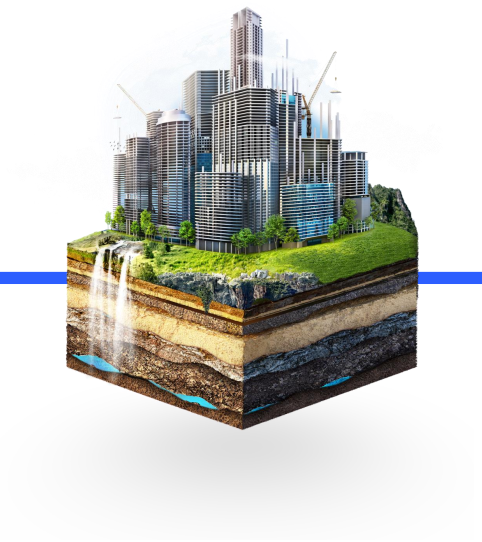
CHEMCO ENVIRONMENT

Metals & Organic contaminant Removal using Reactive Mineral for Groundwater Remediation

Remtech East, Niagara Falls, ON
June 2022

Presented by
Jean Paré, P. Eng.

CANADIAN LEADER IN ENVIRONMENTAL SOLUTIONS



Presentation Agenda

- ✓ ***About us***
- ✓ ***Acknowledgement***
- ✓ ***Chemical Reduction – Technology Review***
- ✓ ***Biogeochemical process – Technology Review***
- ✓ ***Case Studies***
- ✓ ***Conclusions***

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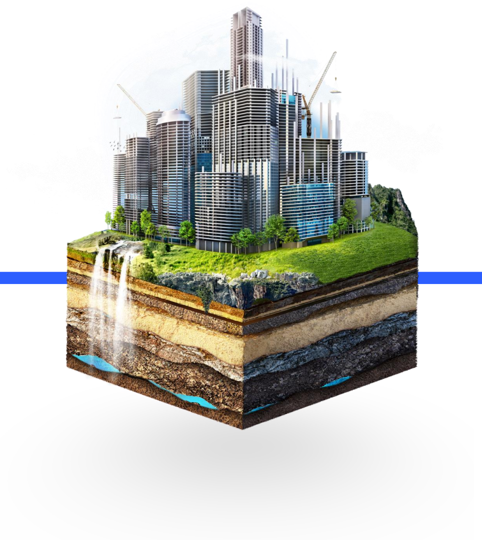

About us

Canadian Company founded in 1988

<u>Production and warehouses throughout Canada</u>

- Quebec
- Ontario
- Alberta
- British Columbia

<u>Sectors of activity</u>:

- Industrial and Municipal Potable & Waste Water
- Contaminated Soil and Groundwater
- Air, Odours and Atmospheric Emissions (Activated Carbon, filtering medias)
- Process Water & Thermal Exchange Fluids (Glycols)
- Drilling Fluids (Oil and Gas & Diamond exploration)
- Aircraft De-icing Fluids

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Our Services

Specialized Products Supply

- Chemical Oxidation
- Chemical Reduction
- Co solvent-Surfactant soil Washing
- Enhanced Bioremediation
- Permeable Reactive Barrier Amendments
- Metals Stabilization
- Activated Carbon Technologies

Excellence & Science through proud Suppliers & Partners

CANADIAN LEADER IN ENVIRONMENTAL SOLUTIONS

ADVANCED OXIDATION TECHNOLOGY (AOT) *Since 2005*

EVONIK Leading Beyond Chemistry *Since 2005*

CARBONE CANADA INC *Since 2014*

BION BIOCONSERVACION *Since 2014*

CARUS® *Since 2014*

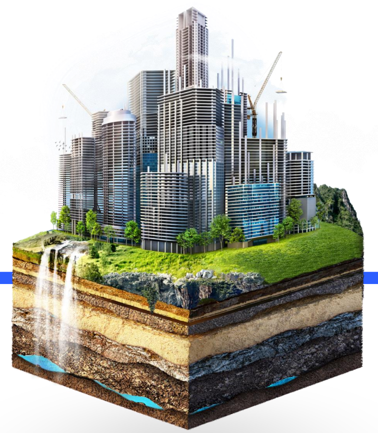
EthicalChem An Ethical Solutions, LLC Division *Since 2016*

EOS EOS Remediation, LLC *Since 2016*

ChemBio Formulation *Since 2017*

SiREM *Since 2017*

Höganäs *Since 2018*



Acknowledgement

- ✓ ***Dan Leigh, Evonik,*** ***Technology Applications Manager - In Situ Reductive Technologies***
- ✓ ***Alan G. Seech, Ph.D., Evonik,*** ***Soil & Groundwater Remediation Lead***
- ✓ ***Josephine Molin, Evonik,*** ***Technology Director Persulfates***

Tuesday Platform

A SESSIONS - Primrose A

A2. Abiotic and In Situ Biogeochemical Processes: Applications and Lessons Learned

8:00	**Abiotic Dechlorination by Natural Ferrous Minerals.** *C.E. Schaefer, D. Nguyen, E. Berns, and C. Werth.* Charles Schaefer (CDM Smith Inc./USA)
8:25	**Mineral Phases from In Situ Biogeochemical Processes: The Key to Abiotic Natural Attenuation?** *P.G. Tratnyek, A.S. Pavitt, and R.L. Johnson.* Paul Tratnyek (Oregon Health & Science University/USA)
8:50	**Development of a ^{14}C Assay to Quantify Abiotic Transformation Rates for Chlorinated Ethenes in Water Supply Aquifers.** *D.L. Freedman, A.A. Ramos Garcia, A. Pullen, J.T. Wilson, B. Wilson, and T. Kuder.* David Freedman (Clemson University/USA)
9:15	**Combined Enhanced Biotic-Abiotic Transformation of Carbon Tetrachloride and Chloroform at the Field Scale: A Biogeochemical Perspective.** *S.D. Justicia-Leon, J. Martin Tilton, C. Divine, S.M. Ulrich, D.L. Freedman, and K. Clark.* Shandra Justicia-Leon (Arcadis/USA)

Tuesday Platfo

A SESSIONS - Primrose A

A2. Abiotic and In Situ Biogeochemical Processes: Applications and Lessons Learned

10:30	**In Situ Biogeochemical Reductive Dechlorination: Performance in Complex Low Permeability Formation.** *J. Studer and N. Glenn.* James Studer (InfraSUR, LLC/USA)
10:55	**Biogeochemically Enhanced Treatment of Chlorinated Organics and Metals.** *D. Leigh, A. Seech, and J. Molin.* Daniel Leigh (Evonik/USA)
11:20	**Using a ^{14}C Assay to Measure Abiotic Degradation of TCE by Magnetic Materials in Aquifer Sediment from the Western USA.** *J.T. Wilson, B. Wilson, D.L. Freedman, and A. Ramos Garcia.* John Wilson (Scissortail Environmental Solutions, LLC/USA)

CANADIAN LEADER IN ENVIRONMENTAL SOLUTIONS

Chemical Reduction Technology Review

In Situ Technologies – Key Drivers

- ✓ Remedial objectives - **Time versus Money**
- ✓ Access to the contaminant of concern (underground infrastructure, public utilities, building, road, etc.)
- ✓ Polishing step to meet low remedial objectives or Risk-Based Criteria
- ✓ **Sustainable Development Contribution** versus remote off-site disposal, environmental footprint, air emission from trucking, etc.)
- ✓ **Improvement of contaminant removal rate** versus natural attenuation

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Chemical Reduction In Situ/Ex Situ – Application range

Chlorinated Compounds

- ✓ PCE, TCE, cDCE, 11DCE, VC
- ✓ 1122TeCA, 111TCA, 12DCA
- ✓ CT, CF, DCM, CM

Herbicides, Pesticides

- ✓ Toxaphène, Chlordane, Dieldrin, Pentachlorophenol

Energetics

- ✓ TNT, DNT, RDX, HMX, Perchlorate

Metals and metalloids

- ✓ As, Cr, Pb, Zn, Cd, Hg, Cu, Cr, Ni, Sb, Co

Under aerobic conditions you can target

HAP, phthalates, perchlorate, petroleum hydrocarbon

- In Red: need to have an organic substrate and/or a ZVI/fermentable carbon combination

ISCR Terminology

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Electron Donor: reducing agents including elemental iron (ZVI), reactive minerals (iron sulfides), fermentable organic carbon (many)

Electron Acceptor: contaminants including pesticides (DDT, Dieldrin), herbicides (2,4-D), chlorinated solvents (PCE, TCE, CT), nitroaromatic explosive compounds (TNT, DNT), and heavy metals (arsenic, chromium)

Biogeochemical Transformation : Processes where contaminants are degraded by abiotic reactions with naturally occurring and biogenically-formed minerals in the subsurface

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Common Chemical Reducing Agents

✓ **Zero valent iron ("ZVI") is still the most common reductant** used in situ for environmental remediation applications.

✓Almost all other reductants are proprietary but most involve the use of some form of ZVI, other zero valent metals, or polysulfide compounds, sometimes mixed with a fermentable carbon substrate.

✓ Until 2004 it wasn't known that chlorinated VOCs were more effectively destroyed by reductant chemicals over oxidants.

Chemical Reduction-Mechanism

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

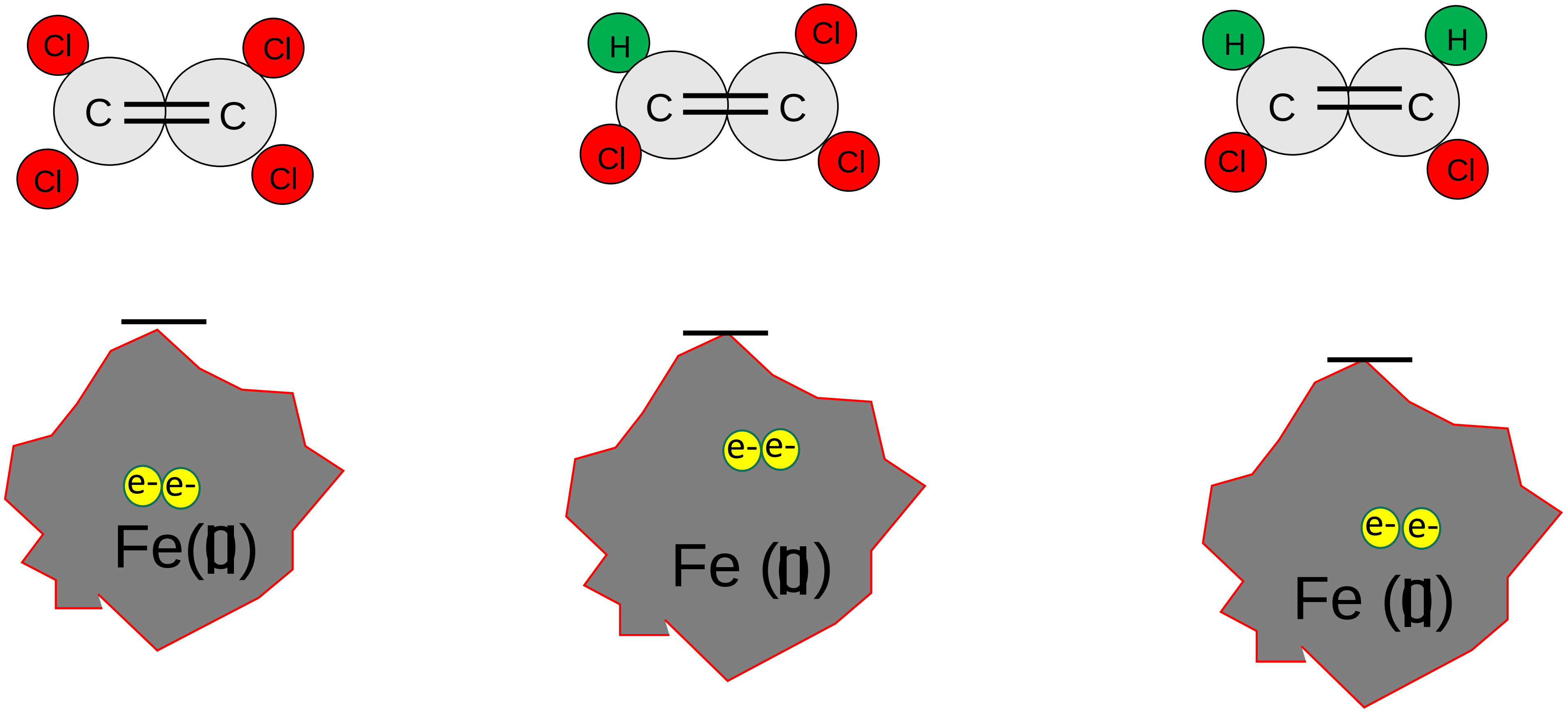
Direct Dechlorination Reactions with ZVI

