Development and Field Trials of a New 100% Soluble Carbon-Iron Product for In Situ Remediation of Groundwater

Kerry Bolanos-Shaw, M.Sc.
Alan Seech, Ph.D.
Andrzej Przepiora, M.Sc., P.Geo.

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Outline of Presentation

- Overview of EHC® *in situ* reductive groundwater treatment product.
- Discussion of reasons for developing EHC®-L and the R&D process.
- Description of the resulting EHC-L product and explanation of how it works.
- Discussion of initial field applications and field data.
EHC® : In Situ Reductive Groundwater Treatment

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
- Zero valent iron (ZVI) provides direct contact chemical reduction and downgradient ferrous iron reactive sites
- Combination of carbon and iron results in very strong reducing conditions
- Very long life from 36 to 72 months
- Emplaced in slurry form via direct push injection, hydraulic/pneumatic fracturing, trenching or soil mixing
### EHC®: In Situ Reductive Groundwater Treatment

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Material</th>
<th>Description</th>
</tr>
</thead>
</table>
| 1. Direct Chemical Reduction           | ZVI alone and EHC                 | • Redox reaction at iron surface where solvent gains electrons and iron donates electrons  
• Abiotic reaction via beta-elimination |
| 2. Indirect Chemical Reduction         | ZVI alone and EHC                 | • Surface dechlorination reactions mediated by magnetite and green rust precipitates formed from iron corrosion products |
| 3. Stimulated Biological Reduction     | Carbon alone and EHC              | • Anaerobic reductive dechlorination involving fastidious microorganisms  
• Strongly influenced by nutritional status and pH of aqueous phase |
| 4. Enhanced Thermodynamic Decomposition| EHC                              | • Energetics of dechlorination more favorable under lower redox conditions generated by combined ZVI corrosion + carbon fermentation (ΔG, Nernst equation, pH, Eh, T, P) |
EHC® PRB Case Study

- Plume extends 2,600 ft / 800 m from grain elevators.
- Discharges into small creek.
- The bedrock rises to an elevation of ca 9 ft / 3 m above the present day water table at the presumed source area.
- PRB installed down-gradient of suspected source area in April 2005.
- The PRB is installed as a line of injection points spaced approximately 10 ft / 3 m apart.
- The PRB extends across the width of the plume and measures ca 270 ft / 90 m long.

Figure courtesy of Malcolm Pirnie Inc.
Field Injection
**Inflowing concentrations measured 85 ft / 26 m upgradient of PRB**

**70 ft / 21 m downgradient from PRB**

**140 ft / 43 m downgradient from PRB**

**600 ft / 183 m downgradient from PRB**

Below detection limit for all analytes

- **Time post injection (months):** -1, 1, 4, 6, 9, 13, 16, 19, 22, 28, 36, 42, 48, 54, 61, 66
- **Conc. (ppb):** 0, 250, 500, 750, 1000, 1250, 1500, 1750, 2000, 2500, 3000

**Analytes:**
- CM
- DCM
- CF
- CT
Effect of EHC PRB on CT Plume

- EHC Treatment Zone
- Monitoring well and CT concentration (ug/L)
- Property Line

March 2005

- SCALE IN FEET
  - 0 300 600
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
- 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.
Results - CVOCs

NW sampling cluster

Conc. (ug/L)

Time post injections (months)

NE sampling cluster

Conc. (ug/L)

Time post injections (months)

SE sampling cluster

Conc. (ug/L)

Time post injections (months)

SW sampling cluster

Conc. (ug/L)

Time post injections (months)

VC
CA
C-DCE
TCE
PCE
EHC®: In Situ Reductive Groundwater Treatment

- EHC is fully proven on hundreds of sites worldwide, results in complete treatment with no daughter product stalls, and has longevity of over 5 years, so

Why develop something new?

