Advances in ISCR: Remedial Amendments and Application Strategies

Intersol 2012

International Conference-Exhibition on soils, sediments and water

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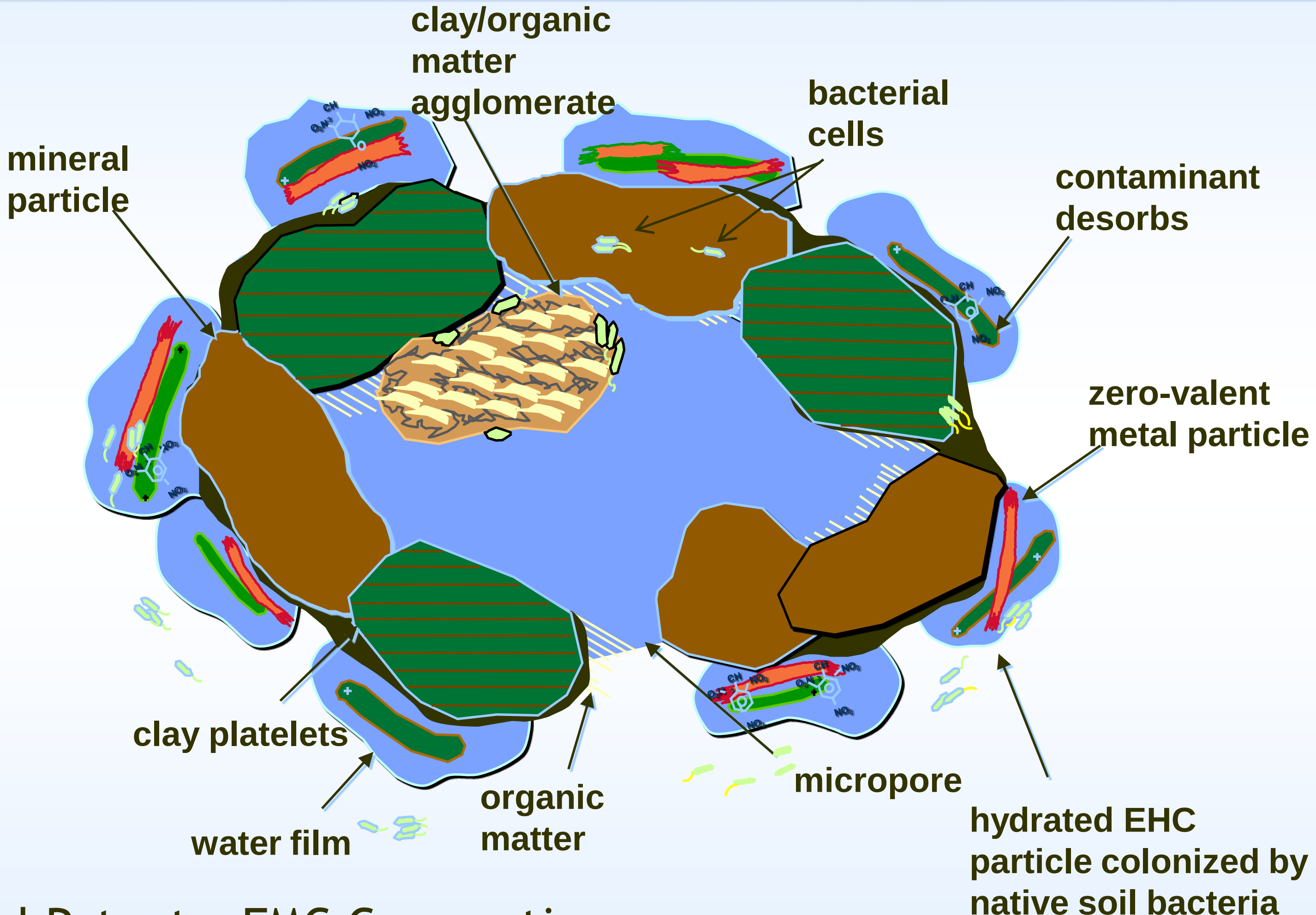
Presentation Overview

- ISCR™ Technologies
  - What is ISCR ?
  - What is EHC® ?
  - Modes of Actions
  - Implementation Strategies
  - Case Studies
  - What is EHC®-L ?
- Technologies Differentiators
  - Reasons to Consider ISCR
  - Conclusions

In Situ Chemical Reduction (ISCR™)



International Patents: FMC Corporation

Environmental Biotechnology's "Development" towards ISCR

Molasses / Vegetable Oil

Lactates / Polylactates

Bacterial inoculation

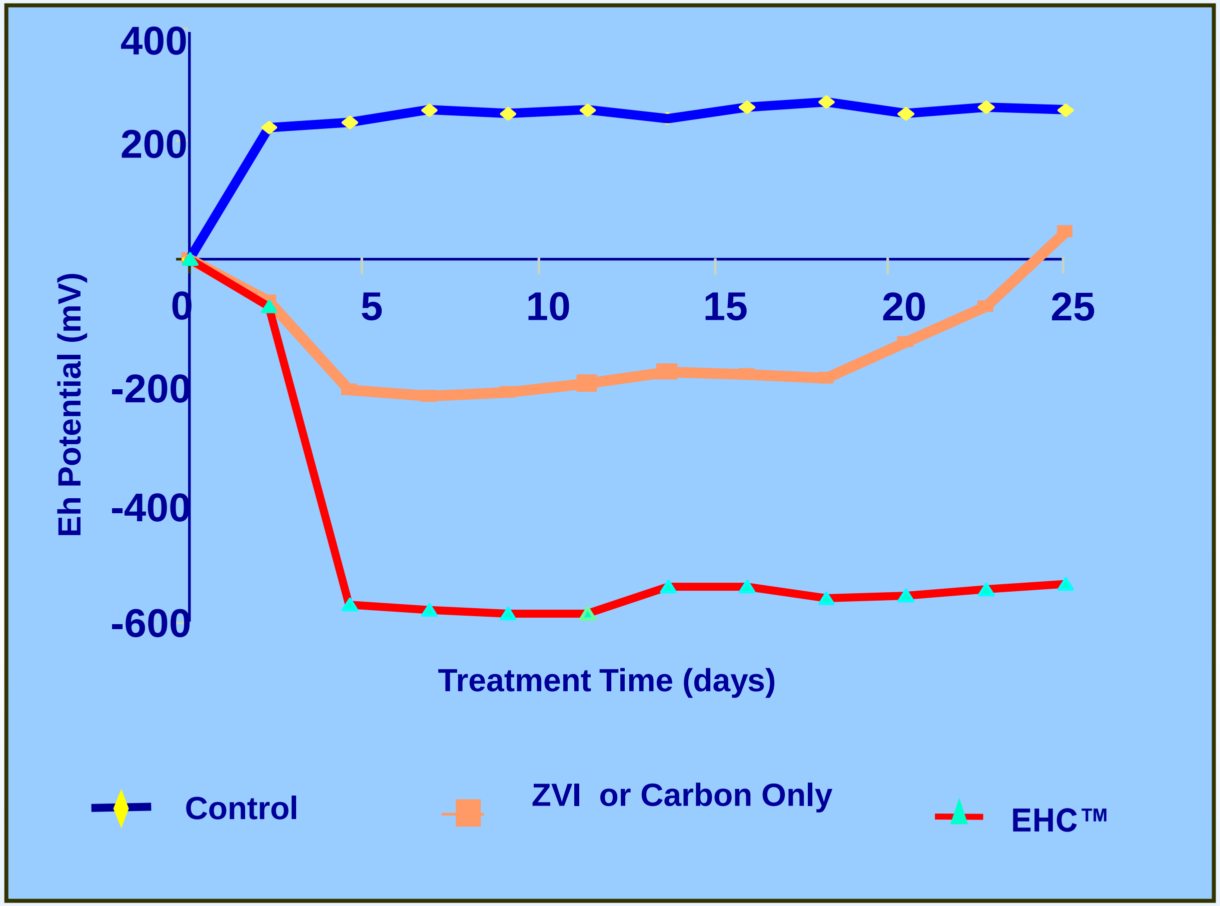
ISRM

ISCR™

- Catabolite accumulation
- Heavy metals mobilized
- Frequent reapplication required
- pH issues

- Less intermediate accumulation
- No metals mobilization
- Long lasting carbon (3-6 yrs)
- ZVI (10-15 yrs)