β elimination (abiotic) pathway

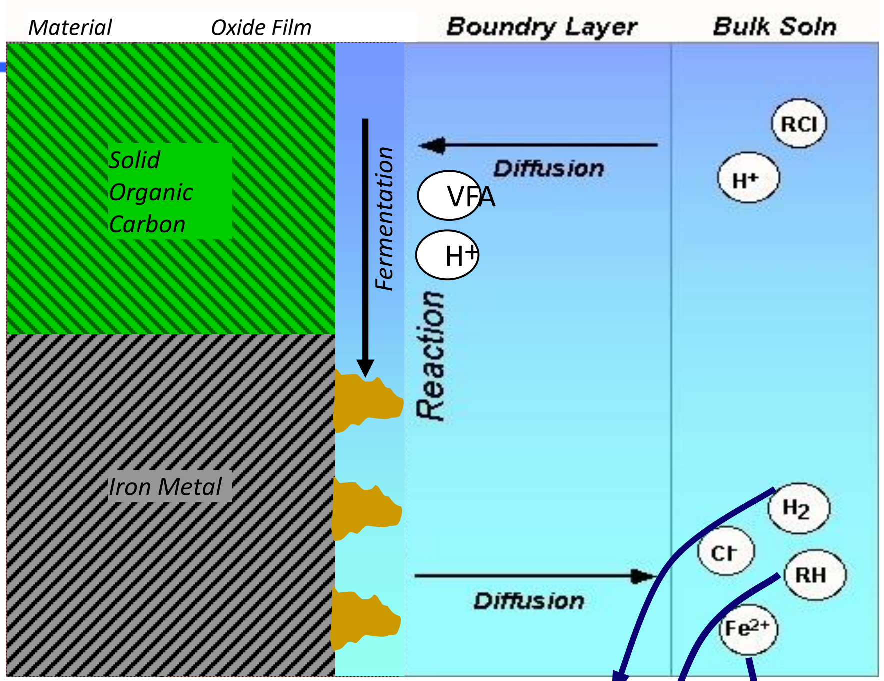
Tetrachloroethylene / Dichloroacetylene

Trichloroethylene / Chloroacetylene

Dichloroethylene / Acetylene



Carbon + ZVI Synergies Generate Multiple Dechlorination Mechanisms: ISCR



3. Biostimulation:

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

1. Direct Iron Effects:

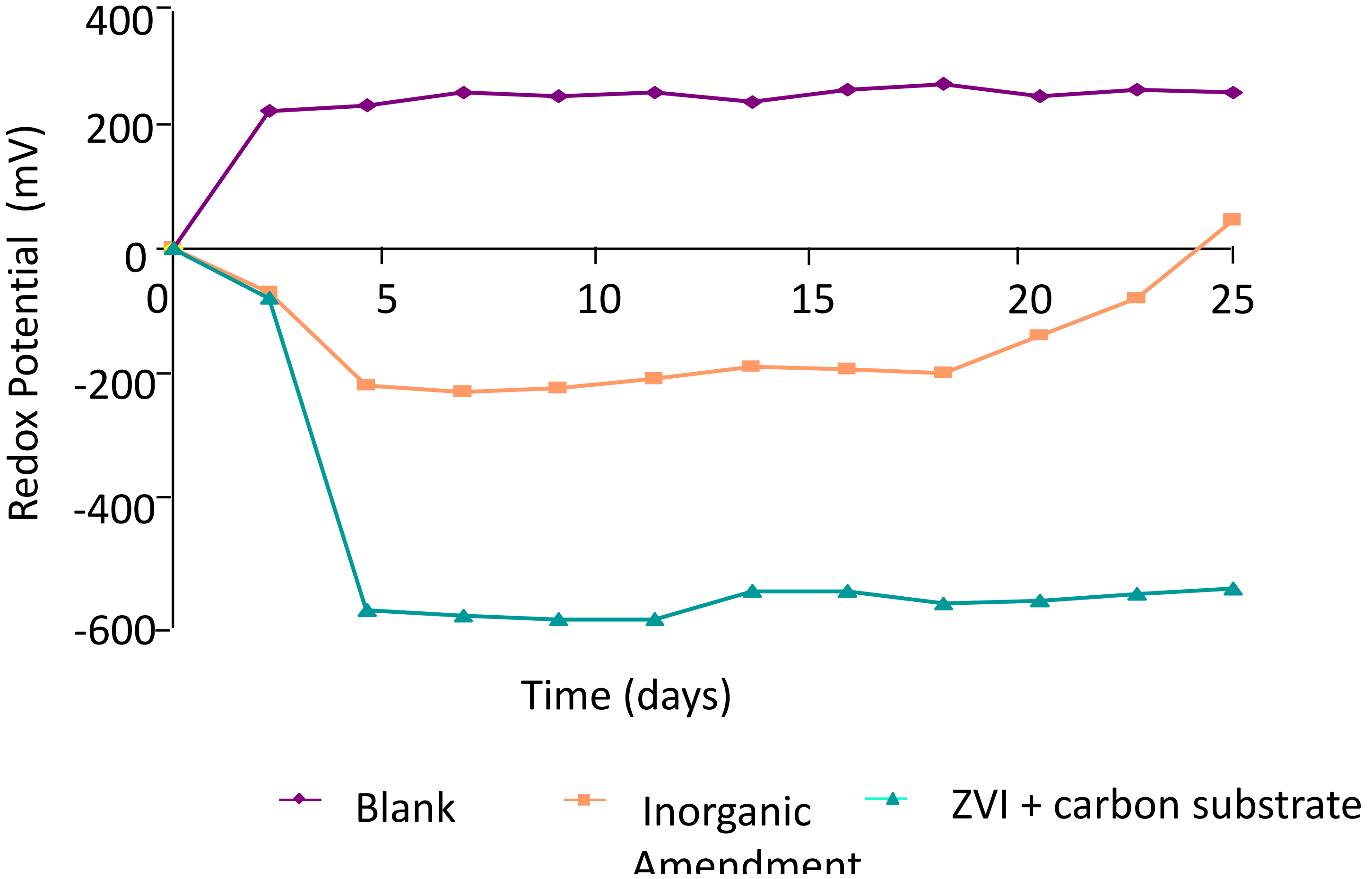
Hydrocarbon generation:

4. Enhanced Thermodynamics:

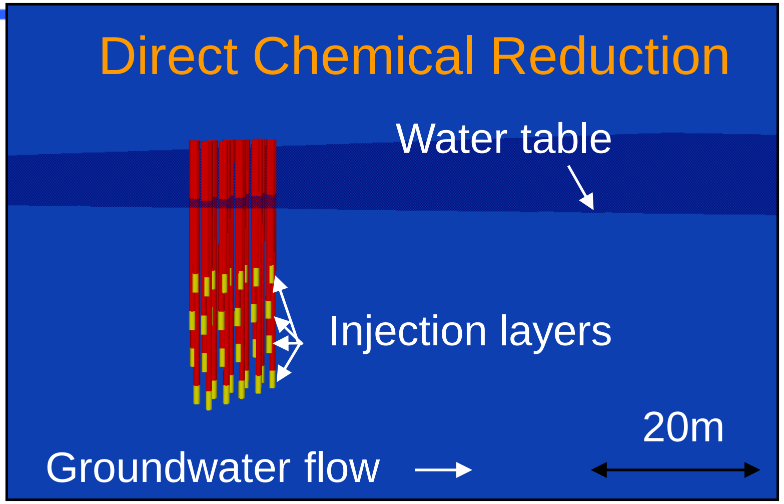
- Very low redox reached by addition of fermentable carbon and ZVI (-500 mV)
- Two processes simultaneously reduce Eh
- Enhances kinetics of dechlorination reactions via higher electron/H^+ pressure

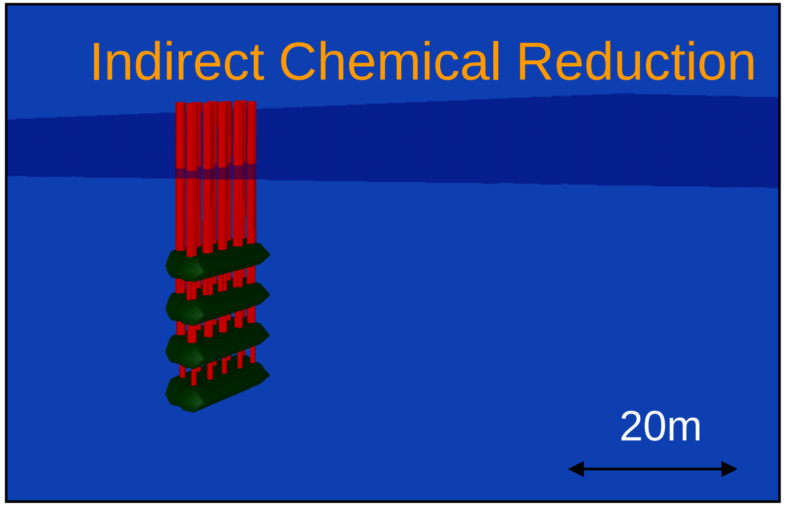
2. Indirect Iron Effects: Dissolved iron precipitates to reactive minerals

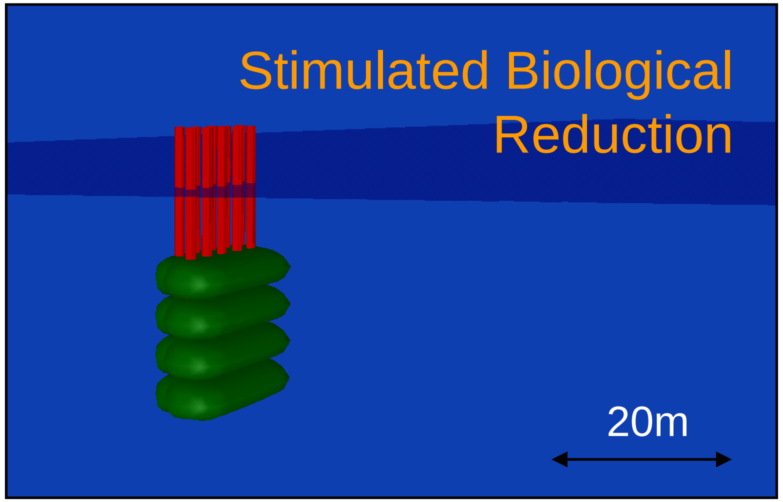
Redox Potential evolution during a reductive phase treatment period

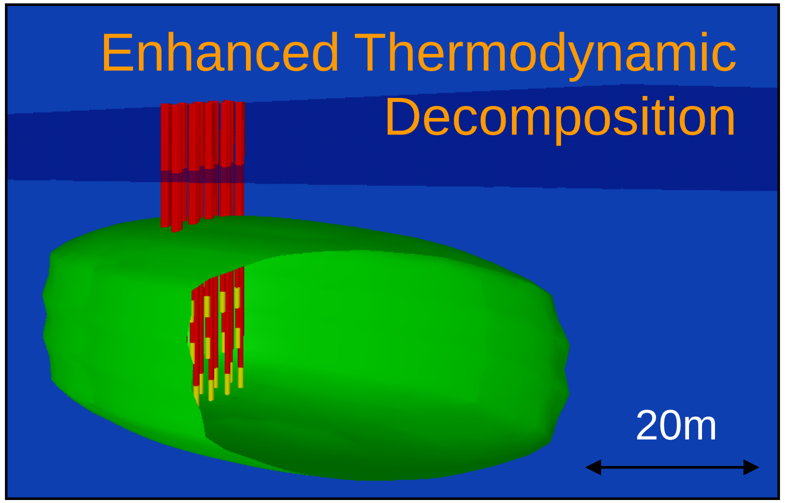


ZVI + Carbone Synergies brings multiples dechloration mechanism









Common Chemical Reducing Agents

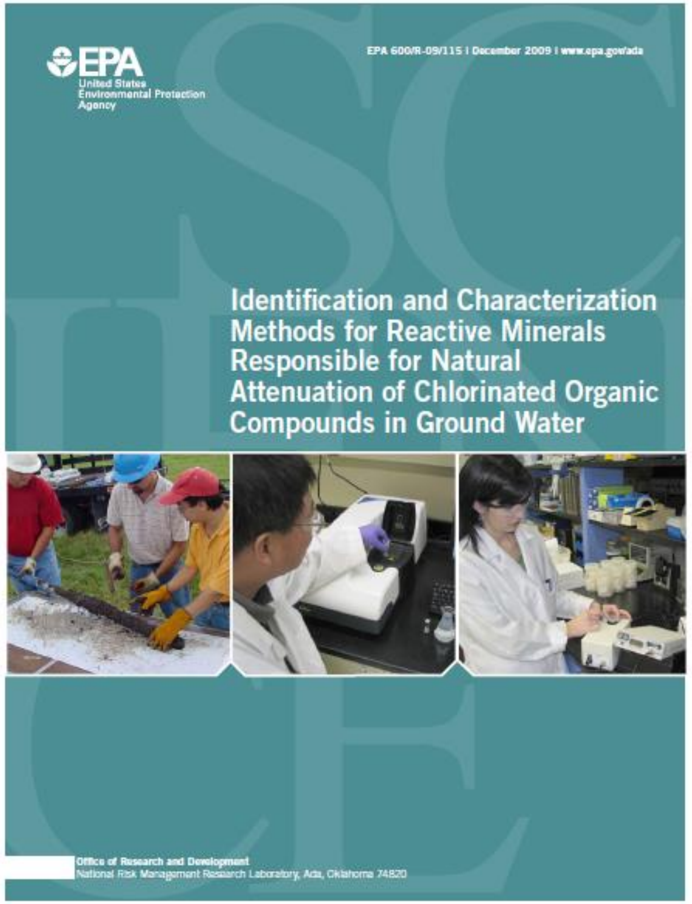
- ✓ Sugars
- ✓ Molasses
- ✓ high fructose corn syrup
- ✓ Whey
- ✓ Fatty acids
- ✓ Lactate
- ✓ Butyrate
- ✓ Propionate
- ✓ Emulsified Vegetable Oils
- ✓ Soybean Oil
- ✓ Complex Fermentable Carbon complex
- ✓ Lecithin
- ✓ Polylactate
- ✓ Zero Valent Iron (ZVI)
- ✓ Soluble Iron Compounds
- ✓ Reactive Minerals

