

Treatability Study Options for Metals Contaminated Sites

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Overview of SiREM Services

Remediation Testing

treatability
studies

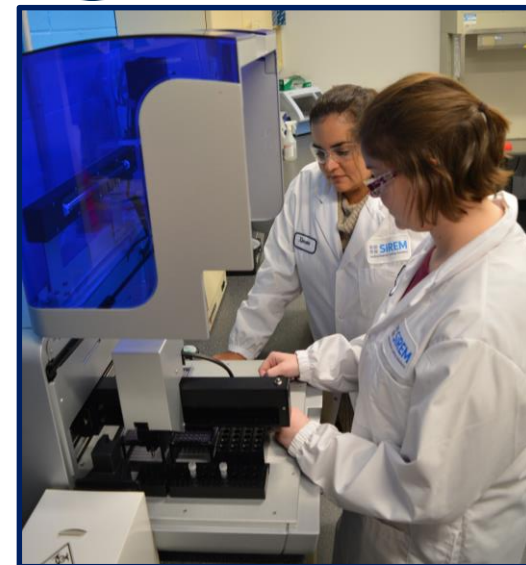


Bioaugmentation



KB-1^{plus}
DGG PLUSTM
Dxo-88

Molecular Testing
gene&trac[®]

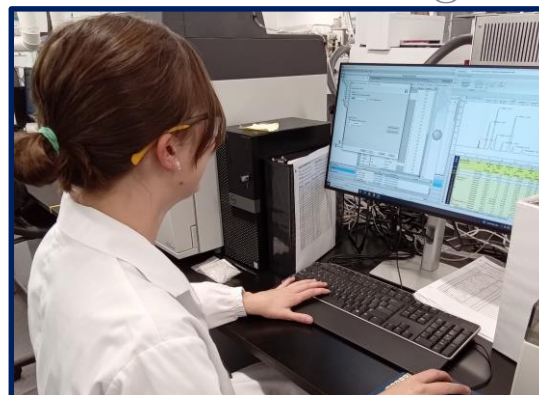


Passive Sampling



WATERLOO
MEMBRANE
SAMPLERTM
SP3TM
SPeeper
PFASsiveTM

analytical
testing



CSIA Iso detect
Environmental Monitoring





Outline

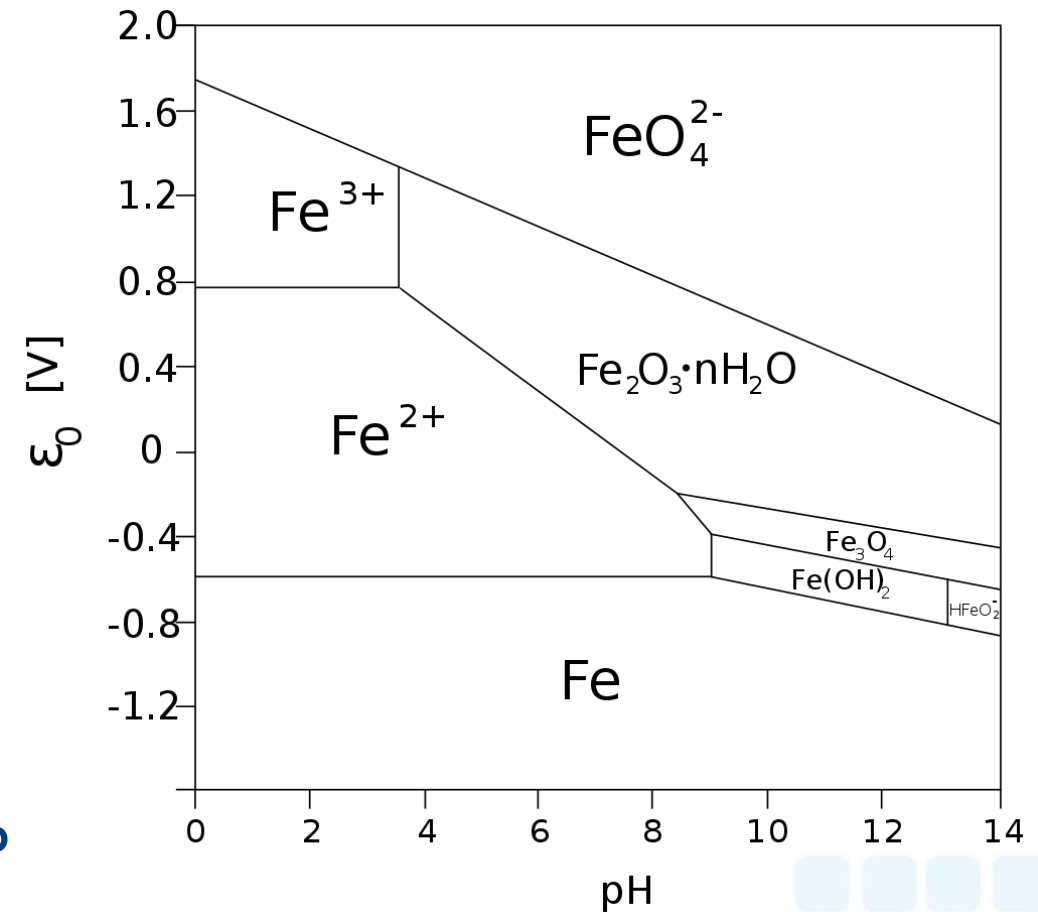
- 1) Why do metals need treatment?
- 2) Why and how should you test remediation technologies for metals treatment before field deployment?
- 3) Case Study 1: PRB Design for Cr(VI) and Chlorinated Ethenes
- 4) Case Study 2: Evaluation of Natural Attenuation of Arsenic at a CCR Site





Metals Treatment

- Metals (Cr, Pb, Cd, Hg)
- Metalloids (As, Sb, Se)
- Can be very toxic at low concentrations
- Have many possible oxidation states
- Remediation strategies often involve precipitation/immobilization
- Amendments can change pH and/or ORP which can impact other geochemistry





What Can Treatability Studies Tell You?

