

A Sustainable Approach to Removal of Dissolved Metals & Metalloids

MetaFix®



GeoForm® ER



GeoForm® Soluble

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October 2024
Soil & Groundwater Remediation
Evonik Corporation

Perspective for the Presentation

- ✓ The goal of our meeting today is to develop a deeper understanding of factors important in selecting a sustainable approach to remediation of soil and groundwater contaminated with dissolved metals or dissolved metals as well as chlorinated VOCs.
- ✓ If we had two hours I would provide short refreshers on the chemistry of chromium, divalent heavy metals, and arsenic but our time is less than one hour so I've decided to focus on only chromium.
- ✓ This presentation has been put together under the assumption that many attendees are not experienced in treatment of sites contaminated with metals or metals along with cVOCs.
- ✓ We have focused on solutions for these sites over the past 10 years and have developed a portfolio of reagents that are very effective for simultaneous removal of dissolved metals and destruction of cVOCs.
- ✓ I will not spend much time on case studies even though we have many available. If you want some more detailed case studies, please reach out to me and I will send them.

“What characteristics qualify an environmental remediation approach as truly sustainable?”



Agenda

What is Sustainable Remediation?

- ✓ Some Definitions
- ✓ Sustained Treatment (Longevity) & Sustained Removal (Permanence)
- ✓ Sustainable Reagents

Processes & Mechanisms in Removal of Dissolved Metals

- ✓ Adsorption, Precipitation, Coprecipitation, Occlusion
- ✓ Reducing Susceptibility to Rebound
- ✓ Short Refresher on Chromium Chemistry

MetaFix® and GeoForm® Reagents for Removal of Dissolved Metals

- ✓ Composition
- ✓ Treatment Mechanisms for Common Metals and Metalloids

Representative Performance Data and Brief Project Snapshots

- ✓ Bench-scale Treatability Results
- ✓ Former Chromium Waste Disposal Site
- ✓ Soil Mixing to Remove SPLP Mercury
- ✓ Industrial Site with Mixed Metals and cVOCs

Questions & Answers

What is Sustainable Remediation?

What is Sustainability?

Some Definitions

National Science and Technology Council: Sustainable Chemistry

- (i) produces compounds or material from readily available and renewable building blocks, reagents, and catalysts
- (ii) uses a process optimized for efficiency
- (iii) employs renewable energy sources

US EPA

Everything that we need for our survival and well-being depends, either directly or indirectly, on our natural environment. To pursue sustainability is to create and maintain the conditions under which humans and nature can exist in productive harmony to support present and future generations.

Applied to Soil & Groundwater Remediation (A. Seech)

- (1) Provide long-lasting treatment mechanisms (reduce the need to repeat treatments)
- (2) with a good degree of permanence (not a transient effect, not subject to rebound)
- (3) and with a smaller carbon footprint

What is Sustainable Remediation?

Sustained Treatment, Sustained Removal, Sustainable Reagents

Sustained Treatment Mechanisms (Longevity)

- Treatment methods that have long duration are more sustainable because they provide greater assurance that adequate removal of dissolved metals will be achieved without repeated applications.

Sustained Removal (Permanence)

- Chemistry and treatment mechanisms that remove dissolved metals in ways resist reversal when soil or groundwater conditions, such as pH or Eh, change are more sustainable. These approaches reduce the probability that time, resources, and energy will need to be expended more than once.

Sustainable Reagents (Smaller Carbon Footprint)

- Reagents that are composed of byproducts from other processes and that can be manufactured without processes that have unusually high energy consumption.

Processes & Mechanisms in Removal of Dissolved Metals

Processes & Mechanisms in Removal of Dissolved Metals

Precipitation: Conversion of a soluble metal into an insoluble form by addition of a chemical to create a supersaturated environment.

- An example of this is conversion of aqueous lead (Pb^{+2}) into lead sulfide (Galena) by enriching the contaminated environment with sulfide (HS^-).

Co-precipitation: A form of adsorption in which soluble species are incorporated within a precipitating solid phase *via* chemical, physical, Van der Waals, or by dipole-dipole interactions.

- An example is removal of dissolved arsenic by its coprecipitation with iron oxyhydroxides (e.g., ferrihydrite).

Adsorption: Binding of a soluble species on the surface of a solid, driven by surface forces/charges.

- An example is removal of tetraethyl lead or methyl mercury by activated carbon or adsorption of arsenite on iron oxide surfaces.

Occlusion: Encasement of metals by formation of insoluble/low solubility layers of mineral precipitates.

- An example is physical protection of newly precipitated Cr(III) species through promotion of long-term precipitation/coprecipitation of iron sulfides and other metals sulfides.

Biogeochemical Remediation: A process that combines physical, chemical, and microbiological mechanisms to remove or degrade contaminants with important contributions from anaerobic carbon metabolism, sulfate reduction, and iron cycling.

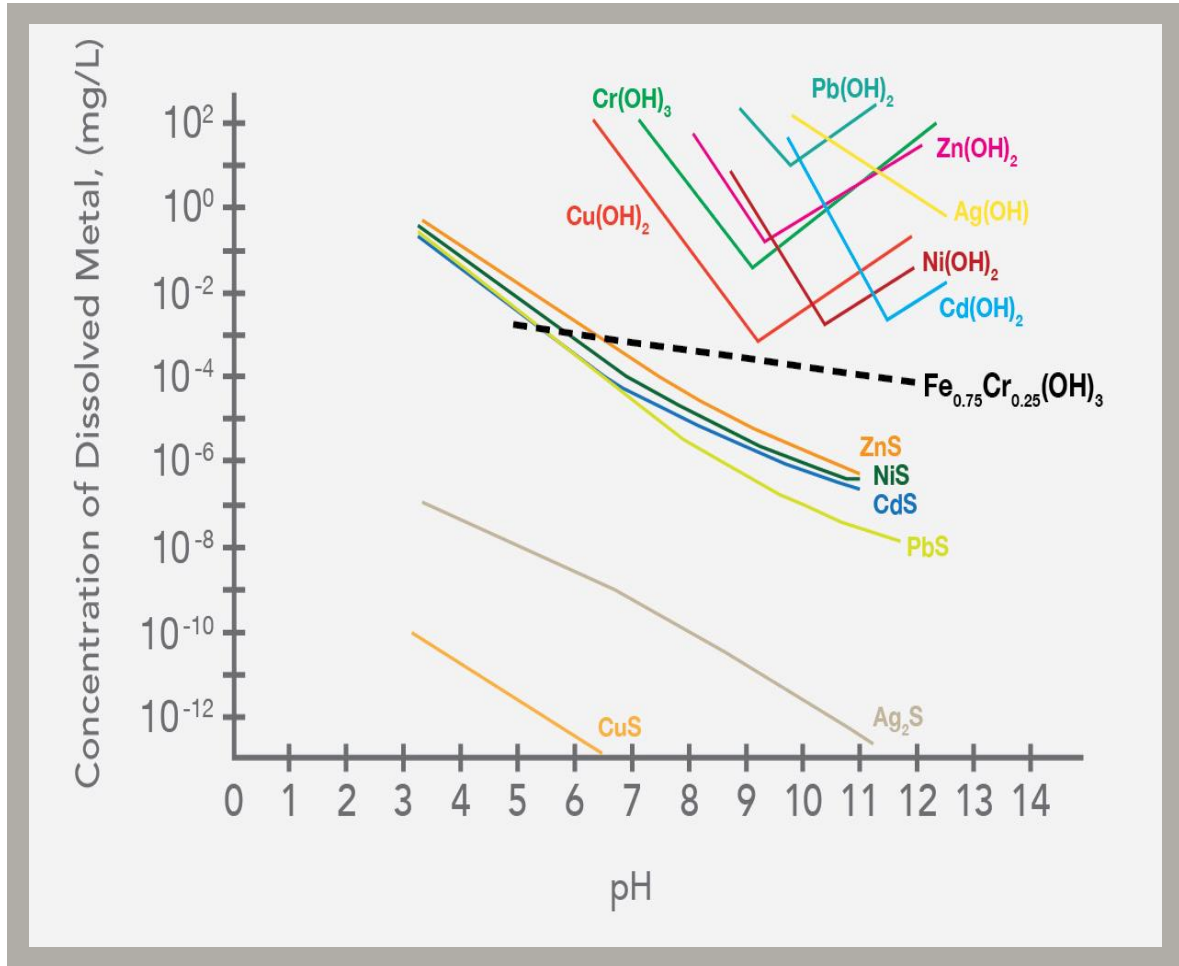
Removal Mechanisms for Dissolved Metals and Metalloids

| Metal | Precipitation as Metal Hydroxides or Iron Metal Oxyhydroxides | Precipitation as Metal Sulfides/Iron Metal Sulfides | Adsorption On & Co-precipitation with Iron Corrosion Products | Precipitation as Metal Carbonates and Phosphates | Adsorption of organometallic species on activated carbon |
|-------------|---|---|---|--|--|
| As (III, V) | - | • | • | - | • |
| Cr(VI) | • | - | • | - | • |
| Pb, Cd, Ni | • | • | • | • | • |
| Cu, Zn | • | • | • | - | - |
| Se | • | • | • | - | - |
| Hg | - | • | • | - | • |



Removal of Dissolved Metals

Metal Sulfides vs Metal Hydroxides (Lower Solubility & Broader pH Range Stability)



EPA 625/8-80-003, 1980; Banerjee et al., 2013. Veolia Water Inc. Environ. Sci. Technol. 1988, 22, 972-977

| Mineral Precipitate | Solubility ($\mu\text{g/L}$) |
|---|--------------------------------|
| Lead Hydroxide $\text{Pb}(\text{OH})_2$ | 2,100 |
| Anglesite PbSO_4 | 30,260 |
| Cerussite PbCO_3 | 7.0 |
| Galena PbS | 3.8×10^{-6} |
| Hydroxypyromorphite $\text{Pb}_5(\text{PO}_4)_3\text{OH}$ | 37 (est.) |
| MCL | 50 |

Reducing Susceptibility to Rebound

The Importance of Redox Longevity

Observations

- Long-lasting reagents allow time for chemical and microbiological processes to work their way through all the oxidized compounds present in the soil/groundwater matrix.
- During an extended reductive phase, a reservoir of redox buffers is created which enable the treatment zone to resist movement back to an oxidized state.
- These redox buffers include (a) reduced iron phases (i.e., Fe(II) minerals), (b) biogenic iron sulfides, and (c) dead microbial cells and associated extracellular polysaccharides (“microbial necromass”).
- As layers of these redox-buffering materials are laid down on the soil or aquifer solids they protect heavy metal precipitates (i.e., divalent metal sulfides), and metalloid precipitates (i.e., Fe-As-S, arsenopyrite) from exposure to oxidizing conditions that may over time result in their dissolution and solubilization of metals/metalloids within.
- This may be particularly important for treatment of chromium Cr(III) which can be re-oxidized in soil or groundwater where the availability and reactivity of MnO_2 is high.