Biogeochemical process Technology Review

Biogeochemical Transformation

- ✓ USEPA Definition: ***Processes where contaminants are degraded by abiotic reactions with naturally occurring and biogenically-formed minerals in the subsurface.***

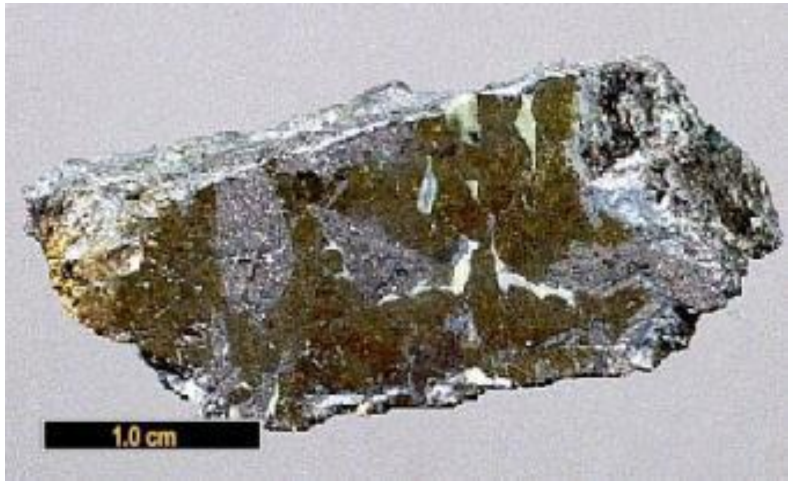
- ✓ Reactive minerals include iron-sulfides (e.g. pyrite, mackinawite, greigite) and oxides (e.g. magnetite)



EPA 600R-09/115 www.epa.gov/ada

Focus on Iron-Sulfide Minerals

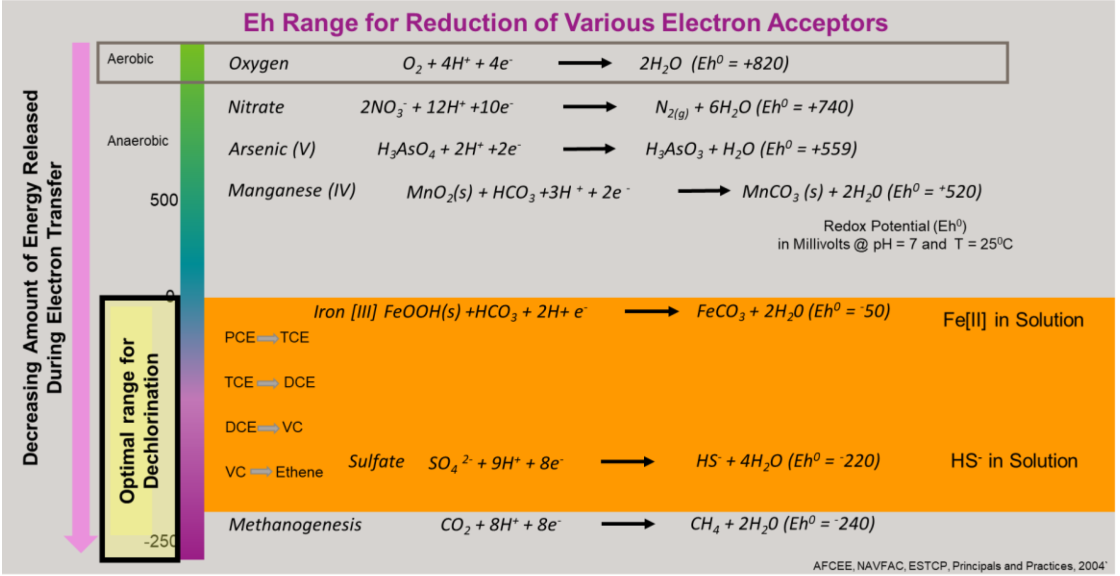
Pyrite (FeS_2)



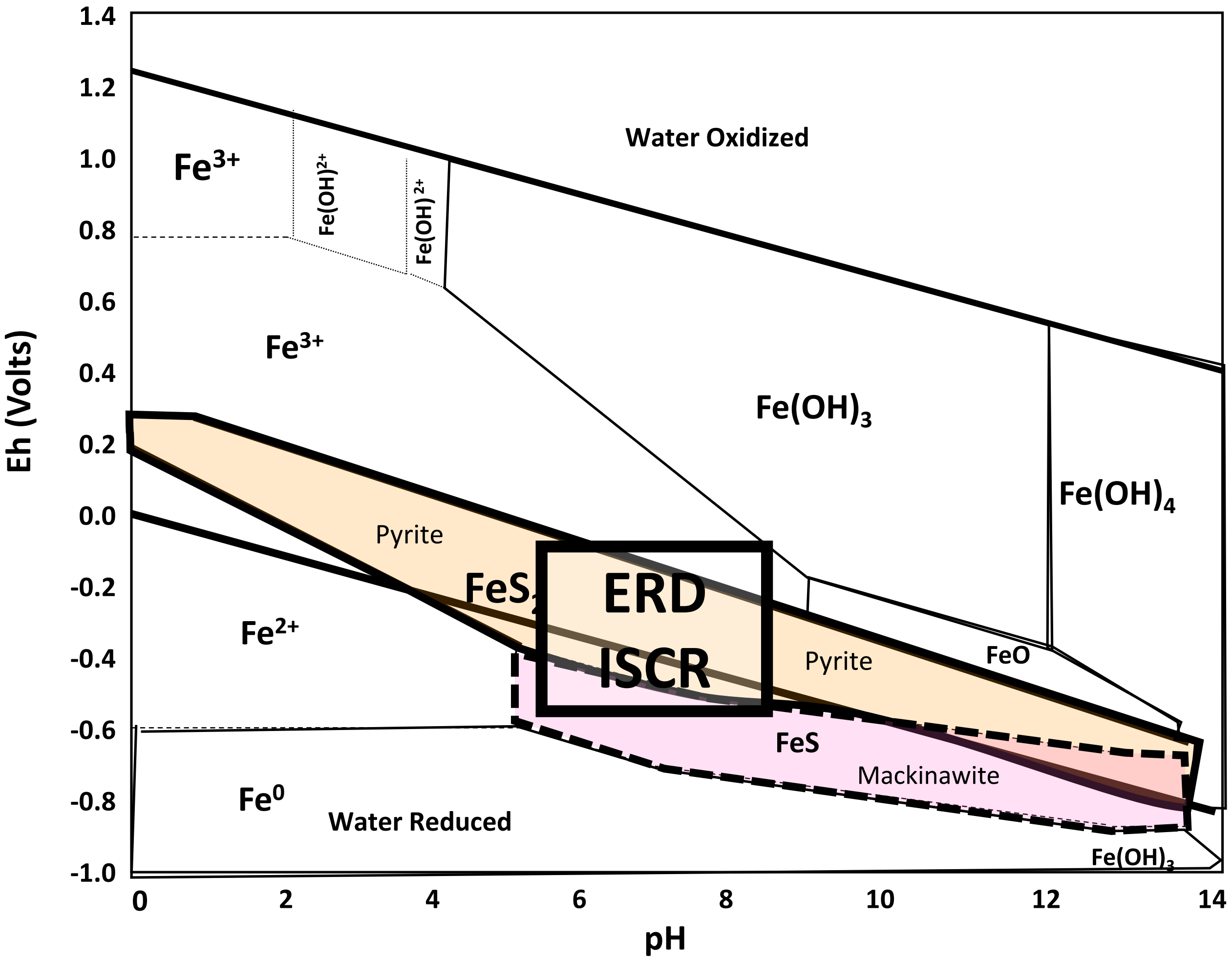
Mackinawite ($Fe_{(1+x)}S$)

Iron-sulfide minerals form, and are stable under ERD/ISCR conditions

FeS minerals conveniently form, and are stable in the same Eh, pH range as biological reductive dechlorination (ERD) and In Situ Chemical Reduction (ISCR)



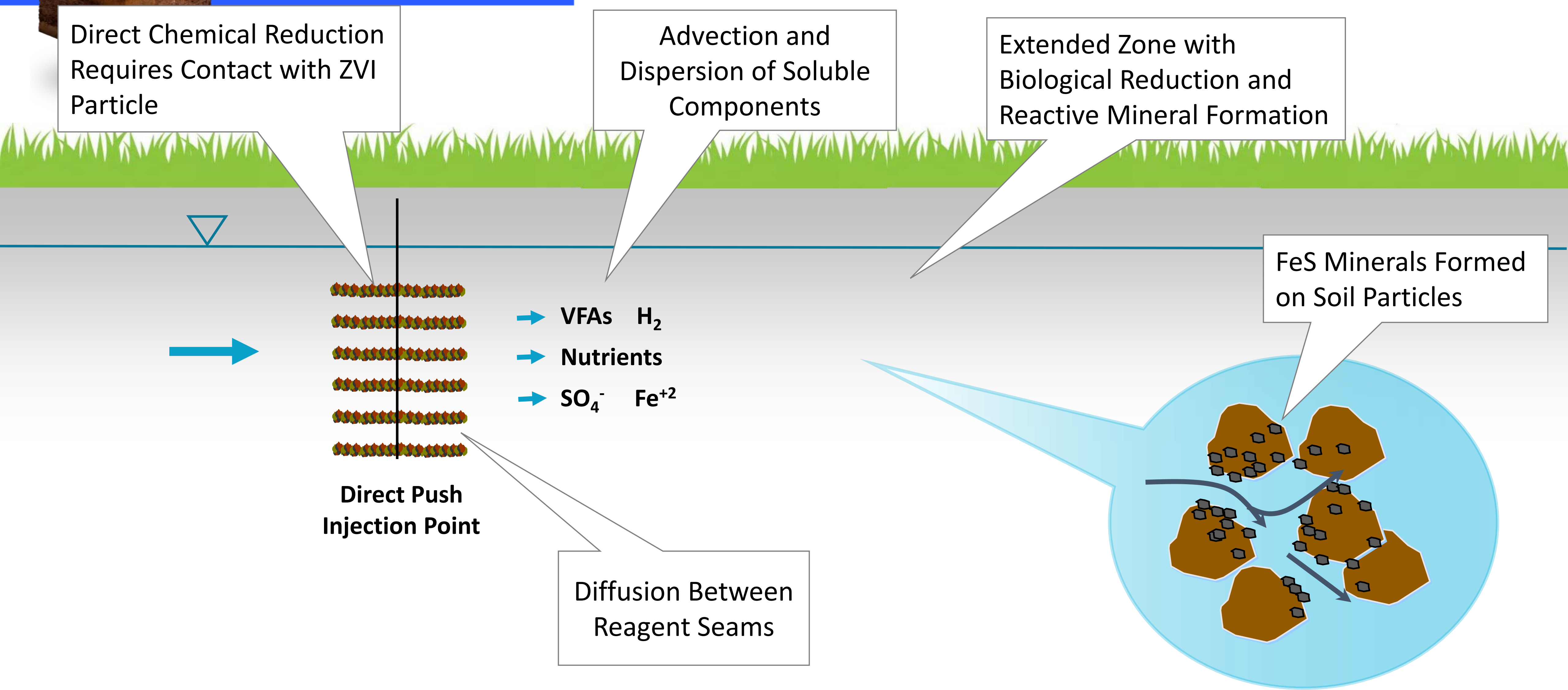
Iron – Sulfur Eh/pH Phase Diagram

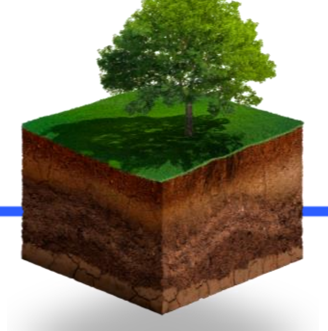


From USGS Water Supply Paper 2254

Fields of stability for solid and dissolved forms of pressure. Activity of sulfur species 96mg/L as SO_4^{2-}, carbon dioxide species 61 mg/L as HCO_3^-, and dissolved iron 56 µg/L