Electron
donor/acceptor/
cometabolite
consumption

Degradation
intermediates/pathways

Effect of controlling variables
(e.g., pH, ORP, amendment
addition, inhibitory effects,
oxidant demand, persulfate
activators)

Contaminant
degradation rates/
lag times

Insight into pilot–test
design





Batch and Column Studies

- Evaluation of Amendments for metals treatment (Cr(VI), As, Cd, Co, Pb, Mn, Ni, Zn)
 - Emulsified veg oils
 - Biogenic hydroxyapatite (from fish bones)
 - Fe, Na, Al and Si oxides
 - Solid carbon amendments with ZVI
 - Zeolite for adsorptive sequestration
- ZVI PRB for redox sensitive metals (i.e., As) Treatment





Flow Through Reactors



- Small horizontal columns represent gravel bed reactors (GBRs)
- End caps are removable to add solid amendments
- Used to study Se reduction and other redox sensitive species





CASE STUDY 1 – PRB DESIGN FOR HEXAVALENT CHROMIUM AND CHLORINATED ETHENES



Chromium

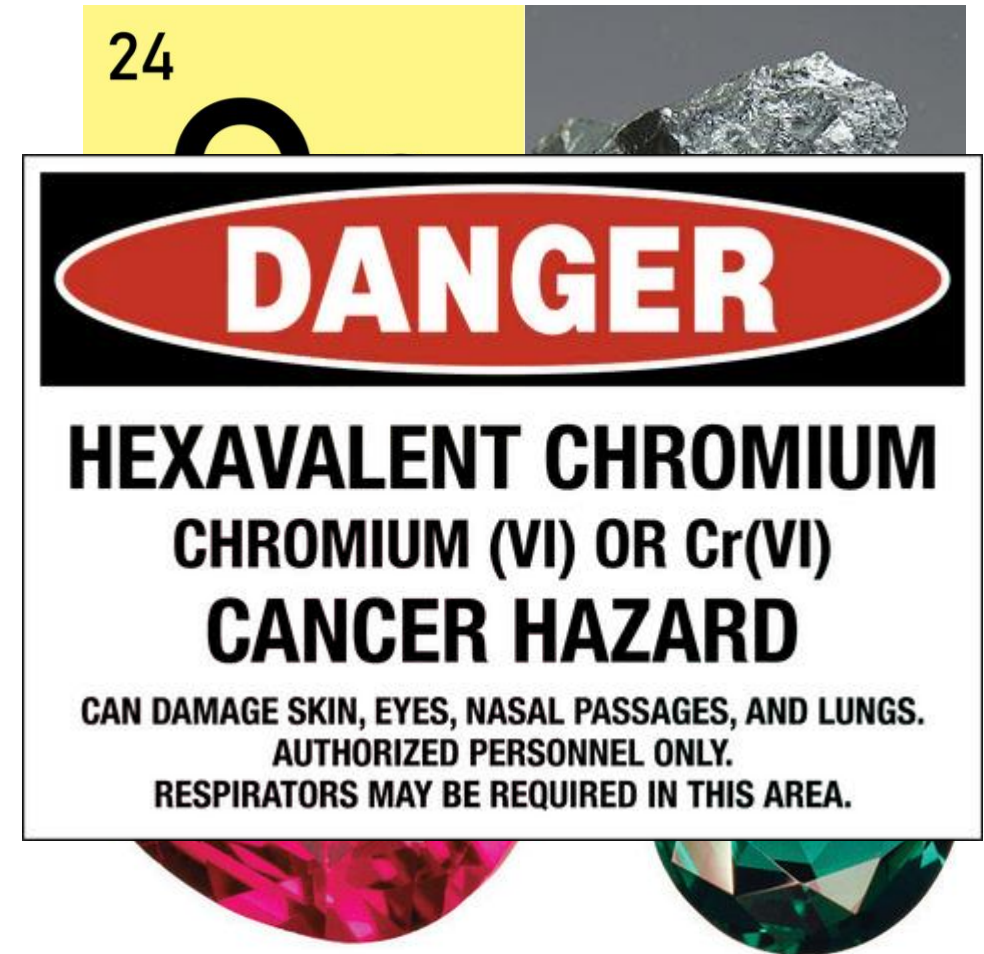
- Transition metal
- Mined as chromite (FeCr_2O_4)
- Used to make stainless steel, chrome plating
- Oxidation states of Cr(III) and Cr(VI)
- Cr(III)
 - Gives rubies and emeralds color
 - Essential nutrient
 - Cr_2O_3 is used as a green pigment
 - Cr_2O_3 is insoluble in water





