COMBINED *IN SITU* TREATMENT OF CHLORINATED SOLVENTS AND HEAVY METALS IN GROUNDWATER USING EHC-M®

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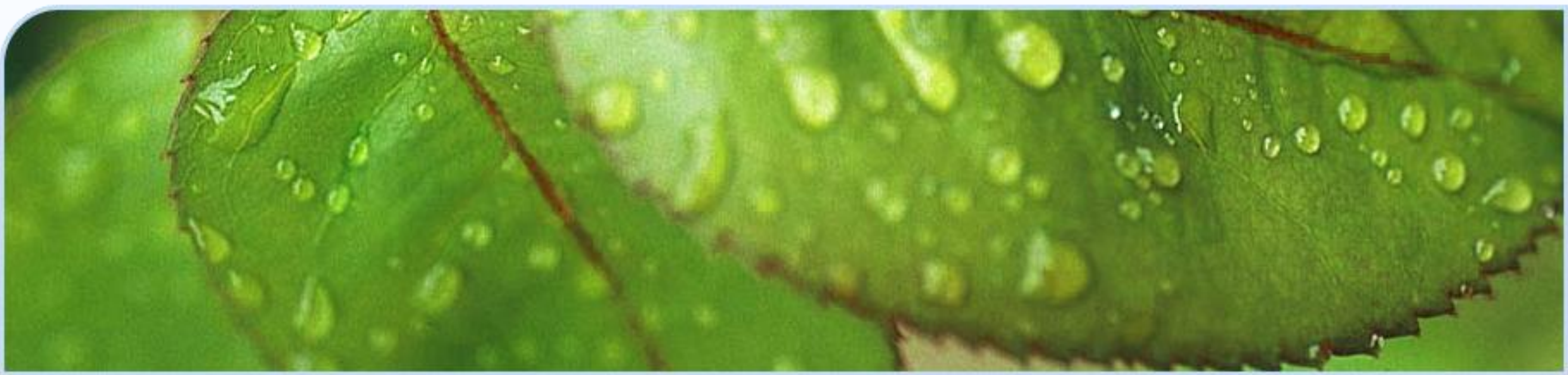
ADVENTUS

Proven Remediation Technologies for Soil, Sediment, and Groundwater



Introduction

- The solubility of metals are impacted by shifts in Eh and pH. Any *In Situ* treatment of organic constituents that alters the geochemistry may therefore mobilize metals.
- Source of metals could be natural or anthropogenic.
- This presentation discusses how various metals could be immobilized *In Situ* and how liberation of metals could be prevented during enhanced anaerobic bioremediation.

Presentation Overview

- Technology Background:
  - Overview of previous research on using ZVI and carbon sources for metals immobilization.
  - EHC Technology overview:
    - CVOCs Treatment Mechanisms.
    - Effect on metals mobility.
- Laboratory Validation
- Field Applications

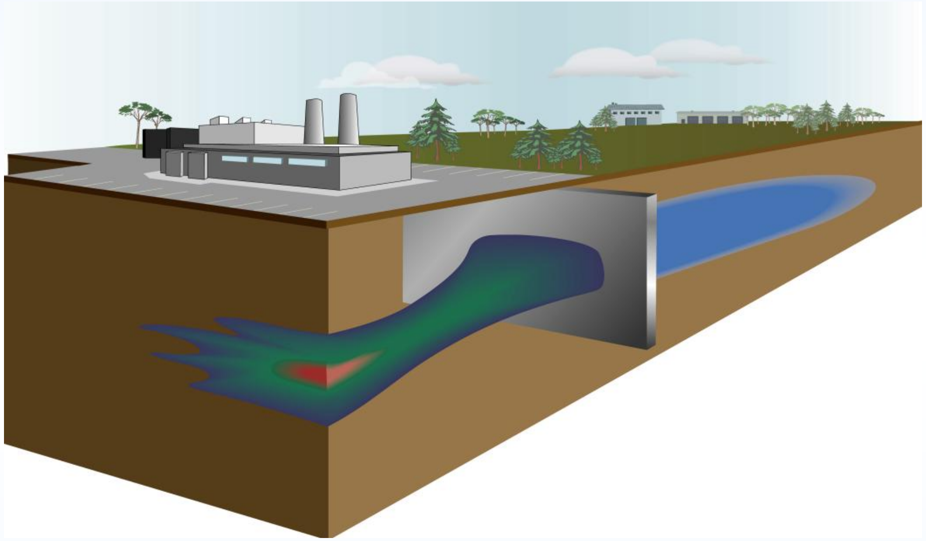
Previous Research on In-situ Reductive Treatment of Dissolved Metals

- Reducible metals are present in natural waters as anions and oxyanions (e.g. Cr, As, Se, Mo, U)

- Immobilized via reductive precipitation on ZVI surfaces and oxyhydroxides

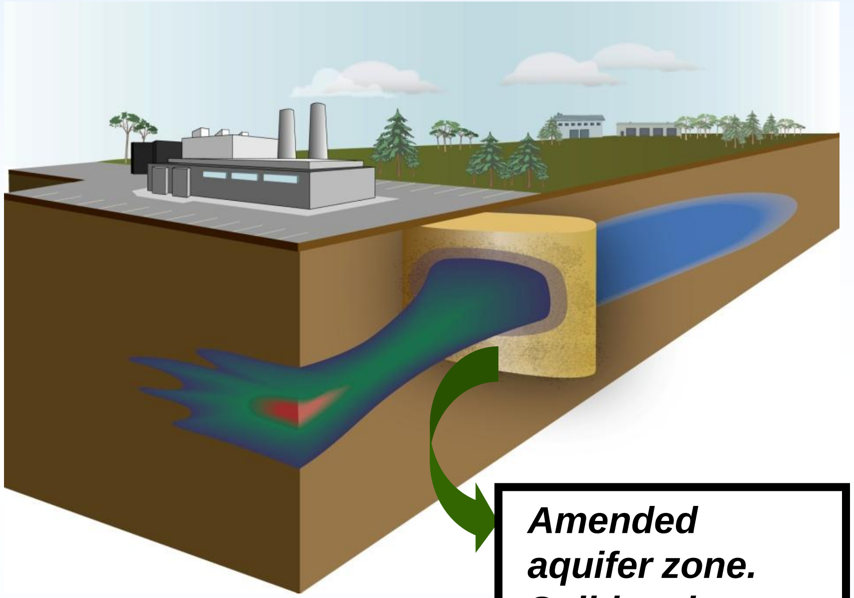
- Puls and Su, EPA Research Lab, OK:

  Reductive precipitation of chromium and arsenic treatment with ZVI PRBs.



Previous Research on In-situ Reductive Treatment of Dissolved Metals

- Metalloids are present in natural waters as divalent cations (e.g. Cu, Zn, Cd, Pb, Hg, Ni)
- Precipitate as metal sulfides.
- Various carbon substrates used to microbially mediate reduction of sulfate present in the groundwater
- Blowes et al., University of Waterloo: Organic substrate PRBs for sulfate reduction and trace metals treatment in acid mine drainage.



Amended aquifer zone. Solid carbon source could be saw dust, wood chips, plant fibers.