Improved Distribution Properties



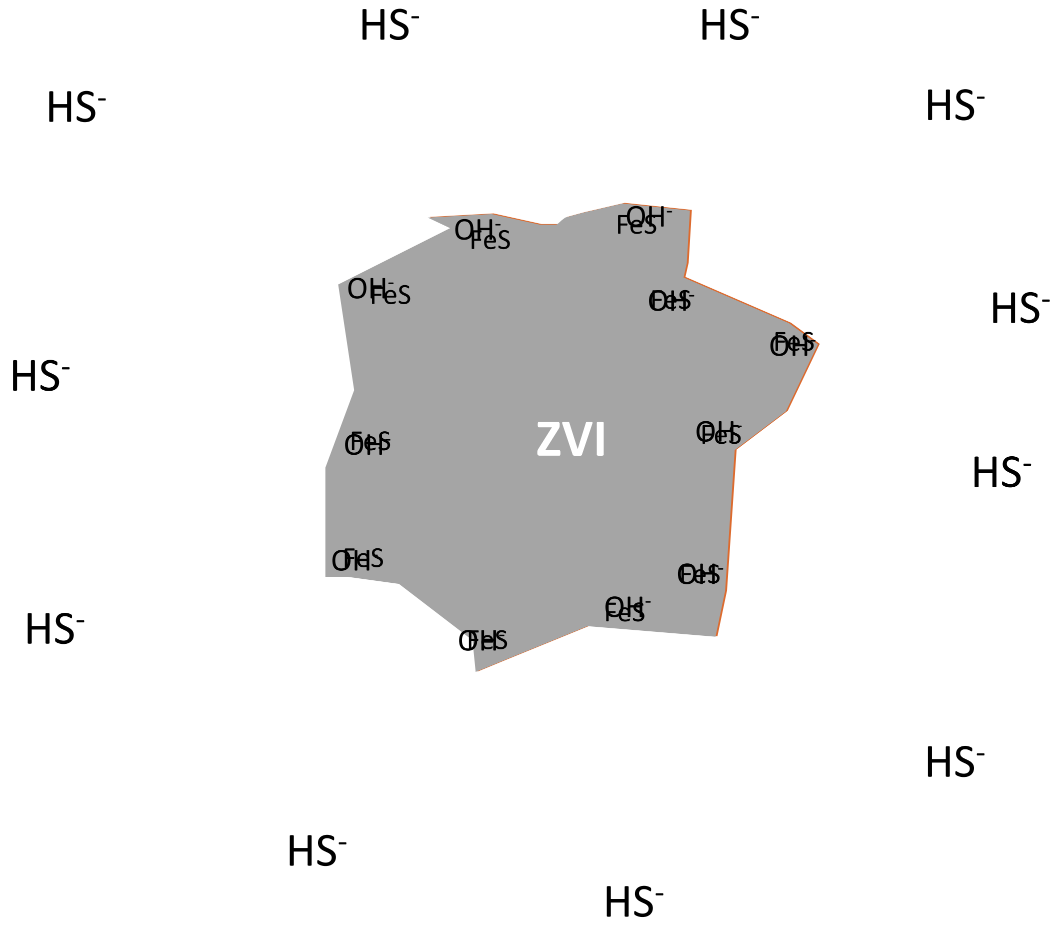


Sulfidation Increases ZVI reactivity and Longevity

“Sulfidation” … can refer to any modification or transformation of a metal-based material by exposure to sulfur compounds of various oxidation states…”

Geoform™ ER In Situ Sulfidation Process:

- ZVI, sulfate (SO_4^{2-}) and organic carbon (**OC**) are distributed in aquifer
- ZVI reacts with water to generate OH^- on surface
- Sulfate is biologically reduced to sulfide (HS^-)
- Sulfide replaces OH^- on ZVI
- Fe^{2+} (ambient, supplied or from ZVI oxidation,) combines with HS^- to form FeS coating on ZVI



Sulfidation of Iron-Based Materials: A Review of Processes and Implications for Water Treatment and Remediation
Dimin Fan, Ying Lan, Paul G.Tratnyek, Richard L. Johnson, Jan Filip, Denis M. O’Carroll, Ariel Nunez Garcia, and Abinash Agrawal, Environmental Science & Technology

Key Advantage 1

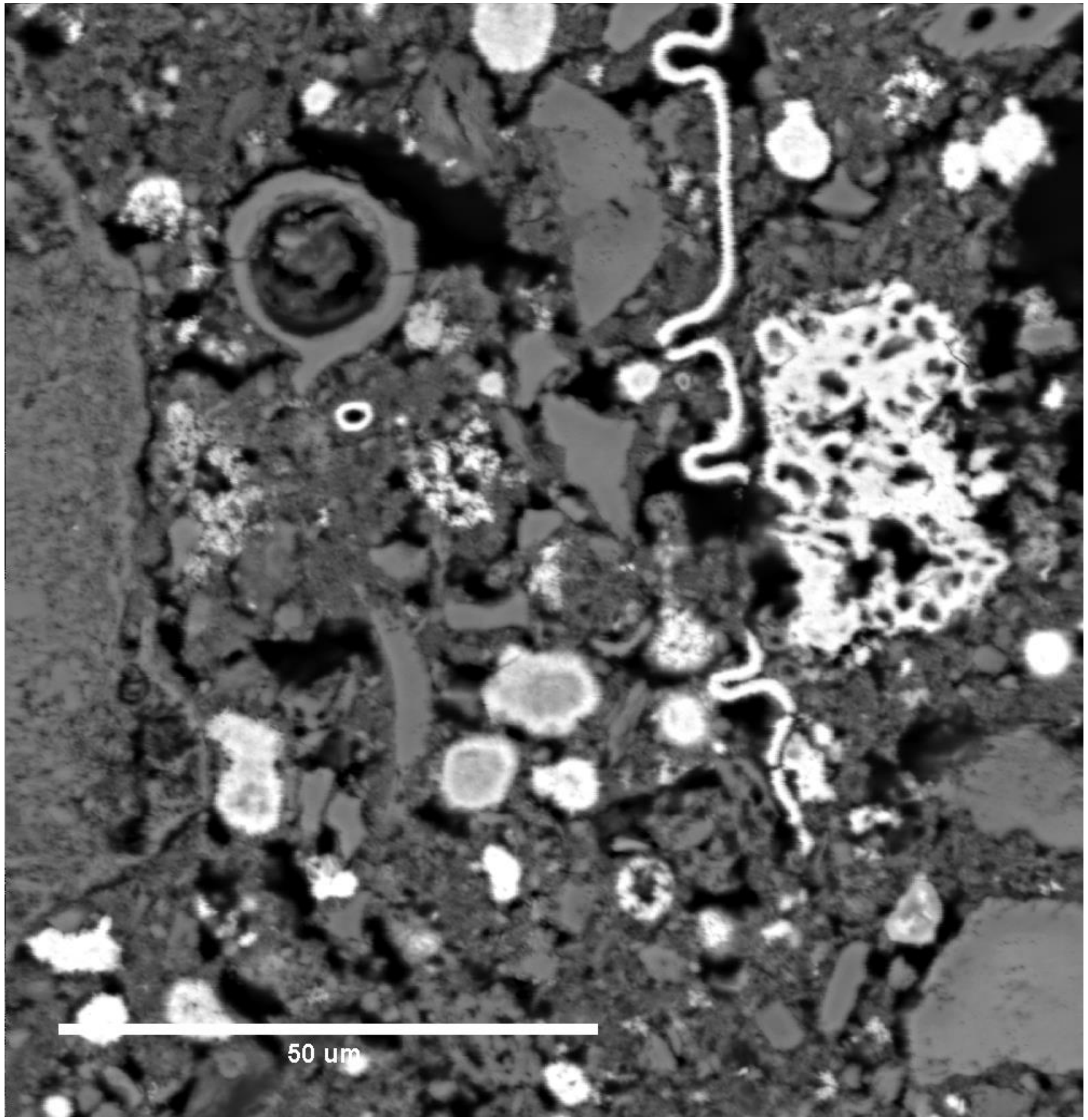
Expanded Surface Area for Abiotic Pathway Without Aquifer Occlusion

- **Produces a very large surface area:**
  3,000 mg/L SO_4 + Fe generates:
  3 μM coating ~ 0.21 M^2 per Liter
  ~ 73.5 M^2 per M^3 of aquifer (@35% porosity)

- **Produce a very small volume:**
  ~2.7 g FeS per Liter (@SO_4 = 3,000 mg/L)
  ~1.9 g FeS_2 per Liter (@SO_4 = 3,000 mg/L)

Volume FeS~ 0.56 cm^3 per Liter
Volume FeS_2 ~0.37 cm^3 per Liter

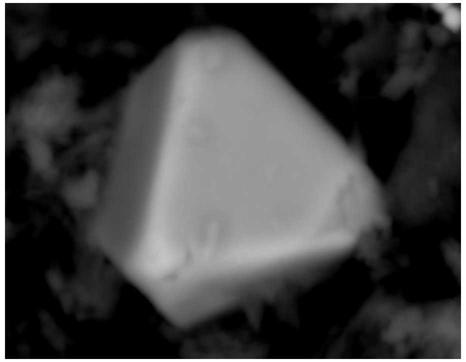
~ 0.1% of aquifer pore space

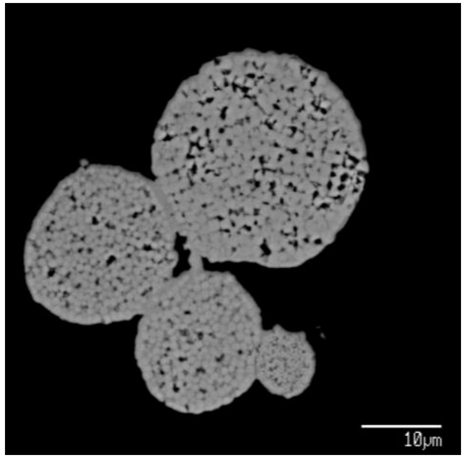


Iron-Sulfide Minerals Occur in Several Forms

Scanning Electron Microscopy (SEM) Images

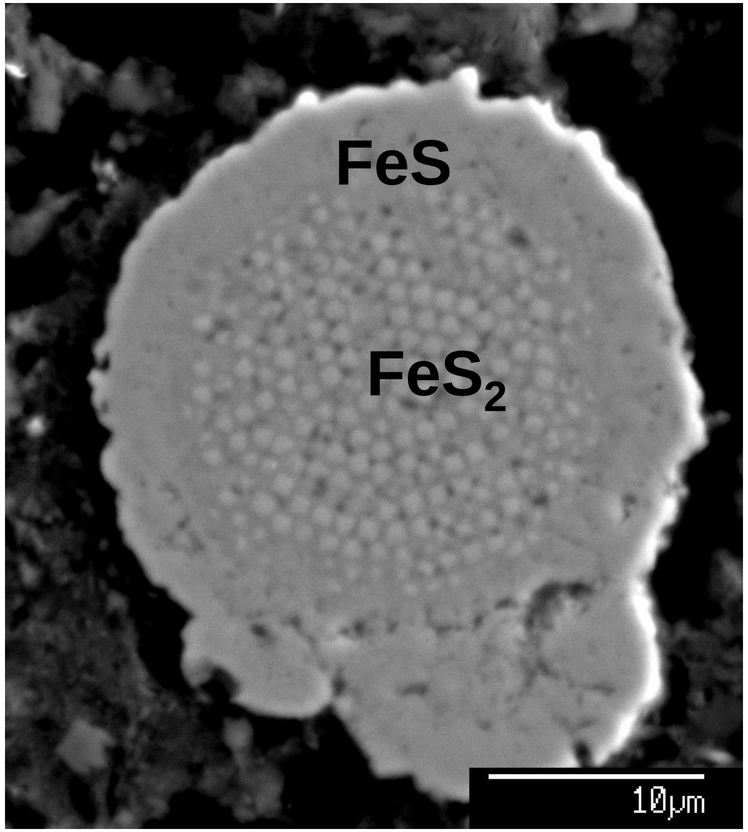
Euhedral Pyrite (FeS_2)



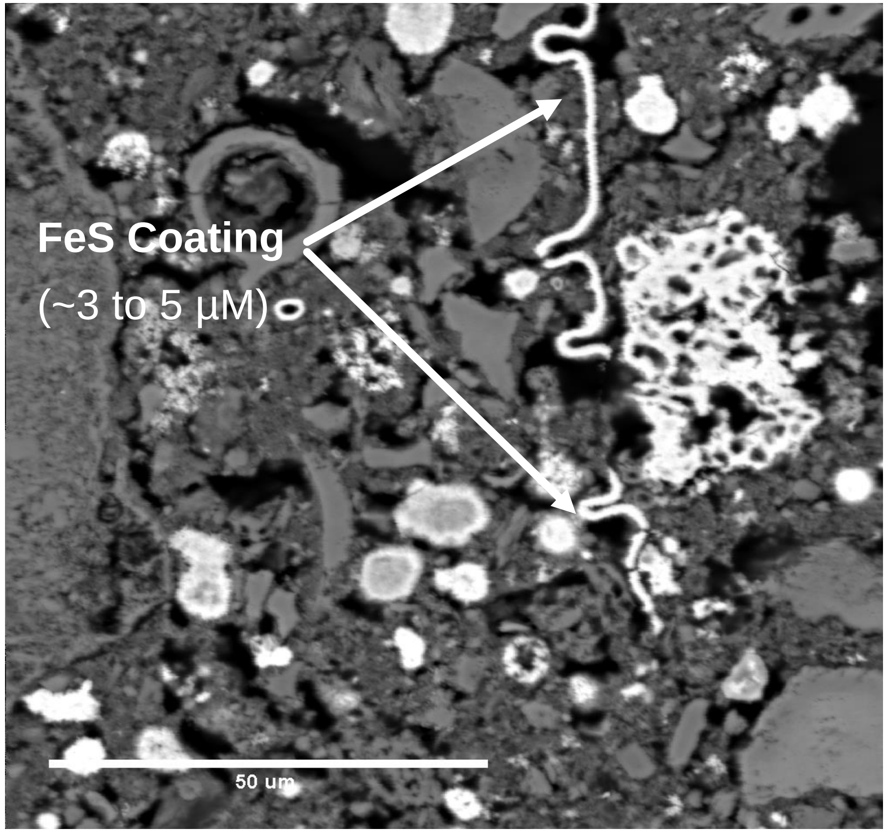


Framboidal Pyrite (FeS_2)

