Chemical Reduction processes for In Situ Soluble Metals Remediation and Immobilization in Groundwater

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SOLUTIONS AND ENVIRONMENTAL PRODUCTS

WATER - SOIL - AIR

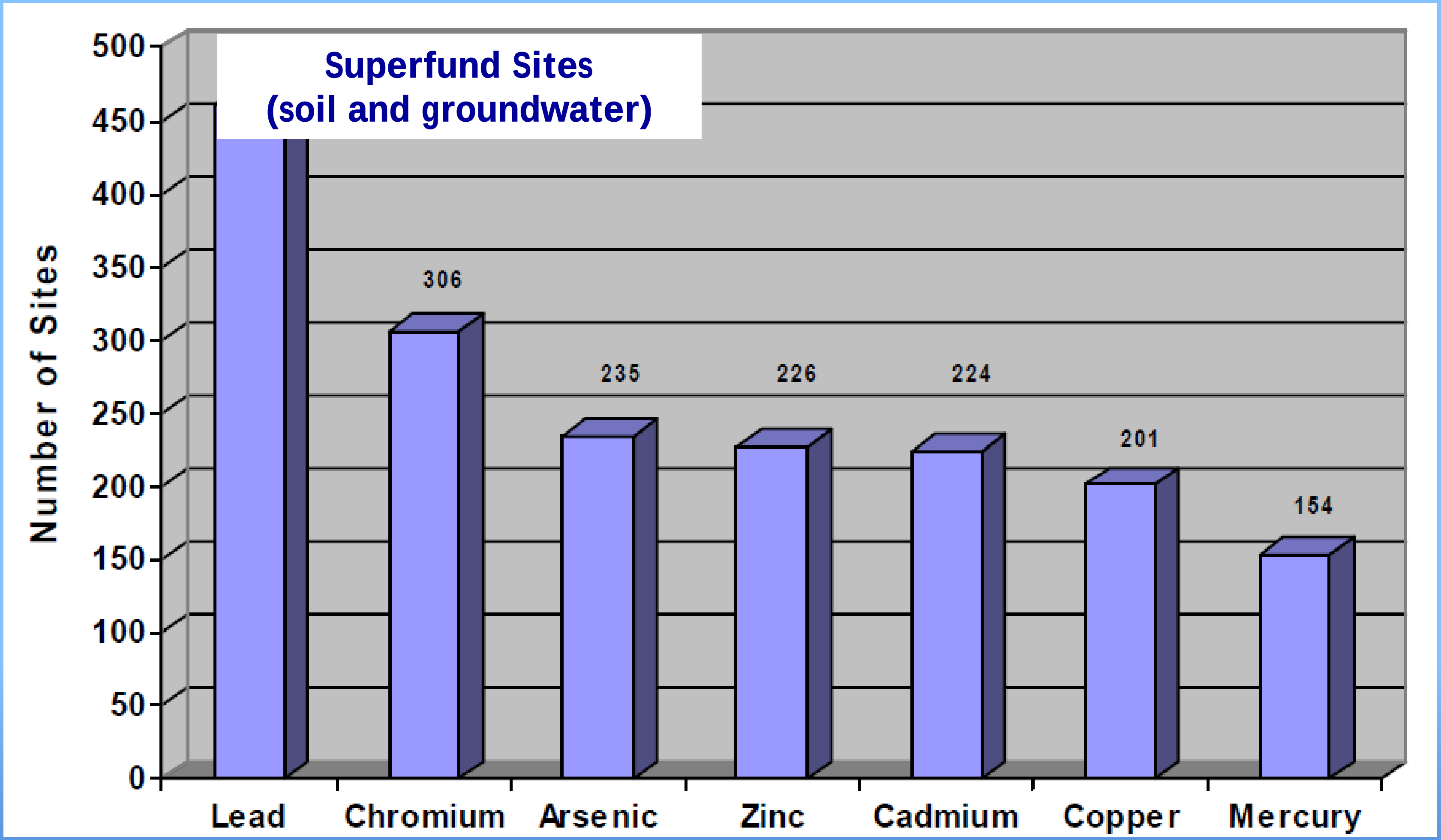
Presentation Outline

- Problem Description
- Technology Review and Performance
- Using ISCR for Toxicity and/or Mobility Control
- Design Parameters
- Case Study Presentation

Problem Description

- **Source of Metals Contaminant**
  - Contaminated Wastewater discharges
  - Direct contact with impacted soil from
    - ⤷ Sludges
    - ⤷ Mining Wastes
    - ⤷ Spills
    - ⤷ Airbone Emissions

Common Metal Impacts



Source: Remediation of Metals – Contaminated Soils and Groundwater, GRWTAC

Technology Review and Performance

Table 1. Remediation Technologies Matrix for Metals in Soils and Ground-Water

Remediation Technology	Metals Treated	Cost	Long-term Effectiveness/ Permanence	Commercial Availability	General Acceptance	Applicability to High Metals Concentrations	Applicability to Mixed Waste (metals & organics)	Toxicity Reduction	Mobility Reduction	Volume Reduction
Capping	1-3	+	«	+	+	«	+	«	+	«
Subsurface Barriers	1-3,5	+	«	+	+	«	+	«	+	«
Solidification/ Stabilization Ex situ	1-3,5	•	•	+	+	+	+	«	+	«
Solidification/ Stabilization *In situ*	1,2,4,6	+	•	+	+	+	+	«	+	«
Vitrification Ex situ	1-3,5	«	+	•	•	+	+	«	+	«
Vitrification *In situ*	1-3,7	«	+	•	•	+	+	«	+	«
Chemical Treatment	2	-	•	•	•	-	-	+	+	«
Permeable Treatment Walls	2	-	•	•	•	-	-	+	+	«
Biological Treatment	1-5	+	«	•	•	«	-	+	+	«
Physical Separation	1-6	•	+	+	+	+	«	«	«	+
Soil Washing	1-3,5-7	•	+	+	+	+	•	«	«	+
Pyrometallurgical Extraction	1-5,7	«	+	+	+	+	«	«	«	+
In situ Soil Flushing	1,2,7	+	«	+	+	+	+	«	«	+
Electrokinetic Treatment	1-6	•	+	+	+	+	-	«	«	+

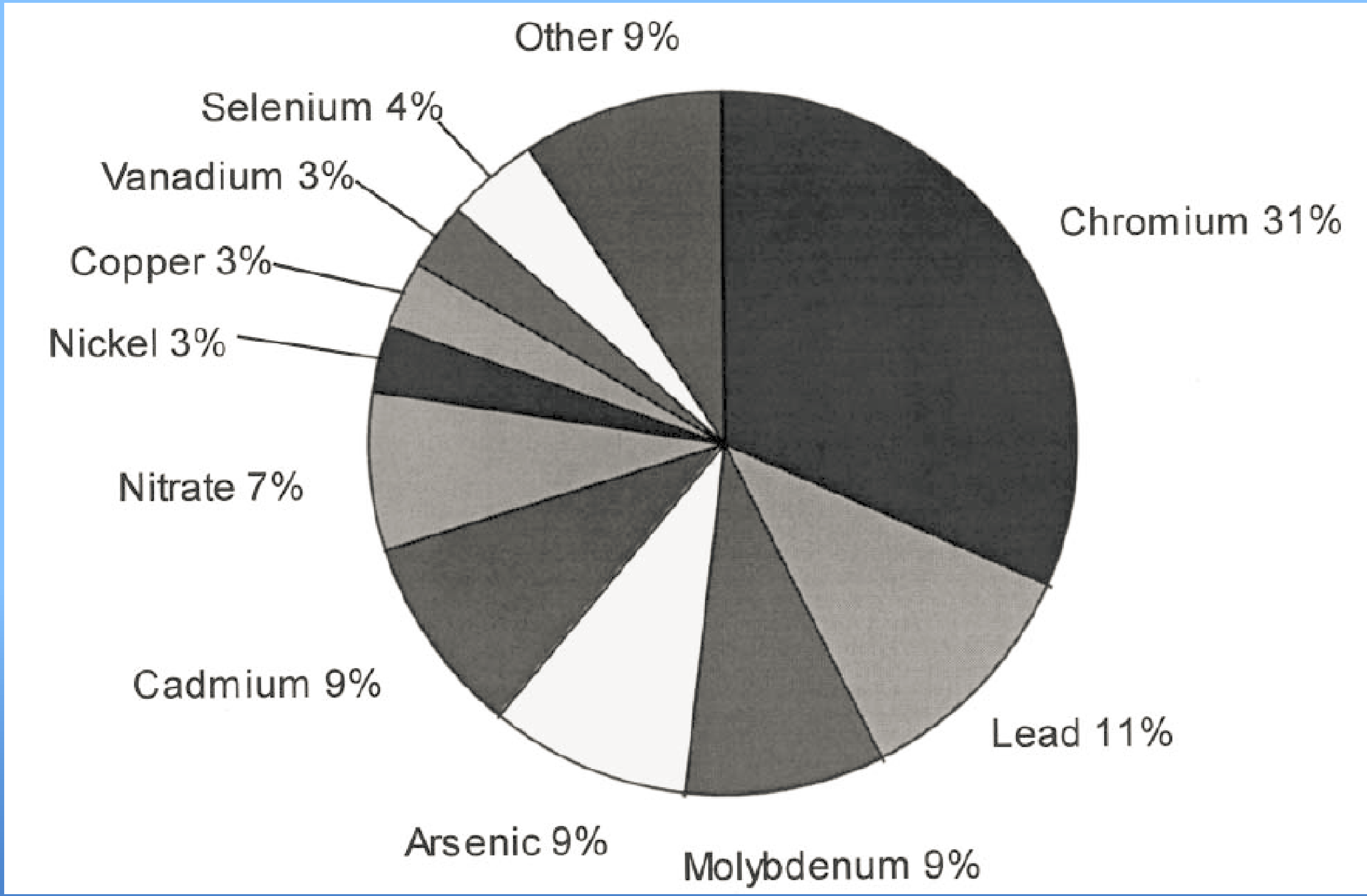
1-Lead, 2-Chromium, 3-Arsenic, 4-Zinc, 5-Cadmium, 6-Copper, 7-Mercury