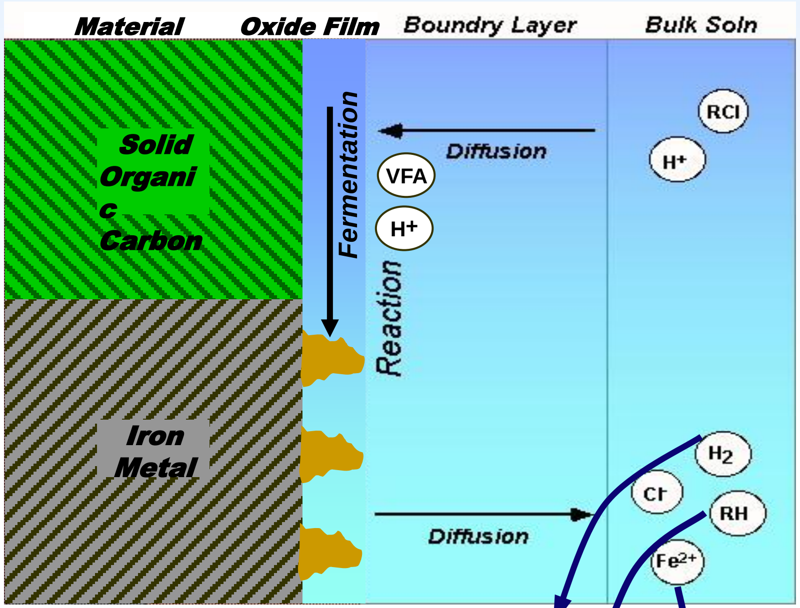
Significantly Lowered Redox (Eh Potential) = ISCR™



- Redox potentials of -600 mV to -800 mV
- Thermodynamics of reductive decomposition become favorable
- Buffering capacity
- Patented

http://www.adventusgroup.com/library/icsr-references.shtml

Carbon/ZVI Synergies: Multiple Dechlorination Mechanisms



1. Direct Dechlorination by ZVI

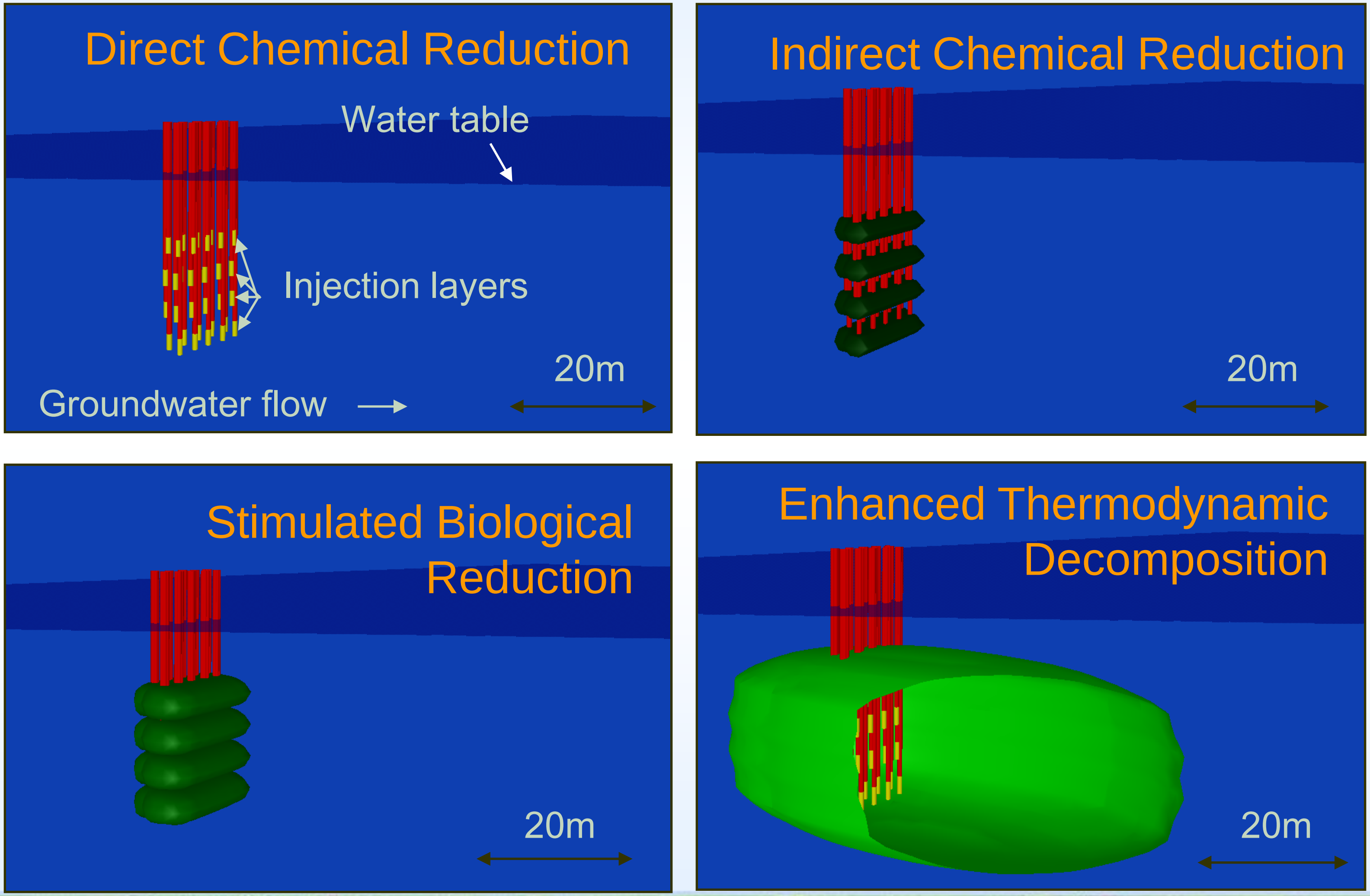
Hydrocarbon generation

2. Indirect Dechlorination by Reactive Mineral Precipitates

3. Biostimulation
- Organic substrate serves as electron donor and nutrient source for microbial activity
- VFAs reduce precipitate formation on ZVI surfaces to increase iron reactivity
- Facilitate consumption of competing electron acceptors such as O_2, NO_3, SO_4
- Increase rate of iron corrosion/H_2

4. Enhanced Thermodynamics
- Very low redox reached by combined chemical and microbiological oxygen consumption (-500 mV)
- Two processes simultaneously reduce Eh
- Enhances kinetics of dechlorination reactions via higher electron/H^+ pressure

ISCR "Four Mechanisms of Action"



What is EHC ?

- EHC is a solid or liquid material that provides:
  - Controlled-release, hydrophilic carbon source (60%)
  - Micro-scale (5- 100 μm) zero valent iron (ZVI) or other reduced metals (Zn, Al), at 5 to >40% weight
  - Major, minor and micronutrients

Contaminants treated

EHC®

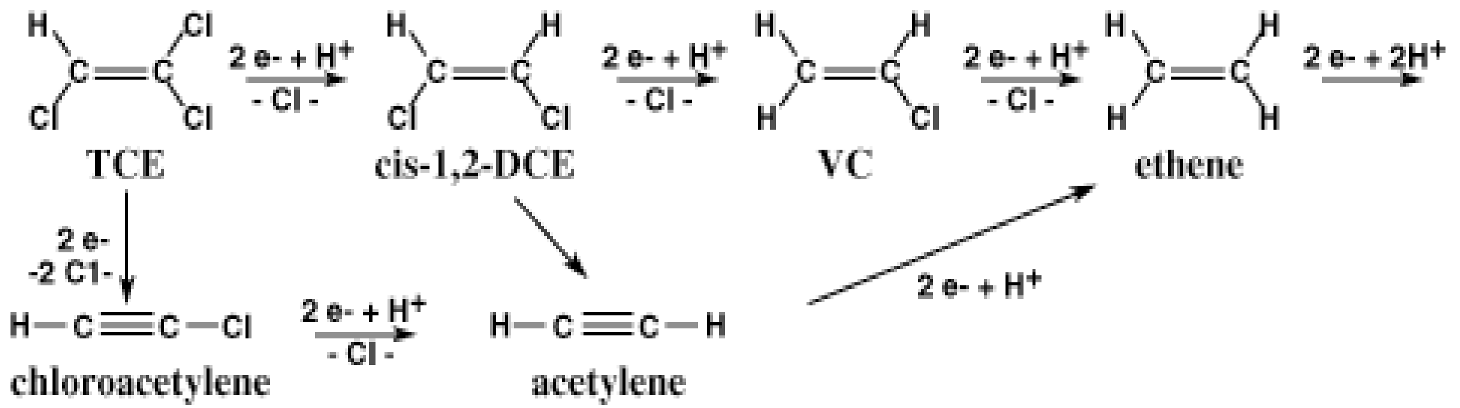
- Chlorinated Solvents
  - PCE, TCE, cis-DCE, 1,1-DCE, VC
  - 1,1,2,2-TeCA, 1,1,1-TCA, 1,2-DCA
  - CT, CF, DCM, CM
- Pesticides
  - Toxaphene, Chlordane, Dieldrin, Pentachlorophenol
- Energetics
  - TNT, DNT, RDX, HMX, Perchlorate