Framboidal FeS_2 and FeS Coating



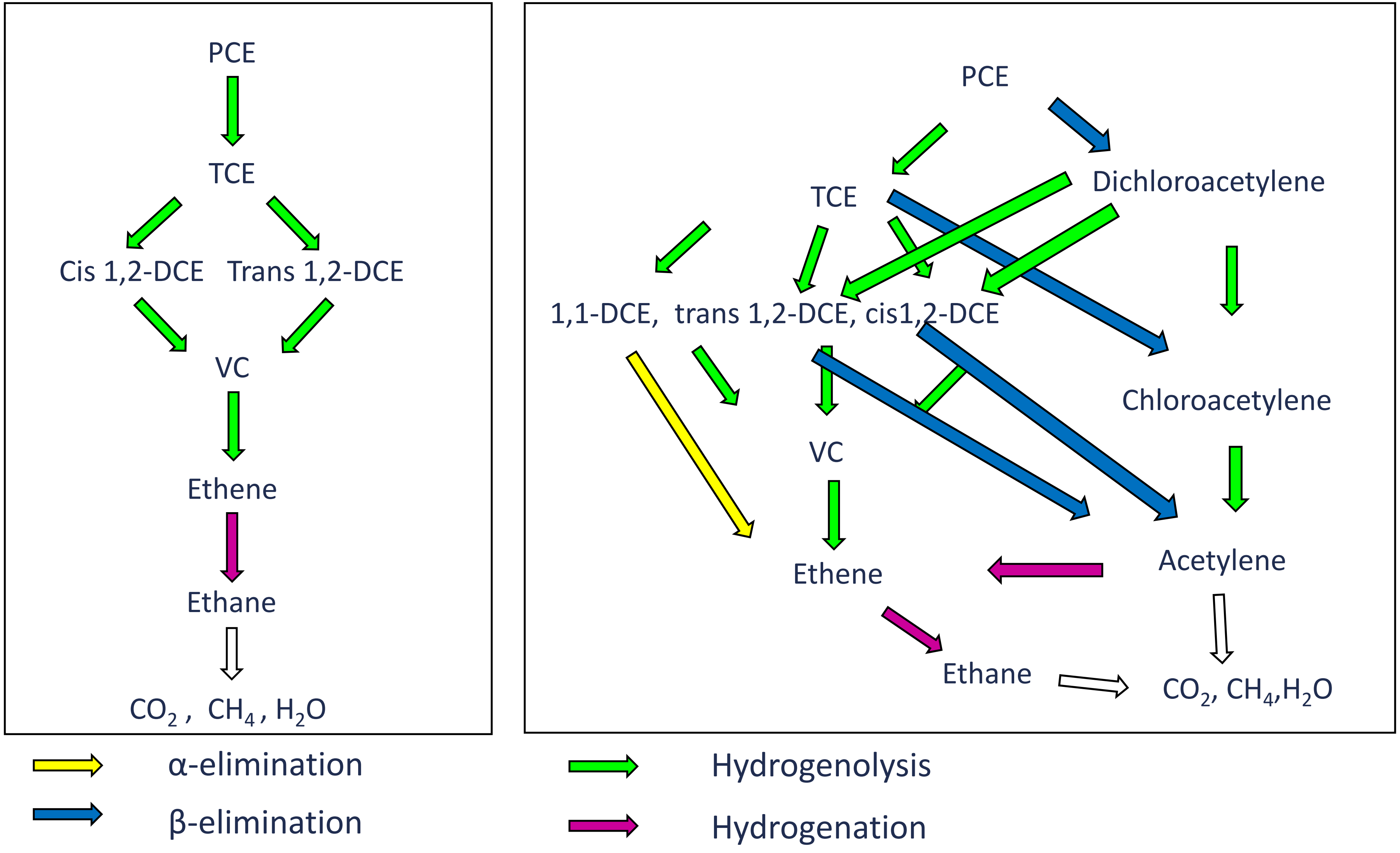
Fe replacement, FeS coating and nano scale FeS_2



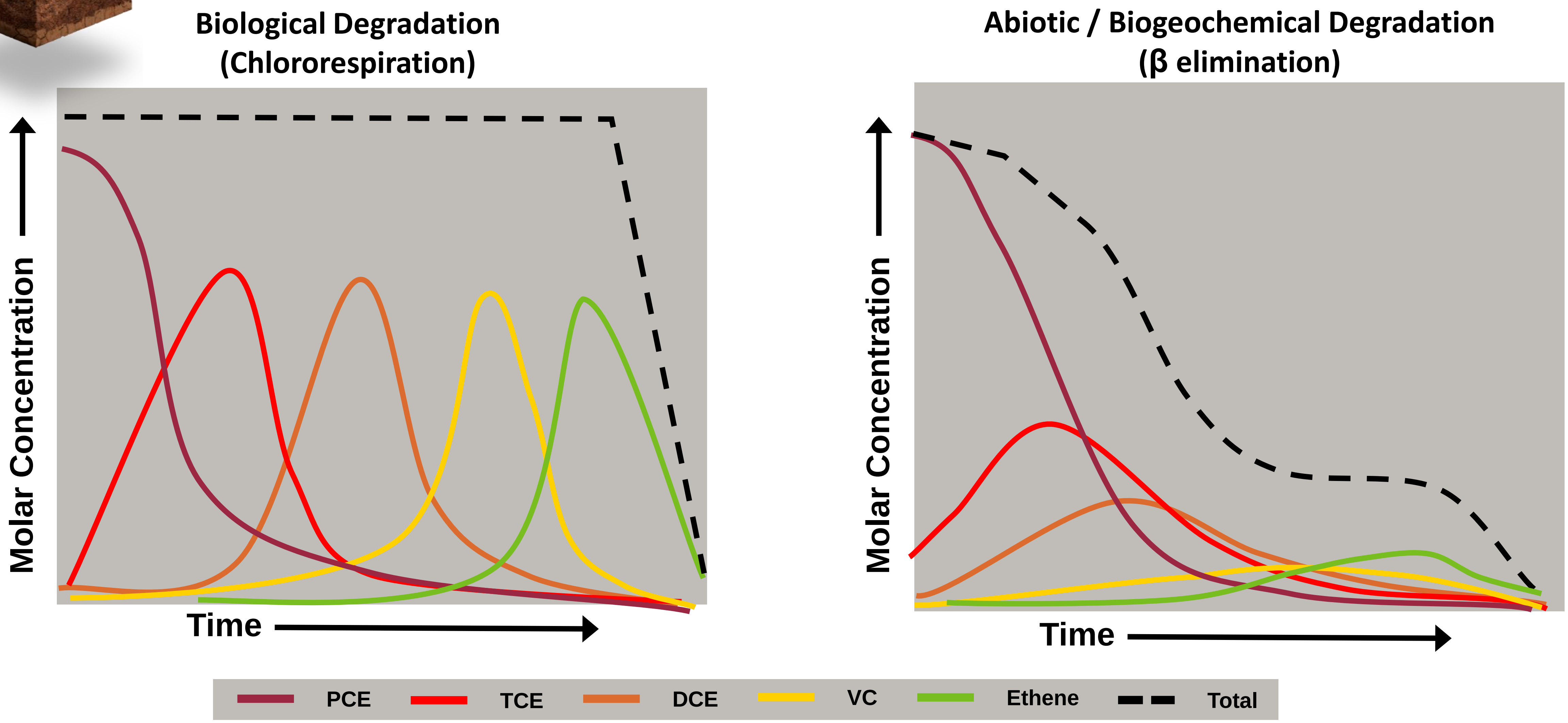
Biotic and Abiotic Reductive Pathways

Biotic

Abiotic



Anticipated Change in Chlorinated Ethene Molar Concentration



Key Advantage 2 - Biogeochemical Process Treat Metals

- Heavy metals and metalloids are a common groundwater contaminant
- Heavy metals are often associated with chlorinated organic plumes
- Some naturally occurring metals increase or decrease in groundwater during the establishment of reducing conditions by ERD and ISCR.

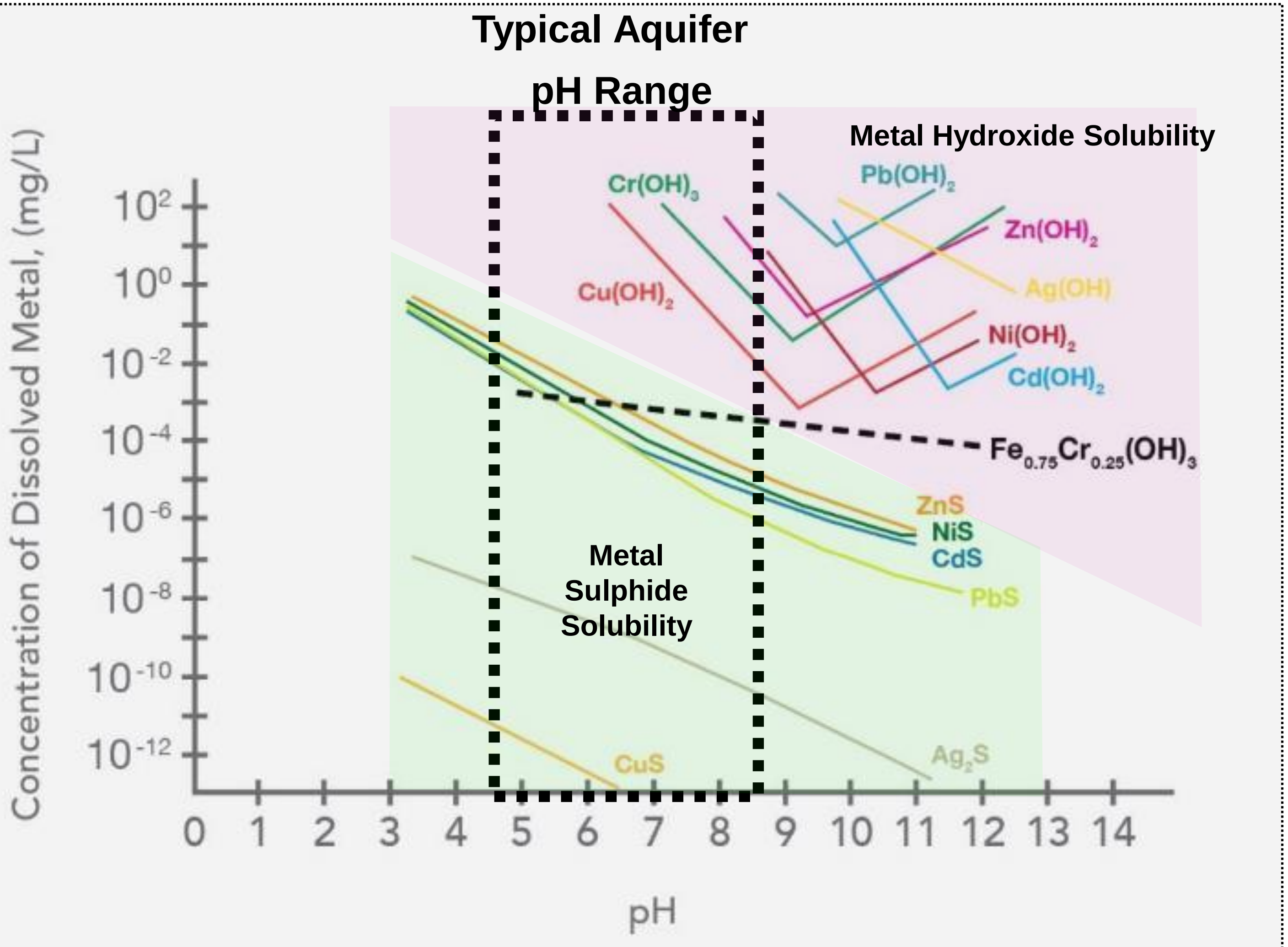
Solid	Arsenic As[V]	→	As[III]	Soluble
Solid	Manganese: Mn [IV]	→	Mn[II]	Soluble
Solid	Iron Fe[III]	→	Fe[II]	Soluble
Soluble	Chromium Cr[VI]	→	Cr[III]	Solid

Many metals can be precipitated as sulphides / iron-sulfides

Arsenic (Arsenopyrite, $FeAsS_2$), Zinc (sphalerite, ZnS), Iron (pyrite (FeS_2), mackinawite (FeS), Cobalt (CoS), Lead (PbS, galena)

Metal-Sulfides are less soluble than metal hydroxides under typical aquifer pH

Aqueous Solubility & Stability of Heavy Metals as Hydroxides, Iron Oxyhydroxides, and Sulfides



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

Case Studies

Case Study:

Evaluation of Biogeochemical Treatment Using Non-Standard Analytical Techniques

Site Conditions:

- Aerobic aquifer
- Ambient Sulfate (SO_4^{2-}) ~ 200 mg/L

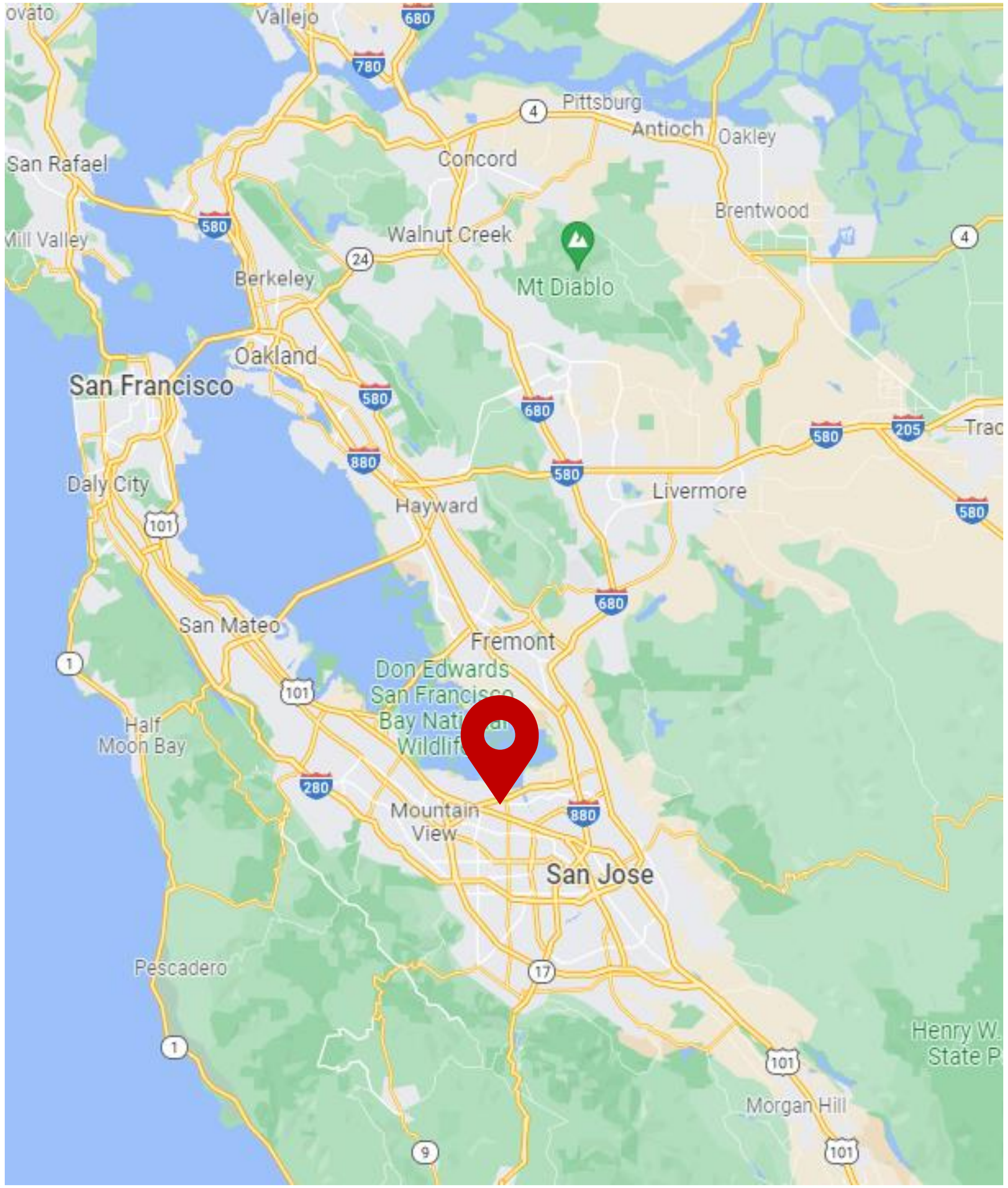
Applied:

- EHC® = ZVI + OC (no added SO_4^{2-})
- GeoForm™ ER = ZVI + OC + SO_4^{2-} + Fe^{2+}

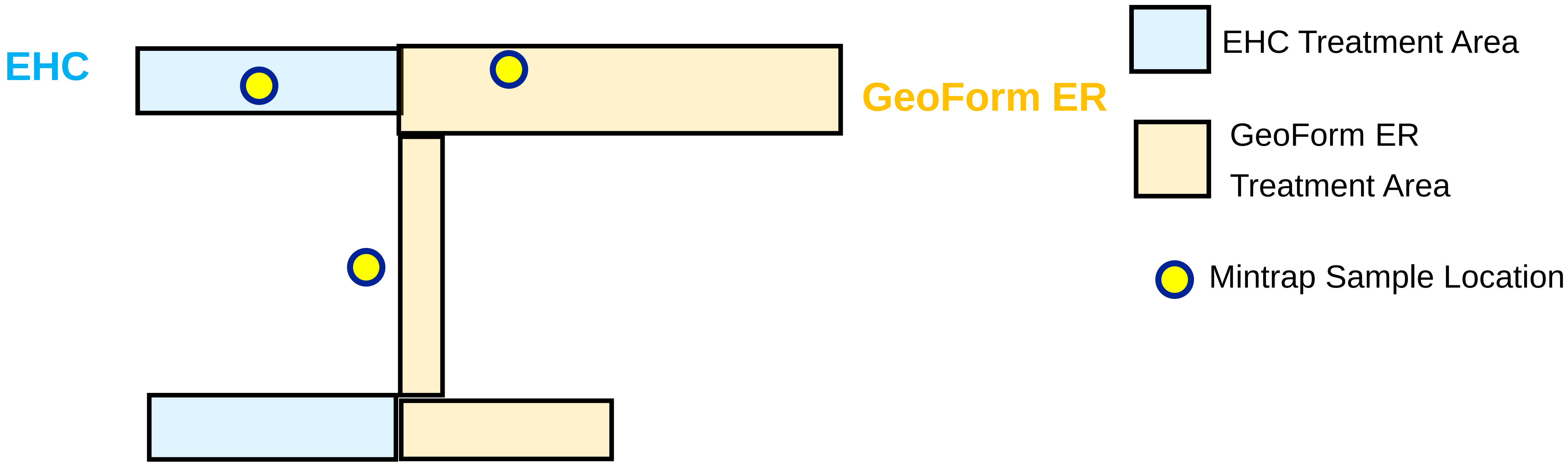
Mintrap™ Installed before treatment and collected ~ 4 months after treatment.

Samples Analyzed for:

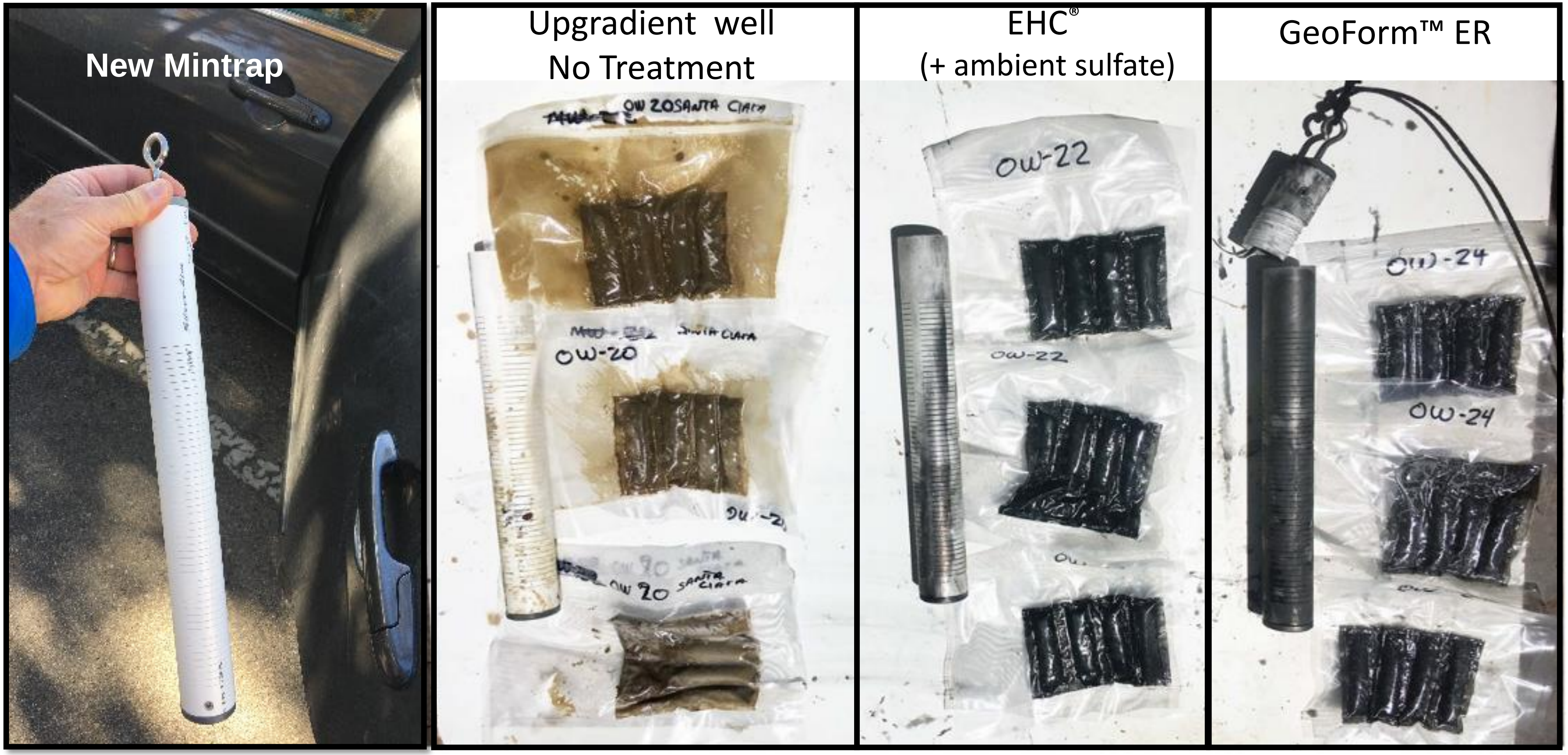
- Total iron and sulphur
- AMIBA
- SEM-EDS - Scanning Electron Microscopy-Energy Dispersive Spectroscopy



EHC® and GeoForm™ Extended Release Application



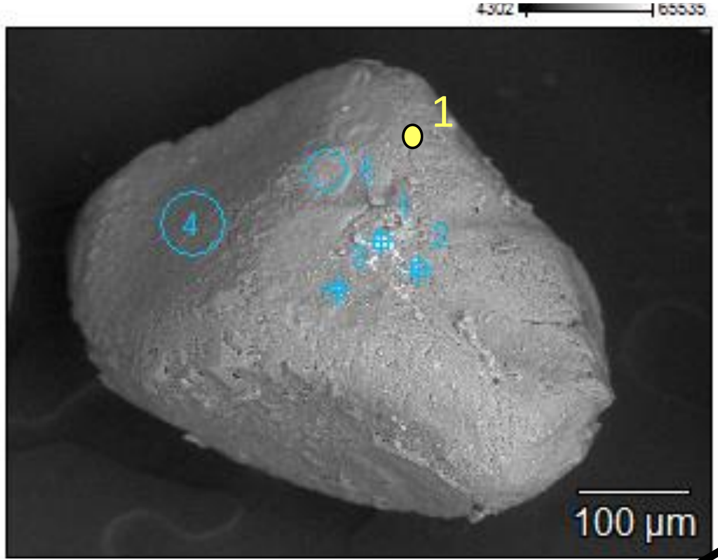
Mintrap™ samples from EHC® and GeoForm™ Extended Release Application



Ulrich, S., Martin Tilton, J., Justicia-Leon, S., Liles, D., Prigge, R., Carter, E., Divine, C., Taggart, D., & Clark, K. (2021). ***Laboratory and initial field testing of the Min-Trap™ for tracking reactive iron sulfide mineral formation during in situ remediation. Remediation. 1–14***. https://doi.org/10.1002/rem.21681

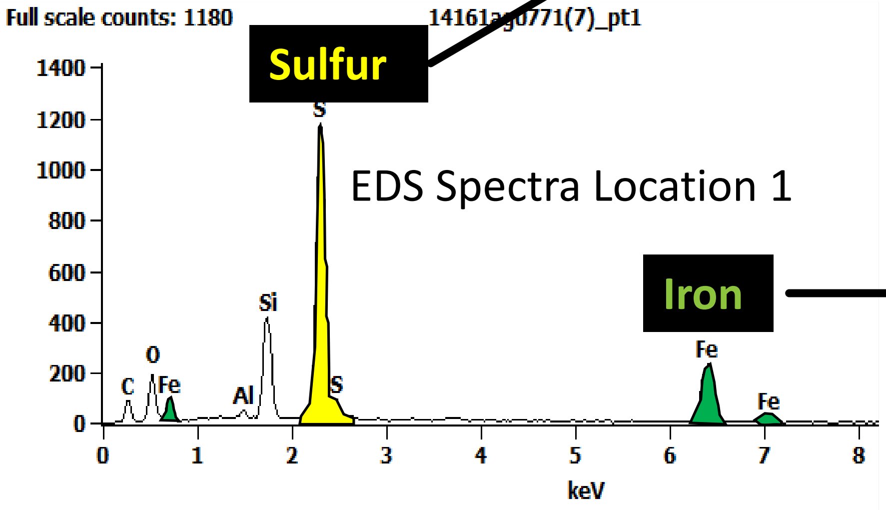
SEM-EDS Results - Following GeoForm™ ER Application

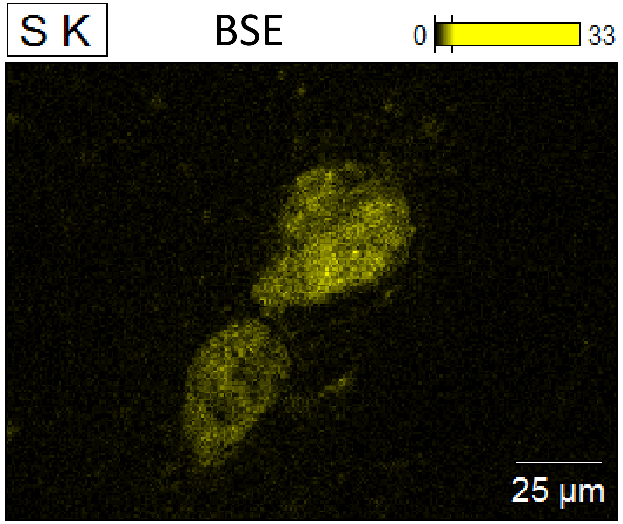
Scanning Electron Microscopy (SEM)-Energy Dispersive Spectroscopy (EDS)