- EHC is a solid powder that cannot fit through well screens and some very tight formations

- For this reason, Adventus focused on developing a 100% cold water soluble product with the same characteristics and benefits as EHC.
Developing EHC®-L: Objectives

1. Create a 100% cold-water soluble product.

2. Find a complex, relatively slow to ferment source of carbon that also contains nutrients.

3. Find a source of soluble iron that will stay in ferrous (Fe2+) form, not precipitate out and have slow release properties.
EHC-L: The Carbon Component

Benefits of Lecithin as a Carbon Source:

- High molecular weight results in slower consumption for extended effective life

- Slower rate of consumption may also reduce incidence of high methane production

- Charged nature of the molecule may enable retention of EHC-L in the reactive zone as opposed to “wash-out” with groundwater flow
EHC-L: The Carbon Component

Composition of Soy Lecithin (from Bailey’s Guide 2005)

<table>
<thead>
<tr>
<th>Polar Lipids</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphatidylcholine</td>
<td>20–22</td>
</tr>
<tr>
<td>Phosphatidylethanolamine</td>
<td>21–23</td>
</tr>
<tr>
<td>Phosphatidylinositol</td>
<td>18–20</td>
</tr>
<tr>
<td>Phosphatidic acid</td>
<td>4–8</td>
</tr>
<tr>
<td>Sphingomyelin</td>
<td>—</td>
</tr>
<tr>
<td>Other phospholipids</td>
<td>15</td>
</tr>
<tr>
<td>Glycolipids</td>
<td>9–12</td>
</tr>
</tbody>
</table>

Major lipids above have a similar C:H:O ratio: e.g., L-a –Phosphatidylcholine (C\textsubscript{42}H\textsubscript{82}NO\textsubscript{8}P):
Benefits of Lecithin as a Carbon Source (continued):

- The two main components of EHC-L (PE and PC) carry both positive and negative charges at the same time (zwitterions) and can therefore provide some buffering for both acids and bases.

- Dissolved phosphorus and nitrogen, major nutrients, will be slowly released in the formation as the lecithin is fermented out.
The soluble ferrous iron (Fe$^{+2}$) in EHC-L can form a variety of iron minerals (e.g., magnetite, pyrite) that are capable of reducing contaminants as they oxidize further to the ferric (Fe$^{+3}$) state (one e$^{-}$ transfer).

Something else important happens: Fe$^{+3}$ can be “recycled” back to Fe$^{+2}$ to repeat the process.
EHC-L: The Iron Component

- As dissolved iron moves down gradient it will precipitate out and coat the matrix with ferrous minerals.

- These minerals can cycle between the ferrous and ferric forms, thereby serving as an iron redox cycle that works as long as other electrons from supplied carbon and eventually indigenous carbon are available.

- Result: a substantial reactive surface stimulating direct chemical abiotic dechlorination can be formed down gradient.
Lecithin Protects Ferrous Iron:

- The anionic functional groups on PC and PE also enable binding of Fe$^{+2}$ iron – thereby reducing its susceptibility to oxidation to Fe$^{+3}$ form during mixing and injection.

- A second mechanism, vesicle formation, also helps to prevent oxidation of Fe$^{+2}$ to Fe$^{+3}$ (*food fortification science literature; Mehansho 2006*).

- Antioxidant nature of lecithin assists with maintenance of iron in the desired Fe$^{+2}$ form.
Like EHC, EHC-L supports degradation of organic constituents by enhancing:

- anaerobic bioremediation processes
- abiotic reduction reactions

EHC-L can also control dissolved phase heavy metals by promoting their adsorption and/or conversion to insoluble forms.
The addition of ferrous iron may also control dissolved phase heavy metals by promoting formation of insoluble forms (e.g., arsenopyrite from arsenic).

Reducible metals (Cr, Mo, U, Se) and metalloids (As, Sb) will also co-precipitate with oxidized iron minerals. Metals present as divalent cations (Pb, Zn, Cd, Cu, Ni) will precipitate as sulfides.
EHC-L Column Test

Influent

Sand Control Column Effluent

1%wt EHC-L Column Effluent

DHC Culture Inoculation

VC
Cis-1,2-DCE
TCE
TOC
The primary lifetime of EHC-L in the subsurface is estimated at 2-3 years, based on long-term column tests (with data from field applications pending), depending on site-specific geochemistry.