In Situ Chemical Reduction/Enhanced Anaerobic Bioremediation of Chlorinated Solvents

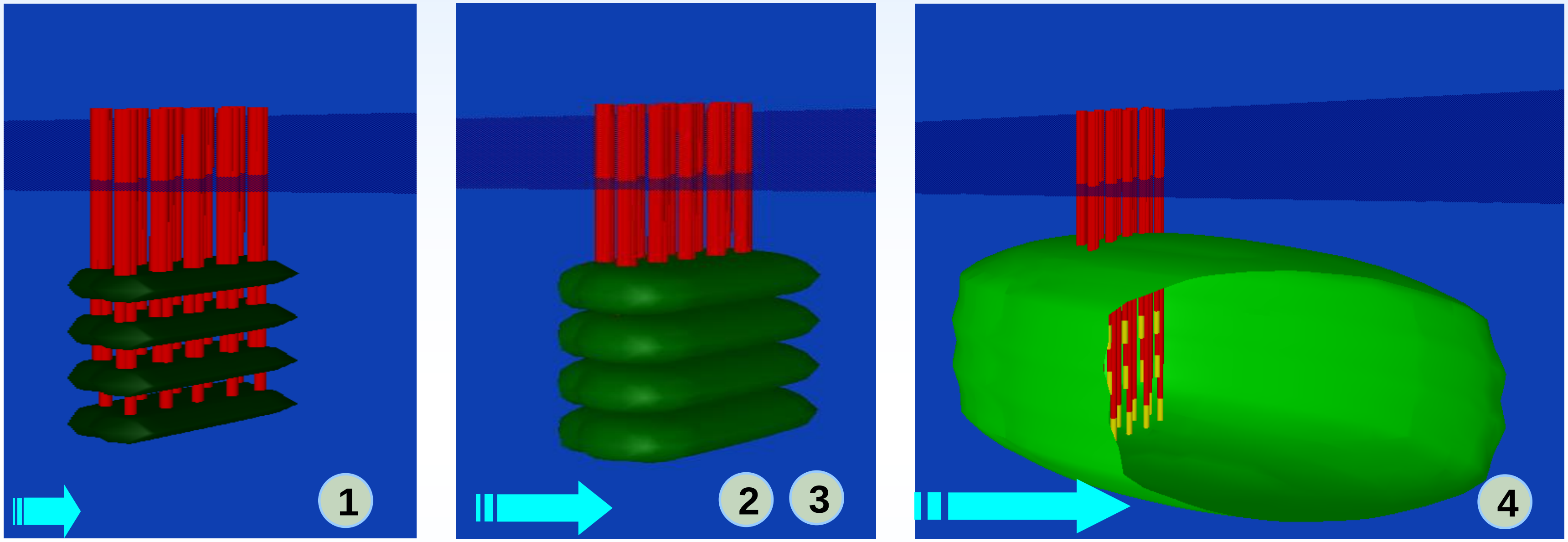
EHC is a hybrid remediation product composed of:

- Controlled-release, food grade, complex carbon
- Micro-scale zero valent iron (5 - 10 μm)
- Major, minor, and micronutrients
- Food grade organic binding agent
- (Sulfate)

CVOC Treatment Mechanisms

Mechanism	Material	Description
Direct Chemical Reduction	ZVI or EHC	• Redox reaction at iron surface where solvent gains electrons and iron donates electrons • Abiotic reaction *via* beta-elimination
Indirect Chemical Reduction	ZVI or EHC	• Surface dechlorination by magnetite and green rust precipitates from iron corrosion
Stimulated Biological Reduction	Carbon Substrates or EHC	• Anaerobic reductive dechlorination involving fastidious microorganisms • Strongly influenced by nutritional status and pH of aqueous phase
Enhanced Thermodynamic Decomposition	EHC	• Energetics of dechlorination are more favorable under lower redox conditions generated by combination of ZVI and organic carbon

EHC Influenced Reductive Treatment Zone



1. Direct ZVI corrosion effects
2. Strongly reduced environment
3. Indirect ZVI effects (H_2 gas and iron corrosion product generation)
4. Biostimulation of the aquifer zone by carbon fermentation products; elevated levels of sulfate with EHC-M

Contaminants Treated

EHC

- Chlorinated Solvents
  - PCE, TCE, cDCE, 11DCE, VC
  - 1122TeCA, 111TCA, 12DCA
  - CT, CF, DCM, CM
- Pesticides
  - Toxaphene, Chlordane, Dieldrin, Pentachlorophenol
- Energetics
  - TNT, DNT, RDX, HMX, Perchlorate

EHC-M

- Heavy Metals including As, Hg, Cr, Pb, Zn, Cd

Effect on Various Metals

Contaminant	Treatment Mechanisms in the ZVI-Carbon zone
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 and 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).

Presentation Overview

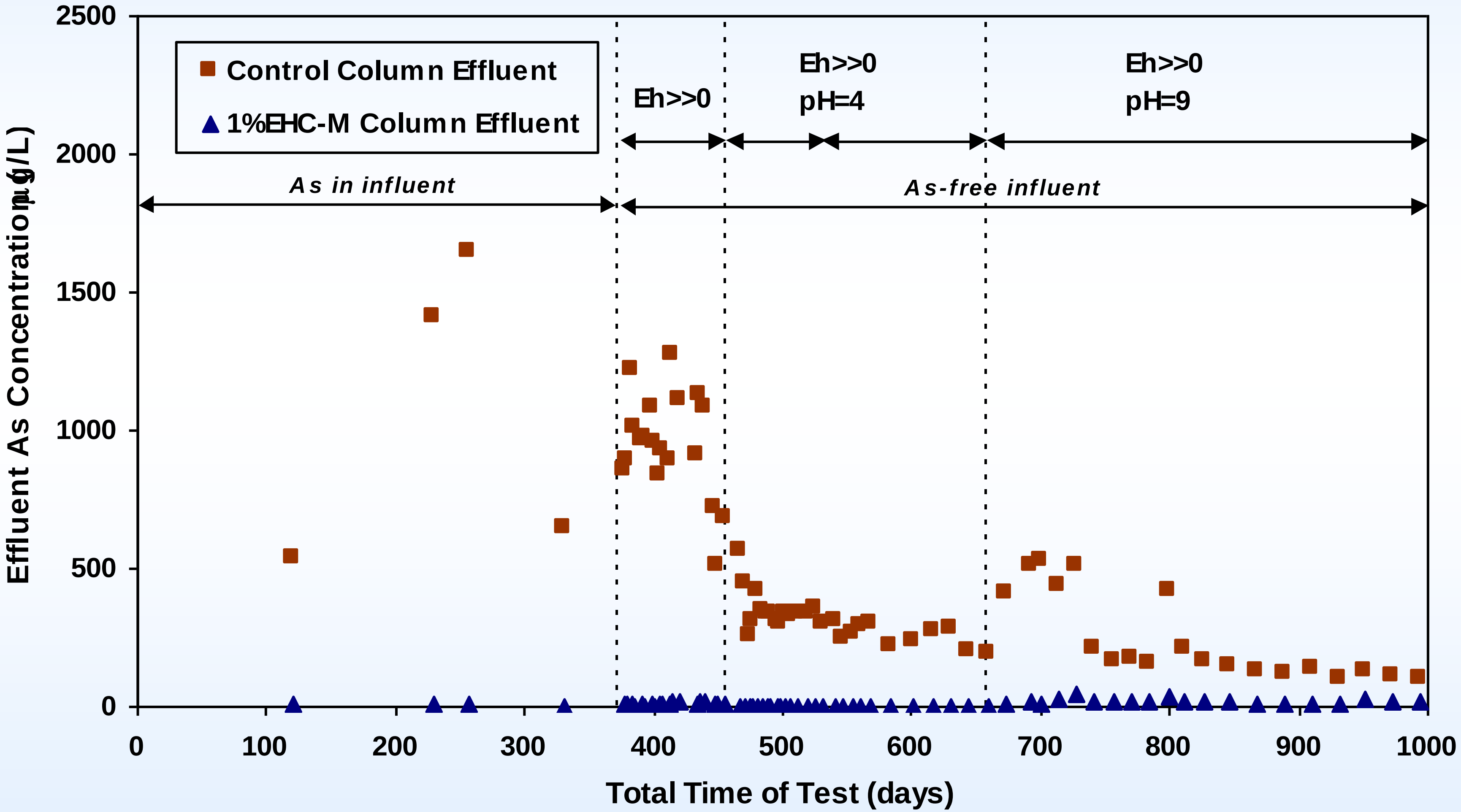
- Technology Background
- **Laboratory Validation**
- Field Applications