+ Good, • Average, « Marginal, - Inadequate Information

Source: Remediation of Metals - Contaminated Soils and Groundwater, GRWTAC

Technology Review and Performance

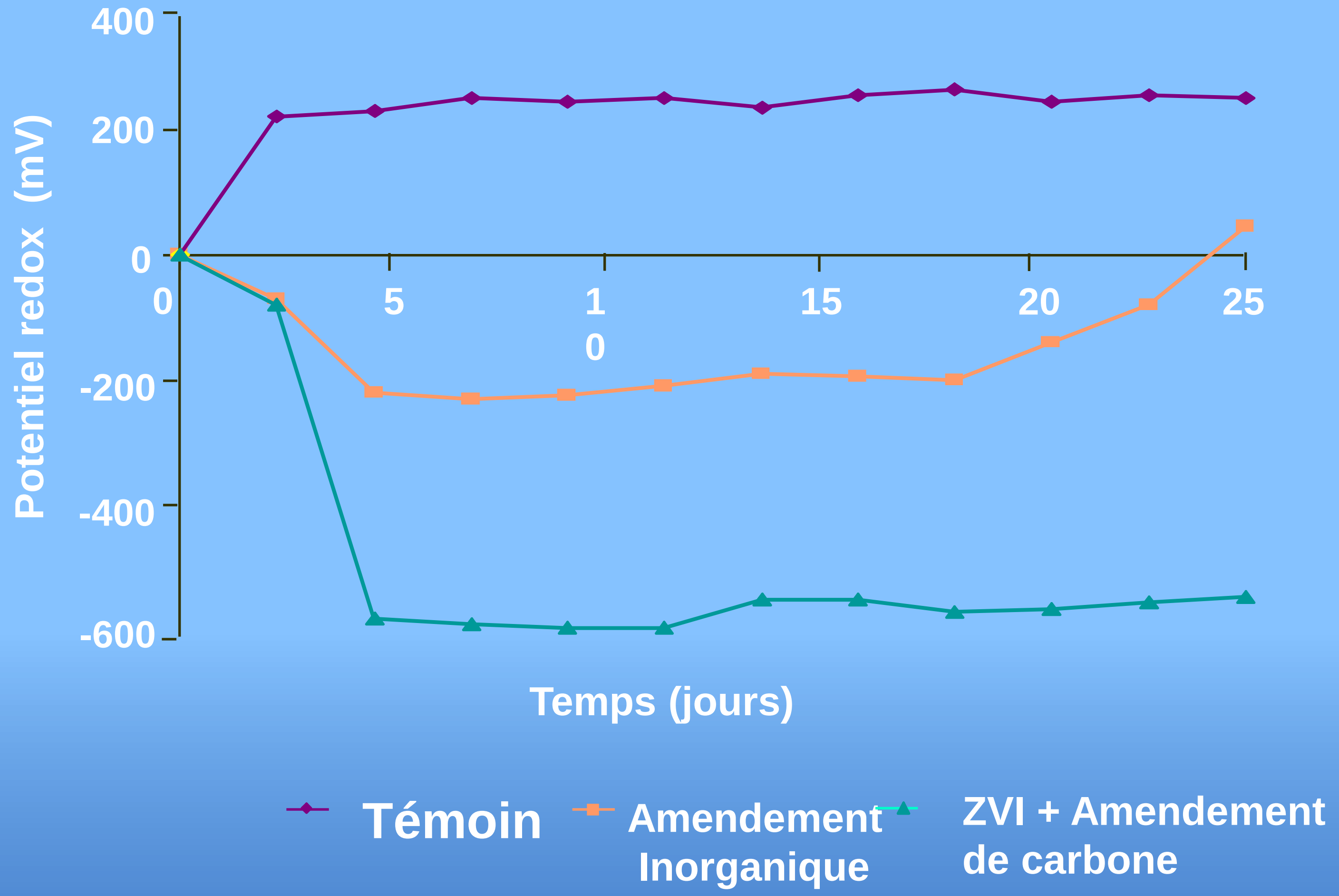
PRB Applications
(2000)



Réduction Chimique
In Situ/Ex Situ - Principes

- Mise en place (In Situ) d'un matériau réducteur ou générant des conditions réductrices pour dégrader les composés organiques toxiques ou immobiliser des métaux
- Le réducteur le plus couramment utilisé est le fer zéro valent (ZVI)
- Introduction possible de substrats organiques pour produire des conditions favorables à la réduction microbienne
- Dégradation/Immobilisation des contaminants par processus abiotiques ou biotiques