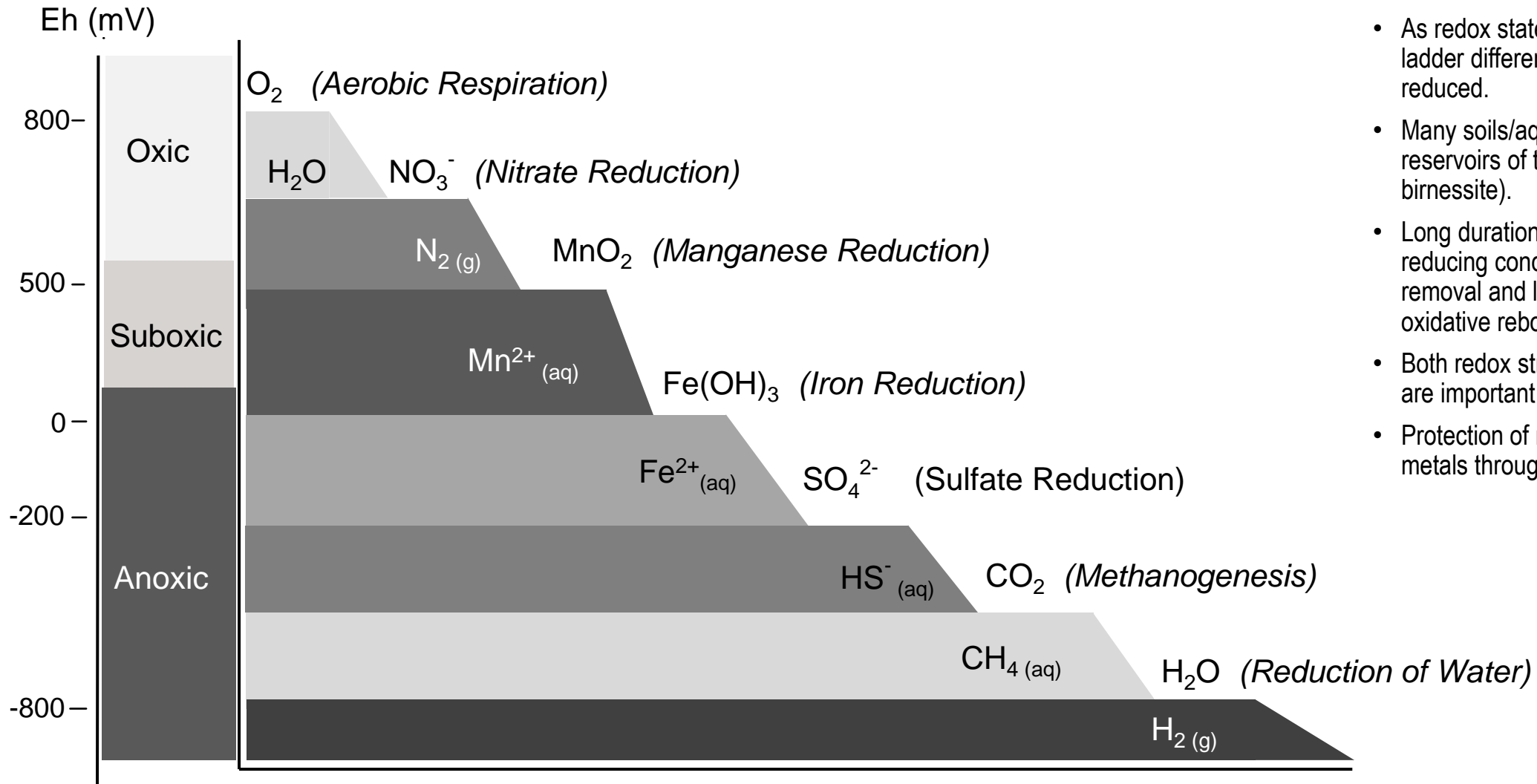
Practical Application

Reagents that provide long-lasting reducing conditions can reduce the probability of re-solubilization of metals/metalloids that have been removed by adsorption or precipitation.

Reagents that promote multiple removal mechanisms (physical adsorption, reductive precipitation, enzymatic reduction) can add another degree of resistance to re-solubilization/rebound.

Reducing Susceptibility to Rebound

The Importance of Redox Strength



- As redox state moves down the ladder different electron acceptors reduced.
- Many soils/aquifer solids have large reservoirs of these (i.e., iron oxides, birnessite).
- Long duration of sufficiently strong reducing conditions supports more removal and limits potential for oxidative rebound.
- Both redox strength and longevity are important: "capacity".
- Protection of recently removed metals through their occlusion.

Short Refresher on Chromium Chemistry

Basics of Chromium Chemistry

Hexavalent chromium, Cr(VI), Anionic

- Soluble, anionic, highly mobile, highly oxidized, very reactive (mobility is reduced as pH increases)
- In acid to near neutral soil or groundwater is present mainly as HCrO_4^-
- At pH >6.5 the dominant form is CrO_4^{2-}
- Cr(VI) is readily reduced to Cr(III) and then rapidly hydrolyzes and precipitates as solid $\text{Cr}(\text{OH})_3$
- Cr(VI) is rapidly reduced by ferrous iron, sulfide, and many organic compounds

Trivalent chromium, Cr(III), cationic

- Insoluble and nearly immobile, but can be reoxidized to Cr(VI)
- Much less toxic, noncarcinogenic, essential nutrient
- Somewhat stable in colloidal precipitate form

Regulatory

- Federal MCL for total chromium is 100 $\mu\text{g/L}$; California MCL is 50 $\mu\text{g/L}$
- California issued a new drinking water standard of 10 $\mu\text{g/L}$ for hexavalent chromium in April 2024.
- Some groups have called for this to be further reduced to approximately 1.0 $\mu\text{g/L}$.
- If this happens the issue of rebound will become even more important.

Short Refresher on Chromium Chemistry

Charge Status and Speciation

Hexavalent Chromium: Cr(VI) is the oxidized, anionic form in most soil and groundwater systems:

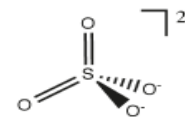
- HCrO_4^- (hydrogen chromate, dominant below pH = 6.5)
- CrO_4^{2-} (chromate, dominant under near neutral pH and dilute solutions)
- $\text{Cr}_2\text{O}_7^{2-}$ (dichromate, acidic systems, particularly with high concentrations)

Trivalent Chromium: Cr(III) is the reduced form and exists mainly in cationic or neutral hydroxides:

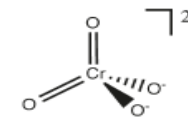
- CrOH^{2+} (minor, only under very acidic conditions)
- Cr(OH)_2^+ (minor, more as pH increases)
- Cr(OH)_3 (dominant at pH between 6.0 and 10.0)
- Cr(OH)_4^- (only significant when pH >10.0)

We should think of hexavalent chromium in the same way as we think of sulfate:

- ✓ *shape governed by tetrahedral oxygen structure*
- ✓ *anion that does not bind to soil or other colloids*



sulfate

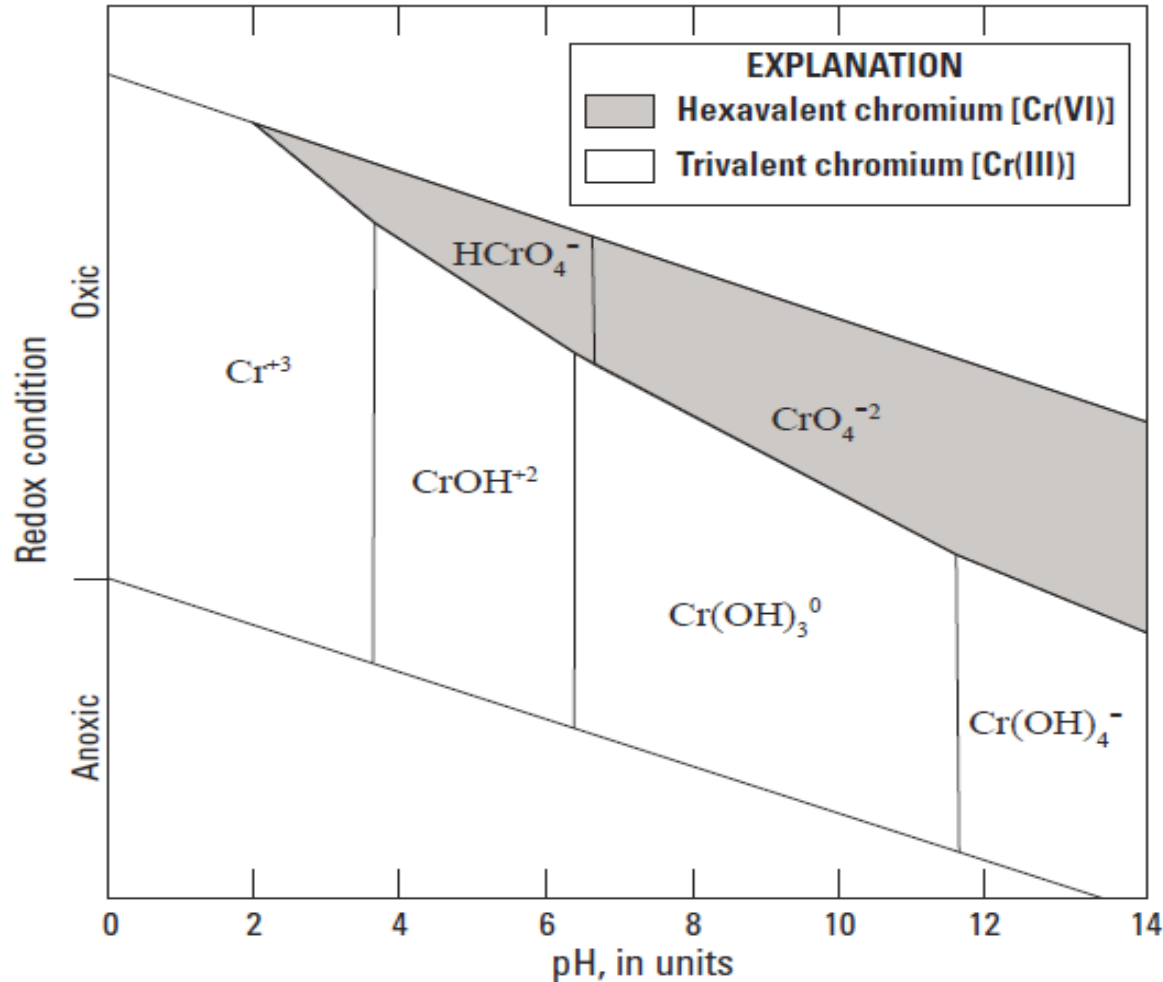


chromate

Do not neglect the possibility that some Cr(III) and Cr(VI) may exist in complexed form with natural humic and fulvic acids, because this has implications for achievement of very low remedial goals.