Summary of Treatment Efficiencies Observed in Internal Lab Tests

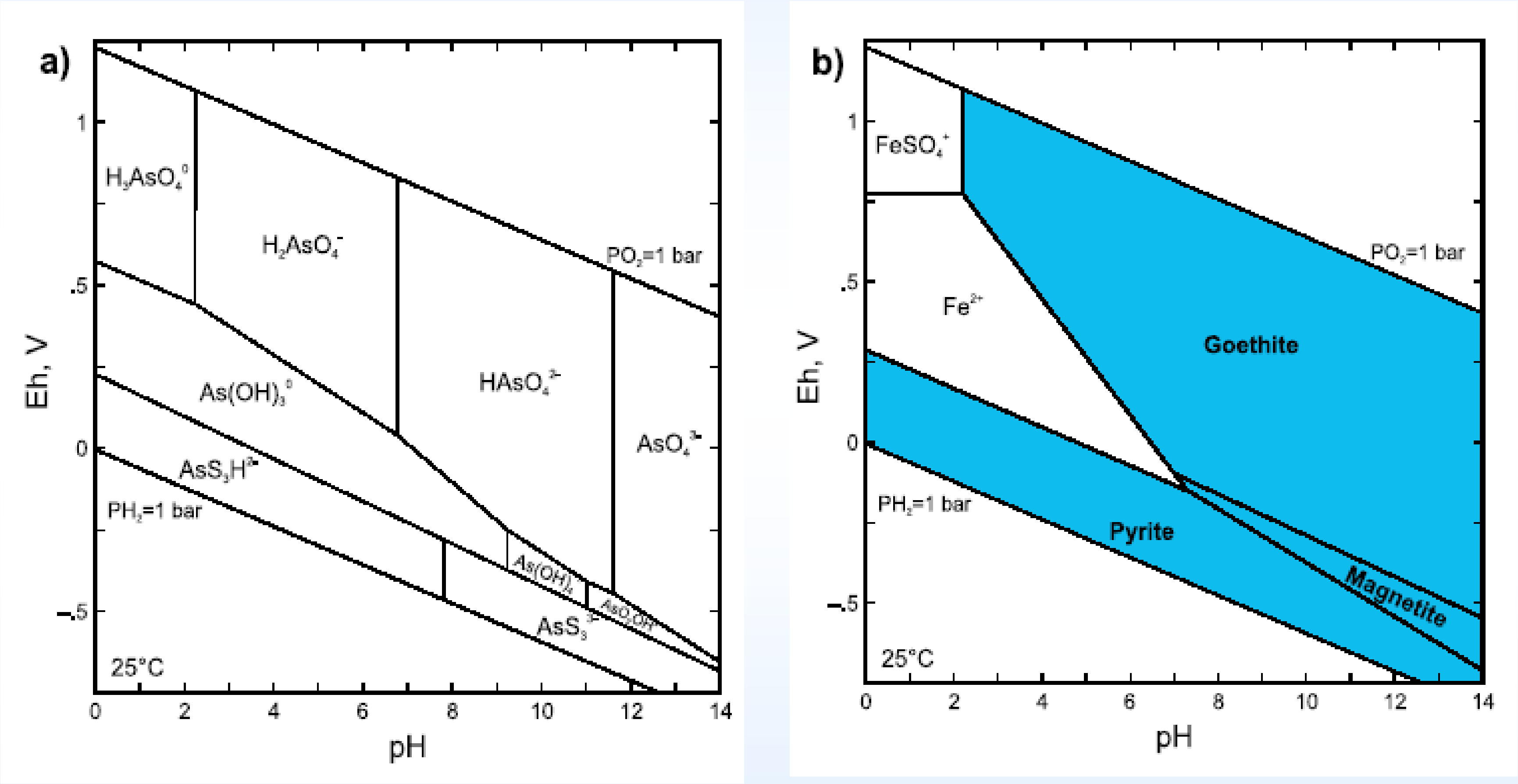
Compound	Influent Concentration Range (ug/L)	Observed Removal Efficiency (%)
Antimony	24,500	>99
Arsenic	500	98
Cadmium	11	>99
Chromium	200	>99
Cobalt	210	>99
Copper	86	>99
Lead	64,000	>99
Mercury	1,020	97
Nickel	350	>99
Zinc	50,400	92

Long-Term Column Test for As Treatment

Column: 13 cm long and 5 cm Ø, Flow rate = 50 mL/d, Residence time = 2 days



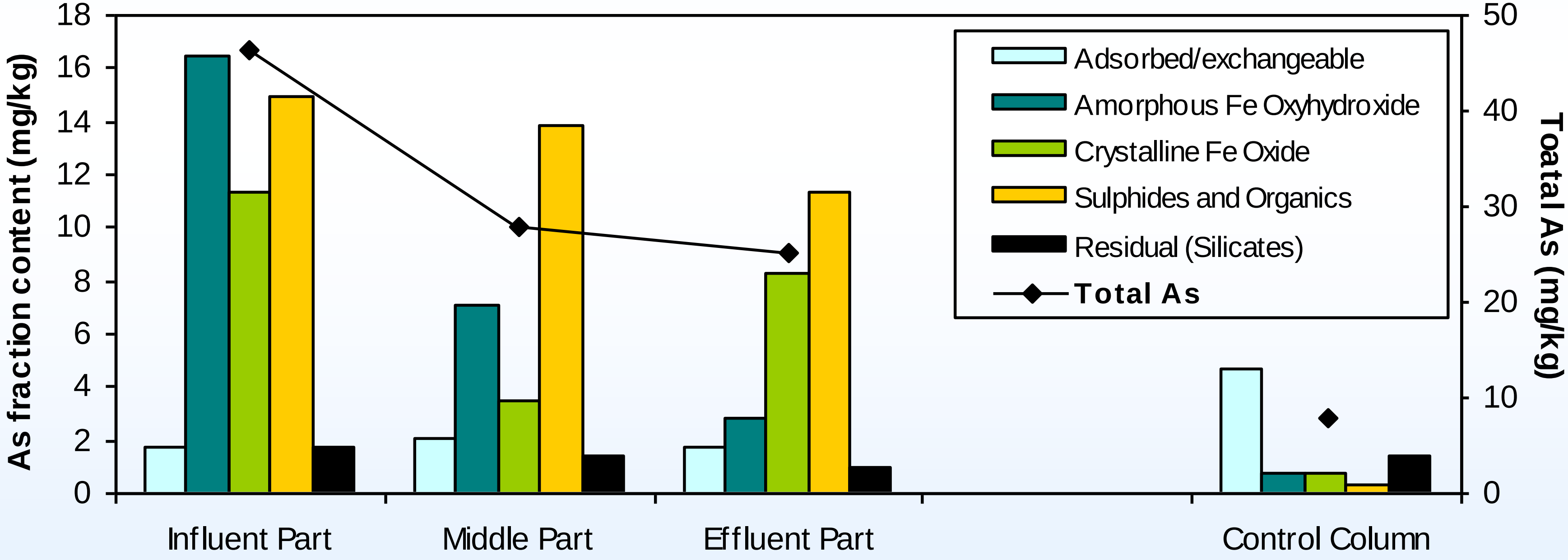
Arsenic Speciation in the presence of dissolved Fe and S