Potentiel Redox des sols durant une phase de traitement réductive

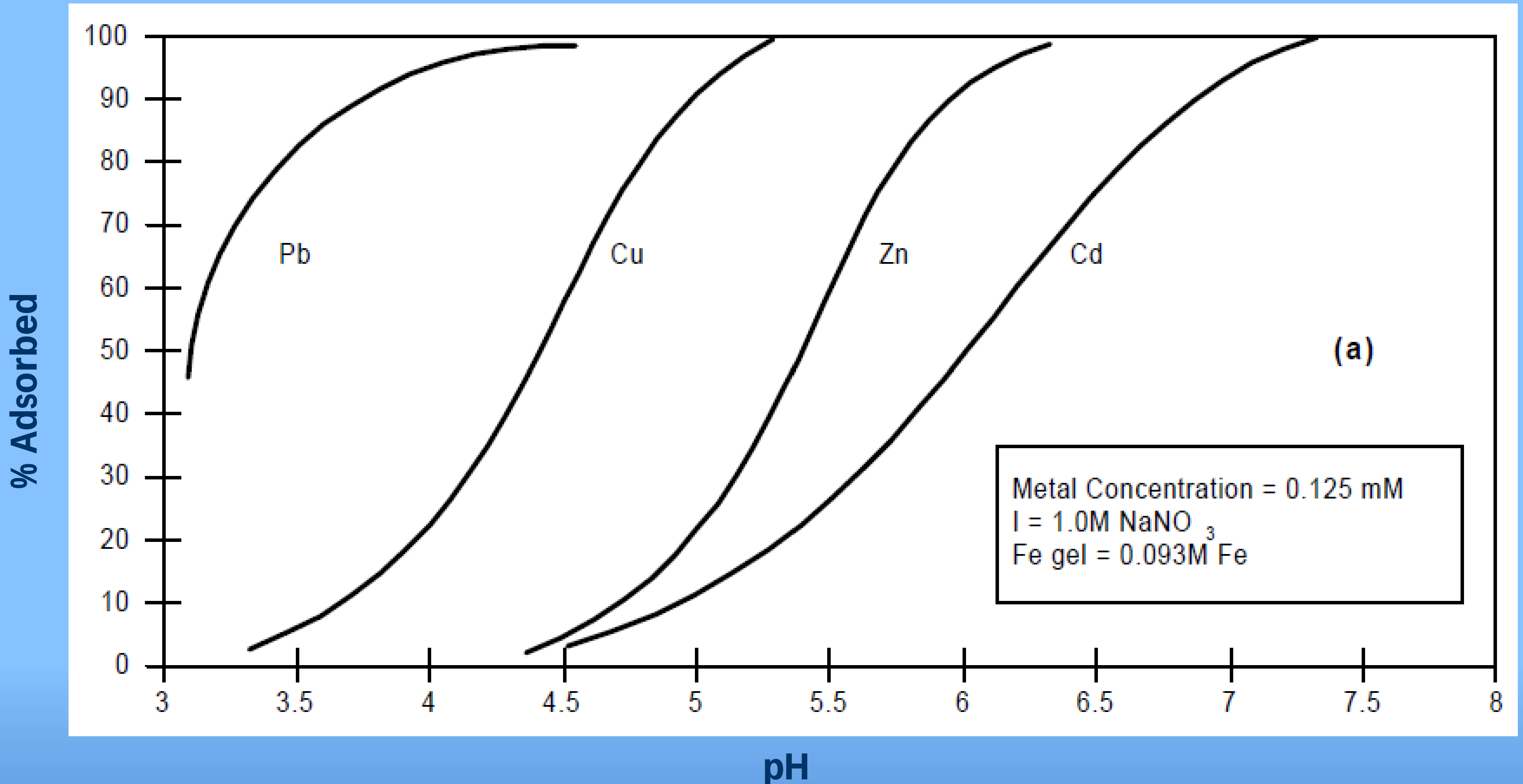


Dissolved Metal Fate (Remediation) Controls

- Depending on their aqueous form, the mobility of trace metals in groundwater is affected by various chemical reactions, including:
    - dissolution-precipitation,
    - oxidation-reduction,
    - adsorption-desorption and complexation.

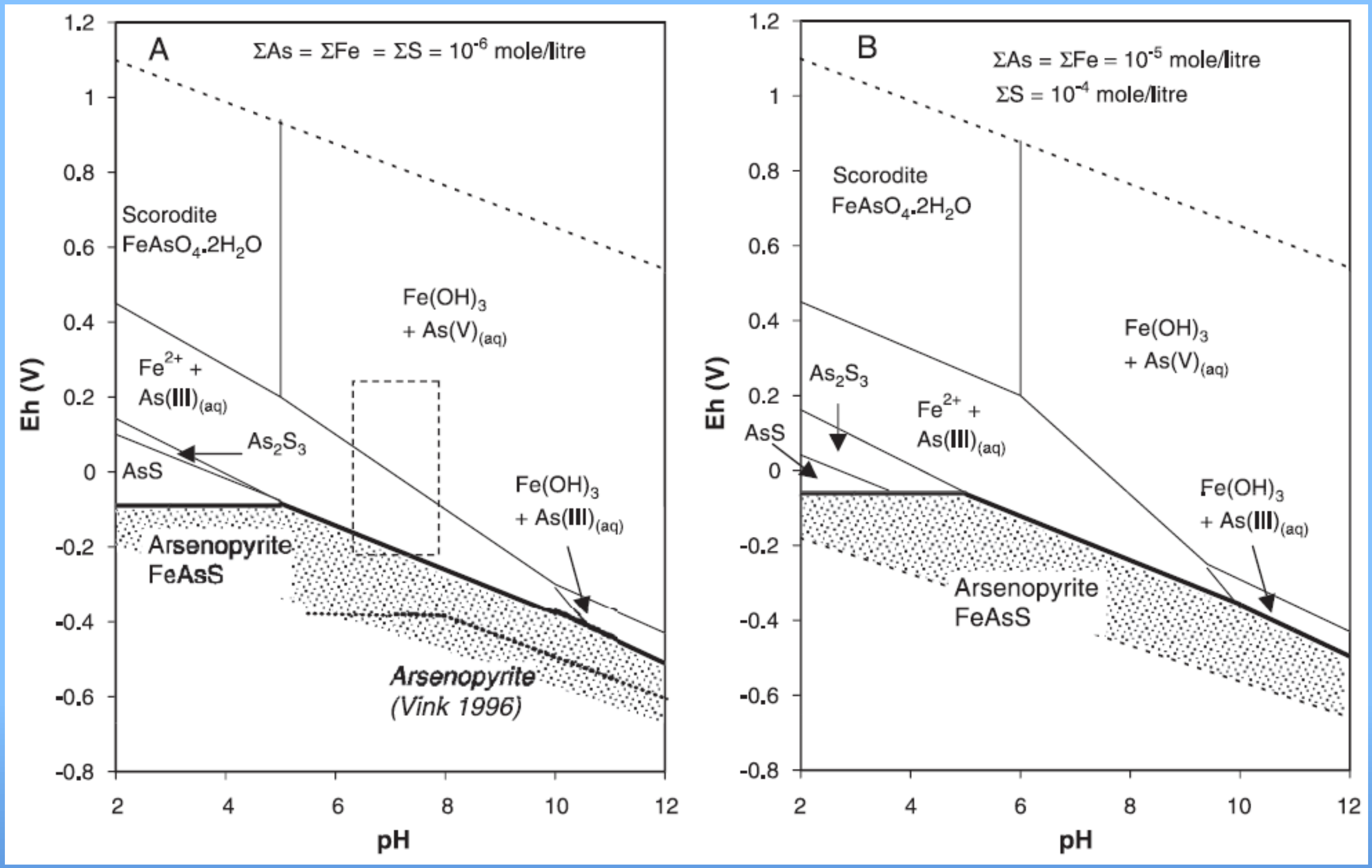
- Precipitation, sorption, and ion exchange reactions can retard the movement of metals in groundwater and at the same time serve as remediation (stabilization) mechanisms.

Adsorption-Desorption: Divalent metals



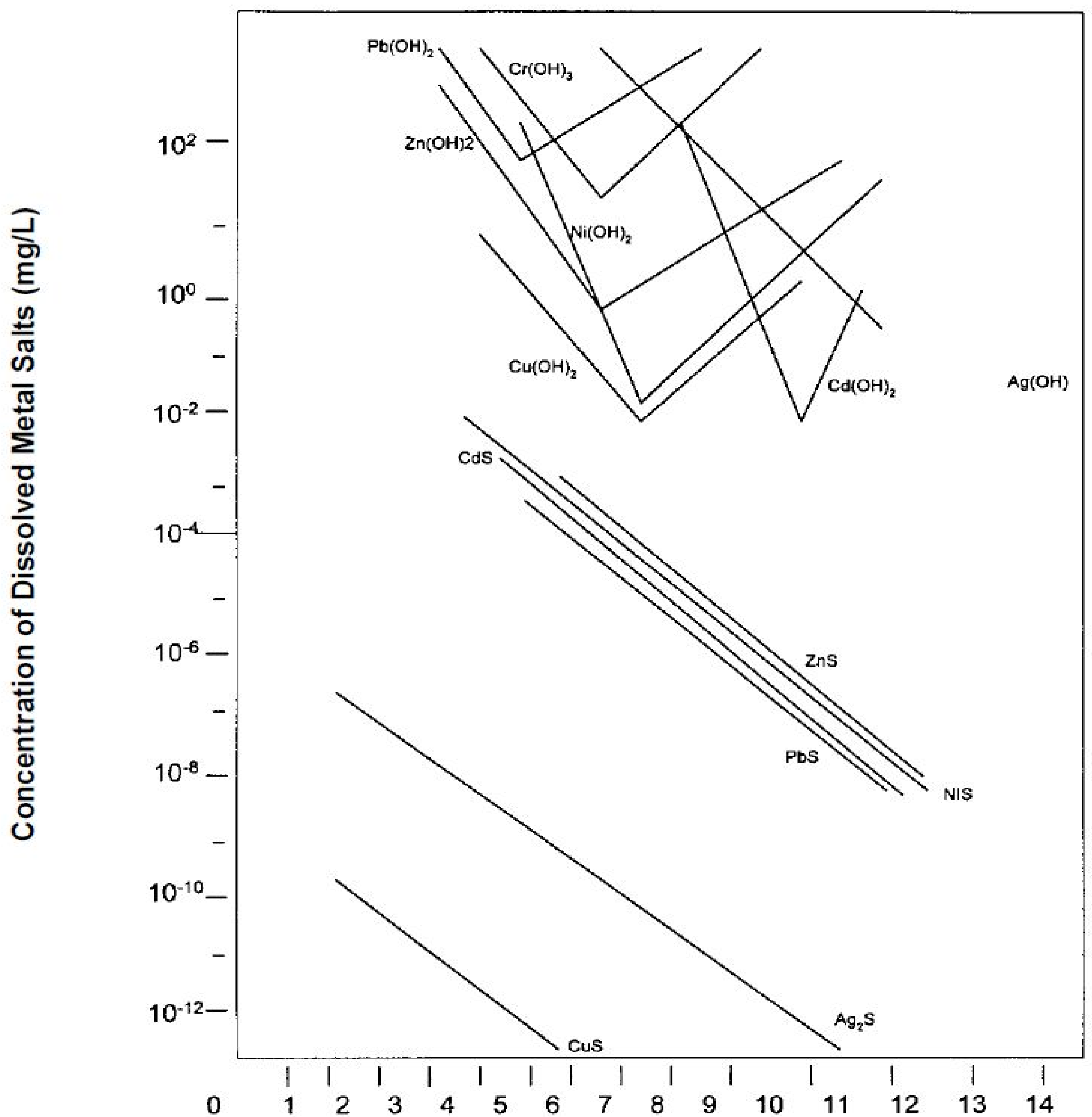
Important adsorptive solids:
hydrous oxides of iron or manganese, clay minerals, and organic matter