Chromium Valence and Speciation

Influence of Changing Eh and pH



- Redox state is the main regulator of chromium valence
- pH has a powerful influence over speciation at any given Eh
- Consistent with the important role of ferrous iron since dissolution of iron-bearing minerals and hence the supply of Fe^{+2} both tend to increase as pH drops ($\uparrow \text{Fe}^{+2} = \downarrow$ hexavalent chromium)
- Observed stability regions will shift if concentrations of solutes increase or decrease
- Phase diagram does not provide insight on the rate at which species change.
- Does not address the fraction of either Cr(III) or Cr(VI) that may exist in complexed form with natural humic and fulvic acids

Influence of redox state and pH on aqueous chromium speciation. (USGS, 2013 SIR 2015-5020)

Short Refresher on Chromium Chemistry

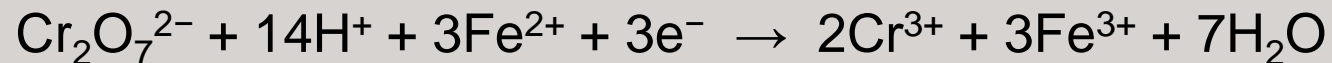
Reduction of Cr(VI) in Soil and Groundwater

- Thermodynamically favorable reaction at pH and Eh common in soil and groundwater
- Can be mediated by flow of e^- from a variety of sources:
 - ✓ Organic matter
 - ✓ Sulfides (HS^-)
 - ✓ Iron sulfides
 - ✓ Ferrous iron (probably dominant reductant)

Generic Reaction for dichromate:



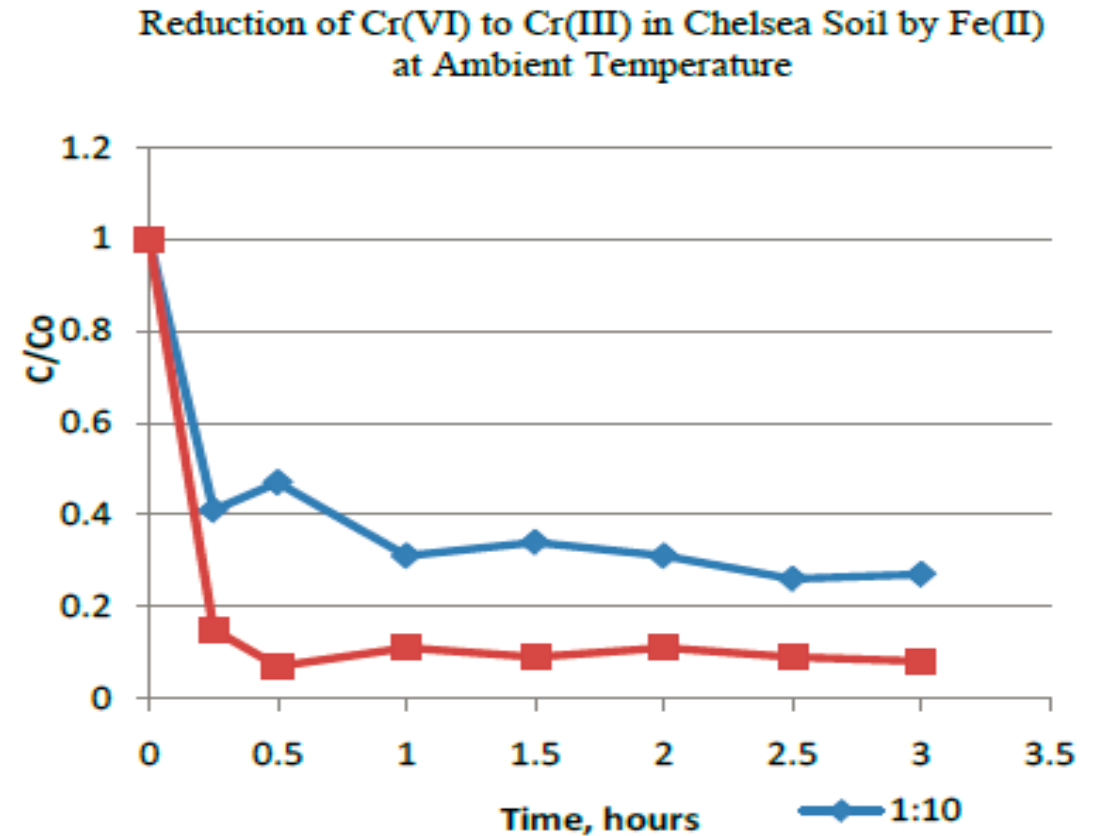
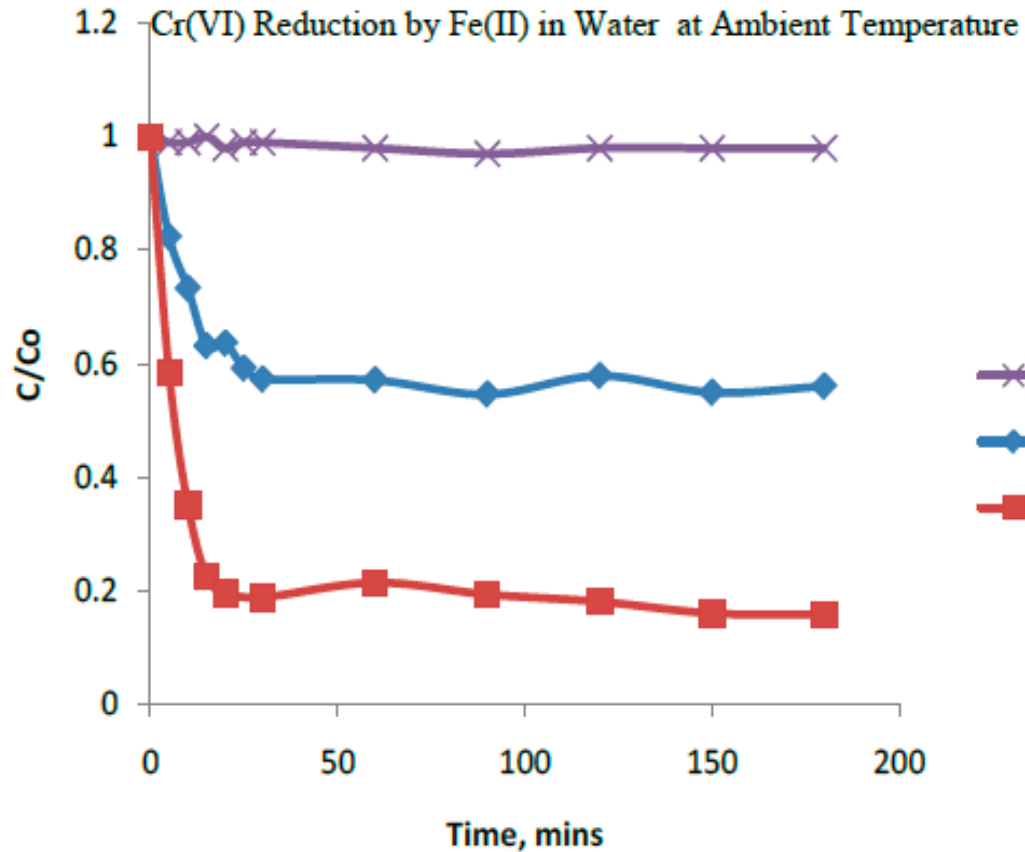
Ferrous Iron Reaction for dichromate:



- Cr(VI) is readily reduced to Cr(III) then rapidly hydrolyzes and precipitates as mainly simple chromium hydroxide if the supply of iron is low.
- The main precipitate is iron-chromium-oxyhydroxide when the supply of dissolved iron is not limited

Short Refresher on Chromium Chemistry

Very Rapid Reduction of Cr(VI) by Fe²⁺ in Water and Soil



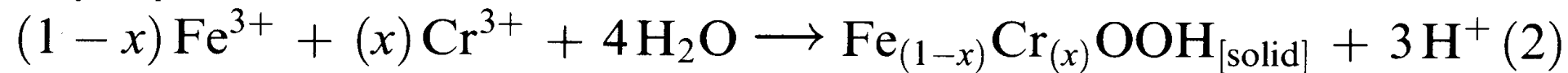
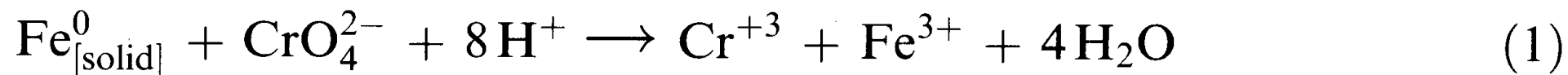
- Rapid reduction is completed in minutes with degree of reduction regulated by supply of ferrous iron.

Ighere, J.O. et al., 2015. *Advances in Chemical Engineering and Science*. 5:15-22.