Hexavalent Chromium

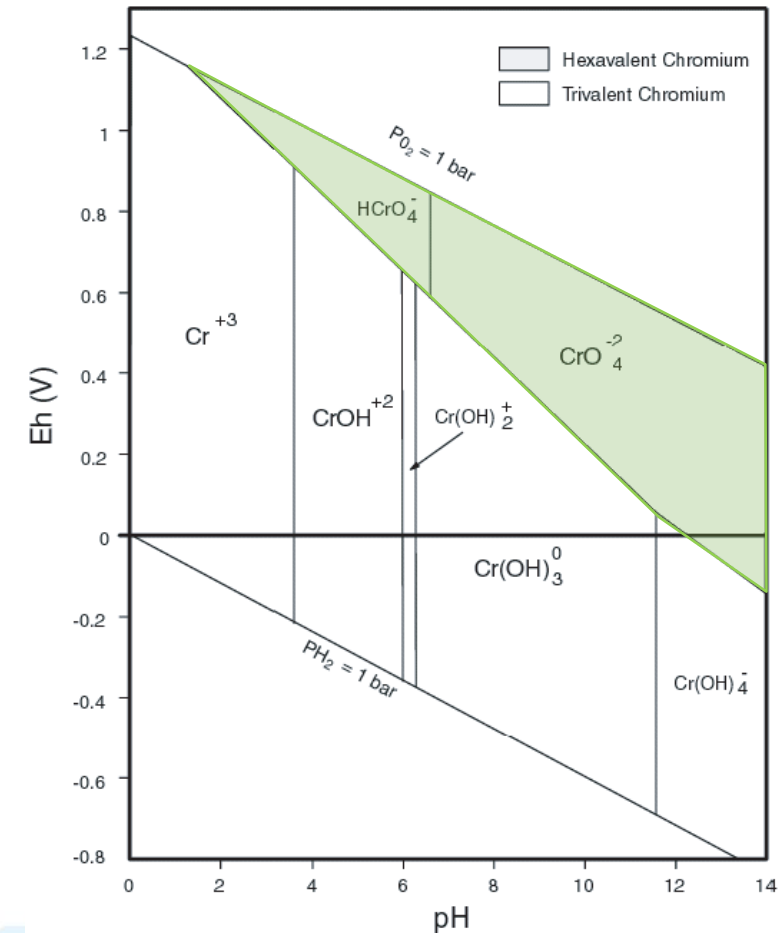
- Cr(VI)
 - Used for metal coatings and pigments
 - CrO_4^{2-} is very soluble in water
 - Known carcinogen
- Health Canada MAC:
50 $\mu\text{g/L}$ Total Chromium in drinking water
- EPA RSL:
0.035 $\mu\text{g/L}$ Cr(VI) in drinking water





Hexavalent Chromium Treatment

- Reduction to Cr(III) reduces mobility and risk
- Chemical Reduction / Precipitation
 - Reduced Iron – ZVI (Fe^0), Ferrous iron (Fe^{2+}) (e.g., ferrous sulfate $[\text{FeSO}_4]$ or ferrous sulfide $[\text{FeS}]$)
 - Reduced Sulfur – calcium polysulfide (CaS_x), dithionite ($\text{Na}_2\text{S}_2\text{O}_4$), hydrogen sulfide (H_2S)
- Biological Reduction
 - Electron donors to stimulate biological activity to generate reducing conditions





Site and Project Overview

- Superfund Site in NE USA, former Cr electroplating facility
- Process waste was discharged directly into wetlands
- Cr(VI): 13-34 mg/L
- TCE: 15-60 $\mu\text{g/L}$



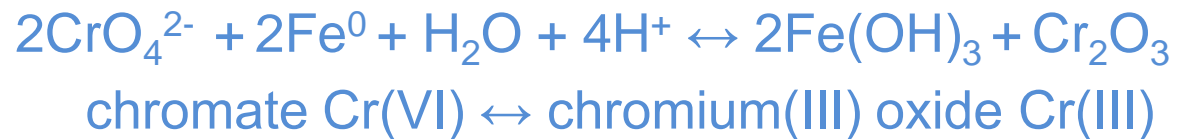
Can a ZVI PRB or other amendments be used to treat the co-contaminants?