Co- precipitation/adsorption of Arsenic in the presence of dissolved Fe and S



From Craw et al. (2003)

Precipitate Stability using hydroxide or sulfide



Reference
EPA 625/8-80-003

Precipitate Stability

Theoretical Solubilities of Selected Metals in Pure Water at 25˚C (mg/L)

Metal	*As Hydroxide*	*As Sulfide*	*As Carbonate*
Cadmium (Cd^{2+})	2.3×10^{-5}	6.7×10^{-10}	1.0×10^{-4}
Chromium (Cr^{+3})	8.4×10^{-4}	No precipitate	—
Cobalt (Co^{2+})	2.2×10^{-1}	1.0×10^{-8}	—
Copper (Cu^{2+})	2.2×10^{-2}	5.8×10^{-18}	—
Iron (Fe^{2+})	8.9×10^{-1}	3.4×10^{-5}	—
Lead (Pb^{2+})	2.1	3.8×10^{-9}	7.0×10^{-3}
Manganese (Mn^{2+})	1.2	2.1×10^{-3}	—
Mercury (Hg^{2+})	3.9×10^{-4}	9.0×10^{-20}	3.9×10^{-2}
Nickel (Ni^{2+})	6.9×10^{-3}	6.9×10^{-8}	1.9×10^{-1}
Silver (Ag^{+})	13.3	7.4×10^{-12}	2.1×10^{-1}
Tin (Sn^{2+})	$1.1. \times 10^{-4}$	3.8×10^{-8}	—
Zinc (Zn^{2+})	1.1	2.3×10^{-7}	7.0×10^{-4}

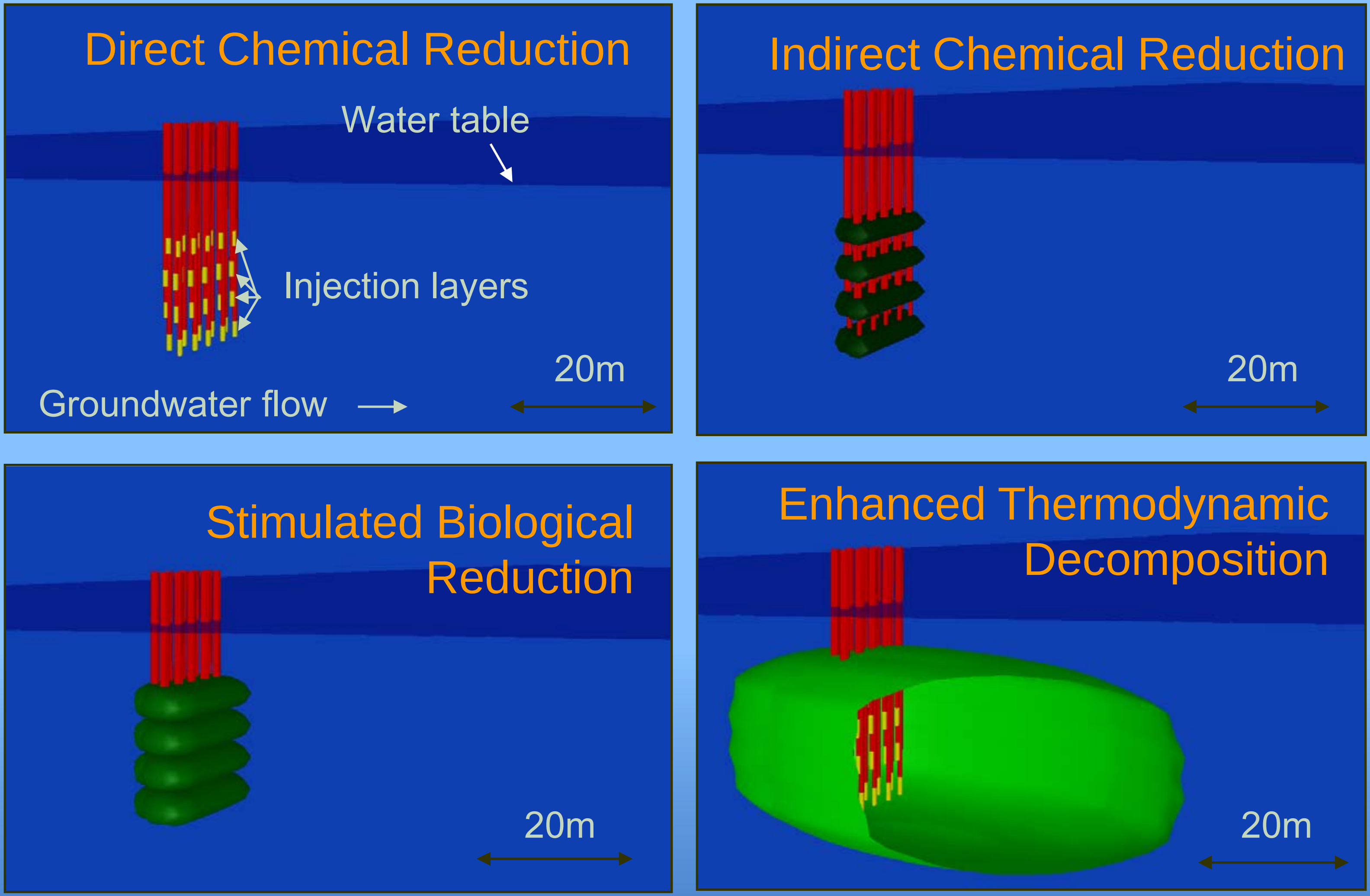
EPA 625/8-80-003

Using ISCR for Metals Toxicity and/or Mobility Reduction in Groundwater

ZVI (40%) + Solid Organic Carbon (50%) + Soluble Organic Carbon (10%) for In-situ integrated biological and chemical reduction (ISCR)