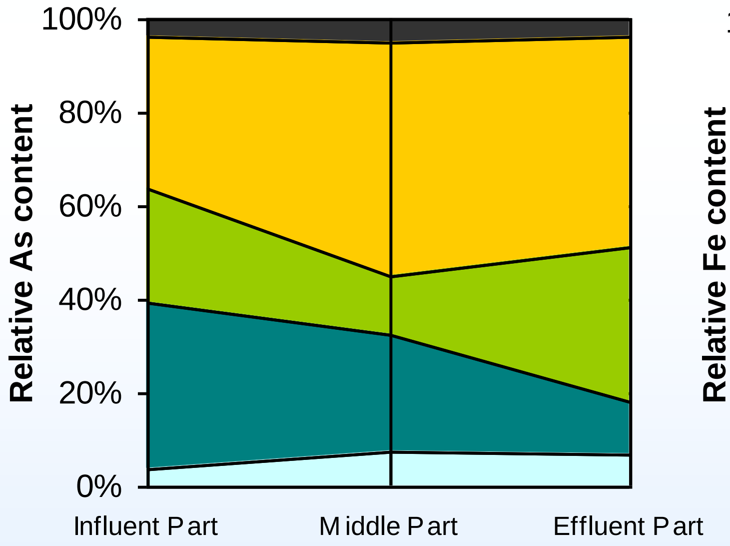
From EPA/600/R-07/140

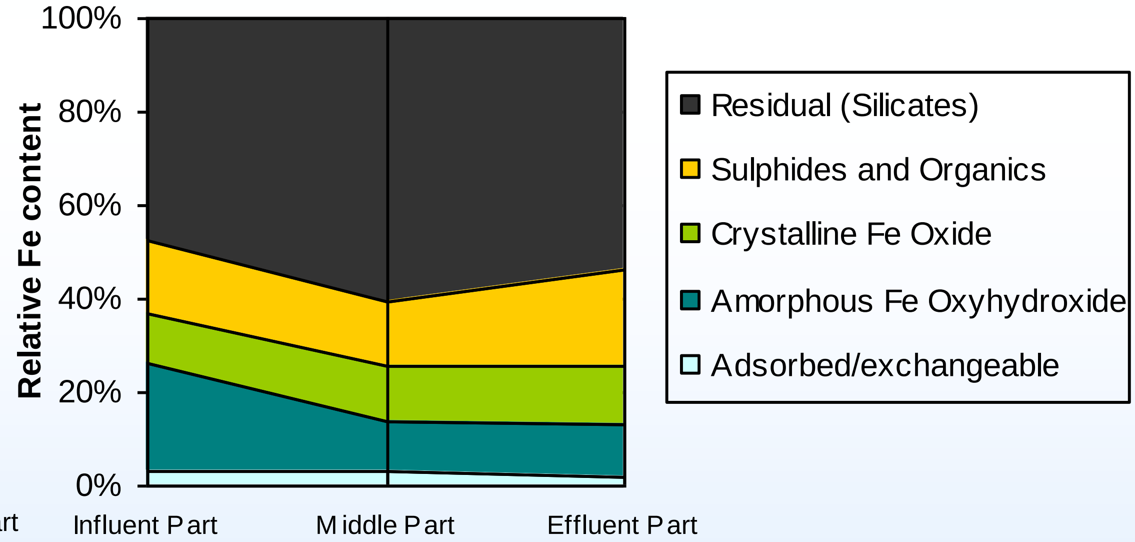
Long-Term Column Test for As Treatment

Solid As Speciation



Long-Term Column Test for As Treatment
Distribution of As and Fe fractions





Mass of As: Fe(II+III) = 1:100

Long-Term EHC-M Column Test for As Treatment

- The majority of As in the EHC-M column was bound in sulfide and iron oxide/oxyhydroxide phases, while most of As in the control column was present in an adsorbed/ exchangeable form.
- The observed changes in solid arsenic and iron distribution along the column confirm the importance of a source ferrous iron from ZVI present in EHC-M.
- Continuous formation of Fe oxide layers protect the precipitated reduced As mineral phases and also aid in re-precipitation and/or adsorption of any As that is potentially mobilized under extreme changes in geochemical conditions.

Presentation Overview

- Technology Background
- Laboratory Validation of Stability
- **Field Applications**

EHC-M Installation Methods

Injection Methods

- Direct injection
- Hydraulic fracturing
- Pneumatic fracturing
- Well injections (EHC-A)

Direct Placement

- Trenching
- Excavations
- Deep soil mixing

EHC-M Installation Methods – Direct Placement

Installation of EHC PRB

Placement at bottom of excavation to treat standing groundwater.

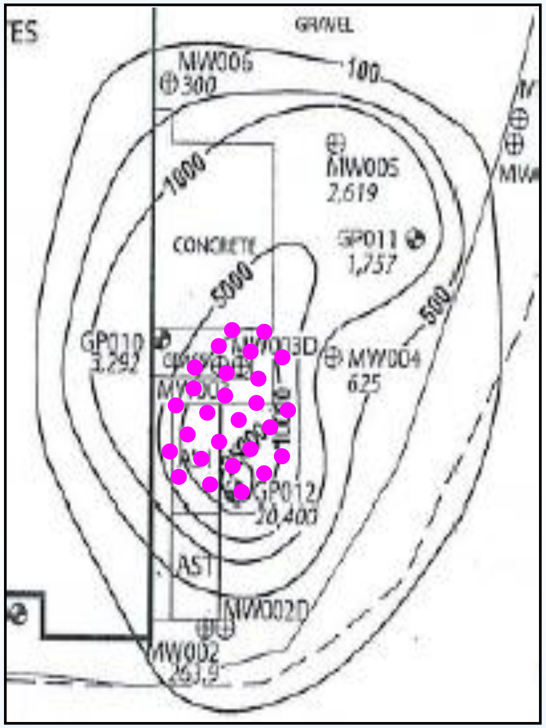
EHC-M Injection Methods
- Pressure-Activated Injection Tip

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!