EHC® -M

- Heavy Metals immobilization including As, Hg, Cu, Cr, Pb, Zn, Cd, Ni, Sb, Co

Modes of Action: Contaminant Reduction Pathways with Fe and C as Drivers

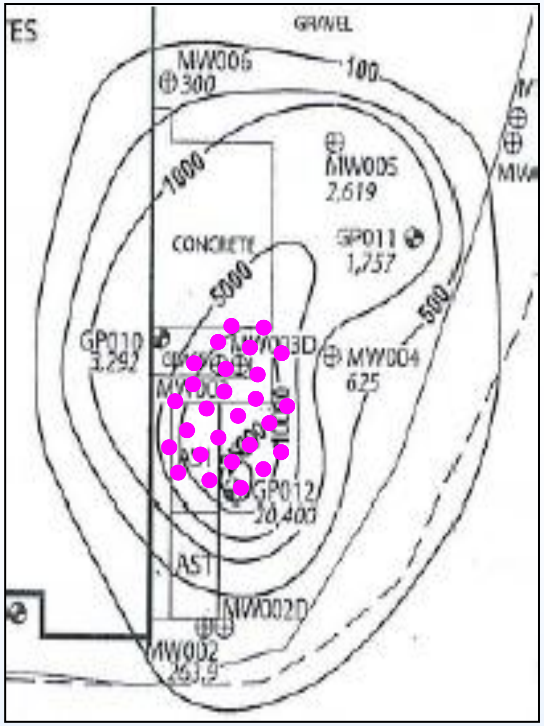
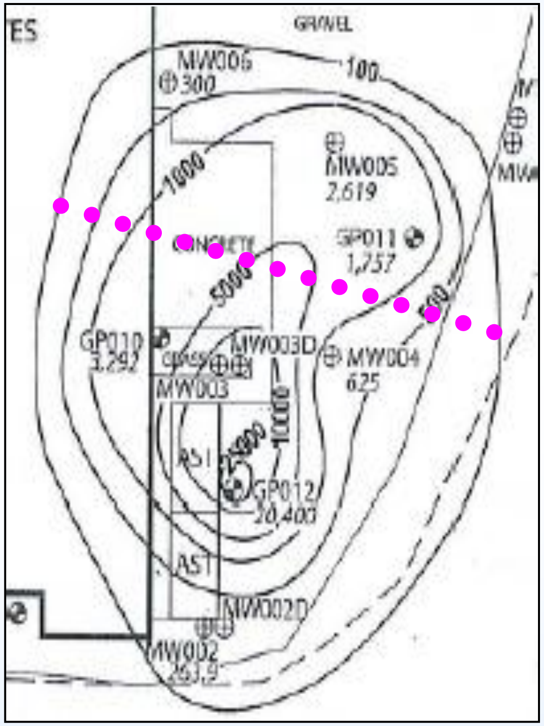
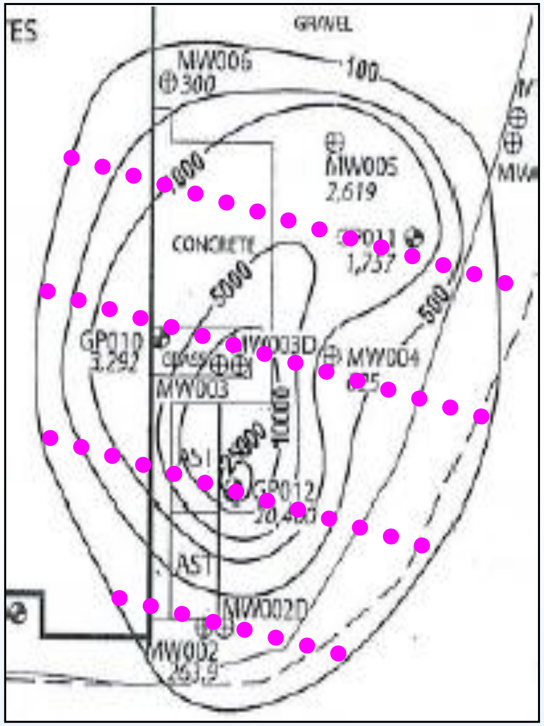
Biological Pathway Driven by Hydrogen from both Fermenting Carbon and Iron



Abiotic Pathway (ß–Elimination): Direct Iron-mediated Chemical Reduction

- Abiotic reactions minimize/eliminate DCE/VC.
- Secondary iron mineral by-products like pyrite (FeS) generate persistent reactive zones supported by modest amounts of background carbon.
- Biological reactions have advantages in physical distribution and longevity.
- Synergy between iron and carbon facilitates more efficient destruction.

EHC Conceptual Remedial Design Strategies

Source Area/ Hotspot Treatment	Injection PRB for Plume Control	Plume Treatment
		
Dosing: 0.15 to 1% wt/wt Spacing: 1.5 to 4.5 m (DPT)	Dosing: 0.4 to 1% wt/wt Spacing: 1.5 to 3 m (DPT)	Dosing: 0.05 to 0.2% wt/wt Line Spacing: based on 1 year g.w. travel distance

EHC installation methods

Injection Methods

- Direct injection
- Hydraulic fracturing
- Pneumatic fracturing
- Well injections (EHC-L)
- Manchettes

Direct Placement

- Trenching
- Excavations
- Deep soil mixing

EHC Direct Injection – URS Site (USA)

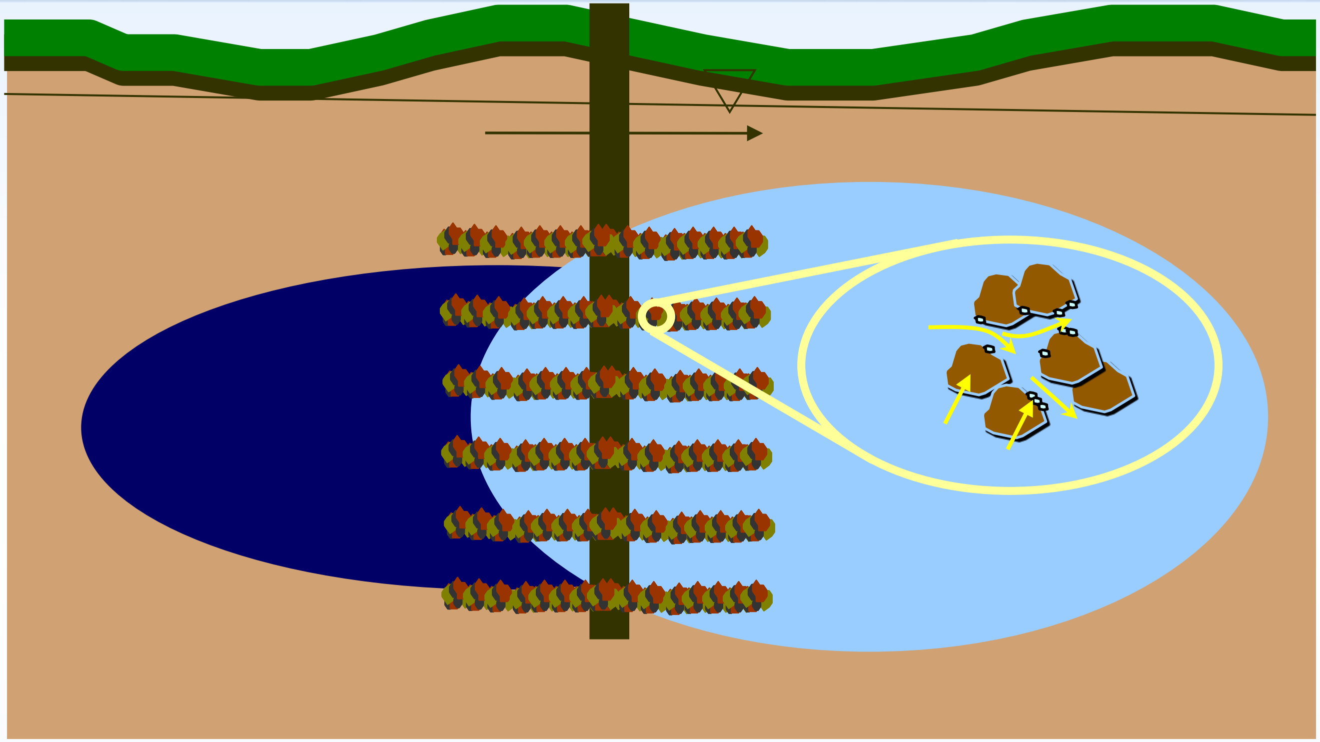
EHC Subsurface Direct Injection Methods

Horizontal Injection Tips

Allows for either top-down or bottom-up injection and directs the slurry laterally into the subsurface.