Short Refresher on Chromium Chemistry

Treatment of Chromium with ZVI

- Reduction of Cr(VI) to Cr(III) by ZVI is followed by its precipitation as mixed Fe-Cr oxyhydroxides with a mineral structure similar to that of goethite (α -FeOOH) with some Cr(III) also deposited into a hematite-like structure (Fe_2O_3).^{1,2}
- Solubility of Fe-Cr oxyhydroxides is less than 0.05 $\mu\text{g/L}$ over a broad pH range of 5.0 to 12.0



- Chromium that has been precipitated as Fe-Cr oxyhydroxide is less subject to dissolution through re-oxidation than that which has been precipitated as simple chromium hydroxide.

1. Blowes et al., 2000. *J. Contam. Hydrol.* 45: 123-137

2. Tratnyek et al., 2003. In: Tarr, M. *Chemical Degradation Methods for Wastes and Pollutants*

Short Refresher on Chromium Chemistry

Remobilization by Oxidation of Cr(III) to Cr(VI)

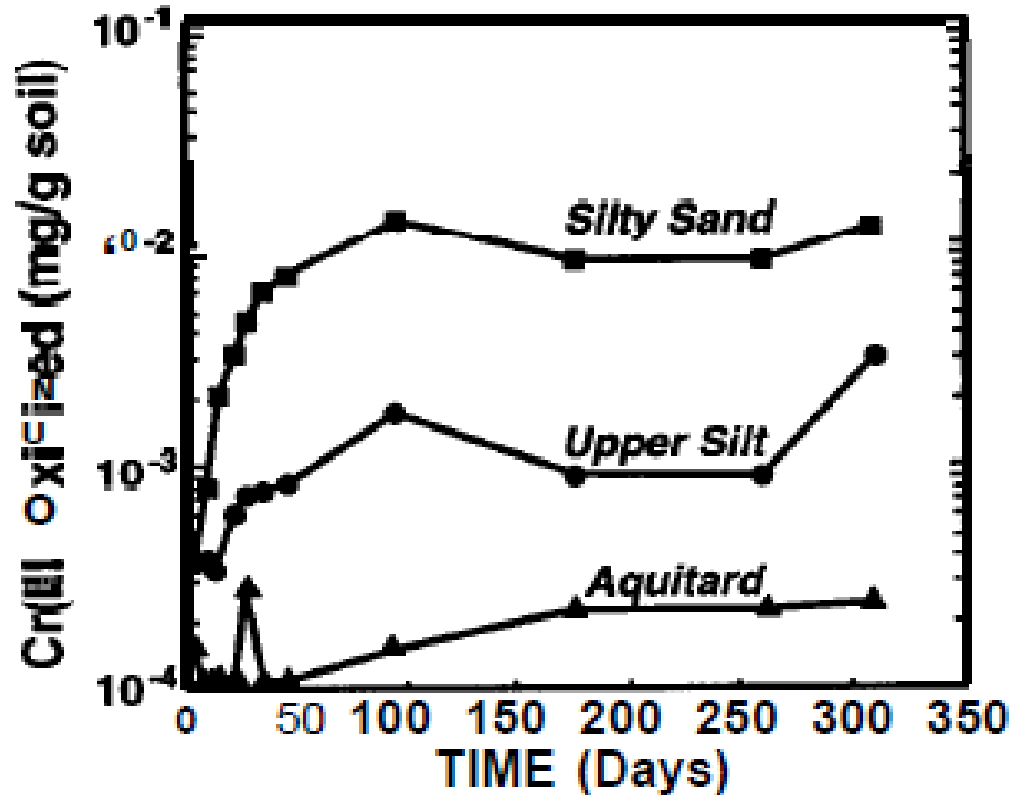


Figure 5. Cr(III) oxidized to Cr(VI) in a suspension of Willamette silt loam.

Palmer and Puls, 1994; EPA/540/5-94/505)

- Rate of process is variable from days to years.
- Has resulted in aqueous Cr(VI) concentrations well above normal remedial standards.
- The rate is governed by the balance of reducing agents and oxidizing agents, particularly MnO₂
- Coarse-grained, oxic, low organic content sites allow more rapid mobilization of Cr(III).
- Fine-grained soils with high organic content may protect Cr(III) from rapid oxidation/mobilization.
- Chromium precipitated under mildly reduced conditions was 3X more susceptible to dissolution than that which has been precipitated under stronger reducing conditions (Varadharajan et al., 2017. *Env. Sci. Technol.* 51: 4918-4927).
- Observation attributed to greater removal of MnO₂ and other oxidants when reducing conditions are strong and long lasting versus milder and short-lived.

MetaFix[®] and GeoForm[®] Reagents for Removal of Dissolved Metals and Destruction of cVOCs



MetaFix® and GeoForm® Reagents

MetaFix® Reagents

- Custom blends of ZVI with reactive minerals, carbonates, and adsorbents.
- Developed in 2014 - 2016 through basic research on removal of targeted metals in a wide range of soils and soil groundwater blends including all major heavy metals and metalloids.
- Excellent track record on arsenic, chromium, divalent metals, and mercury.
- Designed to be effective under a broad range of pH and Eh conditions.
- Performance not inhibited by high salinity or high acute toxicity.

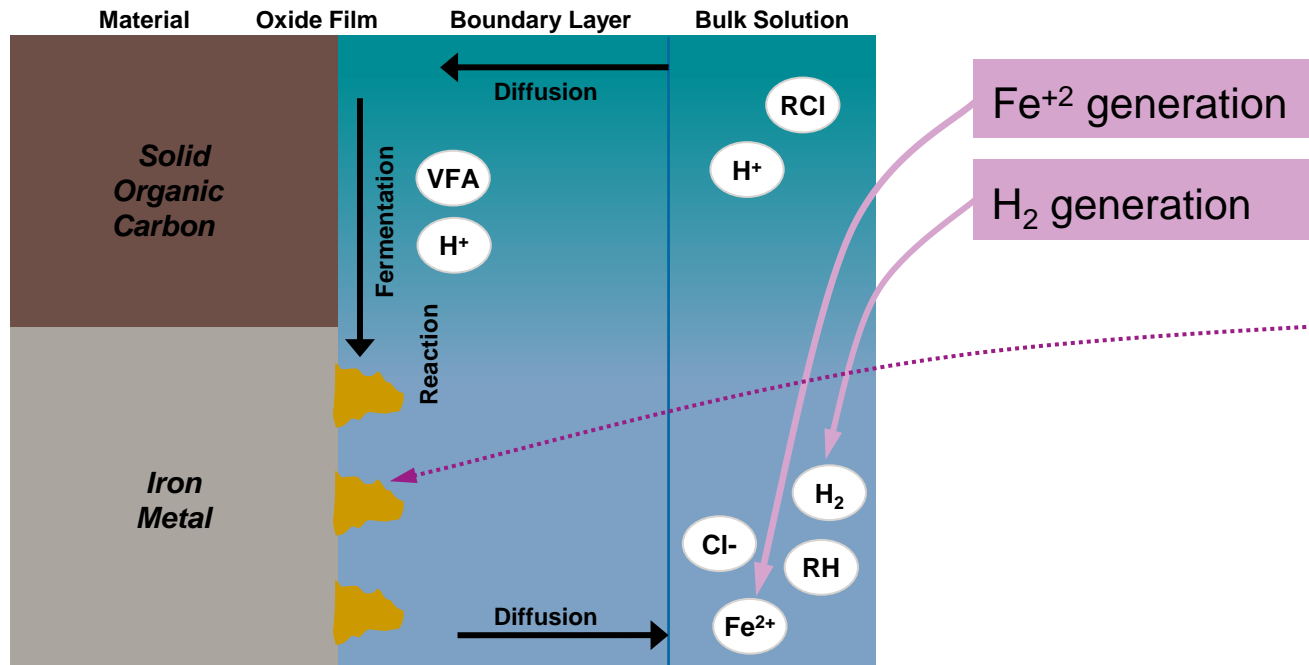
GeoForm® Reagents

- Advanced biogeochemical reagents formulated with ZVI, a blend of rapidly and slowly metabolized organic carbon, soluble iron compounds, soluble sulfate, and important nutrients.
- Ensure rapid removal of DO and nitrate to ensure strong sulfate reducing conditions.
- Provide long-lasting source of reducing equivalents, ferrous iron, and free sulfide.

Treatment of dissolved metals using a combination of MetaFix® and GeoForm® reagents has proven resistant to rebound.

Carbon Fermentation + ZVI Corrosion

Acidity of VFAs balances alkalinity from ZVI



ZVI Reactions:



Production of organic acids (VFAs):

- Serves as electron donor for microbial reduction of cVOCs and other oxidized species such as O₂, NO₃, SO₄
- The release of acids keeps the pH down and thereby serve to reduce precipitate formation on ZVI surfaces to increase reactivity
- Increase rate of iron corrosion/H₂ generation

Favorable thermodynamic conditions for dechlorination:

- Combined oxygen consumption from carbon fermentation and iron oxidation → Strongly reduced environment (-250 to -500 mV)
- High electron/H⁺ pressure

Bacterial Sulfate Reduction

In Situ Generation of Sulfide for Precipitation of Dissolved Metals

- Anaerobic bacteria that use inorganic sulfur compounds (i.e., sulfate, sulfite, thiosulfate) as their terminal electron acceptor during anaerobic respiration and produce sulfide (S^{2-} , HS^- , H_2S).
- This is a large, diverse, almost ubiquitous group of bacteria (40 genera, >120 species).
- Free sulfide promotes corrosion of iron and steel (bad for life of UST, but good for flow of Fe^{2+} from ZVI).
- Require simple organic electron donors (VFAs, ethanol, glucose).
- Steady flow of fermentation products and phosphate from metabolism of plant fiber supports growth and stability of SRB population
- It is important that sulfate must be activated by the enzyme ATP sulfurylase before reduction to sulfide can begin (*n.b.*, importance of bioavailable phosphate, reagent considerations).

