Biogeochemically Enhanced Treatment of Chlorinated Organics and Metals

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Evonik Corporation

International Symposium on Bioremediation and Sustainable Environmental Technologies

Biogeochemical Transformation

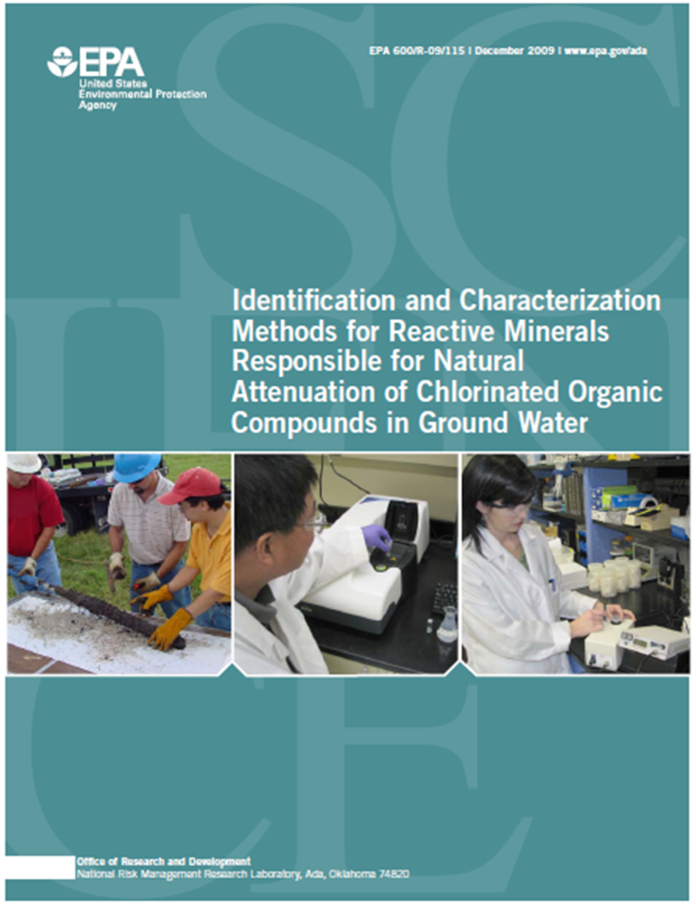
USEPA Definition: ***Processes where contaminants are degraded by abiotic reactions with naturally occurring and biogenically-formed minerals in the subsurface.***

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

Focus on Iron-Sulfide Minerals

Pyrite (FeS_2)

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



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

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Eh Range for Reduction of Various Electron Acceptors

Decreasing Amount of Energy Released During Electron Transfer

Aerobic

Oxygen $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (Eh^0 = +820)$

Anaerobic

Nitrate $2NO_3^- + 12H^+ + 10e^- \rightarrow N_{2(g)} + 6H_2O \quad (Eh^0 = +740)$

Arsenic (V) $H_3AsO_4 + 2H^+ + 2e^- \rightarrow H_3AsO_3 + H_2O \quad (Eh^0 = +559)$

500

Manganese (IV) $MnO_2(s) + HCO_3 + 3H^+ + 2e^- \rightarrow MnCO_3(s) + 2H_2O \quad (Eh^0 = +520)$

Redox Potential (Eh^0)
in Millivolts @ pH = 7 and T = 25^0C

0

Iron [Fe III] $FeOOH(s) + HCO_3 + 2H^+ + e^- \rightarrow FeCO_3 + 2H_2O \quad (Eh^0 = -50)$ Fe[II] in Solution

PCE ⇒ TCE

TCE ⇒ DCE

DCE ⇒ VC

VC ⇒ Ethene

Sulfate $SO_4^{2-} + 9H^+ + 8e^- \rightarrow HS^- + 4H_2O \quad (Eh^0 = -220)$ HS^- in Solution

Optimal range for Dechlorination

Methanogenesis $CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \quad (Eh^0 = -240)$