A key feature of this probe is that it acts as a backflow preventer, keeping injection material IN the ground and not ON the ground!

Hydraulic or Pneumatic Fracturing

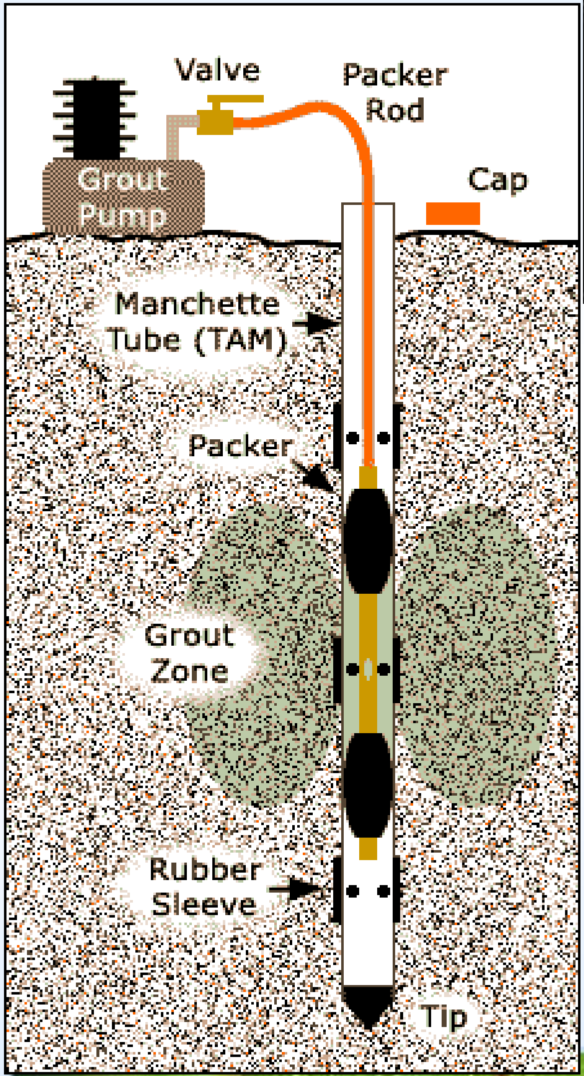


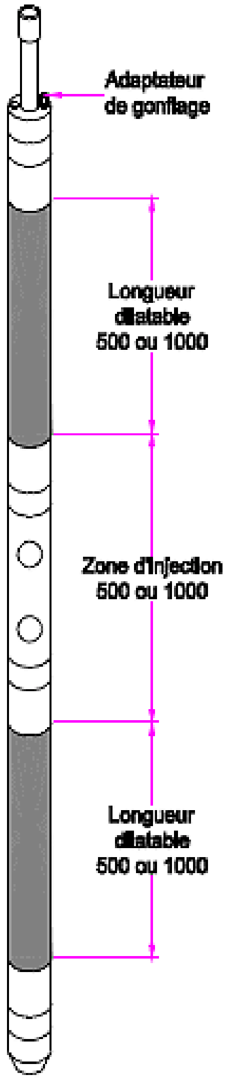
- Roughly horizontal planes of EHC injected via hydro-fracturing or pneumatic fracturing.
- Biochemical zone of dechlorination created through dispersal of dissolved organic carbon and low redox.

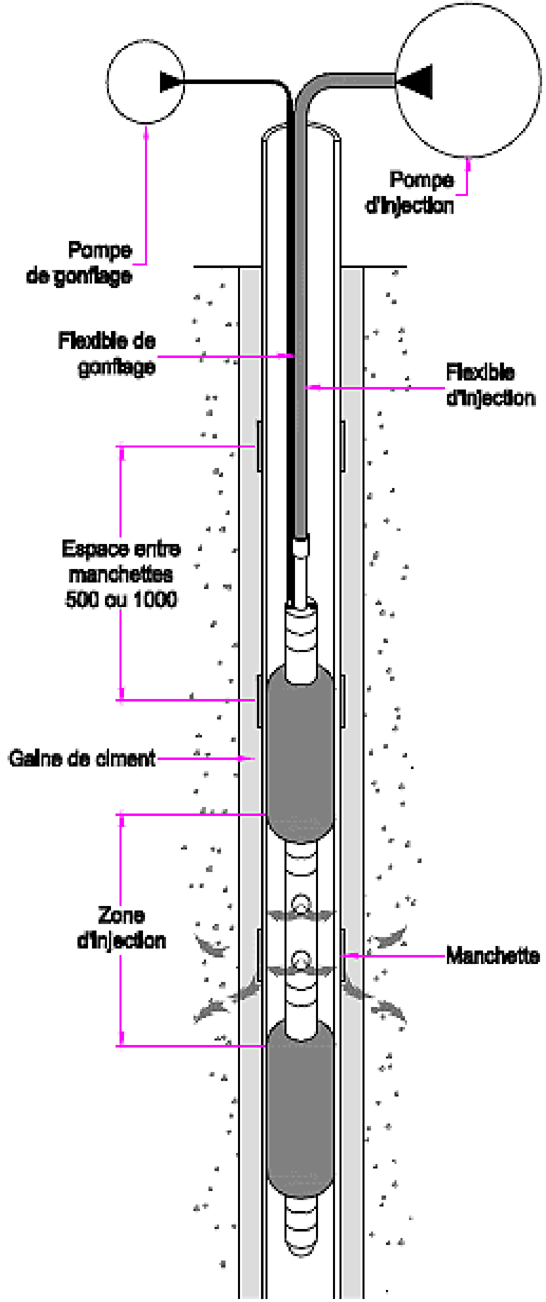
Verification of EHC Placement

Soil cores obtained at the beginning of the installation to verify radius of influence and determine injection spacing