As noted, more permanent benefits (function of TOC) are realized by the electron shuttle between Fe\(^{+2}\) and Fe\(^{+3}\) mediated by reactive mineral formed in and down gradient of the reactive zone.
Most (90%) Lecithin droplets are <3 μm, therefore are expected to easily pass through typical unconsolidated formations (e.g., critical pore size for fine to coarse sand ranges from 12 to 120 μm);

Silt and clay aquifers may require high pressure injections and/or closer IP spacing, due to smaller pores and a higher content of charged particles.
EHC-L: First Field Pilot
EHC-L: Field Results

- To date, over 25 applications of EHC-L have been completed in Canada, the US and Europe.

- Reports from the field confirm the emulsion is easy to work with, completely cold water soluble with no precipitates forming, and negative redox is recorded in the mixing tank.

- Clients have indicated that results look positive, but obtaining actual data has been slow.
### EW-5
- Depth: 80-250
- Screen: 950
- TCE: 1500
- CIS-1,2-DCE: 440
- VC: 120
- TCE: 180
- CIS-1,2-DCE: 1450
- VC: 1.5
- TCE: 2.7
- CIS-1,2-DCE: 2.5

### EW-6
- Depth: 90-250
- Screen: 240
- TCE: 1600
- CIS-1,2-DCE: 600
- VC: 27
- TCE: 210
- CIS-1,2-DCE: 130
- VC: 1
- TCE: 1.4
- CIS-1,2-DCE: 0.93

### PWA-A
- Depth: 145-160
- Screen: NS
- TCE: 80
- CIS-1,2-DCE: 57
- VC: NS
- TCE: 15
- CIS-1,2-DCE: 10
- VC: NS
- TCE: ND
- CIS-1,2-DCE: ND

### PWA-B
- Depth: 115-140
- Screen: NS
- TCE: 260
- CIS-1,2-DCE: 50
- VC: NS
- TCE: 260
- CIS-1,2-DCE: 92
- VC: NS
- TCE: 38
- CIS-1,2-DCE: 11

### PWA-C
- Depth: 50-110
- Screen: NS
- TCE: 550
- CIS-1,2-DCE: 200
- VC: NS
- TCE: 550
- CIS-1,2-DCE: 38
- VC: NS
- TCE: ND
- CIS-1,2-DCE: ND

### PWA-D
- Depth: 32-45
- Screen: NS
- TCE: 73
- CIS-1,2-DCE: 35
- VC: NS
- TCE: 120
- CIS-1,2-DCE: 60
- VC: NS
- TCE: NS
- CIS-1,2-DCE: 6.6

### PWA-B-A
- Depth: 135-152
- Screen: NS
- TCE: 110
- CIS-1,2-DCE: 44
- VC: NS
- TCE: 11
- CIS-1,2-DCE: 56
- VC: NS
- TCE: ND
- CIS-1,2-DCE: ND

### PWA-B-B
- Depth: 105-130
- Screen: NS
- TCE: 74
- CIS-1,2-DCE: 14
- VC: NS
- TCE: 63
- CIS-1,2-DCE: 21
- VC: NS
- TCE: 140
- CIS-1,2-DCE: 35

### PWA-C
- Depth: 30-100
- Screen: NS
- TCE: 340
- CIS-1,2-DCE: 190
- VC: NS
- TCE: 300
- CIS-1,2-DCE: 39
- VC: NS
- TCE: ND
- CIS-1,2-DCE: 0.89

### PWC-A
- Depth: 160-185
- Screen: 340
- TCE: 1500
- CIS-1,2-DCE: 660
- VC: 58
- TCE: 190
- CIS-1,2-DCE: 210
- VC: 0.71
- TCE: ND
- CIS-1,2-DCE: 1.9

### PWC-B
- Depth: 95-155
- Screen: 220
- TCE: 210
- CIS-1,2-DCE: 50
- VC: 25
- TCE: 29
- CIS-1,2-DCE: 9.2
- VC: 0.35
- TCE: ND
- CIS-1,2-DCE: ND

### R2-A
- Depth: 110-130
- Screen: 1200
- TCE: 4000
- CIS-1,2-DCE: 810
- VC: 140
- TCE: 430
- CIS-1,2-DCE: 220
- VC: 0.97
- TCE: ND
- CIS-1,2-DCE: ND

