50 - 150 µm)
- *ca.* 60% fine-grained processed plant fiber particles

Injection methods:

- Direct push, hydraulic and pneumatic fracturing.
- Normally injected as a slurry with 20 to 35% solids.
## ISCR Treatment Mechanisms

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<th>Mechanism</th>
<th>Component</th>
<th>Description</th>
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| **Direct Chemical Reduction**      | ZVI           | • Redox reaction at iron surface where solvent gains electrons and iron donates electrons  
|                                    |               | • Abiotic reaction via beta-elimination                                      |
| **Indirect Chemical Reduction**    | ZVI or Fe(II) | • Surface dechlorination by magnetite and green rust precipitates from iron corrosion |
| **Stimulated Biological Reduction**| Organic Carbon Substrate / H2 | • Anaerobic reductive dechlorination involving fastidious microorganisms  
|                                    |               | • Strongly influenced by nutritional status and pH of aqueous phase          |
Direct Chemical Reduction requires contact with ZVI particle

Extended Zone with Biological Reduction and Indirect Iron Effects

Advection and Dispersion

Diffusion between EHC seams

Bacteria

VFAs
Nutrients
Fe^{+2} H_{2}

H_{2} VFAs
Fe^{+2} H_{2} VFAs

Fe^{+2} H_{2} VFAs
Methods to Determine ROI

Soil Coring

EHC injection point

Sampling locations
• EHC observed to displace into discrete bands.
• Horizontal and vertical fractures observed during coring.
Verification of ZVI / TOC Content in Soil Cores

- At sites with more permeable soils such as gravels or more coarse-grained non-cohesive sands, soil coring has often yielded little visual evidence of discrete EHC seams, suggesting that the EHC amendment has been distributed mainly via permeation into the aquifer matrix.

- When EHC seams cannot be visually identified, the EHC presence can be verified by analyzing the soil for ZVI and/or TOC:
  - Wet magnetic separation process
  - Laboratory analyses of TOC and iron
Wet Magnetic Separation Test

Water and soil mixed in bottle with magnet.

Control – shows no iron.

Core sample – iron indicates EHC presence.
ZVI Content Measured in Soil

- EHC injected from 6.5 to 20.5 ft bgs at an application rate of 0.3% EHC by soil mass (0.12% ZVI by soil mass)
- Soil cores collected 1.5 m from injection points
Hydraulic Profiling Tool

- The HPT uses a downhole transducer to simultaneously measure:
  - The pressure response of the soil to injection of water.
  - The electric conductivity (EC).

- Used to log soil type:
  - A low injection pressure and EC indicates a more permeable formation.
  - A high injection pressure and EC indicates finer grain sediments.
  - An anomaly in the graph with a simultaneous high EC and low pressure reading would indicate ZVI.
• Only thicker fractures were detected by HPT (0.5 to 5 cm).
• This method likely more efficient in homogeneous soils.
Monitoring of Ground Uplift

- When amendments are displaced into discrete seams, there is a disturbance in the subsurface as the fractures are propagated.
- It is possible to measure this disturbance by using uplift stakes or tilt meters.
- This evaluation method is commonly applied during hydraulic or pneumatic fracturing to estimate ROI.

EHC fractures in weathered rock following hydraulic fracturing
This method was used at Colorado site where EHC was injected into sandstone bedrock via hydraulic fracturing.

Majority of fractures propagated >30 ft, median fracture thickness ~8 mm (ranging from 1 to 40 mm).

Tilt meters positioned radially around the injection borehole.

The tilt meters continually measure any change in the tilt of the ground surface.

Data is analyzed using interpretation software to interpret the shape, thickness, extent and orientation of fractures.
• Uplift stakes are installed at ground surface and are measured before and after the injection using surveying equipment.
• Maximum uplift may range from a few mm to several cm - fracture aperture is always greater than the ground uplift due to compression of overburden soil.
• Uplift stakes usually don’t produce useful results at depths greater than 10 m or so, or in windy conditions.
Trenching following Hydraulic Fracturing

• For research purposes, trenches have been excavated following hydraulic fracturing to directly map fracture local and aperture (Murdoch, Clemson University / FRx Inc.).