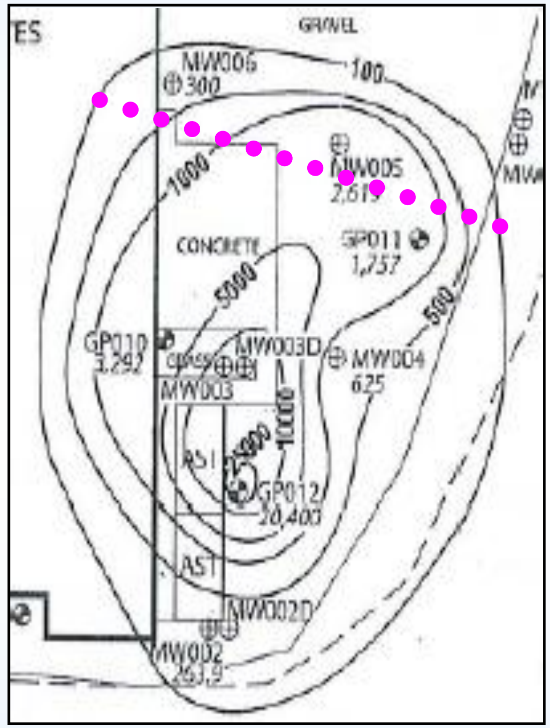
EHC-M Conceptual Designs

Source Area/ Hotspot Treatment



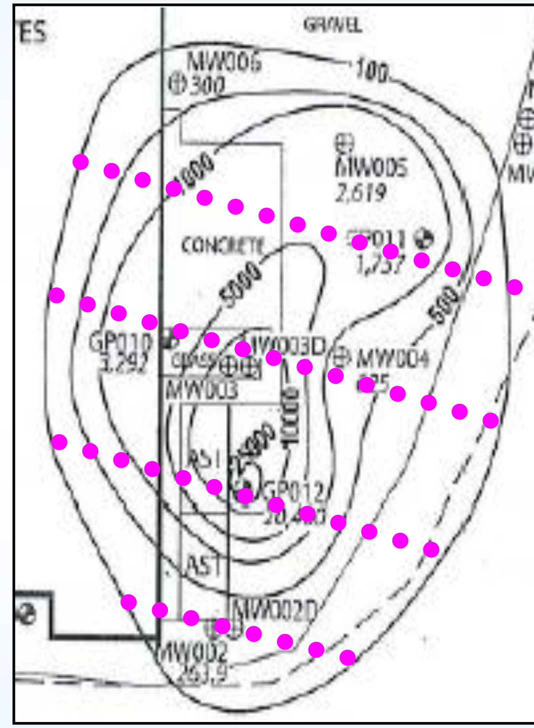
- Dosing: 0.2 to 1% wt/wt
- Spacing: 3 to 5 m (DPT)

Injection PRB for Plume Control



- Dosing: 0.4 to 1% wt/wt
- Spacing: 2 to 3 m (DPT)

Plume Treatment



- Dosing: 0.05 to 0.2% wt/wt
- Line Spacing: 50 m / 1 year gw travel distance

Case Study 1
Mixed plume application

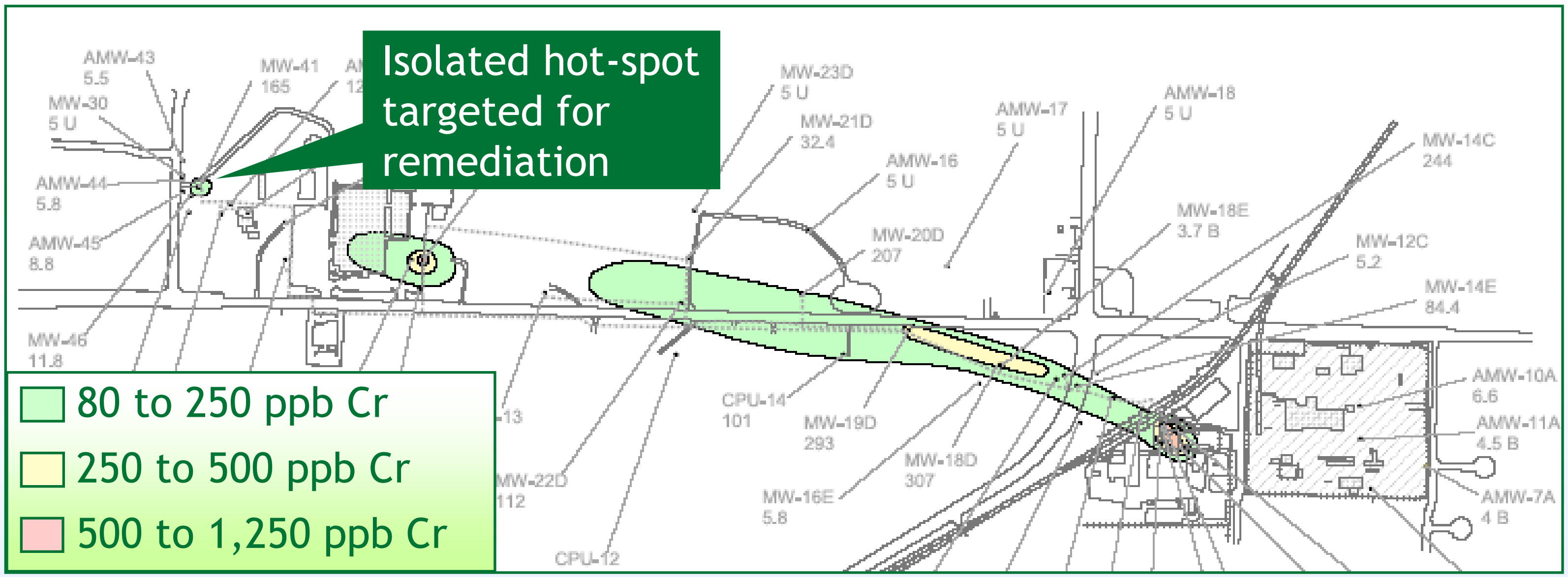
Case Description	
Location	Northwestern US
Type of Site	Industrial facility
Description of Impacts	Cr(VI) and TCE in groundwater; 75 to 85 ft bgs
Objective and Approach	Injection of EHC-M for treatment of isolated hot-spot.

Site Details

Extraction system currently in operation has cleaned up portions of the downgradient end of the plume.

Isolated area experienced rebound when the extraction system was not operated:

- Cr(VI) 165 ppb, TCE 6.1 ppb
- DO 5 mg/L, ORP 200 mV



EHC-M Injection Layout

Treatment Area Dimensions:

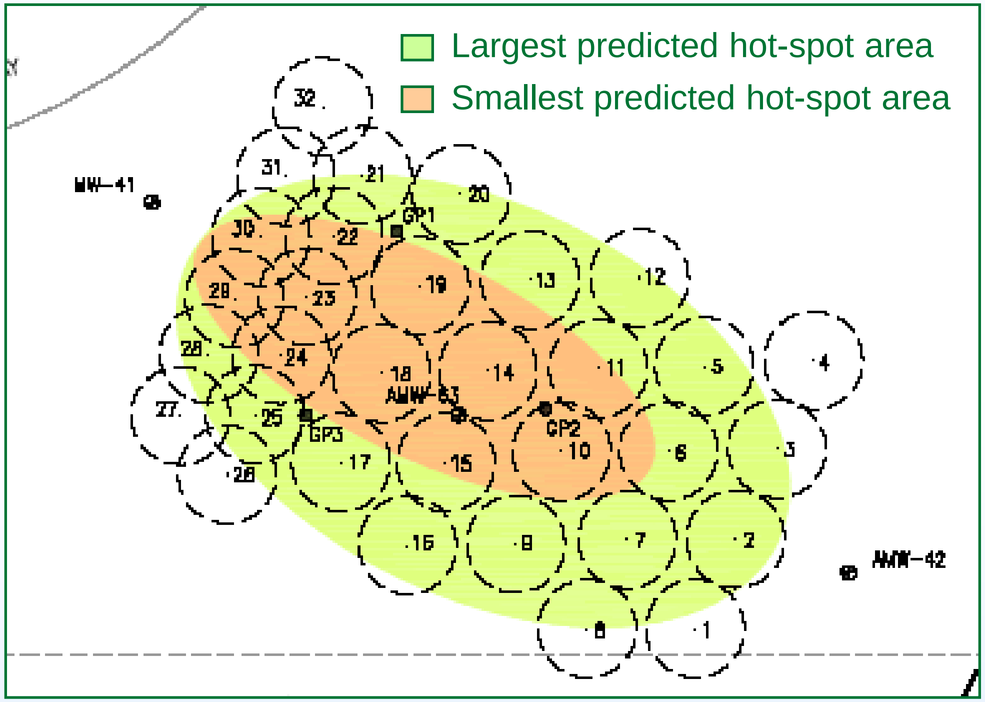
- 100 ft long x 60 ft wide x 10 ft deep (from 75 to 85 ft.

EHC-M Application Rate:

- 0.15% wt/wt
- 9,600 lbs injected

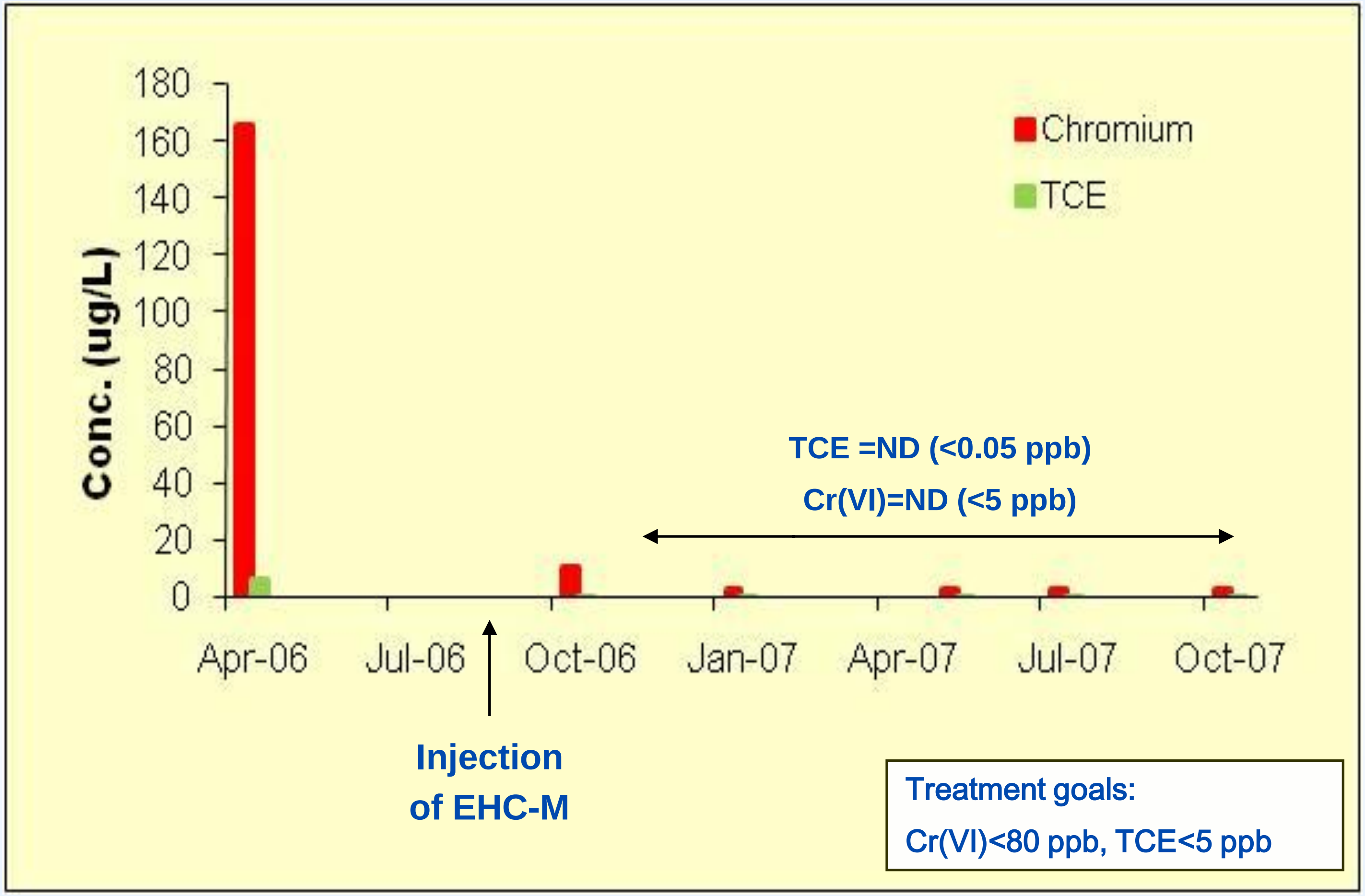
Direct Injection:

- 32 direct push points
- 10 to 15 ft spacing



Field Injection

Field Results – Washington State



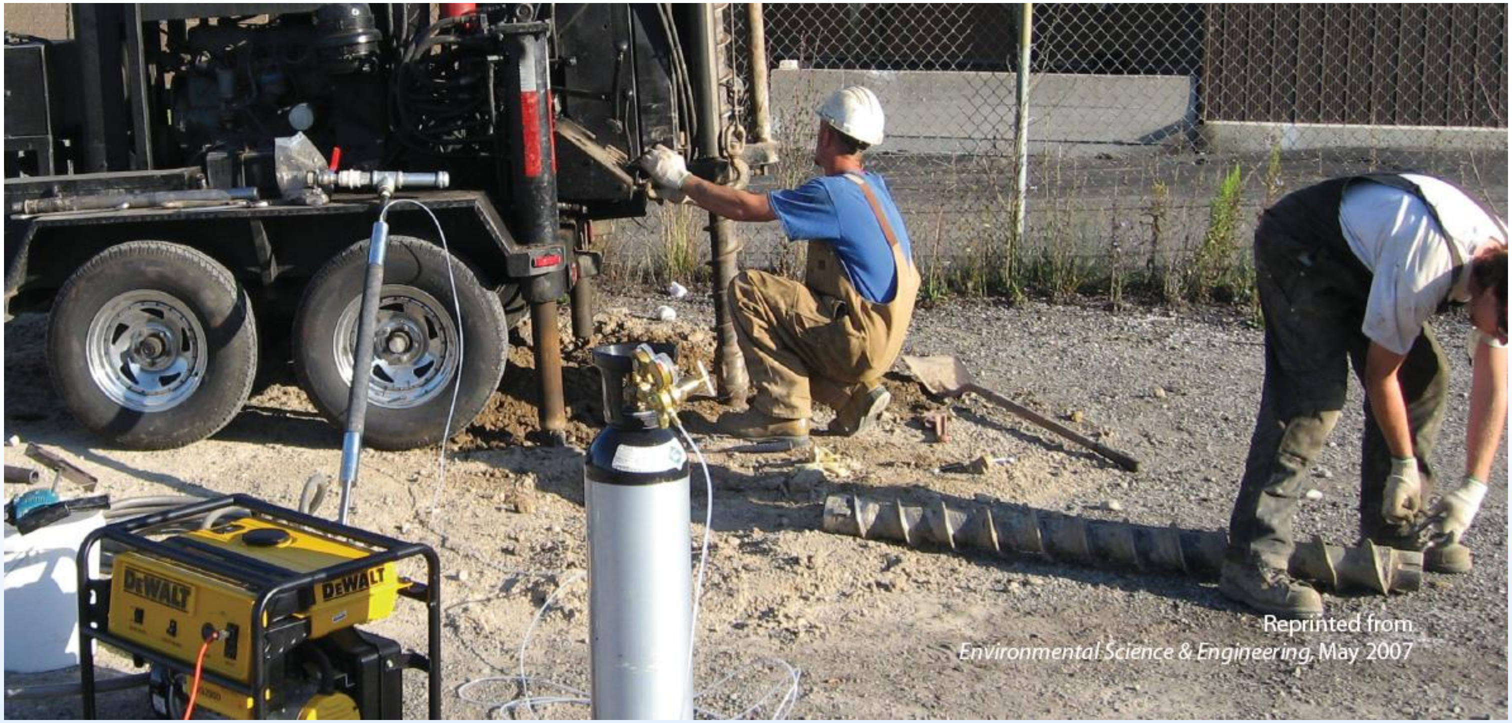
(Courtesy of EA Engineering, Science and Technology, Inc.)