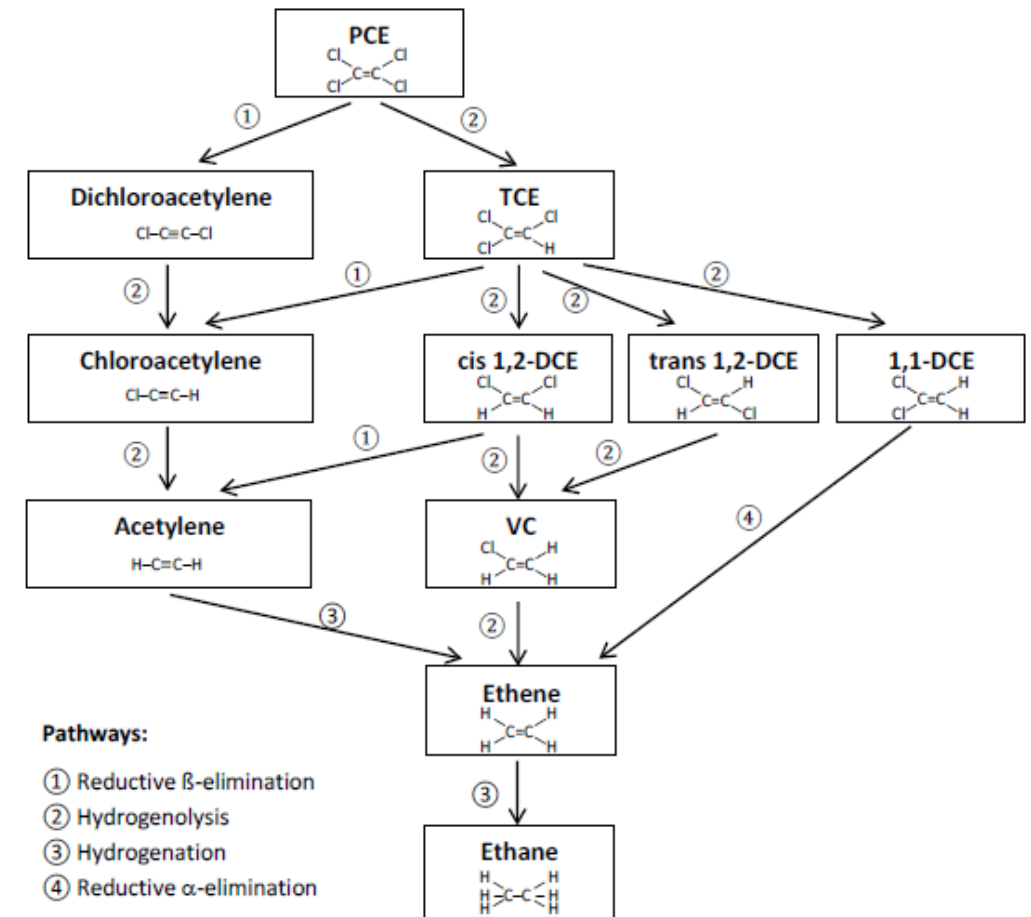


Chemical Reduction of Cr(VI) and TCE with ZVI

Zero-valent iron oxidation \rightarrow Cr(VI) reduction:



Cr(III) precipitates onto ZVI as iron-chromium oxide
and oxyhydroxide complexes





Study Design

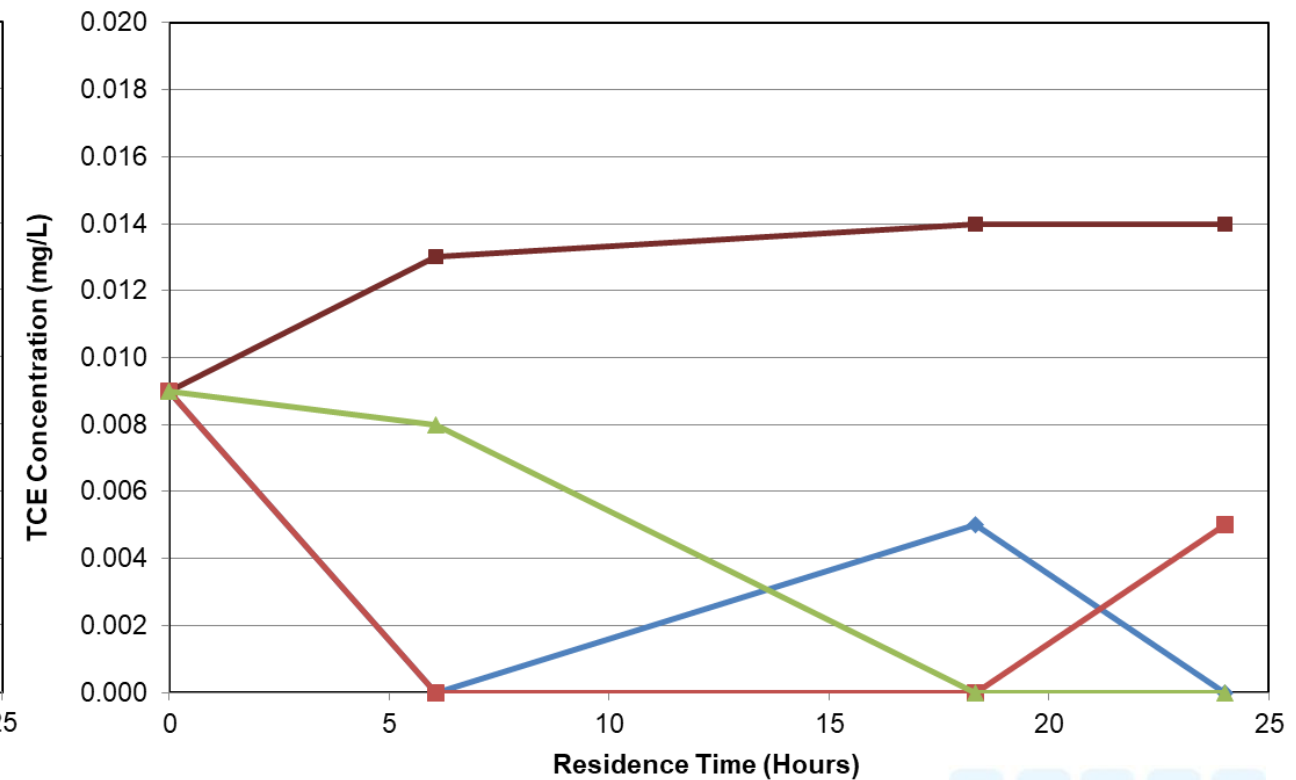
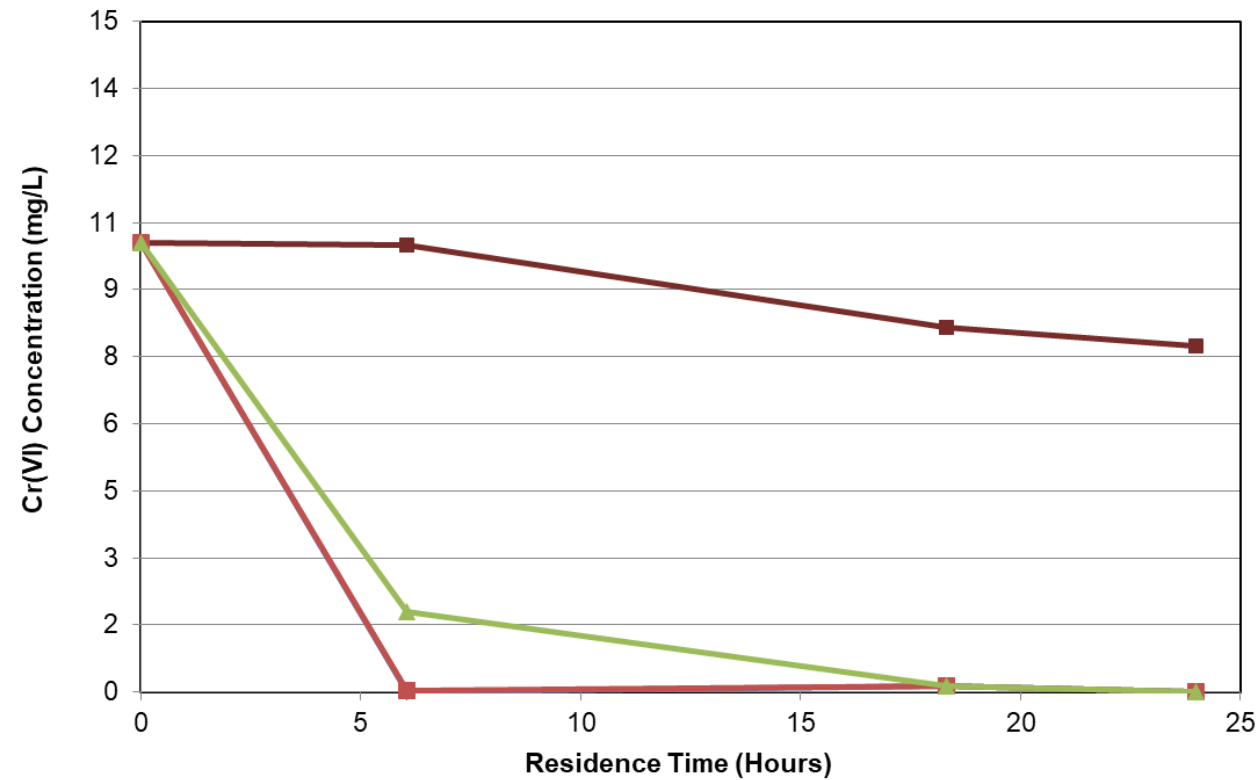
Depth	Amendments
Shallow	0%, 2%, 5%, and 8% Connelly ZVI
Midplume	50%, and 100% Connelly ZVI
Deep	0%, 4%, 7%, and 9% Connelly ZVI 0.50% Metafix®/GeoForm™ 0.10% 3DME®/HRC Primer®