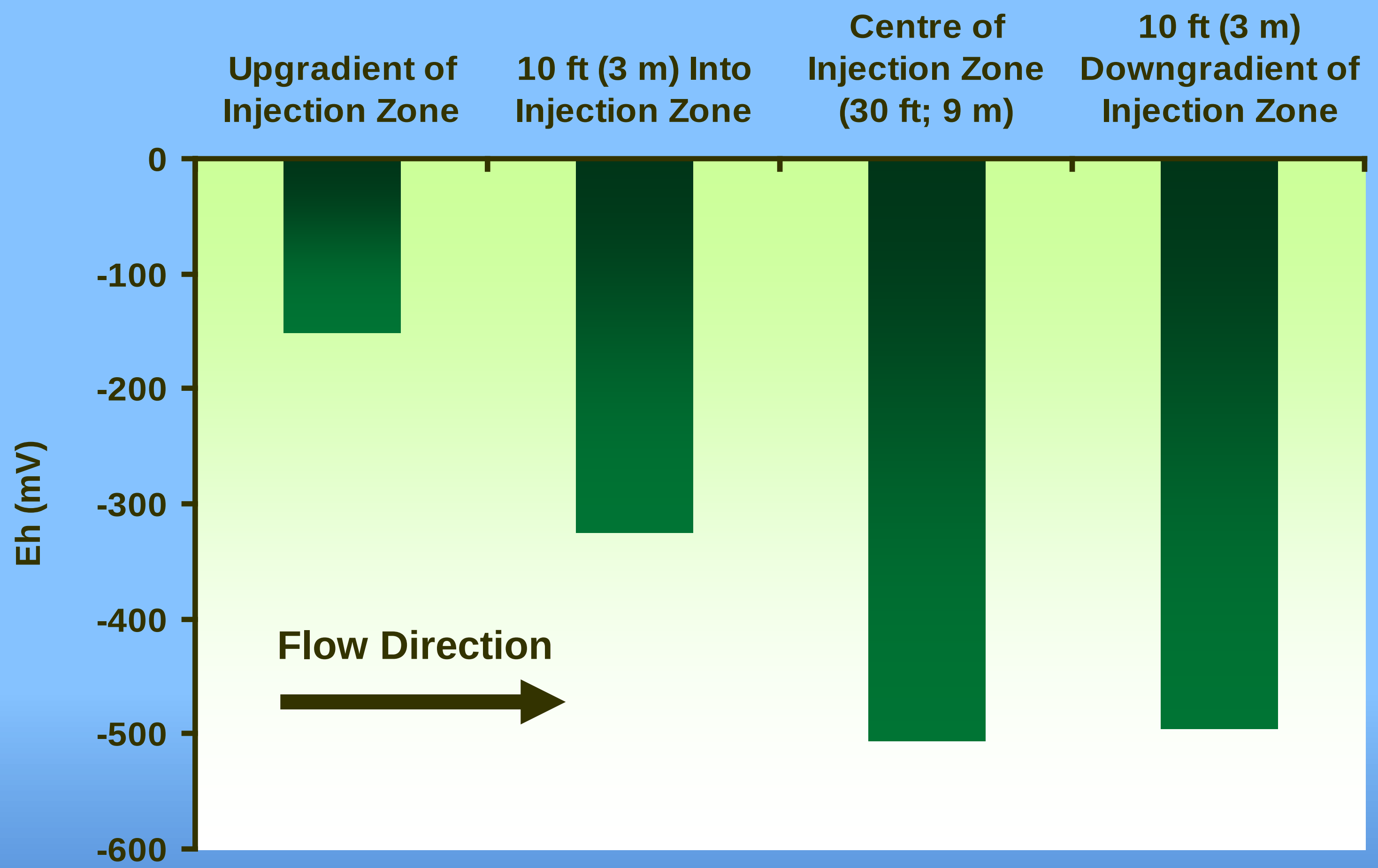
- Major, minor, and micro nutrients are provided
- Balances acidity (VFAs) and alkalinity (ZVI) to prevent acidification of groundwater
- Formulated for injectability
- Product adds sulfate salts and sulfide sources (K and Mg sulfate)
- Very long life from 36 to 72 months
- Emplaced in slurry form via direct push, hydraulic or pneumatic fracturing, trenching or soil mixing

ISCR ZVI + Carbon Treatment Mechanisms



Influence of ZVI + Carbon Substrates on Aquifer Eh Conditions

60 ft (18 m) injection zone



Source: URS

ZVI + Carbon Substrate Treatment Mechanisms

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

ZVI and Carbon Substrates Metals Treated and Mechanisms

Contaminant, metals and metalloids	Treatment Mechanisms in the ZVI-Carbon ISCR 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 • 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)

Design and Field Measurements Requirement

- Total concentration in soil and groundwater of targeted metals
- Dissolved (field filtered) metals concentrations
- pH, Redox Potential (Eh), Dissolved Oxygen
- Cation scan (calcium, sodium, magnesium, silicon)
- Anion Scan (chloride, sulfate, nitrate)
- Total Organic Carbon (TOC), Dissolved Organic Carbon (DOC)
- Alkalinity

These parameters are used to assess the applicability of an ISCR approach and for optimizing the application rate. The same parameters are also recommended monitoring parameters.

Design Considerations ZVI + CS

Are metal levels/mass fluxes and general chemistry amenable to ISCR treatment?

PRB or Plume treatment?

Dose Calculation to create sulfate reducing conditions*

Dose Calculation for sufficient distribution and residence time**

Sufficient SO_4 present ?

Is pH buffer needed (carbonate-based preferable for Me^{2+})

* Terminal electron demand in the calculator

** Guidelines in the calculator

Bench Scale Laboratory testing

- Site groundwater and aquifer material needs to be used.
- Proper sampling and sample handling is essential to avoid sample alteration (aeration) that may result in testing artifacts.
- Flow through column tests are preferable to batch test.
- Field pilot-scale test are strongly recommended as a feasibility step, either following the lab evaluation or stand alone, for As treatment especially.

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
Nickel	350	>99
Zinc	50,400	92

Summary of Removal Efficiencies Observed in the Field

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%
Florida, USA	Arsenic	550	<10	>98%

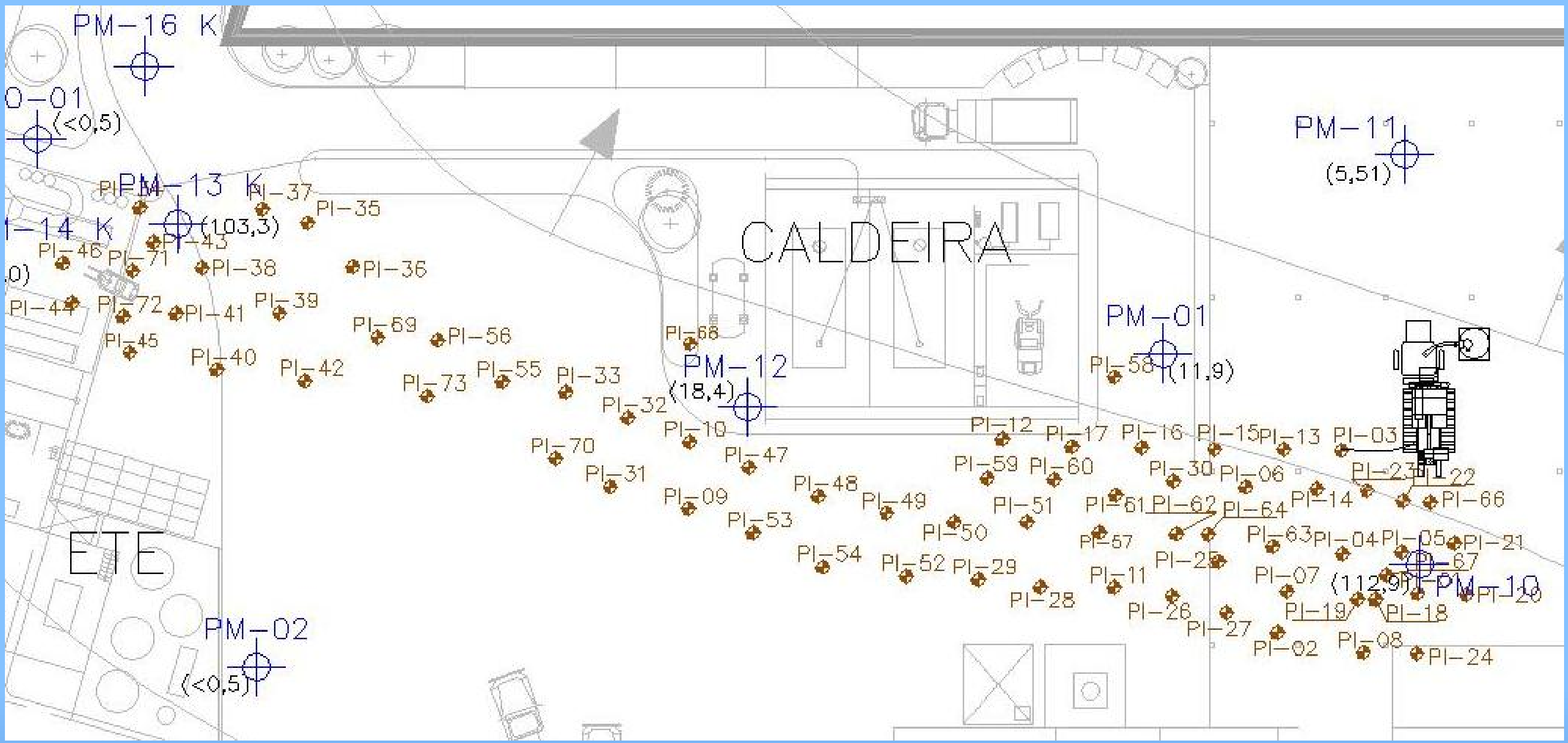
Field Applications of ZVI + Carbon Substrate

- Over 50 world-wide (pilot and full-scale)
- Target concentrations met for various metals including Cr(VI), divalent metals, arsenic
- VOCs present also treated
- Case studies
  - Brazil (Pb)
  - Illinois (Cr, Ni)
  - Ontario (Cu, Ni, Zn)

ZVI + CS
ISCR Groundwater Treatment

CASE STUDY #1
Industrial Site, Rio de Janeiro, Brazil

Full-Scale Application
(March 2011)



- 11,200 kg ZVI+CS injected into a total of 73 points spaced 3 to 4 m apart.
- Application rate of 0.2% ZVI+CS by soil mass.
- $Mg(OH)_2$ added to ZVI+CS slurry to increase the pH.