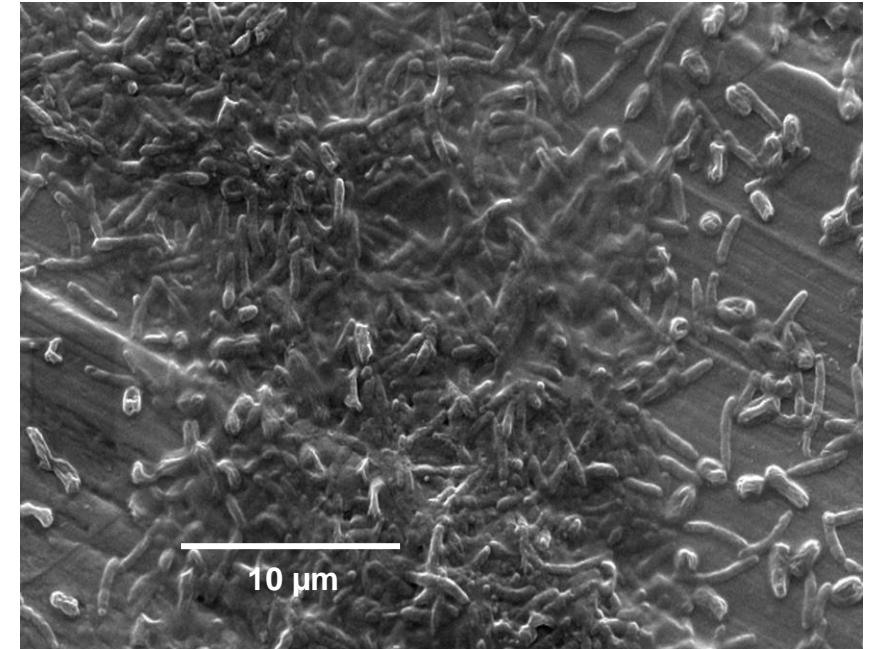
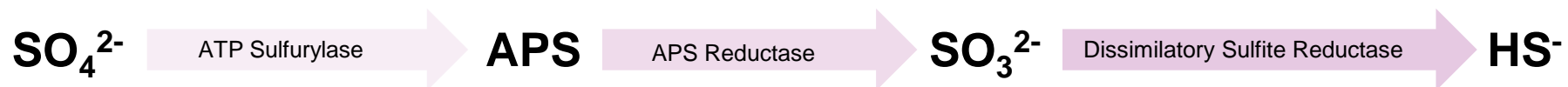


Figure 1. Mixed bacterial biofilm on iron particle.



Tran, T.T.T. et al., 2021. Appl. Sci. 11, 2021

MetaFix® and GeoForm® ER Reagents

Summary of Treatment Mechanisms for Metals and cVOCs

- ✓ ZVI promotes abiotic reduction at particle surfaces and provides a long-lasting source of ferrous iron (i.e., 5 - 15 years).
- ✓ Reactive minerals promote abiotic reduction reactions at particle surfaces and serve as a long-lasting source of both free sulfide and ferrous iron.
- ✓ Reactive minerals also serve as an adsorptive surface for some metals (chromium) and metalloids (arsenic).
- ✓ Slowly soluble carbonate promotes precipitation of some metals as insoluble metal carbonates (e.g., cerussite, PbCO_3).
- ✓ Activated carbon enables removal of organometallic compounds that resist precipitation or coprecipitation (e.g., methyl mercury, tetraethyl lead, organoarsenic compounds).
- ✓ Blend of rapidly and slowly-metabolized organic carbon promotes strong microbial growth for removal of DO, nitrate, and enables sulfate reduction for generation of free sulfide and development of a large microbial biomass.
- ✓ VFAs produced during metabolism of organic carbon will (a) balance alkalinity from ZVI to prevent passivation of ZVI surfaces, (b) increase flow of ferrous iron by increasing ZVI corrosion rate, and (c) ensure adequate supply of simple carbon compounds required for strong bacterial sulfate reduction.
- ✓ Soluble sulfate ensures an adequate supply of free sulfate to be reduced to free sulfide needed in reduction and precipitation reactions and formation of biogenic reactive minerals.

The strong, long-lasting, multiple mechanism conditions created by the MetaFix® + GeoForm® treatment support occlusion of newly precipitated metals and metalloids and prevents their mobilization even if geochemistry changes.

Representative Performance

Bench-scale Treatability Results

Economical bench testing supports reagent selection and required dosage



Vadose Zone Soil Treatment for TCLP Cr(VI)

Batch Microcosm Study

Table 1. Baseline soil characterization.

| Soil ID | DI Water Leaching (ASTM Type I) | | | | Soil | | | TCLP | | | |
|---------|---------------------------------|-----------|-------------------------|-------------------|------|------------|--------------------|------------|----------|-----------|-------------------------|
| | final pH | Pb (µg/L) | Cr ⁶⁺ (µg/L) | Cr (total) (µg/L) | pH | Pb (mg/kg) | Cr (total) (mg/kg) | Pretest pH | final pH | Pb (µg/L) | Cr ⁶⁺ (µg/L) |
| GRM | 8.38 | <30 | 2,630 | 2,740 | 8.21 | 27,200 | 12,500 | 7.49 | 5.27 | 45 | 19,100 |

Table 2. Influence of MetaFix® + Daramend® M treatment on TCLP lead and hexavalent chromium.

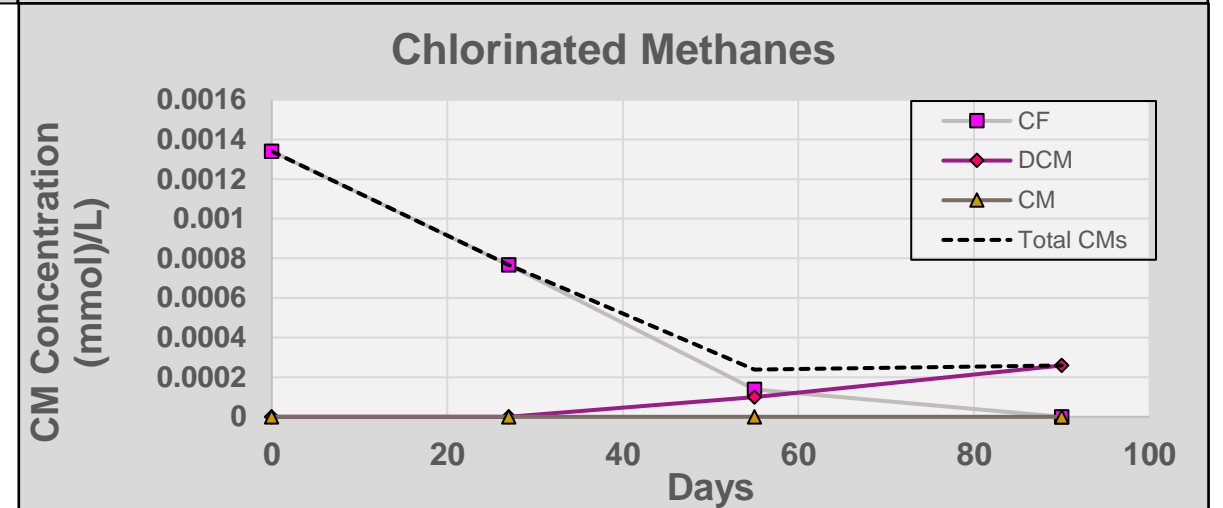
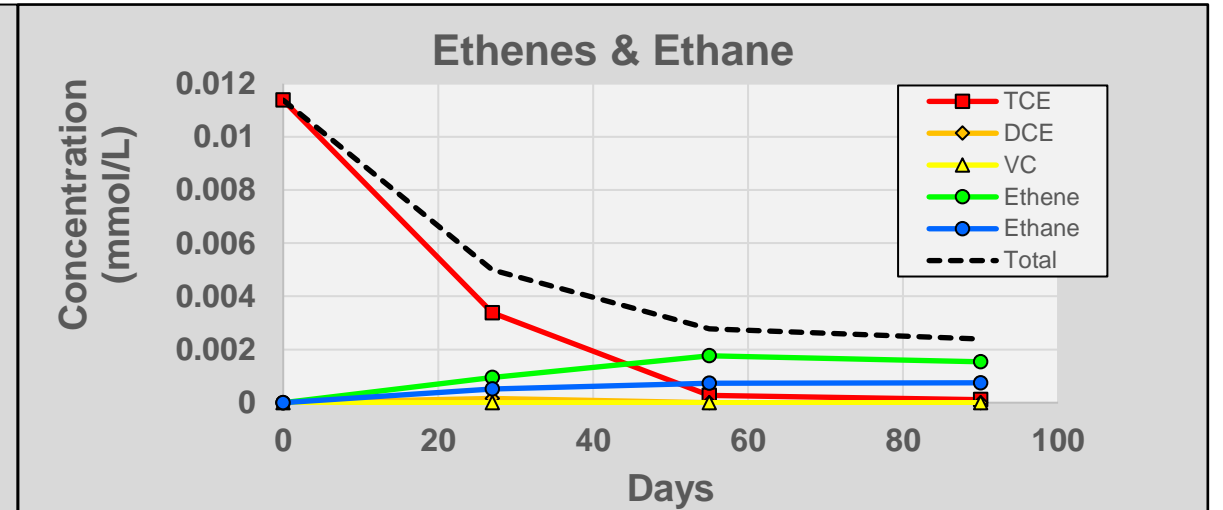
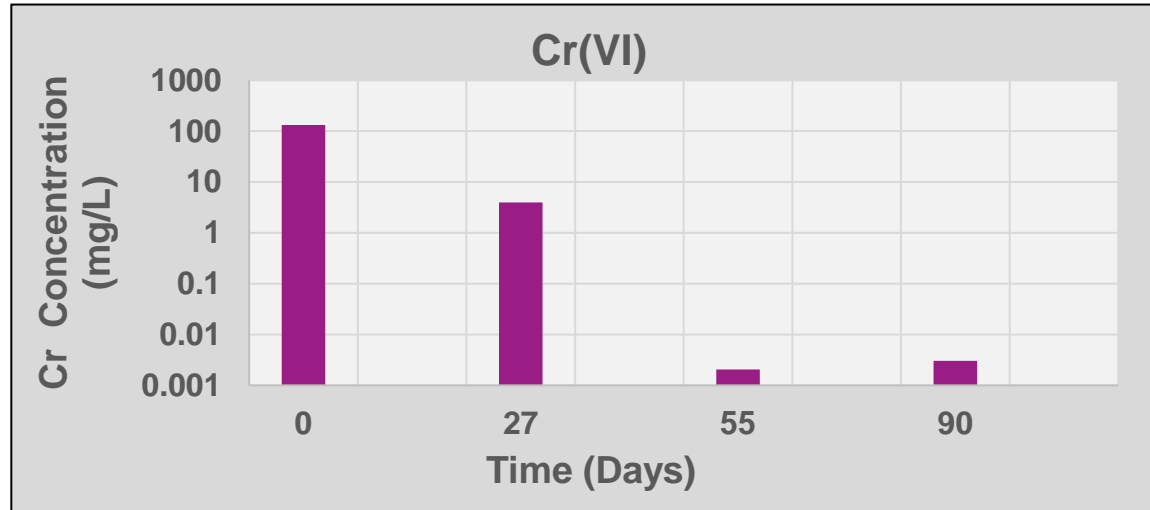
| Control & Treatments | MetaFix® I-3 | MetaFix® I-6A | MetaFix® I-7A | Daramend® M | pH | Pb (µg/L) | Cr ⁶⁺ (µg/L) |
|----------------------|--------------|---------------|---------------|-------------|------|-----------|-------------------------|
| Control | | | | | 8.49 | <30 | 2,220 |
| Treatment 1-L | 0.25 | | | 0.25 | 8.25 | <30 | 1,230 |
| Treatment 1-H | 0.5 | | | 0.5 | 8.25 | <30 | 29 |
| Treatment 2-L | | 0.25 | | 0.25 | 8.41 | <30 | 71 |
| Treatment 2-H | | 0.5 | | 0.5 | 8.17 | <30 | 31 |
| Treatment 3-L | | | 0.25 | 0.25 | 8.35 | <30 | 506 |
| Treatment 3-H | | | 0.5 | 0.5 | 8.28 | <30 | 473 |