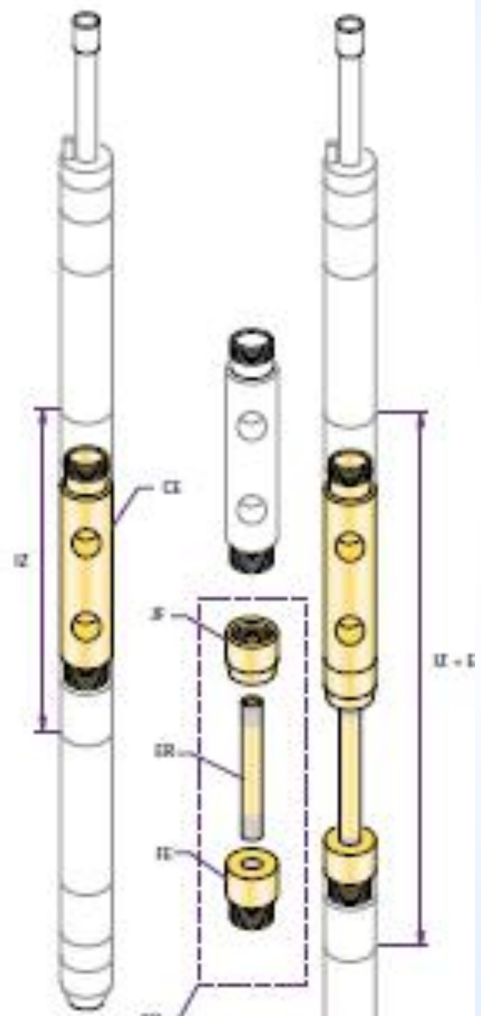
Tube à Manchette







ø 30 mm Packer	NO	YES	N
ø 42 mm Packer	NO	NO	YE



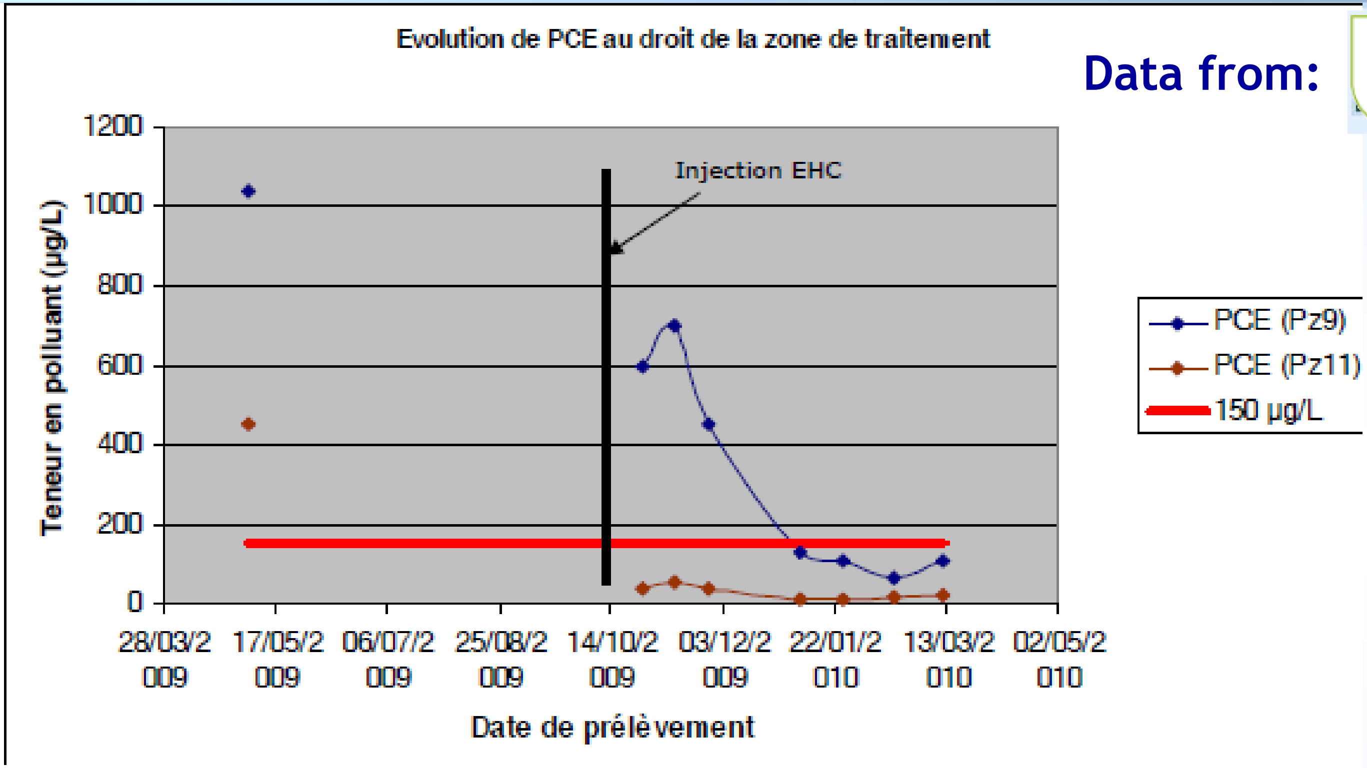
Case Study:
Tube à Manchette - Toulouse, France

Case Study	
Location	Metal jars manufacture – South of Toulouse
Impacts	PCE in groundwater – max 8 mg/L → CVOCs in soil gas → presence in building ambient air
Goals	Protect workers of new activity: • Venting of vapors in unsaturated zone • Injection in impacted aquifer under the building for source reduction below 0.15 mg/L
Remediation approach	3850 kg of amendment injected in 35 points – every 0.5 m from 4 to 9 m deep Injection into highly permeable aquifer through a concrete floor

Data from: VALGO

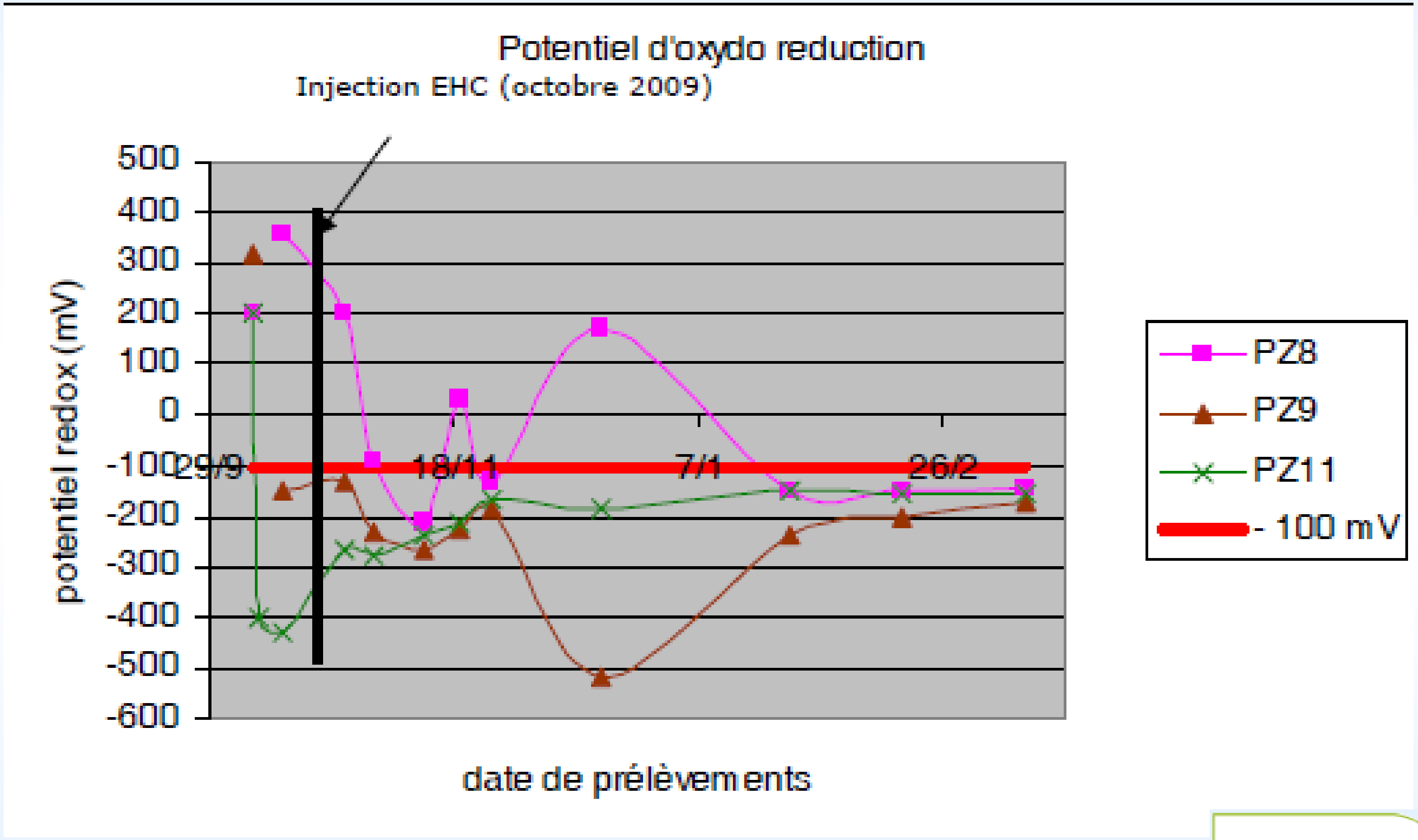
Case Study: Tube à Manchette - Toulouse, France

Data from:



Concentrations en PCE	Diagnostic complémentaire (Mai 2009) - µg/L	Fin du suivi (Mars 2010) - µg/L	Abattement
Pz9	1040	100	**90%**
Pz11	453	20	**95%**

Case Study:
Tube à Manchette - Toulouse, France



Data from: VALGO

EHC Case Study: ARCADIS Site (USA)

Case Description	
Location	Kansas, USA
Type of Site	Grain Silo – Residential Area
Description of Impacts	Groundwater contaminated with CT (2,700 ppb). Plume extended 760 meters from grain elevator, discharging into a creek.
Objective and Approach	Install a PRB across the plume to passively treat the Groundwater. Remedial goal to treat CT to <5 ppb, CF to <100 ppb, Chloromethane (CM) to <20 ppb and methylene chloride (MC) to <5 ppb