Injection set-up

Betomaq grout mixer (model MV 100) ~42% Slurry

The ZVI+CS slurry was continuously prepared on site using a grout mixer, targeting approximately 42% solids.

The slurry was purposefullly mixed thicker than normal (*e.g.*, 29% solids) to limit surfacing during injection.

Gravity feed of slurry to grout pump

Injection pressures were generally below 50 psi at an injection flow rate of 20 L/min.

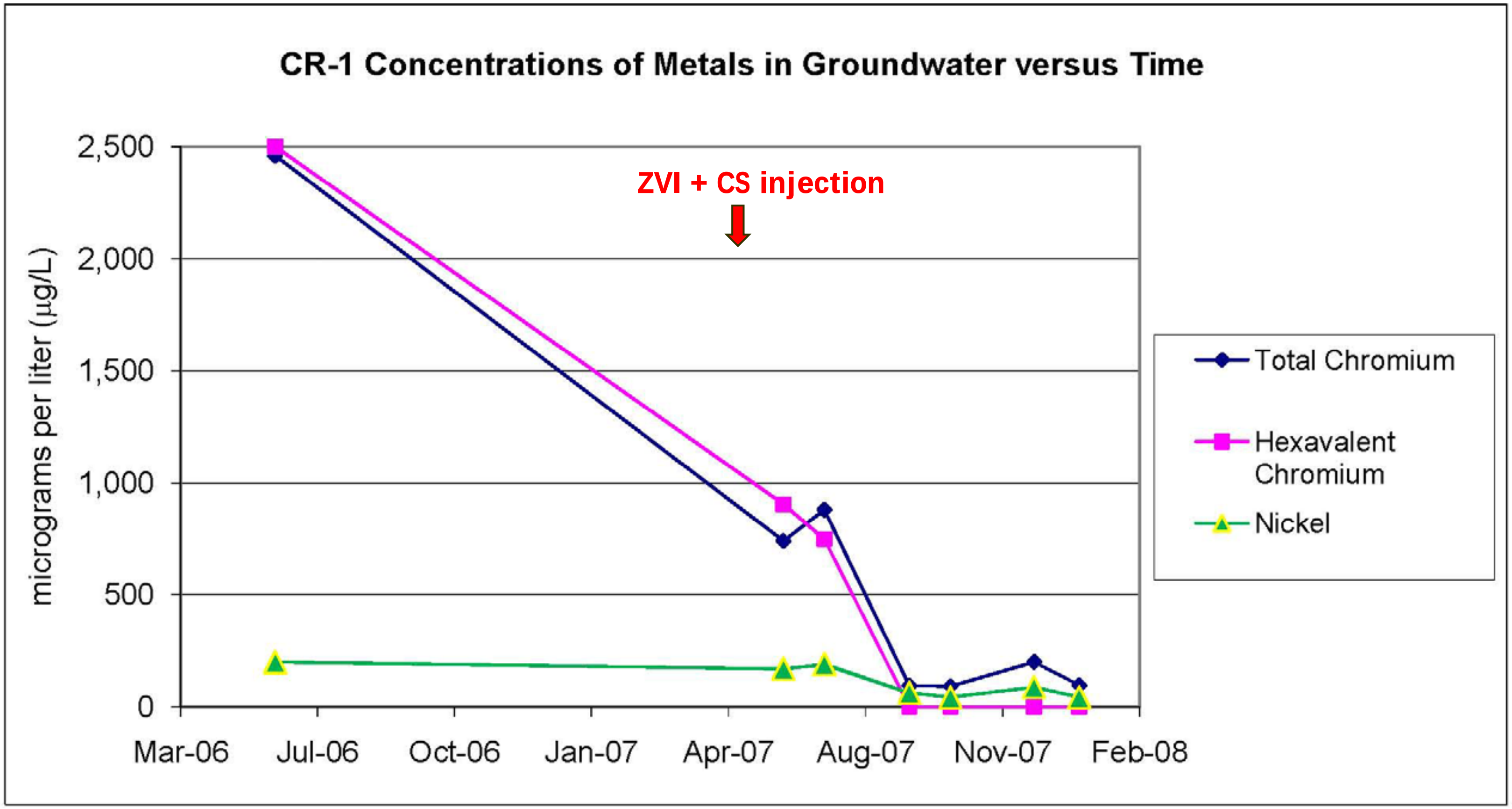
Results
Effect on Dissolved Pb and Geochemistry

	PM-10		PM-01	
	Baseline Nov 2010	~1 year April 2012	Baseline Nov 2010	~1 year April 2012
Dissolved Pb (ug/L)	113	<0.5	12	<0.5
pH	4.45	7.15	5.5	6.6
DO (mg/L)	0.8	1.1	0.4	0.9
ORP (mV)	369	-381	195	-134

Case Study 2
ZVI + CS for Cr(VI) and Ni Immobilization

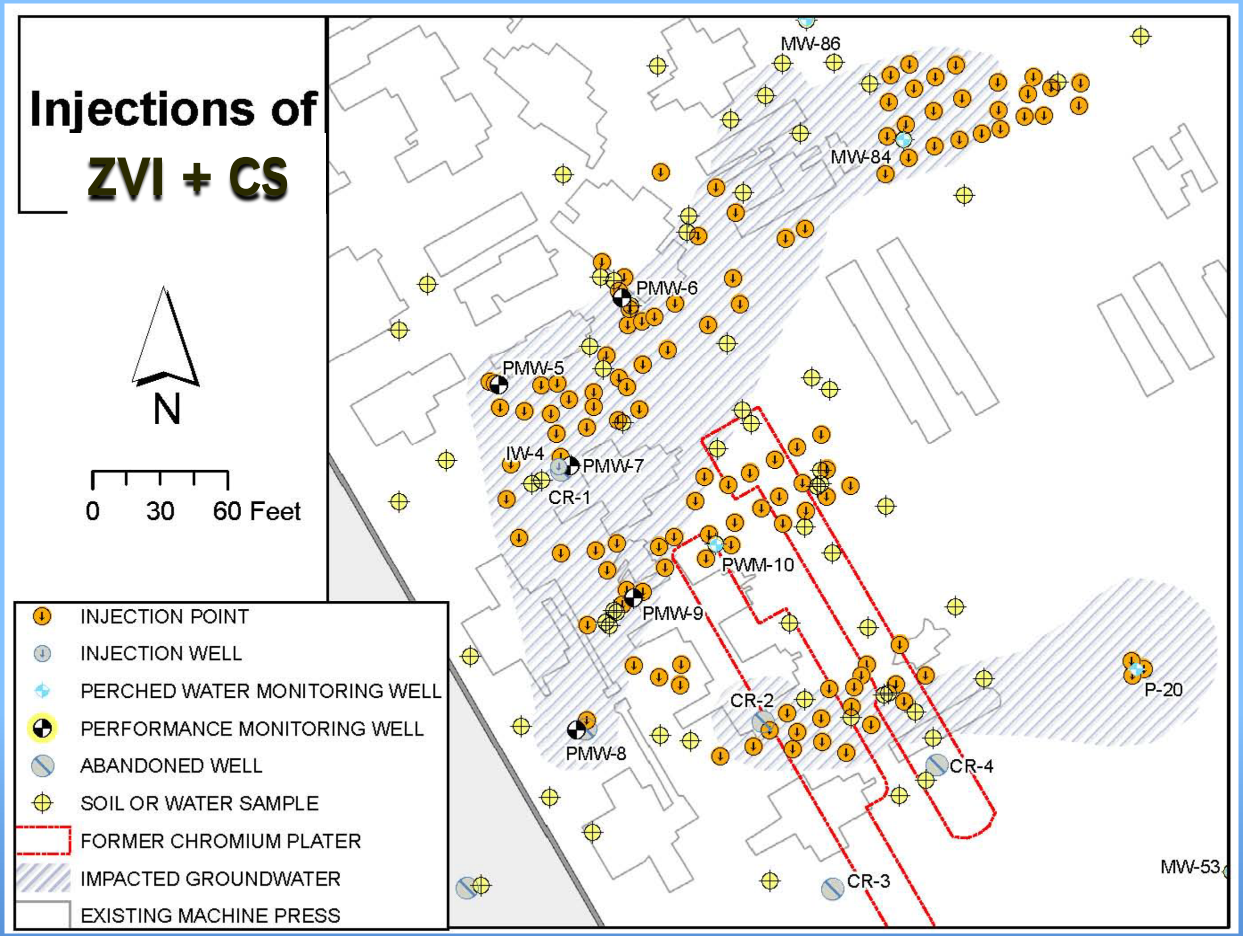
Case Description	
Location	Midwest US
Type of Site	Active industrial
Description of Impacts	Dissolved Cr, Ni plume measuring 250 ft long x 150 ft wide x 10 ft deep (from 13 to 23 ftbgs.
Objective and Approach	Pilot test followed by full-scale injection of ZVI + CS