Chrome Plating Site in Africa

- Vadose Zone treatment by soil mixing
- Treatment objective to pass TCLP
- Remedial Goal of 600 µg/L for Cr(VI)
- Soil in amber glass microcosms with soil water content at 90% WHC
- Reaction period of 28 days
- Low dosage of Treatment 2 was selected for full-scale application
- Economical bench testing to ensure effective reagent chemistry and estimate dosage.

Independent Bench-scale Testing

Treatment of Chlorinated VOCs and Cr(VI)



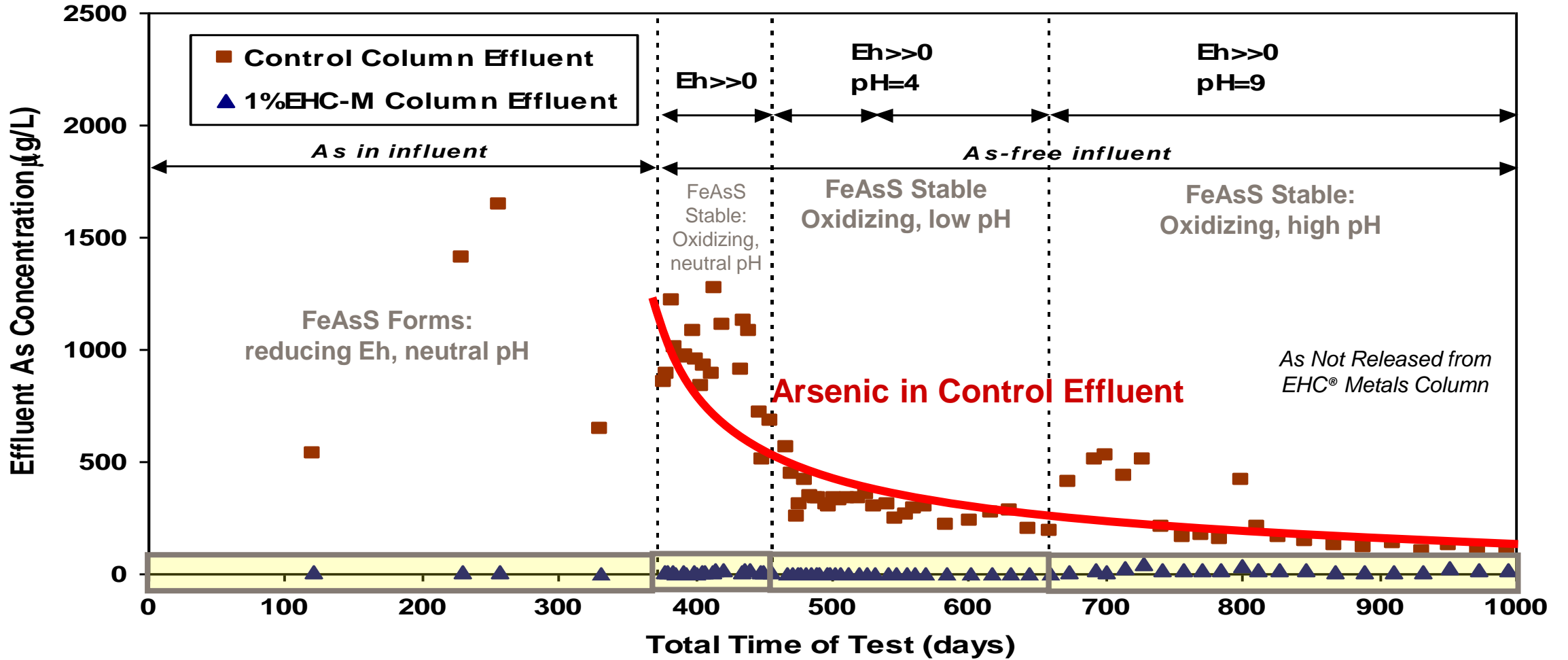
- MetaFix[®] reagent used to simultaneously treat both metals and cVOCs
- Cr(VI) reduced from 132 mg/L to 0.003 mg/L
- TCE and CF removed with very little accumulation of typical partial dechlorination products
- Note production of ethene and ethane

Source: Geosyntec, Guelph ON.

Long-term Arsenic Stabilization by Occlusion

1,000-day Column Study Documents pH/Eh Stability of Precipitated Arsenic (Michigan Site)

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



Representative Performance

Field-scale Project Snapshots

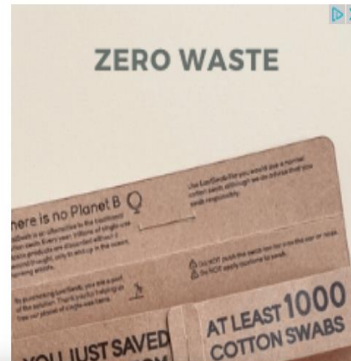


MetaFix® Project Snapshot 1

US EPA Emergency Response for Hexavalent Chromium – Madison Heights, MI



A green liquid that can cause cancer gushed from a wall along a Michigan highway



- Former chromium waste handling site
- Extreme Cr(VI) and elevated TCE
- Site just off I-696 near Madison Heights, Michigan
- Tricia Edwards, USEPA & David Beck, Tetra Tech

- Bench-scale treatability testing
- Pilot-scale demonstration
- Full-scale remediation
- MetaFix® I-3, EHC® Plus, and ELS® Reagents

Treatability Results - Madison Heights Chromium Site

Glass reaction vessels, 28-day reaction period



| Analyte | EP-RW-01-012120 | Test 1 Control | Test 2 I-3+EHC Plus (2 wt.%) | Test 3 I-3+EHC Plus (5 wt.%) | Remediation Goal |
|---|------------------------|------------------------|-------------------------------------|------------------------------|------------------|
| pH (SU) | 6.83 | 8.36 | 7.01 | 6.98 | --- |
| ORP (mV) | 130 | 110 | 100 | 51 | --- |
| Chromium, Hexavalent (µg/L) | <u>302,000</u> | <u>268,000</u> | <u>91,000</u> | <10 | 11 |
| Mercury (µg/L) | <u>1.2</u> | <0.084 | <0.084 | <0.084 | 0.20 |
| Arsenic (µg/L) | <u><167</u> | <u>96.1 (J)</u> | 1.8 (J) | 1.7 (J) | 10 |
| Selenium (µg/L) | <u><122</u> | <u>124 (J)</u> | <u>6.8</u> | <0.79 | 5 |
| Cyanide, Free (µg/L) | 3.9 | <u>29.6</u> | 1.9 (J) | 1.4 (J) | 5.2 |
| Trichloroethene (µg/L) | <u>368</u> | <u>221</u> | 1.9 | 0.37 (J) | 200 |
| cis-1,2-Dichloroethene (µg/L) | 43.2 | 46.7 | 1.4 | 0.36 (J) | 620 |
| trans-1,2-Dichloroethene (µg/L) | <10.9 | 3.2 (J) | <1.1 | <1.1 | 1,500 |
| Chloroethene (µg/L) | <u>14.1</u> | <u>13.8</u> | 3.3 | 0.90 (J) | 13 |
| Perfluorooctanoic acid (PFOA) (µg/L) | 0.0905 | 0.0827 (J) | 0.0218 (J) / 0.0200 (J) | 0.0218 (J) | 12 |
| Perfluorooctane sulfonate (PFOS) (µg/L) | <u>20.2 (J)</u> | <u>3.47 (J)</u> | <u>0.617 (J) / 0.558 (J)</u> | <u>0.467 (J)</u> | 0.012 |

Objectives & Results

- Determine if removal of dissolved Cr(VI) could be achieved at such high initial concentrations.
- Clear dosage response
- Complete removal at 5% w/w
- TCE removal without accumulation of DCE or VC