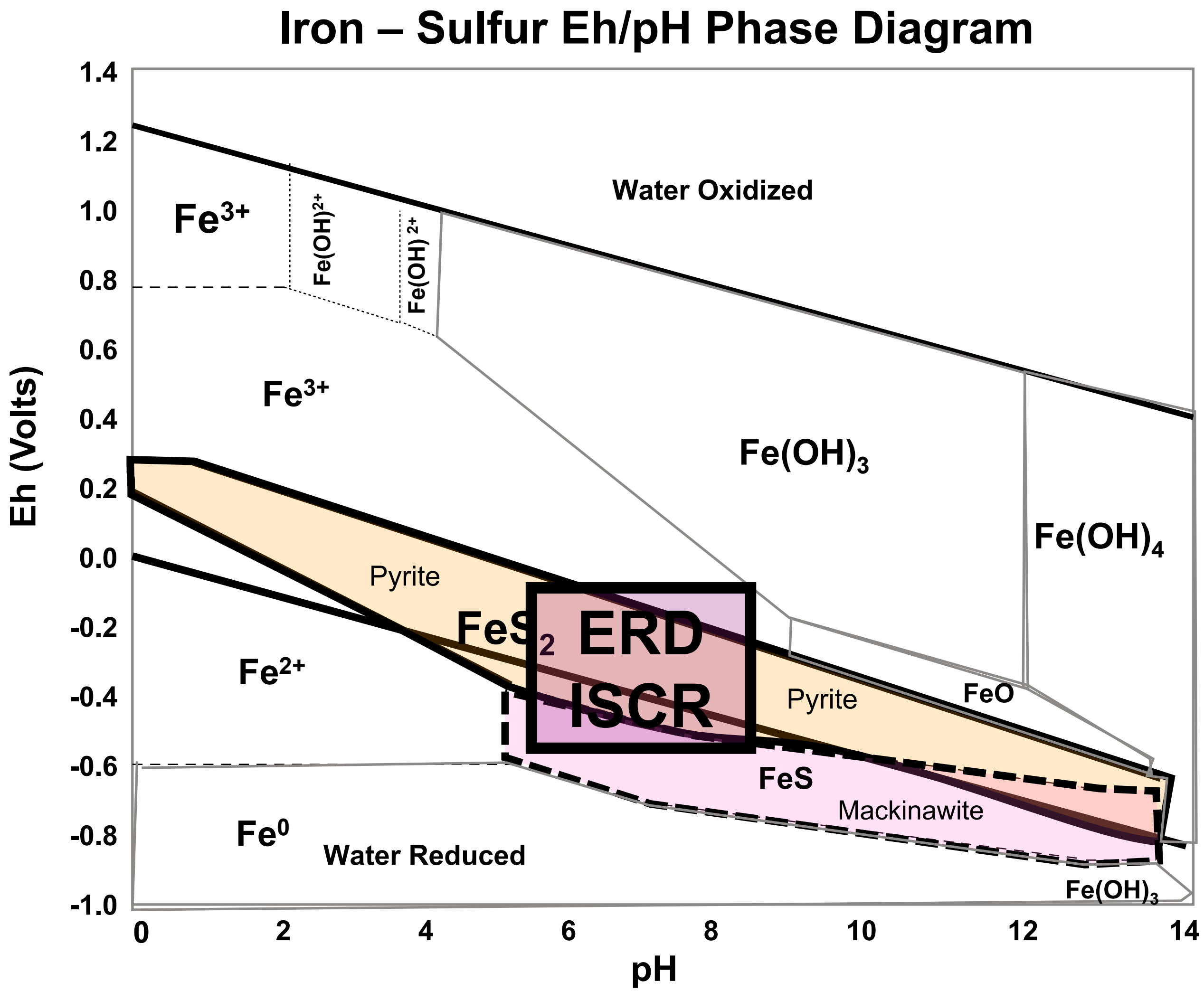
-250

AFCEE, NAVFAC, ESTCP, Principals and Practices, 2004`

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)

Pyrite (FeS_2) Mackinawite ($Fe_{(1+x)}S$)

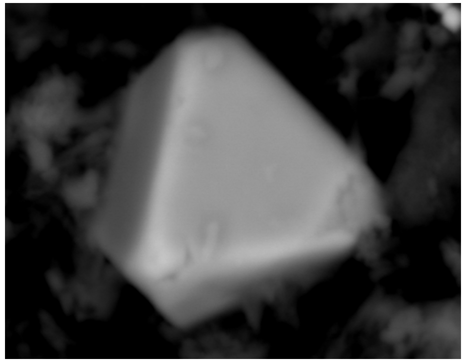


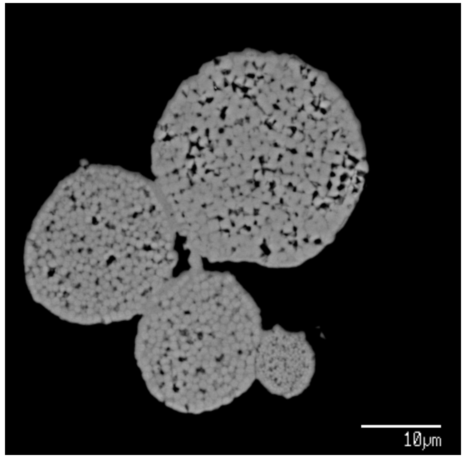
From USGS Water Supply Paper 2254
Fields of stability for solid and dissolved forms of pressure. Activity of sulfur species 96mg/L as SO_4^{2-}, carbon dioxide species 61 mg/L as HCO_3^-, and dissolved iron 56 µg/L