Results – Pilot test

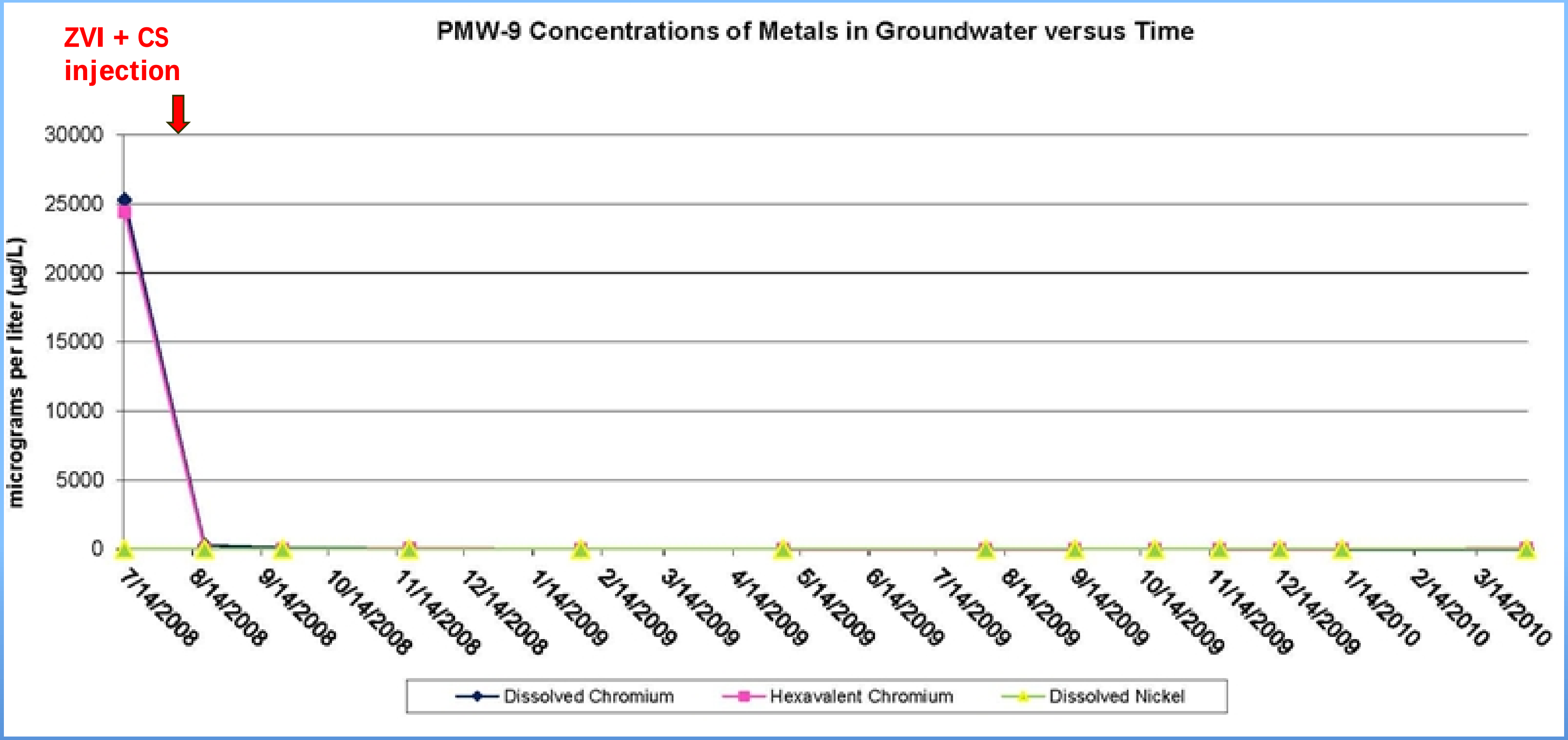


Full-scale Injection design

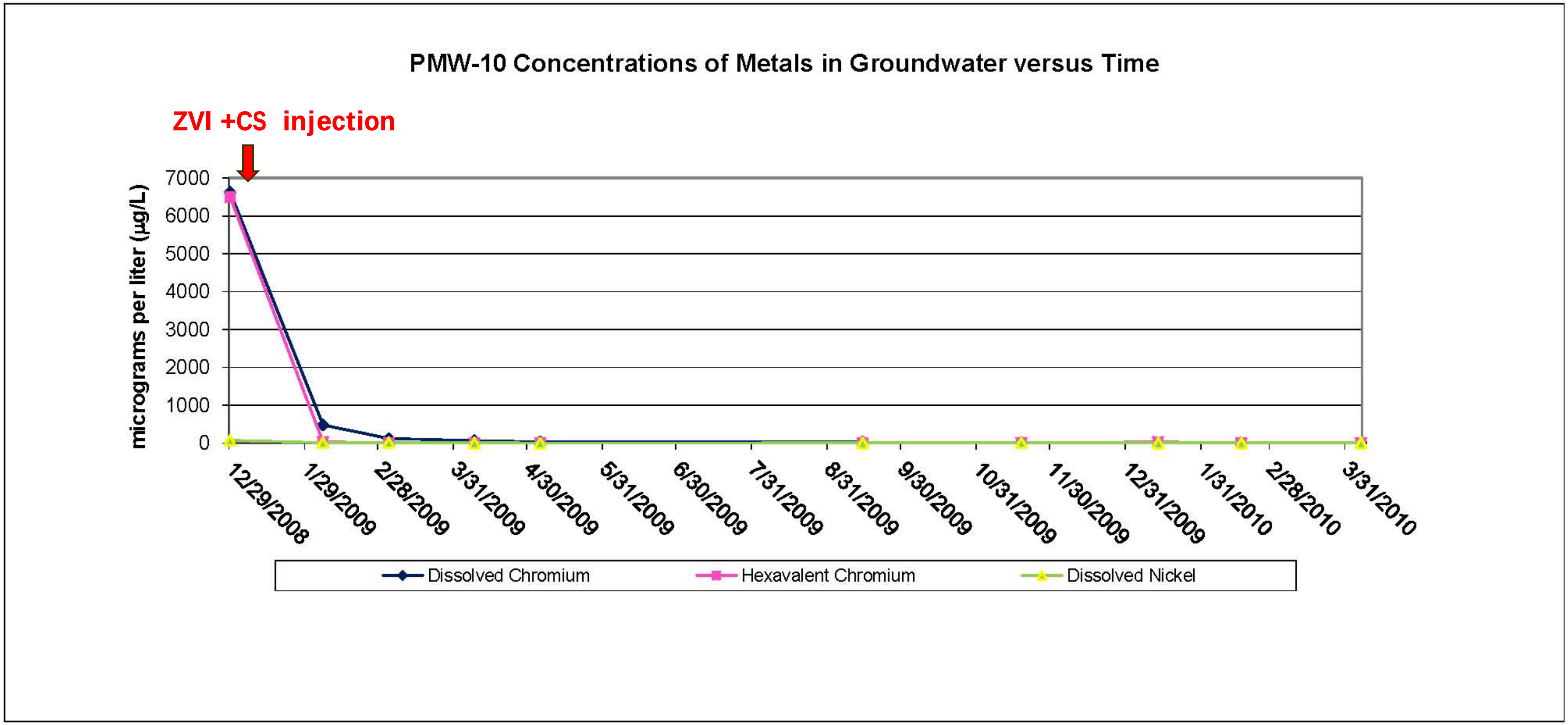
- 450 lb of ZVI + CS injected at each location (0.5% to soil mass).
- Spacing of 8 to 10 ft between injection points.