Full Scale Implementation



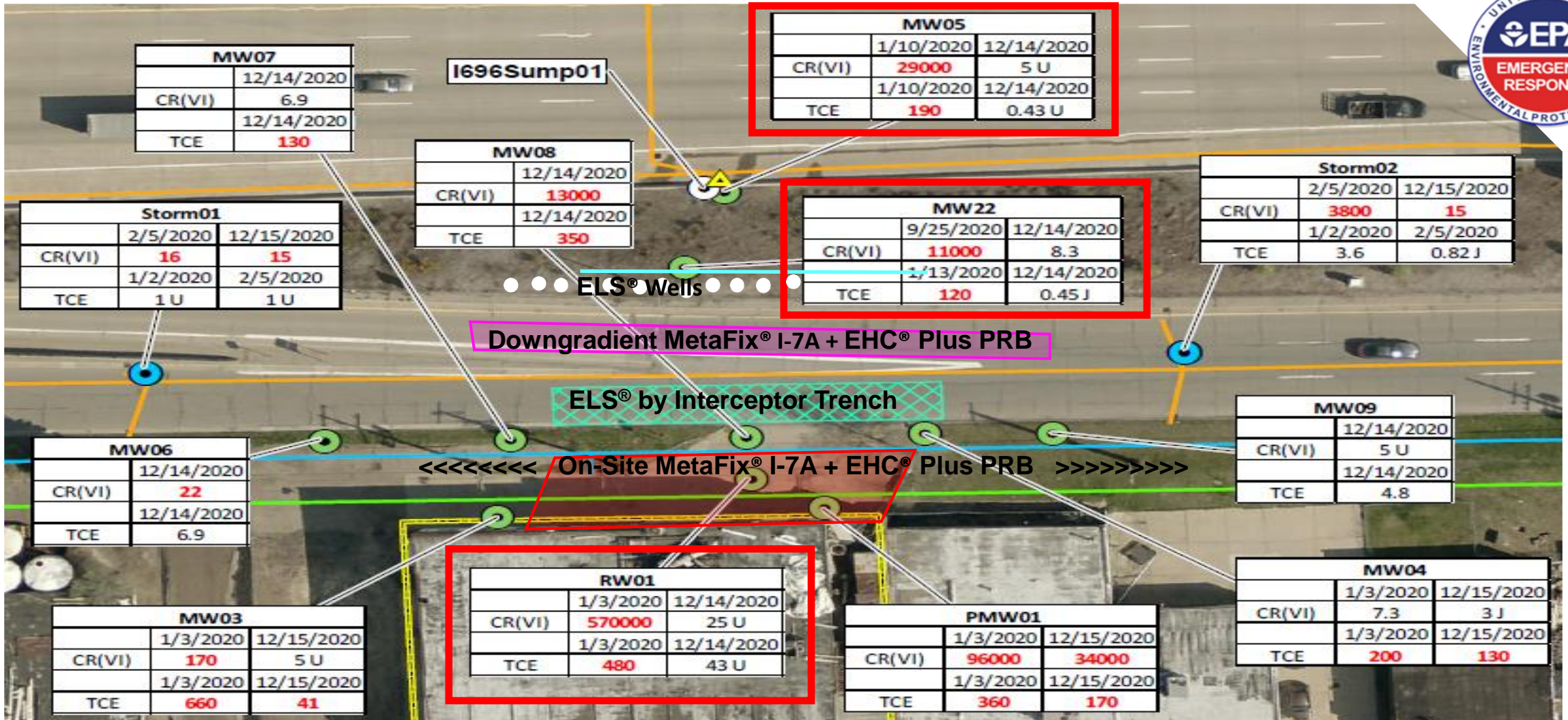
ELS® Embankment Wells

MetaFix® + EHC® Downgradient PRB

ELS® Interceptor Trench

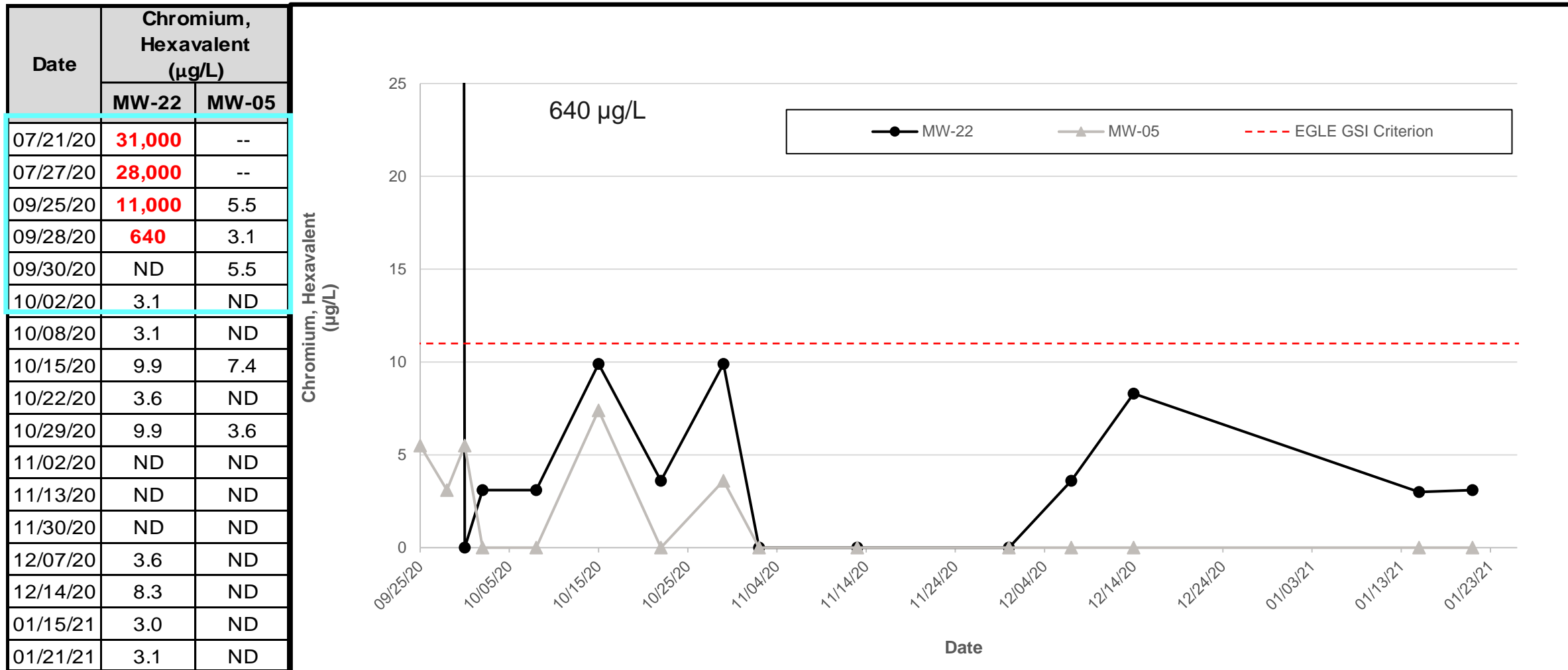
MetaFix® + EHC® On-Site PRB

Madison Heights Chromium Site





Initial Monitoring Results – Madison Heights, MI



MetaFix® Project Snapshot 2

On-Site Treatment of Mercury: Bench-scale Treatability Test

- Mercuric chloride was used as a catalyst in chemical synthesis at this former chemical plant

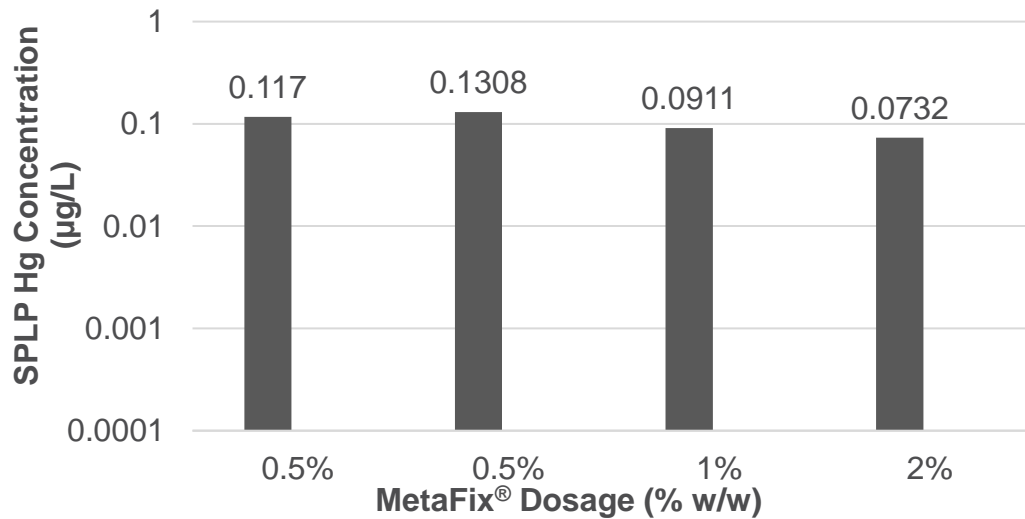


- Soil mercury concentrations ranged from 300 to 420 mg/kg.
- The remedial goal was to stabilize the soil and to then dispose of the treated soil at an offsite landfill and the land will be developed for residential use.
- Results from bench-scale testing indicated that a MetaFix® dosage of 0.5% (w/w) would achieve the remedial objective for mercury (i.e., 1.0 µg/L SPLP).

| Parameter | Control (untreated) | MetaFix® 0.5% (w/w) | MetaFix® 1.0% (w/w) |
|-------------------|---------------------|---------------------|---------------------|
| Soil Moisture (%) | 18.3 | 18.5 | 20.0 |
| pH | 8.6 | 8.0 | 7.9 |
| Total Hg (mg/kg) | 315 | 293 | 314 |
| SPLP Hg (µg/L) | 35.1 | <1.0 | <1.0 |

MetaFix® Project Snapshot 2

On-Site Treatment of Mercury: Pilot-scale Demonstration



Pilot-scale Demonstration

- Four treatment cells, each with 50 m³ soil
- A range of MetaFix® dosages compared including 0.5% 1.0%, and 2.0% (w/w)
- MetaFix reagent mixed into the soil with an excavator bucket and a screening bucket
- Sufficient water added to increase soil moisture content to near but below the point of saturation (ca. 90% WHC)
- Soil was covered with HDPE to prevent drying and support creation of anaerobic conditions
- Reaction period was 7 days
- Even the lowest dosage achieve the remedial objective of 1.0 µg Hg/L in SPLP testing
- Decision was to use 0.5% w/w reagent dosage for full-scale application

MetaFix® Project Snapshot 2

On-Site Treatment of Mercury: Full-scale Treatment

Allu Screening Bucket



Full-scale Application

- The MetaFix® dosage of 0.5% w/w selected for the full-scale treatment.
- Full scale implementation utilizes an integrated soil mixing system where soil crushing/screening and reagent dosing/mixing are completed in a single step.
- Reaction period was the same as in the pilot-scale demonstration (7 days).
- Several thousand tons successfully treated to below the remedial goal of less than 1.0 µg/L SPLP.