EHC PRB Case Study

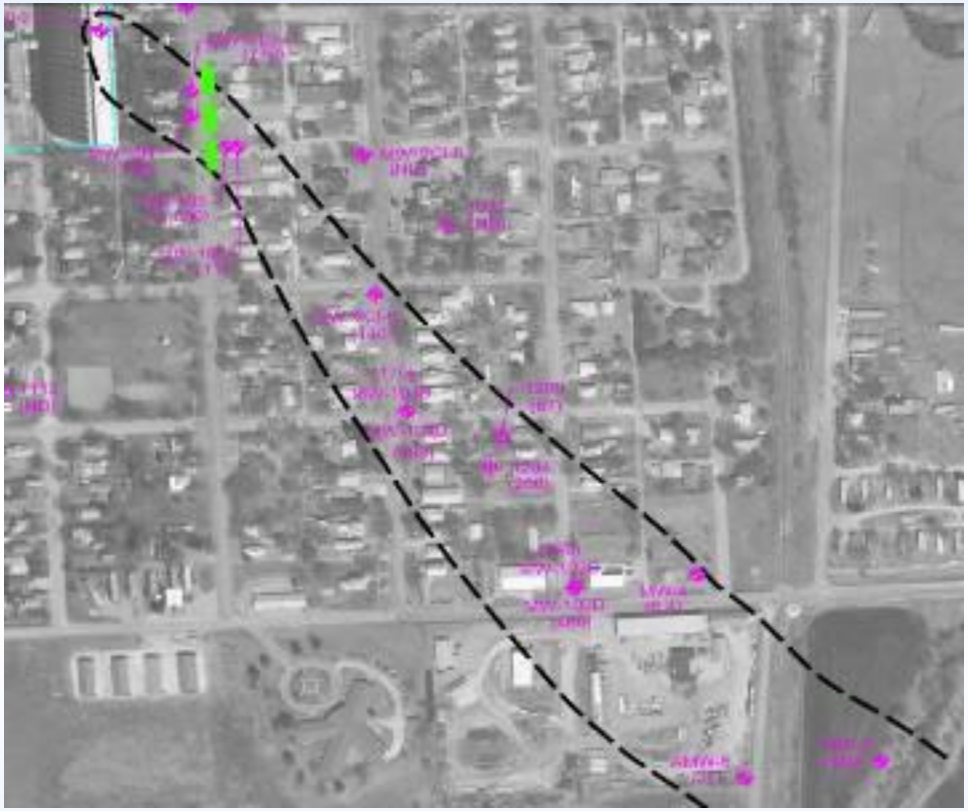
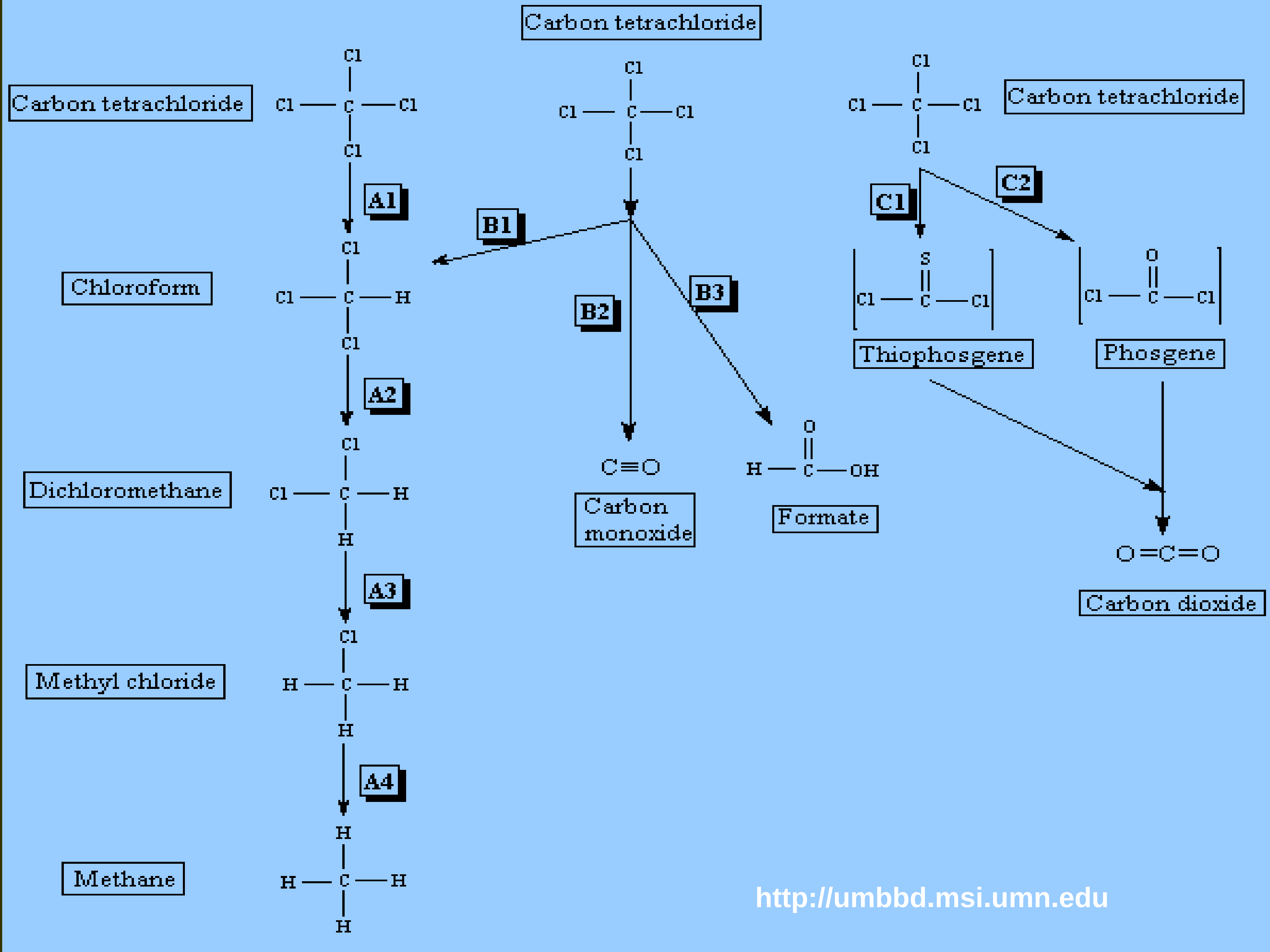


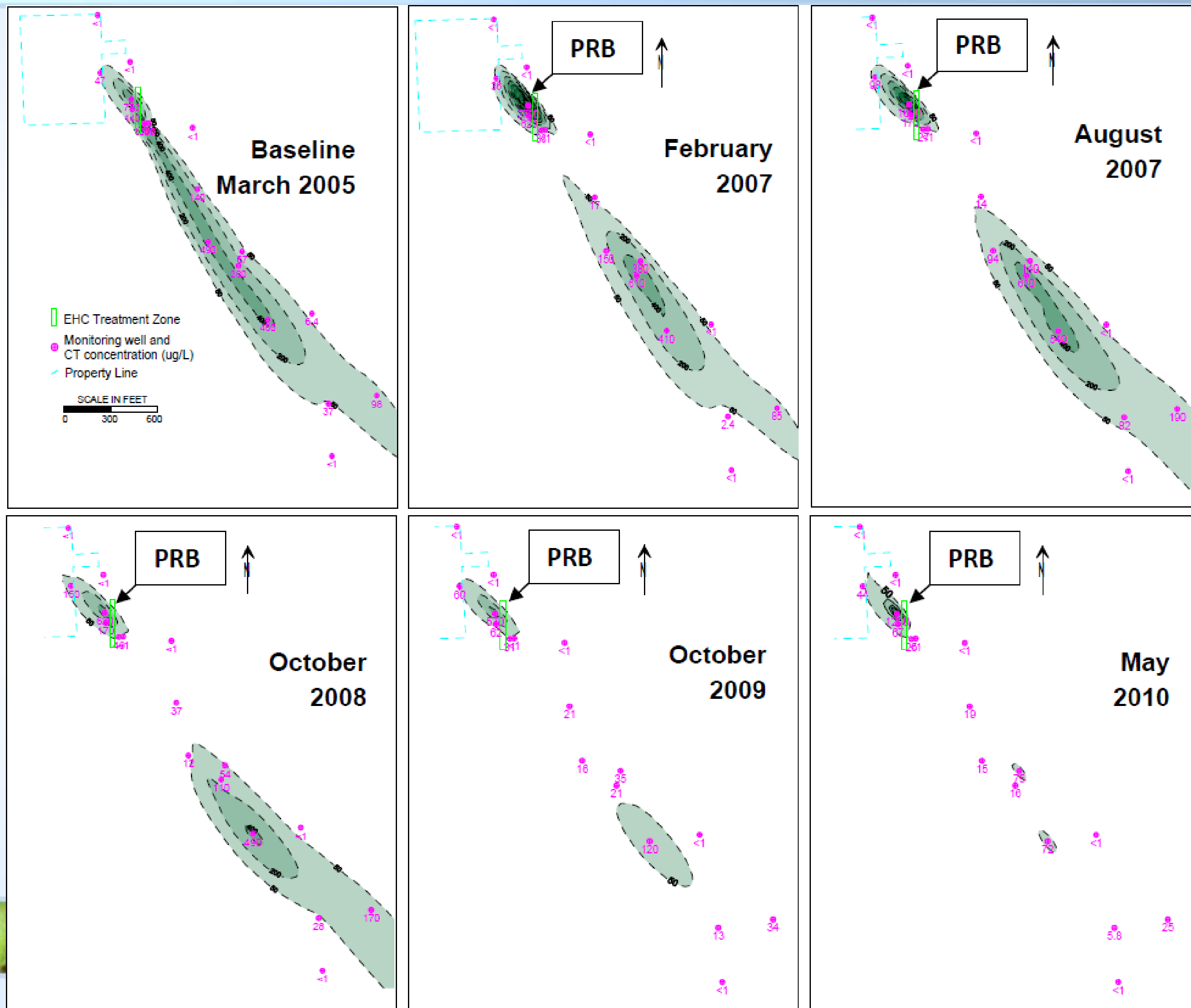
Figure courtesy of Malcolm Pirnie / Arcadis