Results – Full-scale



Results – Full-scale



Case Study 3
Trace metal groundwater plume

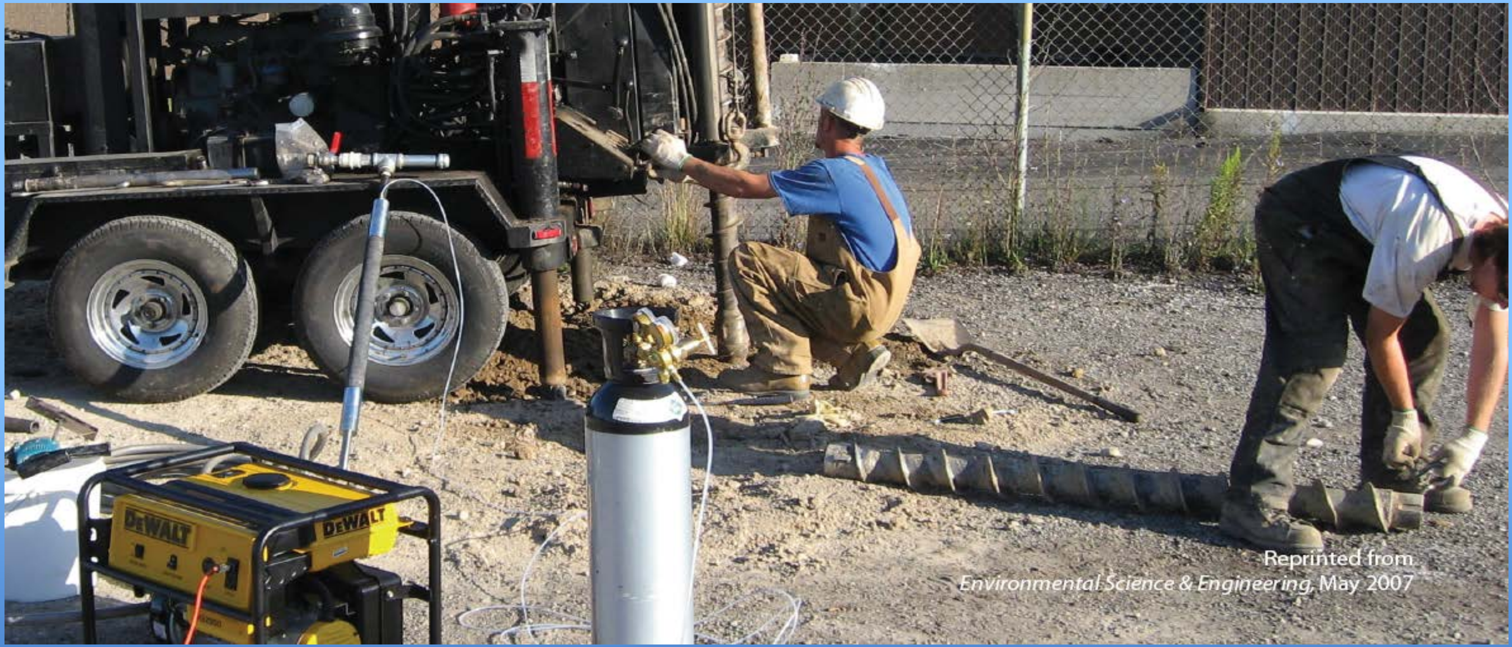
Case Description	
Location	Ontario Canada
Type of Site	Industrial
Description of Impacts	Copper, Cobalt and Nickel
Objective and Approach	ZVI + CS injected along site boundary for plume cut-off.

Plume Treatment, Heavy Metals, Ontario

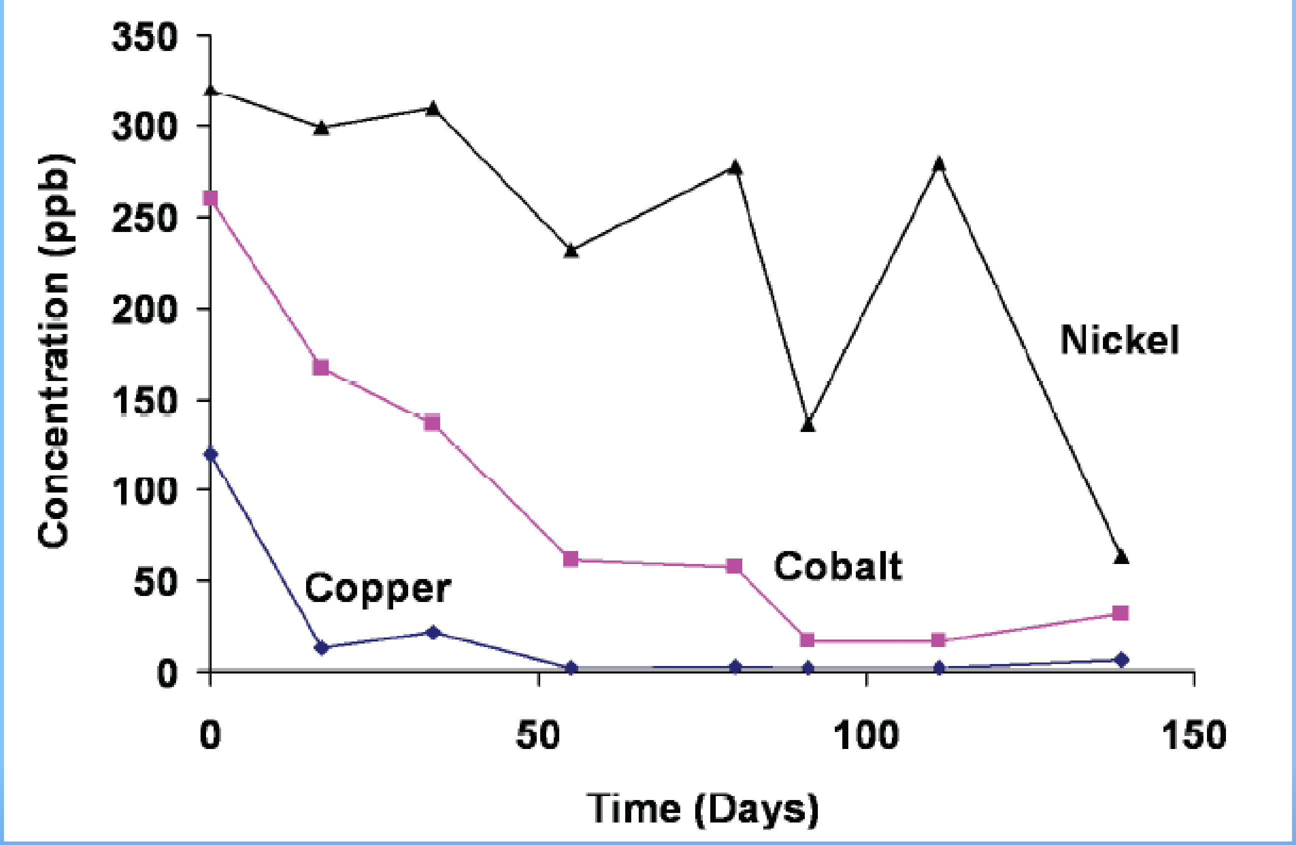
ZVI + CS injections along site boundary cut off plume of dissolved cobalt, nickel and copper

Installation method - Ontario site

- Total of 600 kg ZVI + CS injected into area measuring 9 m L x 7 m wide x 7 m deep (0.08% to soil mass).
- ZVI + CS slurry injected via open bore holes using packers - total of 12 locations.
- Reactive gas also added to facilitate anaerobic conditions



Field Results - Ontario site



- Sulphate reducing conditions (Eh<-250 mV) achieved in days
- Remediation objectives were met for all metals
- Regulatory approval was obtained.

(Courtesy of Vertex Environmental Solutions)

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- **Consulting and Technology Site Assessment:** technology support and selection (chemical oxidation and reduction, co solvent-surfactant soil washing and enhanced bioremediation);
- **Products supply, logistic and storage**: nutrients, bacterial preparations strains, oxidants, reducing agents, catalysts, oxygen and hydrogen release compounds, co solvent-surfactant blends
- **Laboratory Services and Analysis**: Groundwater Parameter Analysis, Tracer Study, Soil and Groundwater Oxidant Demand Evaluation (SOD), Bench Scale Treatability testing in saturated and unsaturated conditions.

Acknowledgement

- FMC Environmental Solutions
- Vertex Environmental

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Thank you for your attention !

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