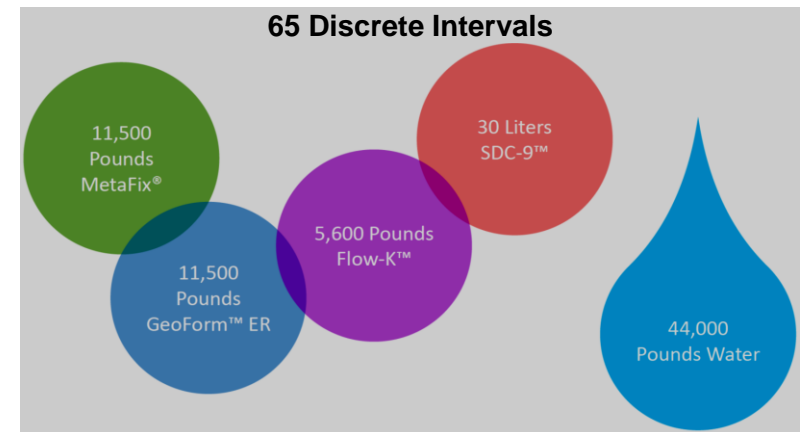
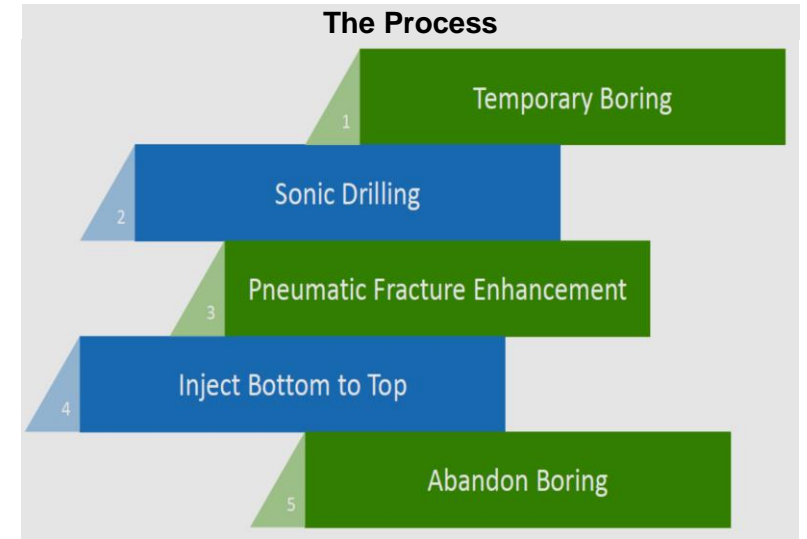
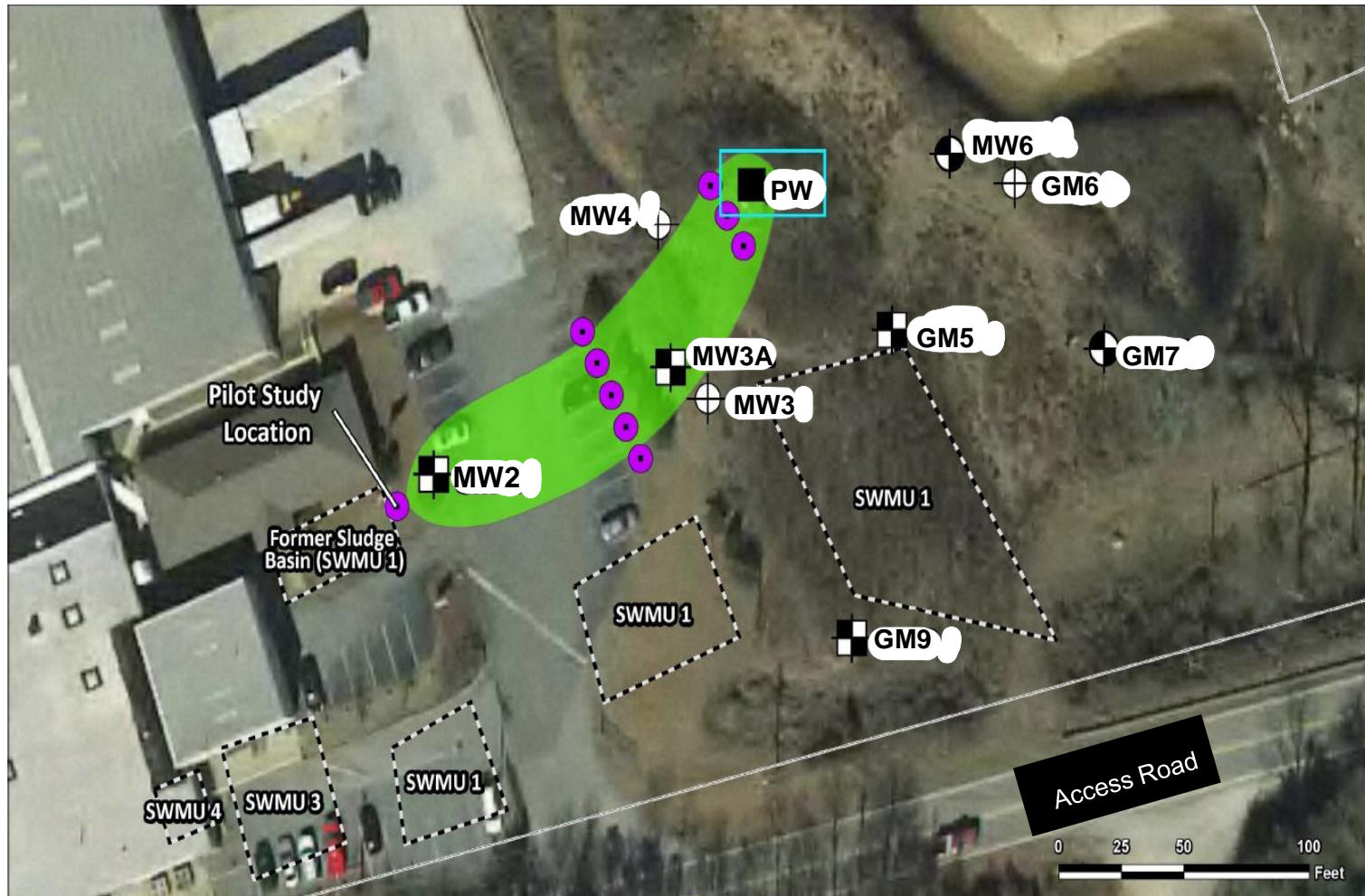
Project Snapshot 3 MetaFix® with GeoForm® ER

Removal of Dissolved Cd, Ni, and Zn
In Situ BioGeoChemical Reduction of cVOCs
Industrial Facility
SE USA



MetaFix® I-7A with GeoForm® ER Project Snapshot

Full-scale Treatment of Metals and cVOCs



Source: Rogersadcallcott.com

MetaFix[®] I-7A with GeoForm[®] ER Project Snapshot

Full-scale Treatment of Metals and cVOCs

Table 1. Groundwater chemistry at MW3A.

| Sample Date | pH (s.u) | Spec. Cond. (µs/cm) | DO (mg/L) | ORP (mV) |
|-------------|----------|---------------------|-----------|----------|
| 5/3/2021 | 5.6 | 456 | - | - |
| 11/1/2021 | 5.6 | 463 | 0.51 | 149 |
| 2/2/2022 | 5.7 | 465 | 0.73 | 166 |
| 5/2/2022 | 6.5 | 599 | 0.36 | -5.7 |

Table 2. Contaminant concentrations at MW3A.

| Sample Date | PCE (µg/L) | TCE (µg/L) | cDCE (µg/L) | tDCE (µg/L) | VC (µg/L) | Cd (µg/L) | Ni (µg/L) | Zn (µg/L) |
|-------------|------------|------------|-------------|-------------|-----------|-----------|-----------|-----------|
| 5/3/2021 | 13.9 | 43.3 | 4.4 | <1.0 | <1.0 | 0.015 | 0.036 | 0.418 |
| 11/2/2021 | 7.7 | 31.7 | 53.0 | <2.0 | <2.0 | 0.373 | 0.410 | 6.0 |
| 2/2/2022 | 7.0 | 33.0 | 53.0 | <2.0 | <2.0 | 0.505 | 0.115 | 1.33 |
| 5/2/2022 | <1.0 | 1.6 | 28.4 | <1.0 | 5.0 | 0.021 | 0.046 | 0.29 |
| 12/30/2022 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <0.002 | <0.010 | <0.010 |
| 11/2/2023 | 1.5 | 4.8 | 1.8 | <1.0 | 6.6 | <0.002 | 0.011 | 0.052 |
| GWPS | 5.0 | 5.0 | 70 | 100 | 2.0 | 0.005 | 0.700 | 5.0 |

Source: Rogersadcallcott.com

Summary & Conclusions

1. Dissolved metals and metalloids can be effectively removed by promoting reactions including adsorption, precipitation, and coprecipitation using iron and iron sulfide-based chemistry that results in more complete and more permanent removal than hydroxide precipitation chemistry.
2. Our understanding of metals chemistry in the environment has improved; however, treatability testing remains an important part of responsible selection of reagents and effective determination of required reagent dosage.
3. Treatment chemistry employed to promote metals removal should be carefully considered because rebound may be observed if the treatment chemistry converts dissolved metals using mechanisms that are subject to reversal. An example is re-oxidation of Cr(VI) that has been reduced to Cr(OH)₃ by high pH treatments (e.g., lime, fly ash, polysulfide) when pH buffers back to the native neutral or acidic range.
4. Susceptibility to this type of rebound can be minimized through use of treatments that generate strong, long-lasting reducing conditions under which continuous precipitation and coprecipitation reactions result in occlusion of the metals and thereby shield them from dissolution by oxidation or changes in pH conditions.
5. At sites where both metals and chlorinated organics require treatment, a combination of enhanced adsorption/precipitation/coprecipitation reactions with reductive biogeochemical treatment can enable simultaneous removal of dissolved metals and destruction of the chlorinated contaminants.

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Questions
are
Welcome!



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