Case Study 2
Trace metal groundwater plume

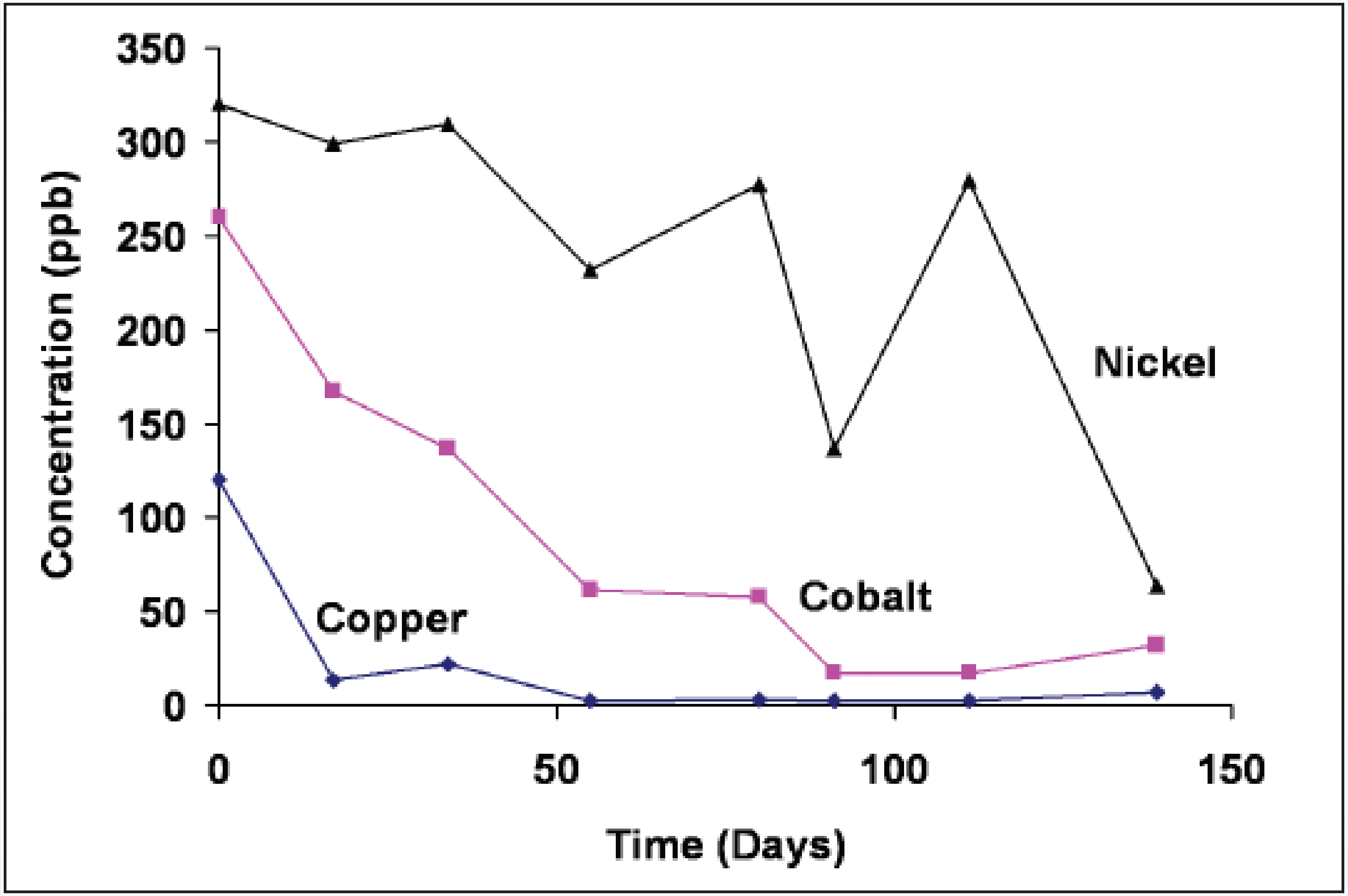
Case Description	
Location	Ontario Canada
Type of Site	Industrial
Description of Impacts	Copper, Cobalt and Nickel
Objective and Approach	EHC-M injected along site boundary for plume cut-off.

Installation method

- Total of 600 kg EHC-M injected into area measring 9 m L x 7 m wide x 7 m deep (0.08% to soil mass).
- EHC-M slurry injected via open bore holes using packers - total of 12 locations.