- CT plume extends 760 m from grain elevators.
- Discharges into small creek.
- The bedrock rises to an elevation of ca 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 3 m apart.
- The PRB extends across the width of the plume and measures 83m long.


Carbon tetrachloride
Carbon tetrachloride
Carbon tetrachloride
A1
A2
A3
A4
B1
B2
B3
C1
C2
Chloroform
Dichloromethane
Methyl chloride
Methane
Carbon monoxide
Formate
Thiophosgene
Phosgene
Carbon dioxide
http://umbbd.msi.umn.edu

Field Injection

Effect of EHC PRB on CT Plume



Cost Summary

Materials:

- EHC used was approx. € 300 / m^2 of PRB cross-section (83 m long x 3 m deep on average).

Treatment Amounts and Duration:

- Using estimated linear groundwater velocity of 0.55 m/day and a porosity of 30%, the PRB is treating an estimated total of 14,600 m3 of groundwater per year (83 m long x 3 m average depth x 365 days x 0.55 m/day x 30%).

- With an estimated life of at least 5 years, the PRB is expected to treat a total of 73,000 m3 of groundwater during its life-time, at a product cost of about €1 / m^3.

Comparison of EHC to Other Technology Offerings

PRODUCT	CARBON	ZVI	NUTRIENTS	BUFFERING	LONGEVITY (MONTHS)	COST
ISCR EHC®	Yes	Yes	Yes	Yes	12 - >60	€3/kg
Lactate-based hrc's	Yes	No	No	No	6 - >12	€5.0 – 8.0
Iron	No	Yes	No	No	80 – 120+	€0.2 – 0.5
Molasses	Yes	No	Yes	No	1 - 2	€0.5 – 1.0
Vegetable Oil	Yes	No	No	No	12 - >60	€3.0 – 6.0
Chitin	Yes	No	Yes	No	6 - 24	€2.0 – 3.0

Other EHC Formulations

EHC-L (phasing out EHC-A)

- Cold-water soluble EHC formulation
- Contains soluble carbon and ferrous iron

EHC-F

- Fine Iron with soluble carbon
- Suitable for fractured rock/injection permeation

EHC-G

- Granular iron
- Suitable for deeper/hydro fracturing applications

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ISCR Reagents for Groundwater Remediation: EHC-L®

EHC-L is a fully soluble product based composed of slow-release carbon and ferrous iron.

- Lecithin phospholipids (PC, PE, and PI) provide an excellent, slowly-metabolized source of carbon and nutrients.
- Ferrous iron provided as an organo-iron complex.
- The mixture is very resistant to oxidation during mixing and injection due to the antioxidant characteristic s of PE and PC.

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EHC-L: Treatment

- The addition of soluble carbon to the subsurface will support the growth of indigenous microbes in the groundwater environment.

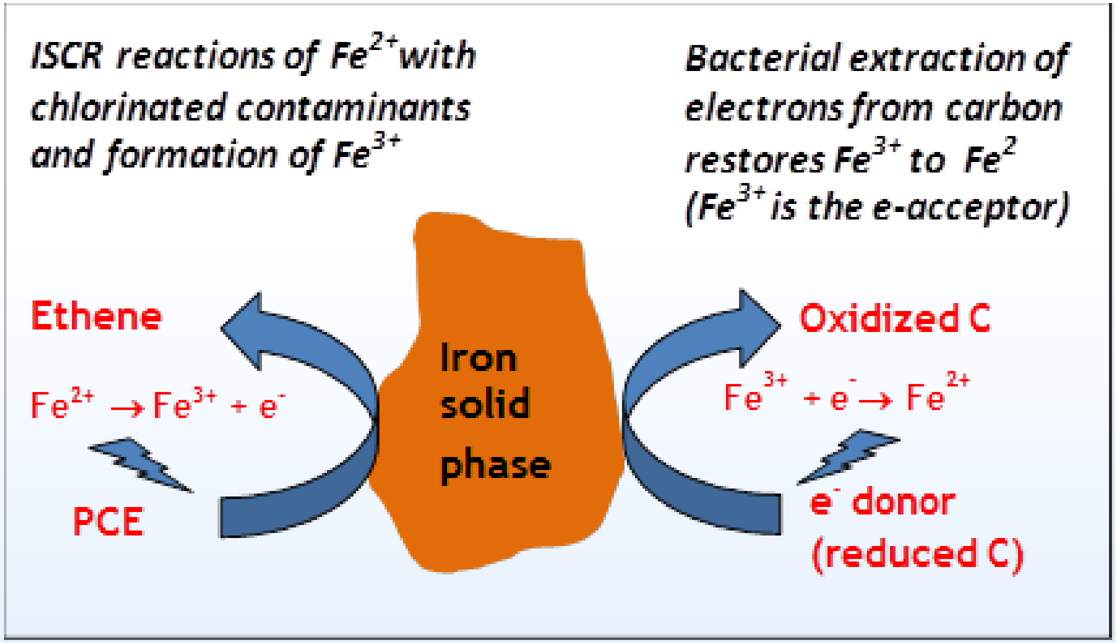
- As bacteria feed on the soluble carbon, they consume dissolved oxygen and other electron acceptors, thereby reducing the redox potential in groundwater.

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

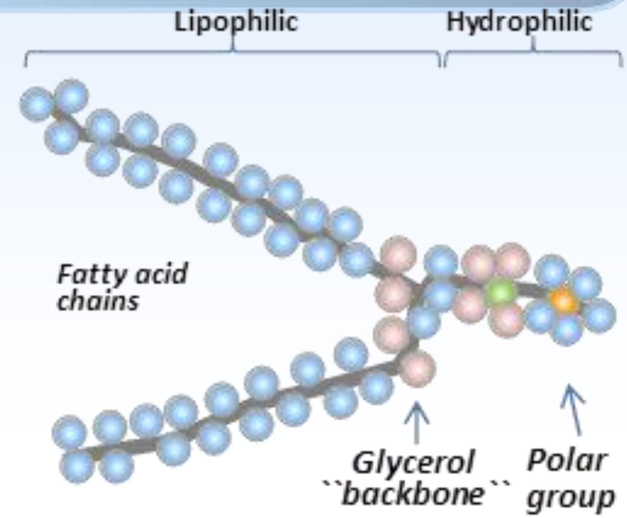
EHC-L: Iron component action

❖ 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: Carbon component action



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: Carbon component action

Benefits of Lecithin as a Carbon Source (continued):

❖ Components of EHC-L 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.

EHC-L: Iron – Carbon Synergy

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.