Iron-Sulfide Minerals Occur in Several Forms

Scanning Electron Microscopy (SEM) Images

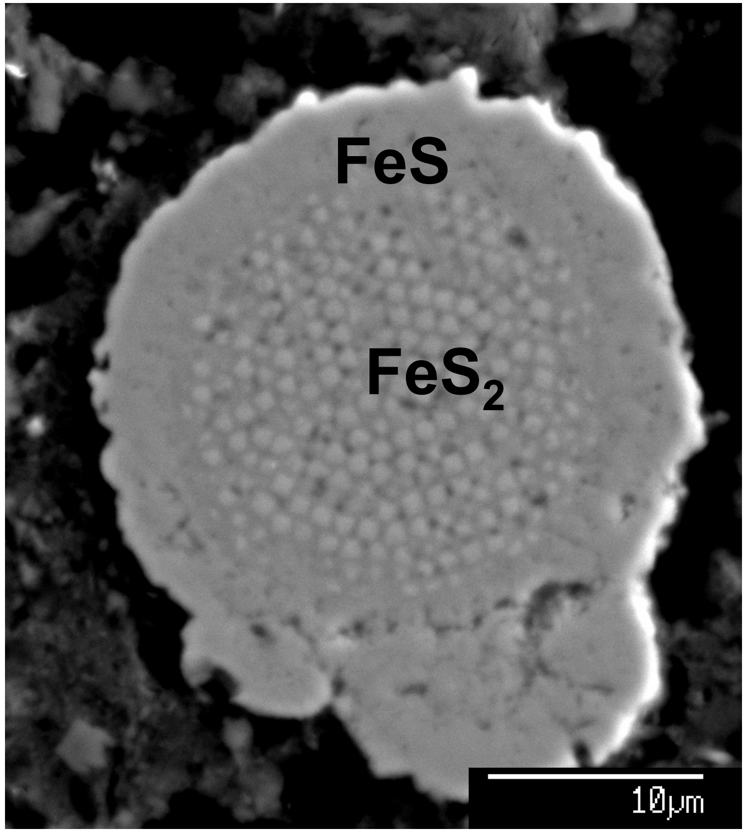
Euhedral Pyrite (FeS_2)



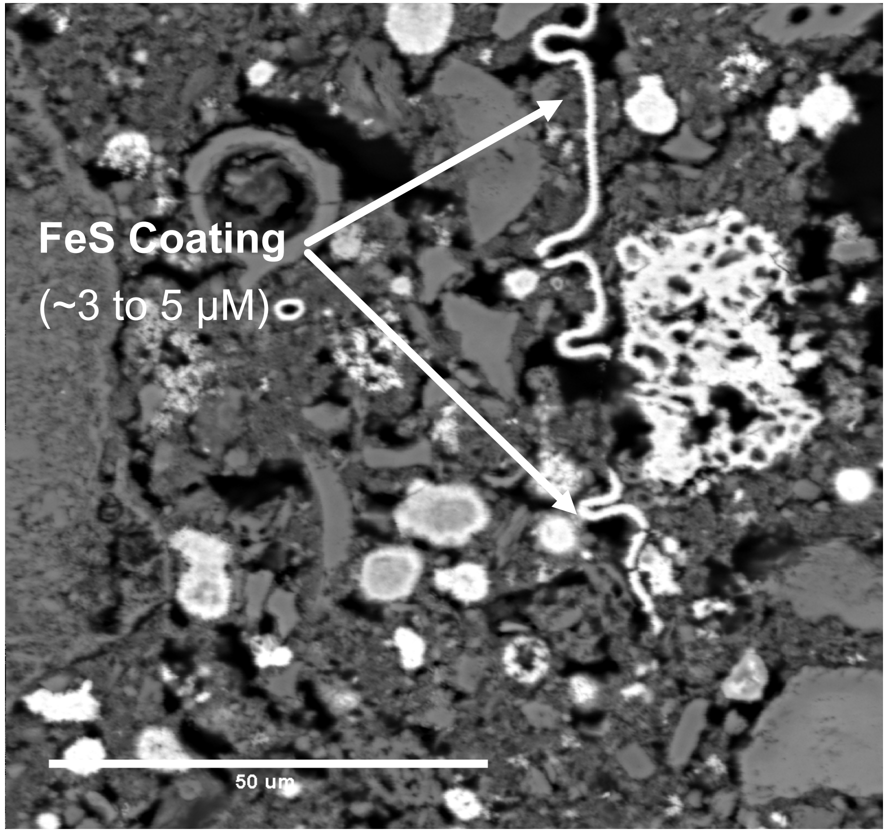


Framboidal Pyrite (FeS_2)