Field Results

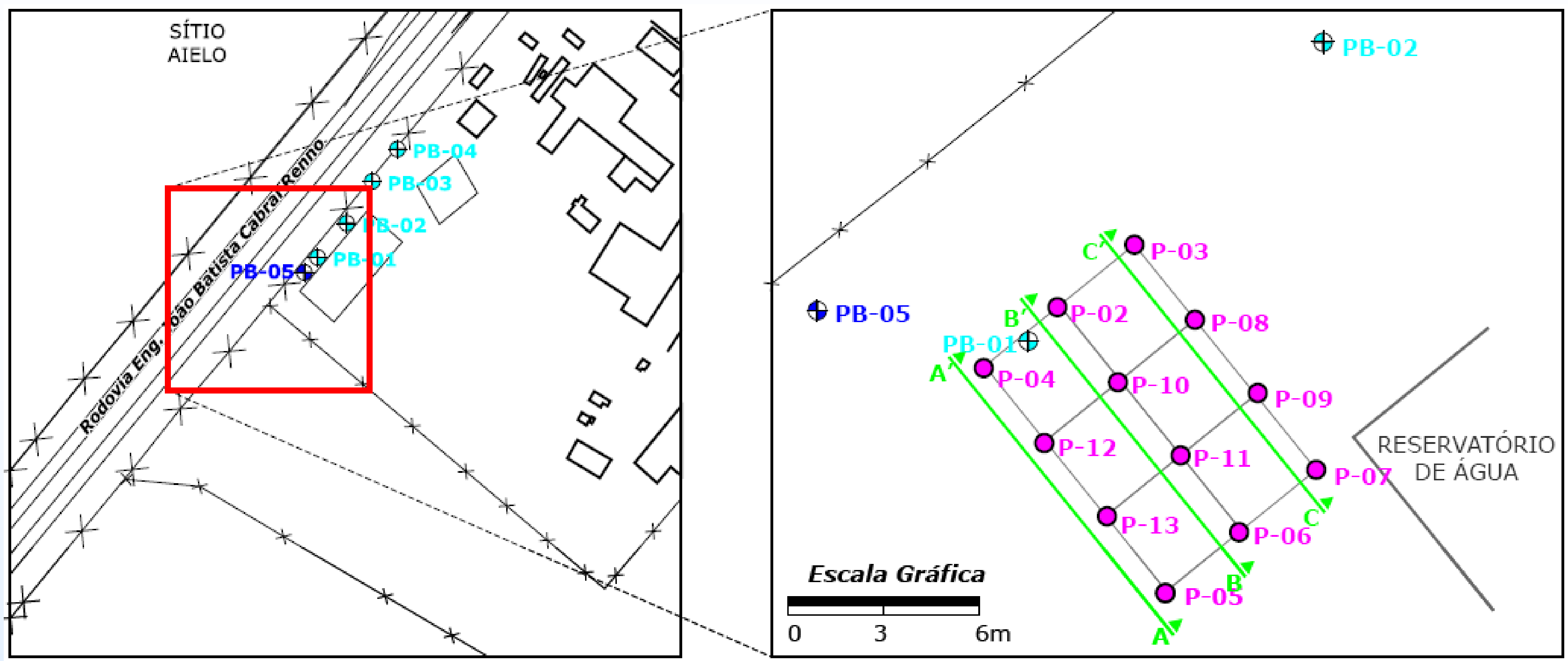


Case Study 3
EHC-M and pH Adjustment for Lead Immobilization

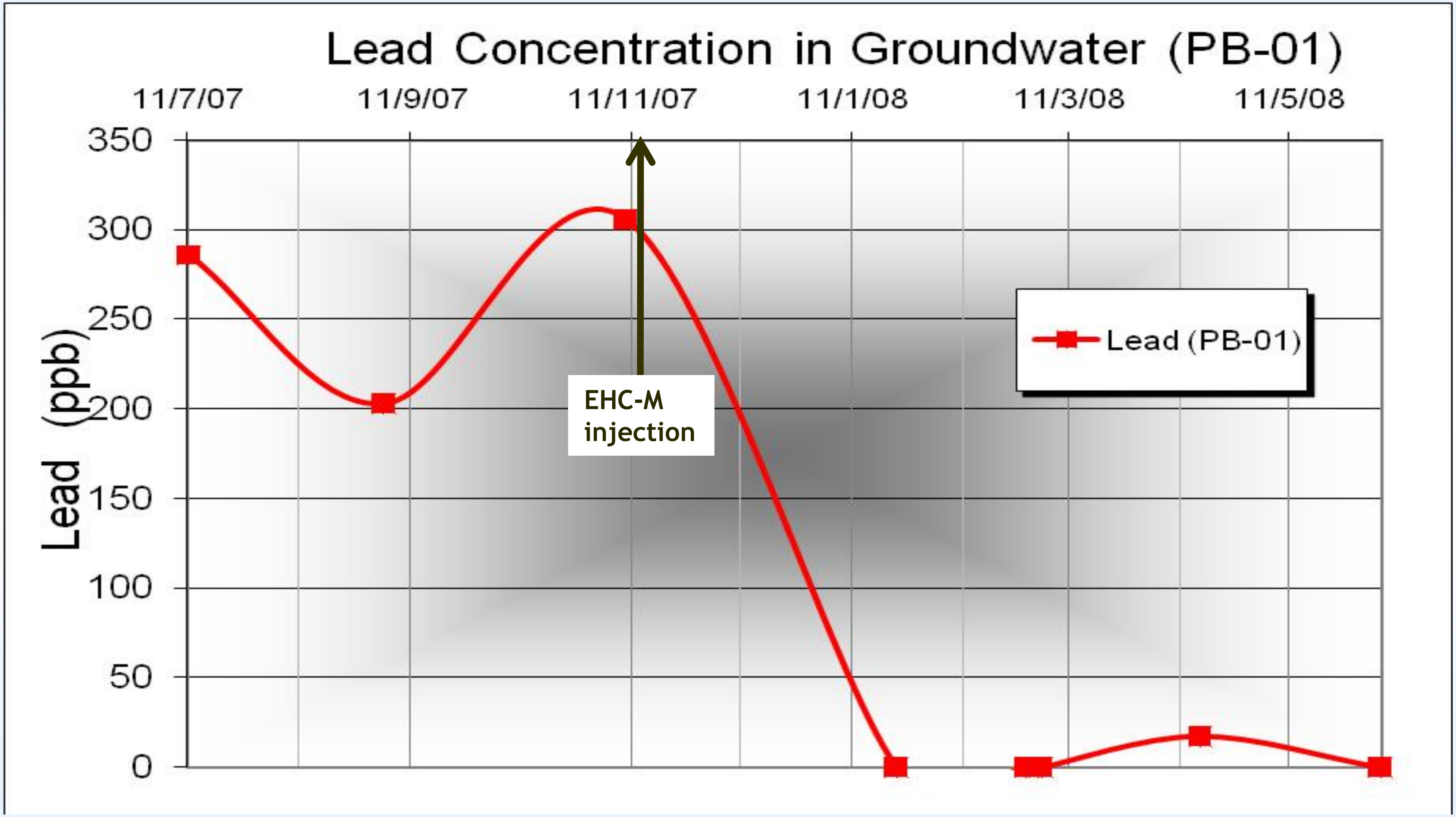
Case Description	
Location	Sao Paulo, Brazil
Type of Site	Former battery recycling facility
Description of Impacts	Dissolved lead plume measuring 250 m long x 150 m wide x 15 m deep (from 15 to 30 m bgs); pH of 4 to 5.
Objective and Approach	Pilot study injection of EHC-M. Treatment included pH adjustment using dolomite.

Injection design

- 1,000 kg of EHC-M was injected from ca 17 to 27 m bgs (0.05% to soil mass).
- 5,000 kg dolomite injected to upper 5 ft of treatment zone (0.5% to soil mass based on pH titration testing).



Pilot Study Results



Summary of Treatment Performance

Location	Compounds Treated	Baseline Conc. (µg/L)	Post Treatment Conc. (µg/L)	Removal Efficiency
Washington, USA	Chromium(VI)	165	<5	>97%
	TCE	6.1	<0.5	>92%
Ontario, Canada	Copper	120	10	92%
	Cobalt	260	40	85%
	Nickel	320	70	78%
Sao Paulo, Brazil	Lead	306	<10	>97%

Summary

- Combination of iron and carbon promotes:
  - Chemical and biological degradation of chlorinated organics
  - Immobilization of reducible metals and metalloids

- EHC-M effective for:
  - Chlorinated solvents
  - Immobilization of metals
  - Mixed plumes