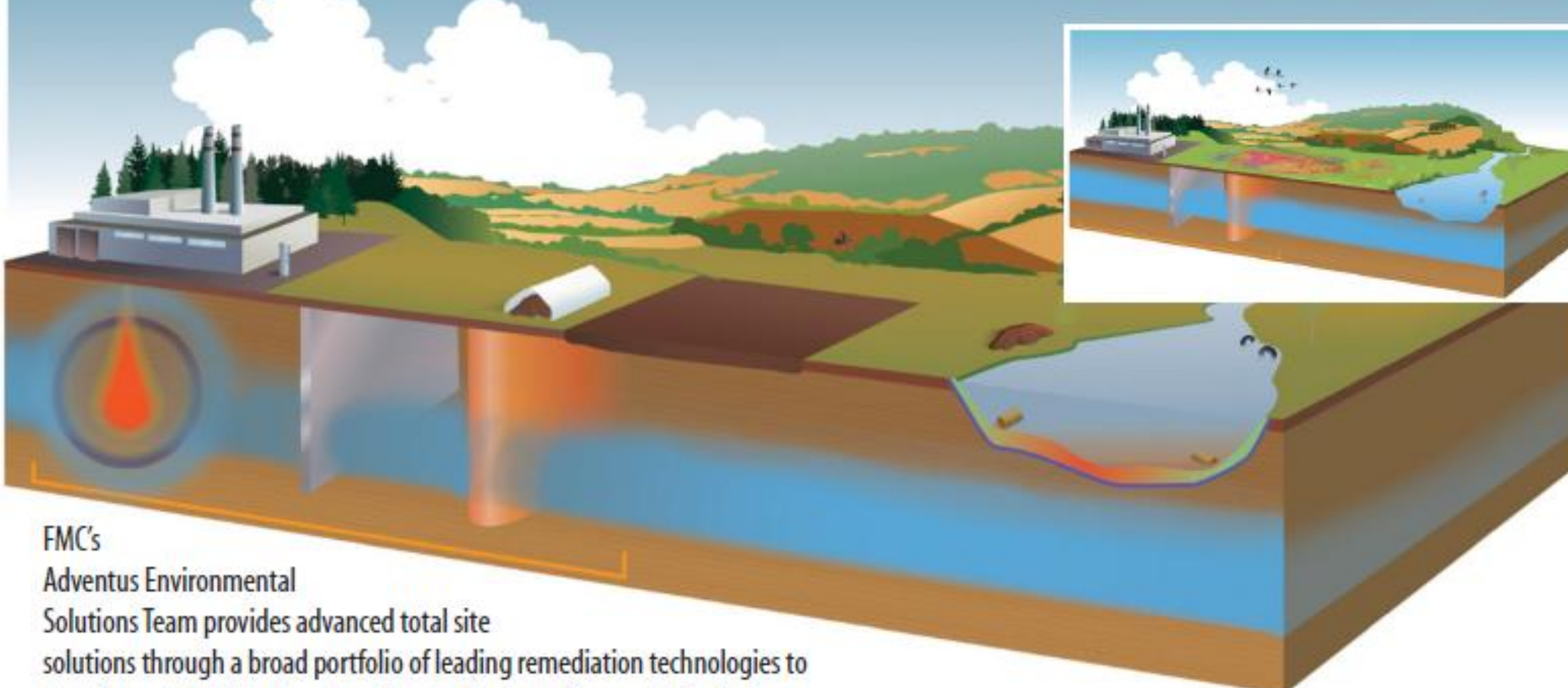
EHC-L: Longevity

❖ 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.

EHC-L: Onsite Mixing & Application

ISCR / ISCO Environmental Solutions



FMC's
Adventus Environmental
Solutions Team provides advanced total site solutions through a broad portfolio of leading remediation technologies to treat impacted soil, sediment, and groundwater environments, including:

- **In Situ Chemical Oxidation (ISCO) technologies**
- **In Situ Chemical Reduction (ISCR) technologies**
- **Oxygen Releasing Compounds, and more**

Visit us online today to learn more about our field-proven environmental solutions to successfully address most constituents of interest.

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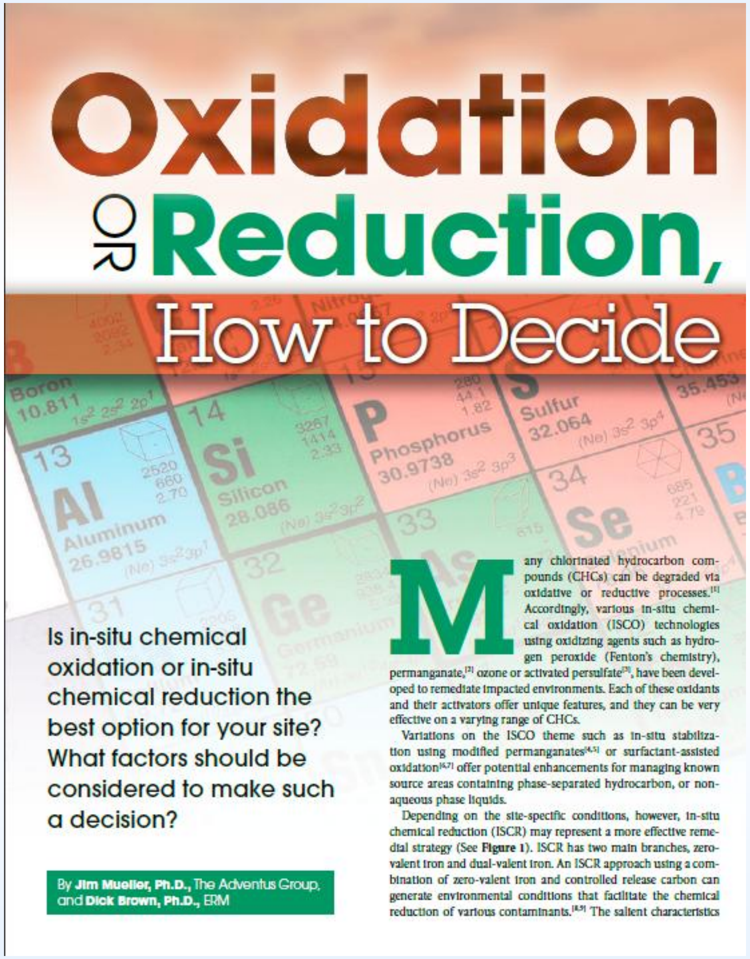
ISCO or ISCR: How to Decide?



Oxidation or Reduction, How to Decide

Is in-situ chemical oxidation or in-situ chemical reduction the best option for your site? What factors should be considered to make such a decision?

By Jim Mueller, Ph.D., The Adventus Group, and Dick Brown, Ph.D., ERM

Many chlorinated hydrocarbon compounds (CHCs) can be degraded via oxidative or reductive processes.[1] Accordingly, various in-situ chemical oxidation (ISCO) technologies using oxidizing agents such as hydrogen peroxide (Fenton's chemistry), permanganate,[2] ozone or activated persulfate[3], have been developed to remediate impacted environments. Each of these oxidants and their activators offer unique features, and they can be very effective on a varying range of CHCs.

Variations on the ISCO theme such as in-situ stabilization using modified permanganates[4,5] or surfactant-assisted oxidation[6,7] offer potential enhancements for managing known source areas containing phase-separated hydrocarbon, or non-aqueous phase liquids.

Depending on the site-specific conditions, however, in-situ chemical reduction (ISCR) may represent a more effective remedial strategy (See **Figure 1**). ISCR has two main branches, zero-valent iron and dual-valent iron. An ISCR approach using a combination of zero-valent iron and controlled release carbon can generate environmental conditions that facilitate the chemical reduction of various contaminants.[8,9] The salient characteristics

PE News April, 2008

ISCR

- Chlorinated compounds
  - Ethenes
  - Ethanes
  - Methanes
  - PCBs
  - Pesticides w Cl > 20%
- Non-Chlorinated
  - Nitrated (Explosives)
  - NDMA
- Inorganics
  - As
  - Cr
  - Perchlorate

ISCO

- Chlorinated Compounds
  - Ethenes
  - Ethanes
  - Methanes
  - PCBs
  - Pesticides w C=C
- BTEX & PAHs
- Other Organics
  - MTBE, 1,4-Dioxane
  - Explosives
- Metals
  - As

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ISCR Global Use

USA
- Over 1,000 sites in 48 states
- Florida DEP acceptance
- L.A. RWQCB general waiver list

International
- REACH certified
- Applied in:

Australia	Belgium
Brazil	Canada
Czech Rep.	Colombia
China	Denmark
Finland	France
Germany	Hungary
Ireland	Israel
Italy	Latvia
Portugal	Spain
Sweden	Taiwan
UK	

Packaging
50 lb (25 kg) bags
2,000 lb (1000 kg) IBC

Thank you for your time and attention !

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