### R2-B
- Depth: 95-105
- Screen: 380
- TCE: 225
- CIS-1,2-DCE: 25
- VC: 74.5
- TCE: 62
- CIS-1,2-DCE: 16
- VC: 0.9
- TCE: ND
- CIS-1,2-DCE: 0.52

### R2-C
- Depth: 15-95
- Screen: 5.3
- TCE: NS
- CIS-1,2-DCE: 10
- VC: NS
- TCE: NS
- CIS-1,2-DCE: NS
- VC: 0.42
- TCE: NS
- CIS-1,2-DCE: NS

### MW-60D
- Depth: 175-185
- Screen: 210
- TCE: 1100
- CIS-1,2-DCE: 10.4
- VC: 45
- TCE: 180
- CIS-1,2-DCE: 1450
- VC: ND
- TCE: ND
- CIS-1,2-DCE: 14

### MW-60I2
- Depth: 80-90
- Screen: 280
- TCE: 3800
- CIS-1,2-DCE: 1000
- VC: 60
- TCE: 330
- CIS-1,2-DCE: 250
- VC: 1.2
- TCE: ND
- CIS-1,2-DCE: 0.68

### MW-60I1
- Depth: 120-130
- Screen: 400
- TCE: 1100
- CIS-1,2-DCE: 11
- VC: 45
- TCE: 210
- CIS-1,2-DCE: 350
- VC: 1.1
- TCE: ND
- CIS-1,2-DCE: 1.2

**Injections took place at EW-5 early August 2011.**
**Only have 90 day data available at this time, further reductions expected in following sampling events.**
**Client pleased with results thus far; indicated that they are significantly better than results of previous EOS injection in 2008.**
EHC-L: Project Data #2

Site: Real Time Wells  Domain: All Sensors  Channel: ORP (mv)

Data collection time: Feb 25 2012 05:30 PM
Mesh Size: 21 x 20 x 3
Contour Depth: 66.865 AMSL ft

Date Exported: Mar 06 2012 04:36 PM

www.Groundswelltech.com
EHC-L: Project Data #2

Site: Real Time Wells
Domain: All Sensors
Channel: pH (pH)

Data collection time: Feb 26 2012 05:30 PM
Mesh Size: 21 x 20 x 3
Contour Depth: 66.865 AMSL ft

Data Exported: Mar 06 2012 04:37 PM

www.AdventusGroup.com
Injections took place Nov 21 – 23, 2011. 
Mg(OH)$_2$ was also injected for pH buffering. 
SDC-9 inoculum was injected at the same time.
### EHC-L: Project Data #3

<table>
<thead>
<tr>
<th></th>
<th>MW-103R U</th>
<th></th>
<th>MW-301 U</th>
<th></th>
<th>MW-302 U</th>
<th></th>
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</thead>
<tbody>
<tr>
<td>cis-1,2-Dichloroethene</td>
<td>3.3</td>
<td>8.9</td>
<td>14</td>
<td>ND</td>
<td>1.6</td>
<td>29</td>
</tr>
<tr>
<td>Tetrachloroethene</td>
<td>110</td>
<td>39</td>
<td>30</td>
<td>3</td>
<td>3.1</td>
<td>1.5</td>
</tr>
<tr>
<td>Trichloroethene</td>
<td>5.8</td>
<td>11</td>
<td>3.7</td>
<td>36</td>
<td>74</td>
<td>9.1</td>
</tr>
<tr>
<td>Vinyl chloride</td>
<td>ND</td>
<td>1.9</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Injections took place.
EHC-L: Summary

- The base composition of EHC-L is a slow release carbon source (lecithin), ferrous iron, and a redox buffer – all components are food-grade.

- These components are designed to enhance both microbially-mediated reductive dechlorination and abiotic dechlorination by formation of reactive reduced iron minerals.

- EHC-L is easy to prepare for injection using equipment that is readily available and widely-used in the groundwater remediation industry.
Questions are Welcome!

For more information please contact:

FMC Adventus Environmental Solutions
1345 Fewster Dr.
Mississauga, ON
Canada L4W 2A5
Ph: 905.273.5374

Or visit our website: www.AdventusGroup.com