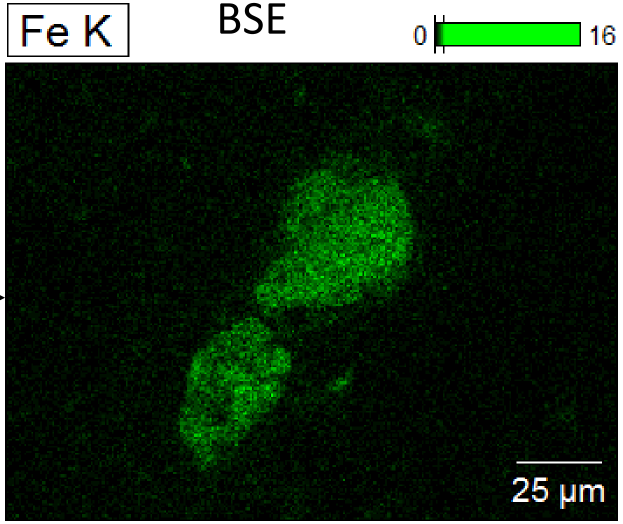
SE EDS Location map

(SE – Secondary Electrons – Show Morphology)



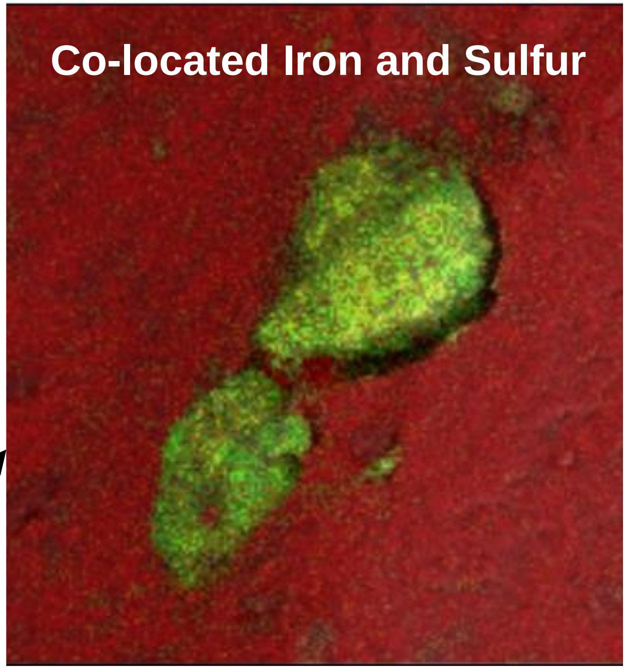


(BSE – Backscatter Electrons)
(Identifies Elements on Surface)



AMIBA Results	
AVS (FeS)	CrES (FeS_2)
51%	49%

BSE

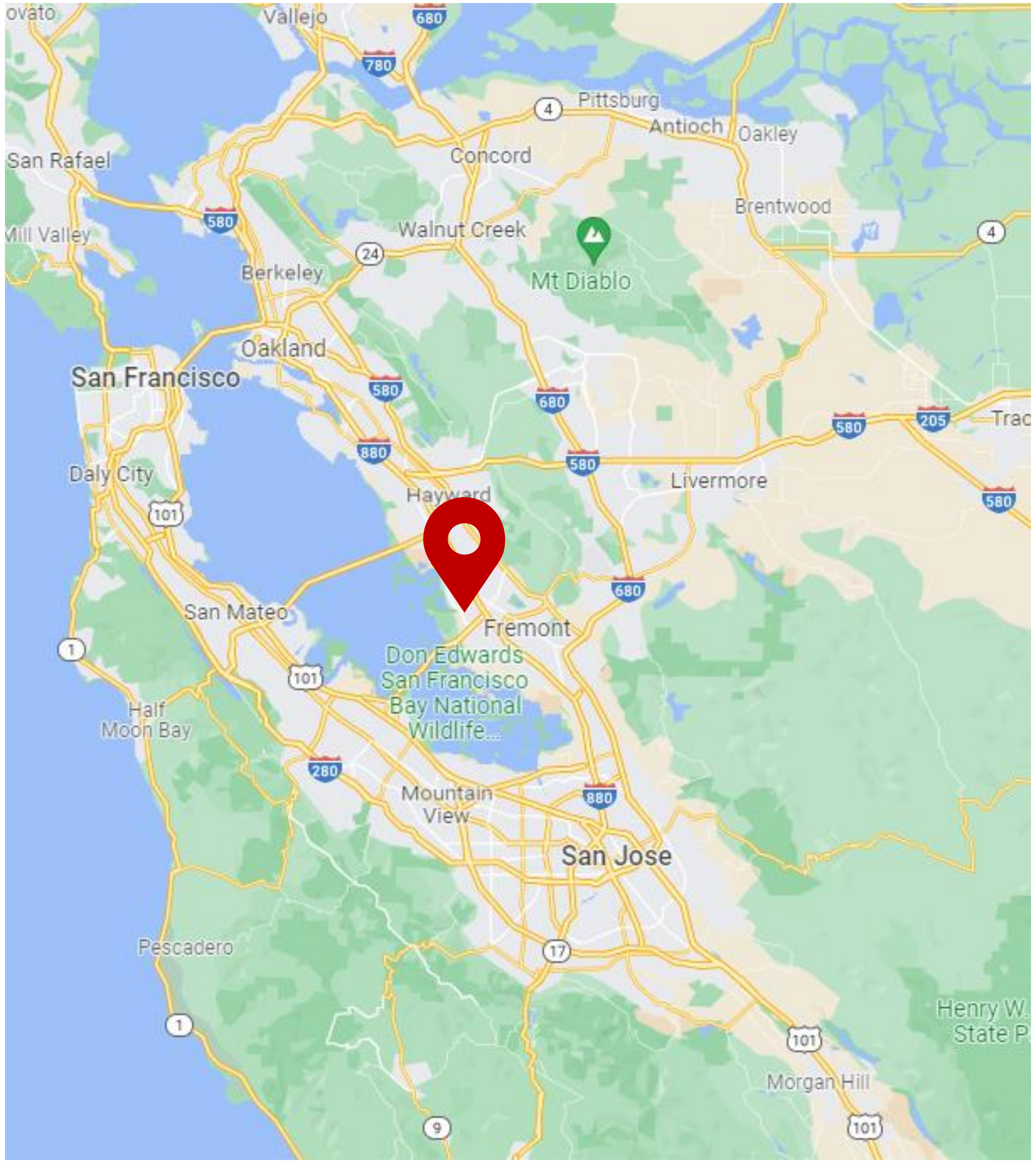


X-ray overlay map
red = Si,
green = Fe,
yellow = S.

Case Study:

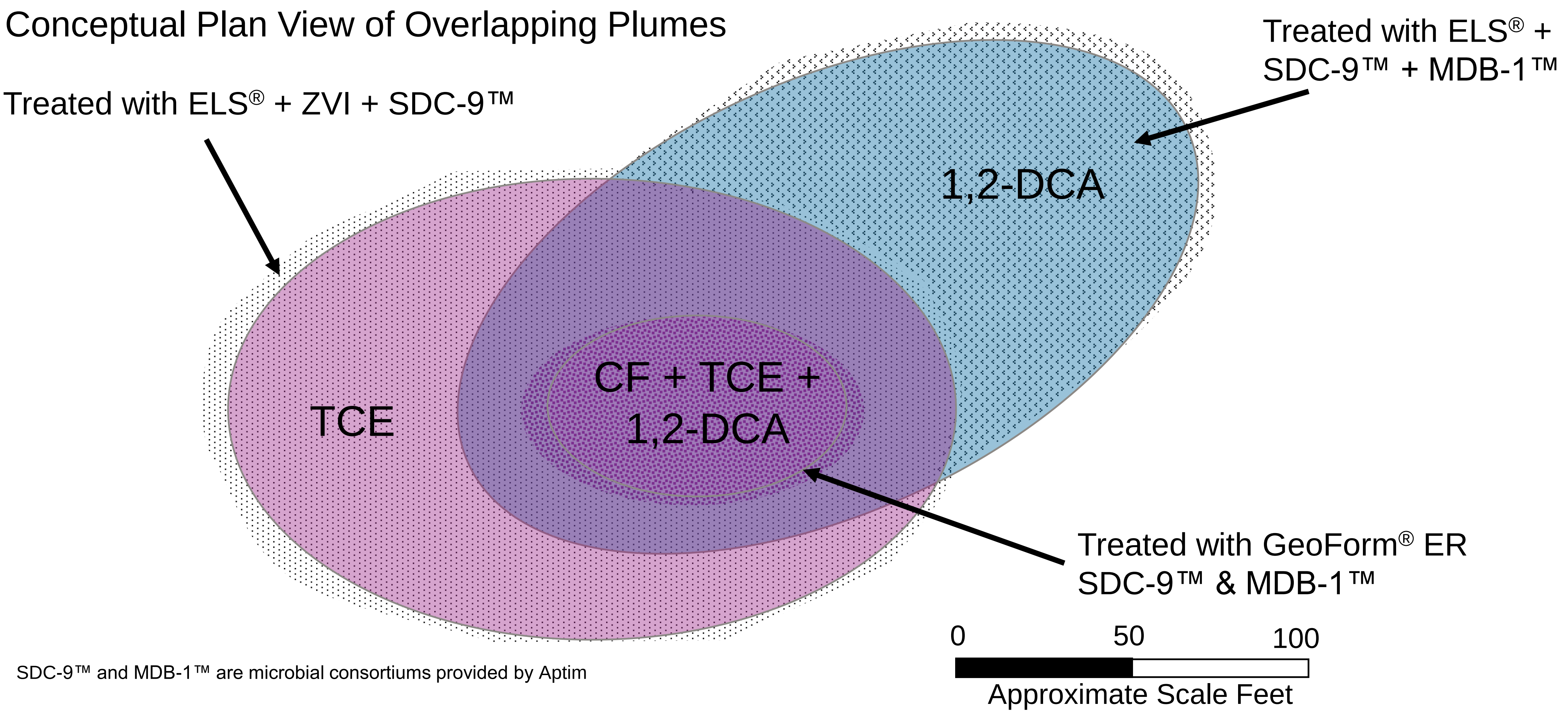
Combined ISCR and BGCR Treatment of Chlorinated Organics

- Site Overview
  - Elevated sulfate groundwater (~ 400 to 700 mg/L)
  - High Concentration TCE
    - Permeable Reactive Barrier Application
  - Mixed plume (TCE, 1,2-DCA, CF)
    - One recalcitrant hot spot treatment
- Both properties being developed
- Client wanted aggressive approach
- Evaluated biogeochemical enhanced treatment for both sites



Case Study: BGCR Treatment of Mixed Chlorinated Organics

Sequential Treatment of Mixed Plume

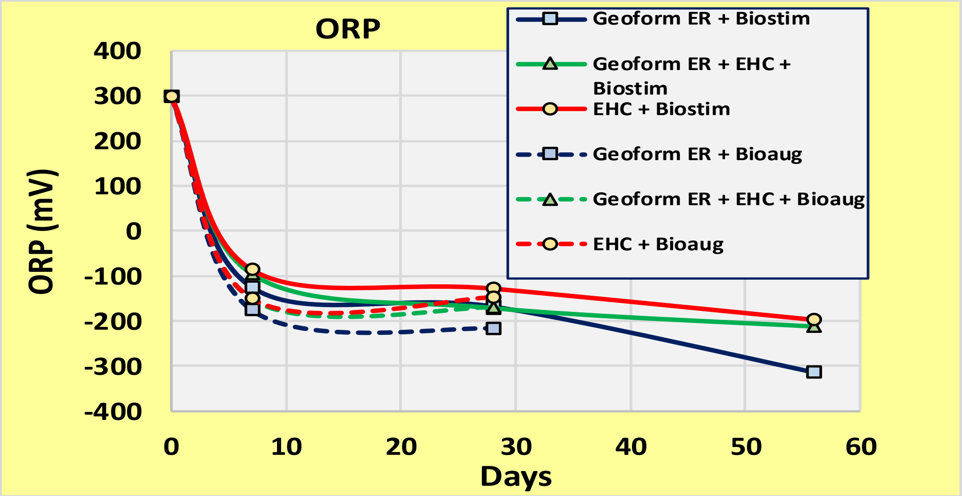


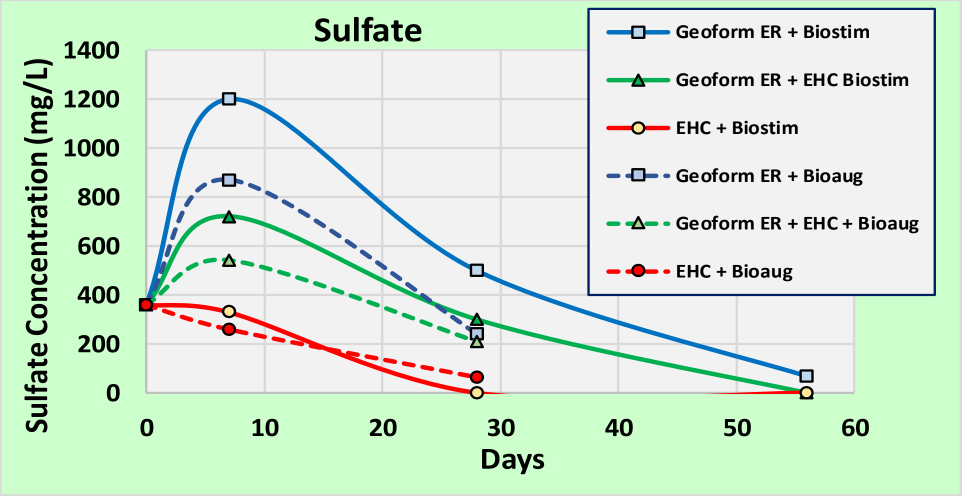
SDC-9™ and MDB-1™ are microbial consortiums provided by Aptim