Total of 12 columns with different amendments





ZVI Amended Columns

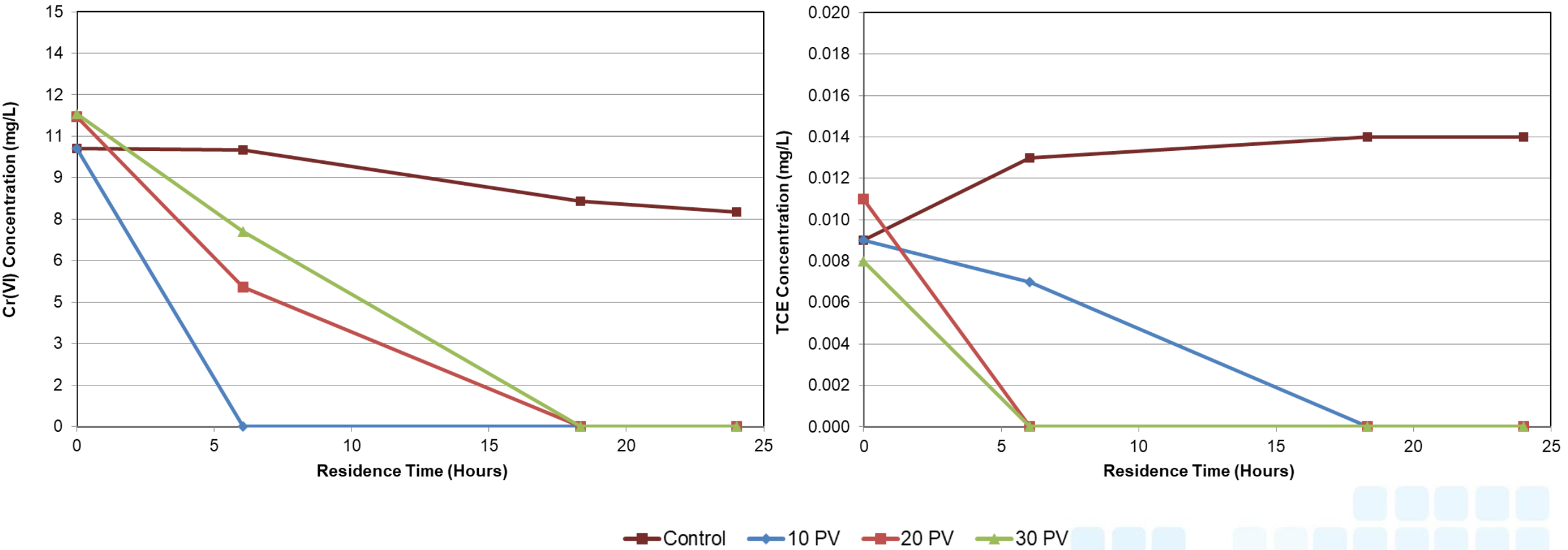


Control 4% ZVI 7% ZVI 9% ZVI





MetaFix[®]/GeoForm[™] Amended Column





Pilot Design Optimization

- Shallow and Deep Zones:
 - ZVI reduced Cr(VI) and TCE concentrations
 - 75% w/w chosen as amendment amount
 - Trenched PRB selected as implementation strategy
- Midplume Zones:
 - Injectables reduced Cr(VI) and TCE concentrations
 - Direct injection selected as implementation strategy to supplement solidification/stabilization



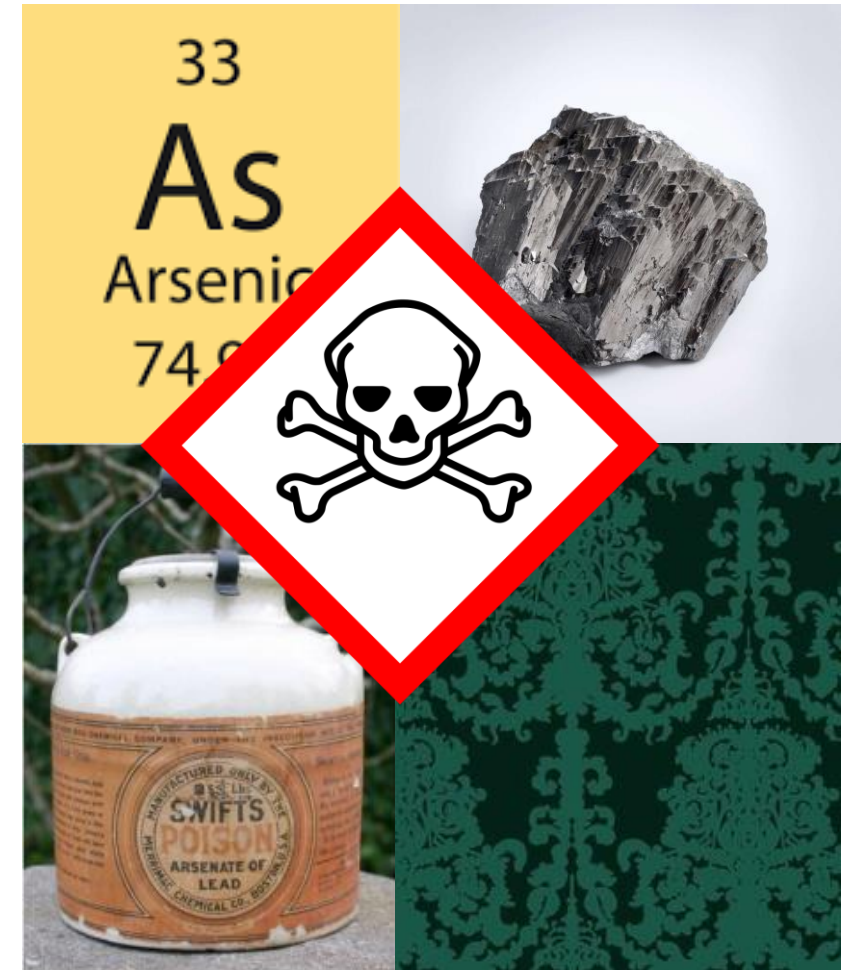


CASE STUDY 2 – EVALUATION OF NATURAL ATTENUATION OF ARSENIC IN GROUNDWATER AT A COAL COMBUSTION RESIDUAL (CCR) SITE



Arsenic

- Metalloid
- Mined in combination with other metals
- Used to make semiconductor devices
- Oxidation states of As(III) and As(V)
- Health Canada MAC and EPA MCL:
10 µg/L





Arsenic Treatment

- As(III) is considered more toxic and more difficult to remove
- Enters groundwater through natural microbial processes, reductive dissolution of Fe oxides, or anthropogenic sources (burning coal)
- Adsorption, complexation, and precipitation with Fe and Fe oxyhydroxides