• Actual fracture extent has generally been found to exceed the predictions from uplift data (FRx Inc.).

• In general, it has been found that material emplaced via hydraulic fracturing propagate primarily horizontally out to a distance greater than 5 m with a vertical rise of ca 1 m (FRx Inc.).
• Elevated levels of TOC and Fe confirms EHC presence
• A sharp drop in ORP and increase in EC is expected within the EHC injection zone → changes to these and other redox indicator parameters confirm EHC zone of influence.
• Response in EC and ORP have been observed in 24 hours within placement zone.
Dissolved Fe Measured Within and Downgradient from EHC Injection Zones
TOC Measured Within and Downgradient from EHC Injection Zones

![Graph showing TOC measured at different locations over time.](image-url)
EHC Case Study – Source Area Treatment
Former Dry Cleaner, Oregon

• Primary CVOCs included chlorinated ethenes at concentrations up to:
  - PCE ~ 22,000 ug/L
  - TCE ~ 1,700 ug/L
  - DCE ~ 3,100 ug/L
  - VC ~ 7 ug/L

• Site-Specific Challenges:
  - Low permeability lithology – high degree of sorbed impacts expected
  - Large seasonal variation in groundwater table (range from ca 2.1 to 4.6 m bgs) → 2.5 m smear zone
  - Groundwater flow direction change with season
Test Injection using Direct Push
Displacement of liquid vs. solid amendments
Displacement of liquid vs. solid amendments: Direct push injection test
A total of 10,000 lbs (4,649 kg) of EHC was injected into 32 injection points targeting an area measuring 77 m² x 6 m deep (from 3 to 9 m bgs).

Application rate of 0.6% EHC to soil mass.

Figure from Hart Crowser.
EHC® Effect on Geochemistry

**Total Organic Carbon**

- X-axis: Time post EHC injection (months)
- Y-axis: Conc. (mg/L)

**ORP**

- X-axis: Time post EHC injection (months)
- Y-axis: ORP (mV)

**Dissolved Oxygen**

- X-axis: Time post EHC injection (months)
- Y-axis: Conc. (mg/L)

**Sulfate**

- X-axis: Time post EHC injection (months)
- Y-axis: Conc. (mg/L)

Legend:
- NW sampling cluster
- NE sampling cluster
- SW sampling cluster
- SE sampling cluster
EHC® Case Study Results

**NW sampling cluster**
- Concentration (ug/L)
- Time post injections (months)

**NE sampling cluster**
- Concentration (ug/L)
- Time post injections (months)

**SE sampling cluster**
- Concentration (ug/L)
- Time post injections (months)

**SW sampling cluster**
- Concentration (ug/L)
- Time post injections (months)
Increase in ethene & ethane confirms complete dehalogenation
Ethene levels of up to 760 ug/L measured in July 2007 (11-month data) → 96% increase compared with maximum baseline levels
Correlation observed between total CVOC concentrations and ethene plus ethane measured in GW following initial acclimatization period of 7 months
Summary of Results

• Most commonly, EHC has been found to distribute into discrete seams during direct injection, as would be expected when a solid material is injected into an aquifer at a pressure exceeding the combined lithostatic pressure and cohesive strength of the soil.

• Observed ROI:
  • Direct push: ~1.5 to 2.5 m
  • Fracturing: 3 to 20 m
  • Permeation (non-cohesive sands and gravels): ~1.5 m
Complete degradation of targeted constituents has been achieved at numerous sites where the distribution could be viewed as “non-homogenous”

Uniform distribution is NOT required during injection, but rather the creation of a sufficiently uniform network of “reagent seams”.