Case Study: Chlorinated Ethene (CE) Treatment at Bay Area Site

- **Bench Test compared:**
  - EHC® ISCR Reagent (no added sulfate)
  - GeoForm® Extended Release + EHC®
  - GeoForm® Extended Release

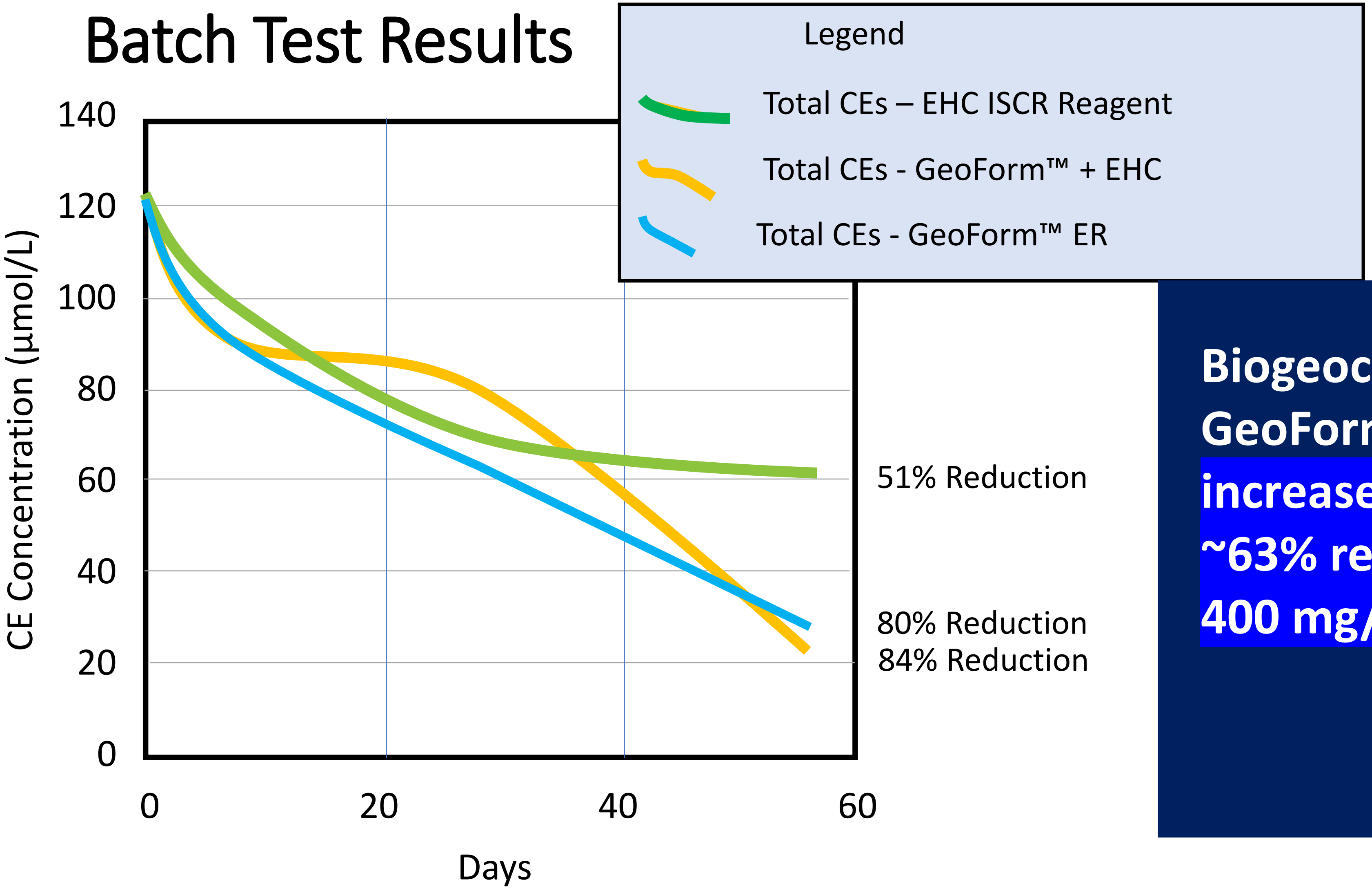
- EHC® similar to GeoForm® ER except EHC® does not contain ferrous iron and sulfate as does GeoForm® ER
- With ambient sulfate (~ 400 mg/L)
- With and without bioaugmentation (SDC-9™)





Case Study - Chlorinated Ethene (CE) Treatment at Bay Area Site

Batch Test Results

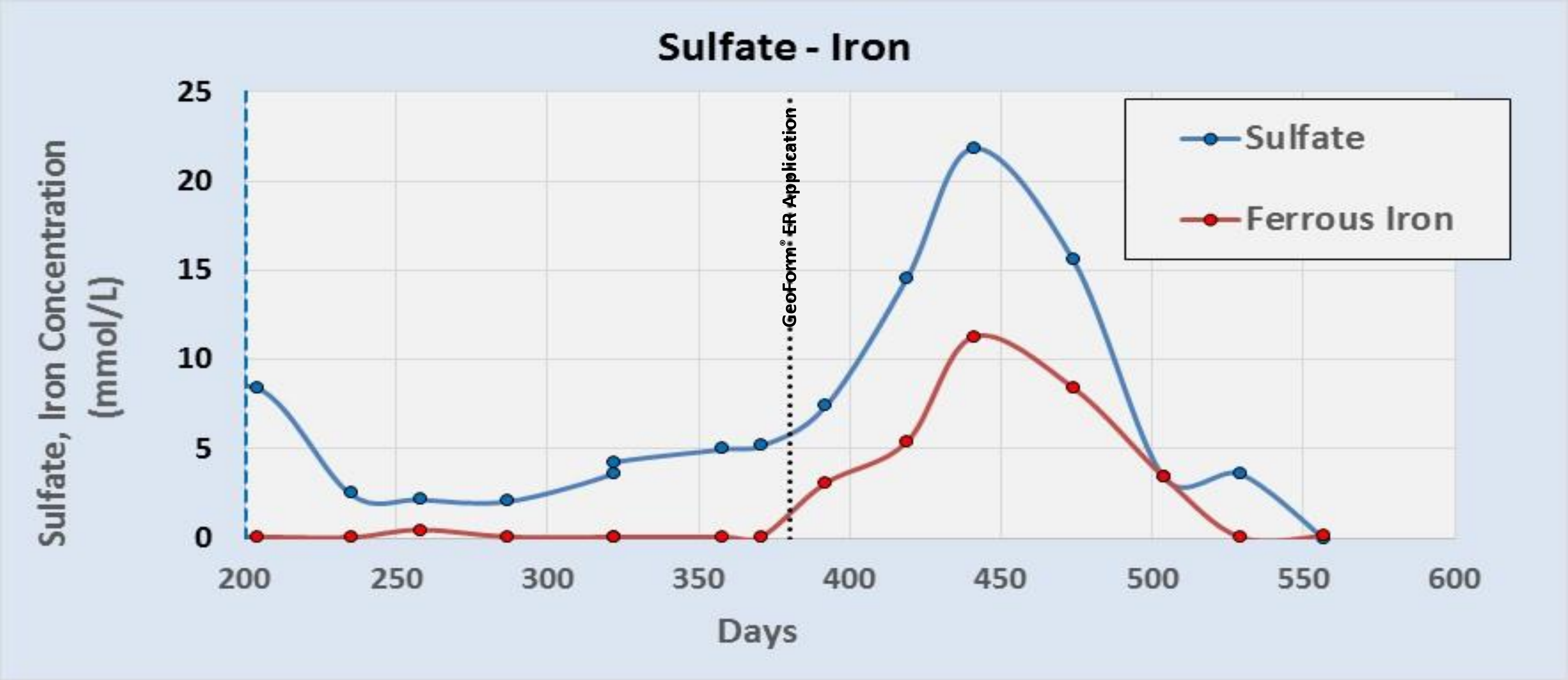


GeoForm® Extended Release Increases EHC® Degradation Rates

Biogeochemically enhanced GeoForm® Extended Release increased CE degradation rate ~63% relative to EHC® (ISCR) (with 400 mg/L ambient sulfate).

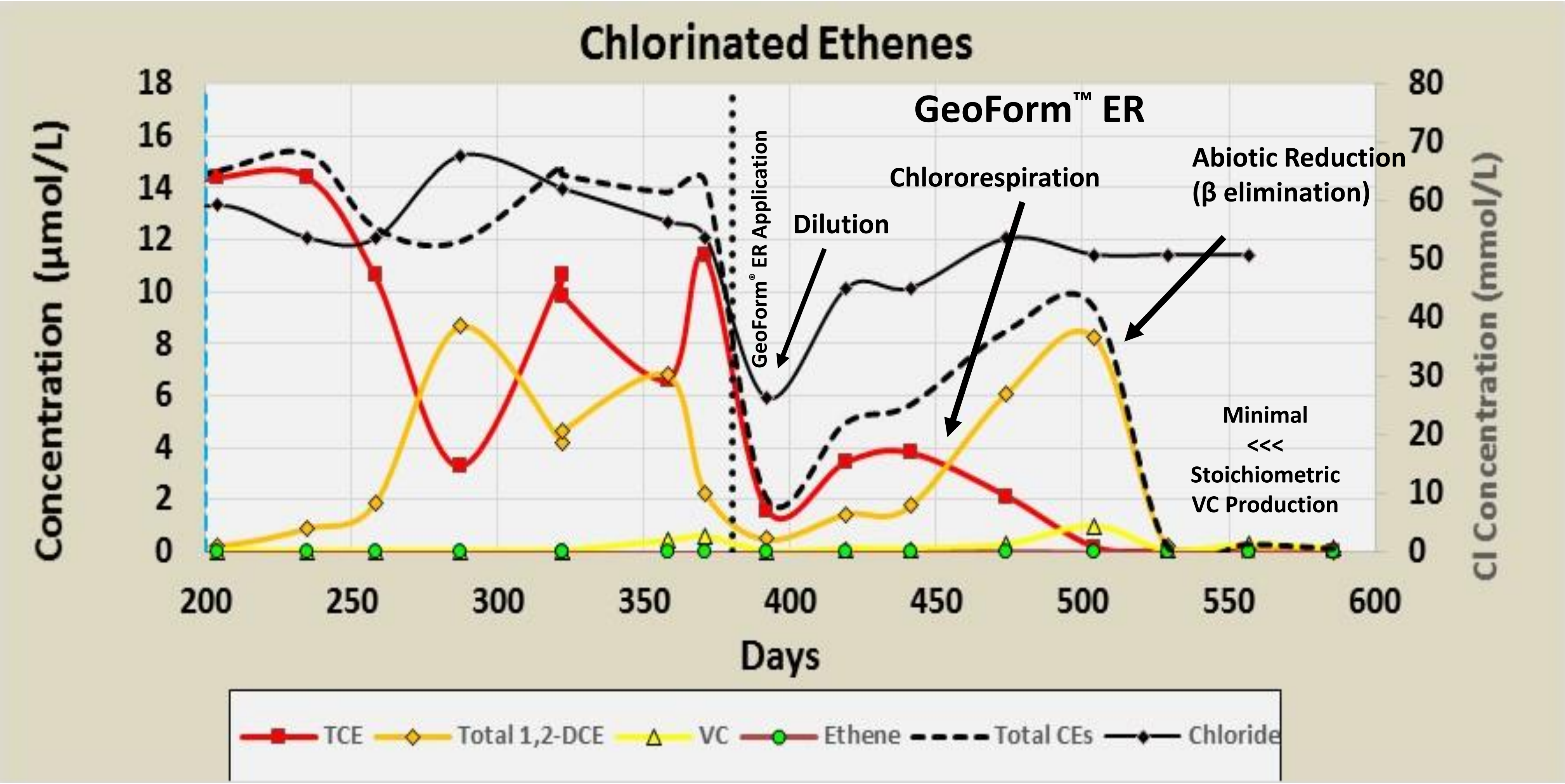
Case Study: Mixed Chlorinated Organics at Bay Area Site

Sulfate & Iron Temporarily Increase Following GeoForm™ ER application



Case Study: Mixed Chlorinated Organics at Bay Area Site

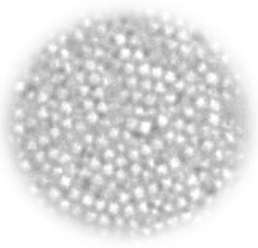
Biogeochemical Treatment of Chlorinated Ethenes (CEs)



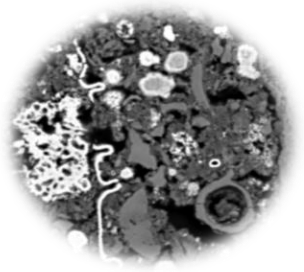
Conclusions

Presentation Summary

- Biogeochemical Reduction (BGCR) is a naturally occurring process.
- BGCR processes occur with, and will improve ERD and ISCR processes.



- Most site conditions can be modified to optimize BGCR processes.
- BGCR processes enhance the reactivity and longevity of Zero Valent Iron (ZVI)



- BGCR sequesters & stabilize toxic metals from groundwater.

CHEMCO ENVIRONMENT

CANADIAN LEADER IN ENVIRONMENTAL SOLUTIONS

Thank you for your attention !!
Questions ?!?

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June 2022

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