Background

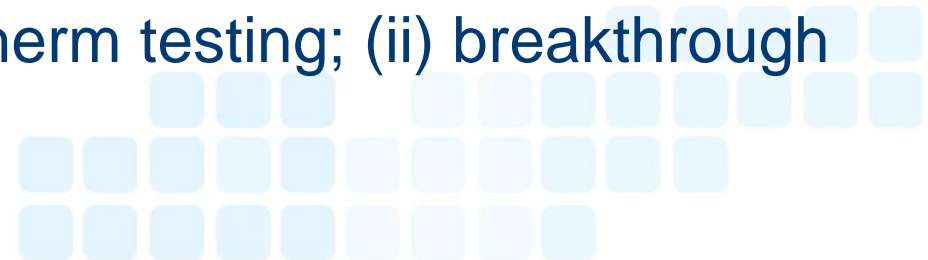
- A CCR Pond has been decommissioned and isolated from the shallow sandy aquifer by a cement-bentonite wall (CBW).
- Dissolved As has persisted in shallow groundwater outside the east section of the CBW.
- The shallow saturated sand layer thickness vary from 5 to 15 ft and is underlain by a marl layer (homogeneous silty and sandy clays).





Objectives

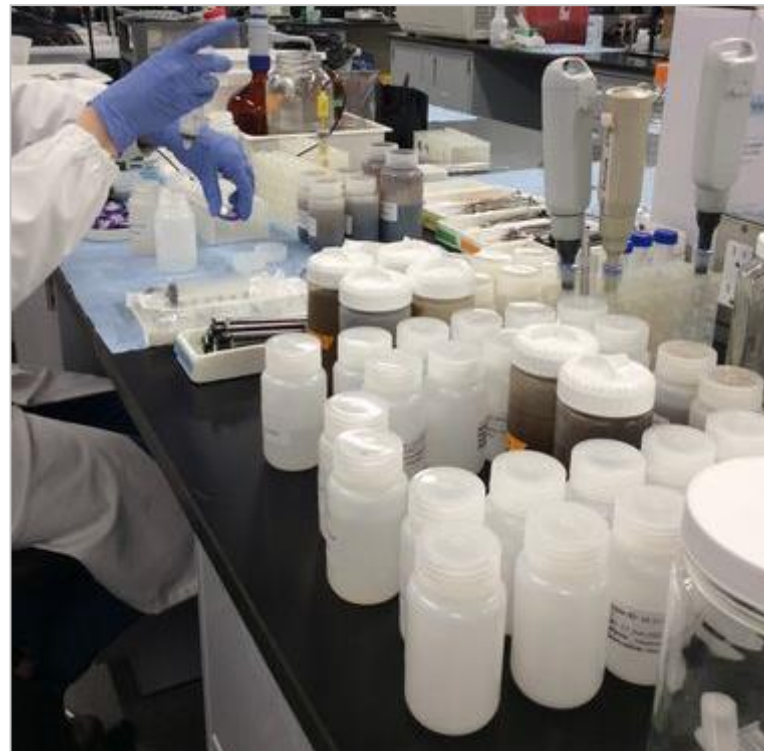
- USEPA Tiered approach to evaluation of natural attenuation of inorganics was used to support the use of MNA for As management at the site.
- Tier I analysis showed that As concentrations in shallow monitoring wells had been decreasing and the As plume extent has stabilized.
- Laboratory tests were performed as part of Tier II and Tier III evaluations:
 - Tier II: (i) aqueous As and Fe speciation; (ii) bulk soil chemical composition of arsenic, iron and sulfur; (ii) mineralogical composition; and (iii) speciation of solid-bound arsenic. Tests were done on both the sand aquifer material and the top marl layer.
 - Tier III: Evaluation the rate of arsenic attenuation and the stability of the solid-bound arsenic using: (i) adsorption isotherm testing; (ii) breakthrough column testing; and (iii) desorption testing.





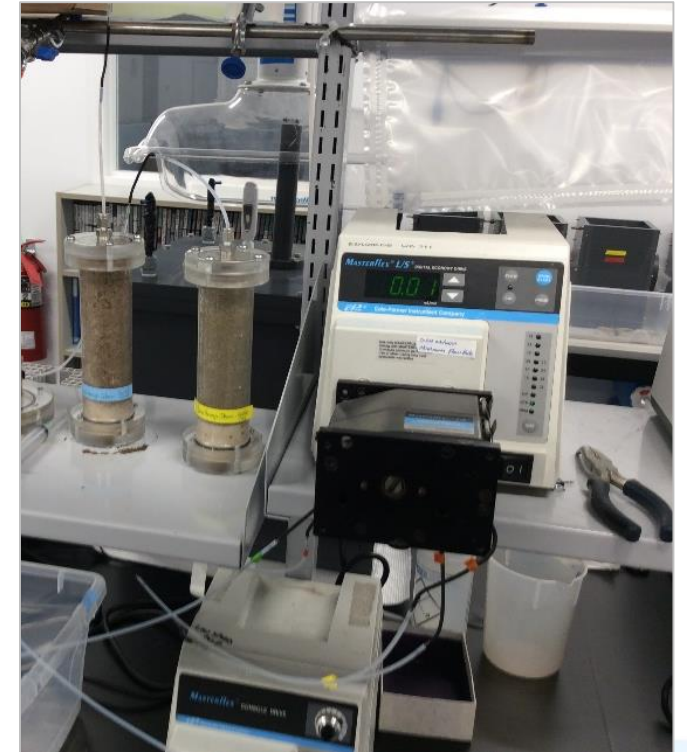
Adsorption/Desorption Reactors and Columns

Geologic Material Characterization



Reactors for Adsorption and Isotherm Testing and Desorption Testing

Columns for Breakthrough Testing





Tier II and III Conclusions (As Attenuation)

Arsenic Attenuation Processes	Site-Specific Evaluation Supported by Testing
1. Adsorption to Fe oxyhydroxides and Fe sulfides, or other mineral surfaces such as clay minerals, if present.	<ul style="list-style-type: none">• Relatively low concentration of amorphous Fe oxides found in the shallow aquifer solids, while both Fe oxides and Fe sulfides were detected in marl.• As is present as a non-charged As(III), thus less amenable to adsorption onto iron oxides vs. As(V).• Distribution coefficients from an isotherm test for As(III) were low, but significant in zone if groundwater flow rate low or the zone is stagnant.• As content in the geologic material associated with iron oxides was low.
2. Co-precipitation of arsenic as a trace component in iron oxyhydroxides or sulfides.	<ul style="list-style-type: none">• Solid-bound As not found on Fe oxides in the shallow geologic material.• Dissolved Fe present in site groundwater. Precipitation of iron oxides under aerobic conditions in column test caused consistent removal of dissolved As in the geologic material, likely preceded by oxidation of As(III) to As(V).• Co-precipitation of As with Fe oxides likely occurs at the As plume boundaries, where aerobic-anaerobic transition redox zones exists.
3. Precipitation of arsenic sulfides.	<ul style="list-style-type: none">• As sulfides were not found in site geologic material.• Dissolved sulfate present in site groundwater, but sulfate reduction not likely in shallow groundwater based on ORP and lack of sulfide in material.



Tier II and III conclusions (As mobilization)

Arsenic Mobilization Processes	Site-Specific Evaluation Supported by Testing
1. Desorption at high pH from Fe oxyhydroxides and sulfides. Reductive dissolution of Fe hydroxides.	<ul style="list-style-type: none">• Limited release of As observed in desorption test with arsenic-free site water and geologic material from the center of arsenic plume.• Partial mobilization of As observed at alkaline pH conditions, which indicated desorption may occur if the pH increases above 8, based on a zero point of charge (ZPC) value for native Fe oxides determined.
2. Reduction of As as a trace component in Fe oxyhydroxides or sulfides.	<ul style="list-style-type: none">• Partial release of As observed in highly reducing conditions under which iron oxides are expected to undergo reductive dissolution.• Highly acidic conditions in the TCLP leach did not cause arsenic release from the sand and marl.
3. Oxidation of As sulfides.	<ul style="list-style-type: none">• Highly oxidizing conditions did not cause arsenic release in the sand material which did not contain iron sulfides.• No release of arsenic was observed from Cooper Marl under aerobic conditions suggesting potential occlusion of surface by secondary minerals.



What Happened?

- The As attenuation and mobilization data was provided to the regulator
- Regulator agreed that MNA was an appropriate remedy

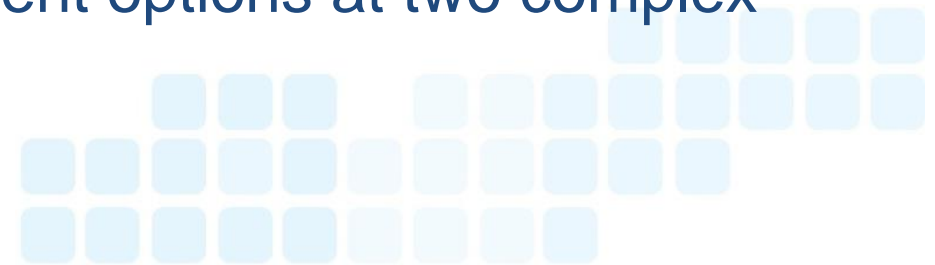
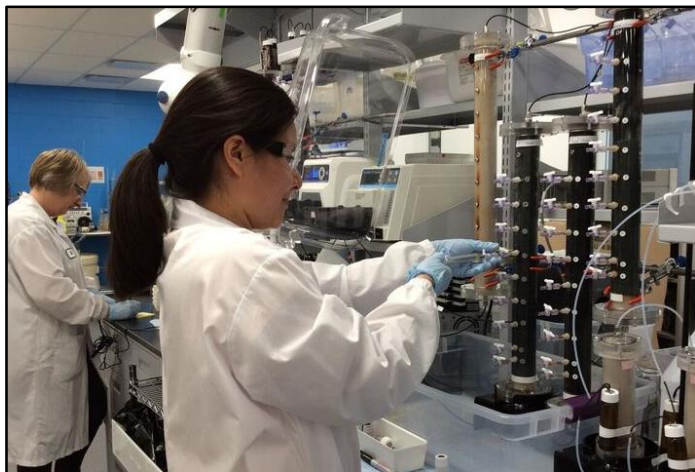




Conclusions



- Metals remediation projects can be complex
- Treatability studies can test amendments before field application or assist with testing for MNA projects leading to more informed field pilot scale designs
- Cr(VI) and As treatability studies showed viable treatment options at two complex sites



Questions

Questions



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