Framboidal FeS_2 and FeS Coating



Fe replacement, FeS coating and nano scale FeS_2



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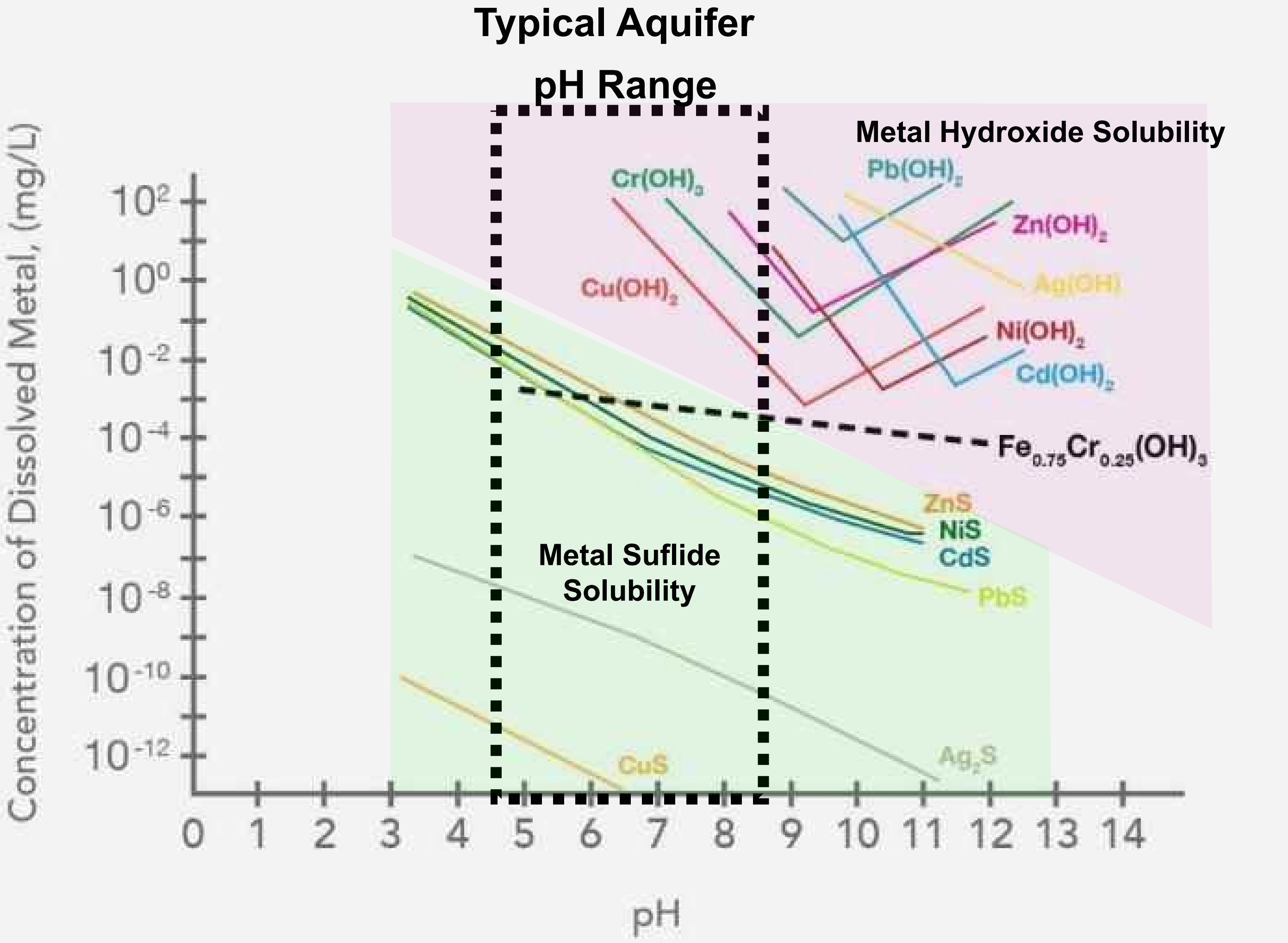
Metal-Sulfides are less soluble than metal hydroxides under typical aquifer pH

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

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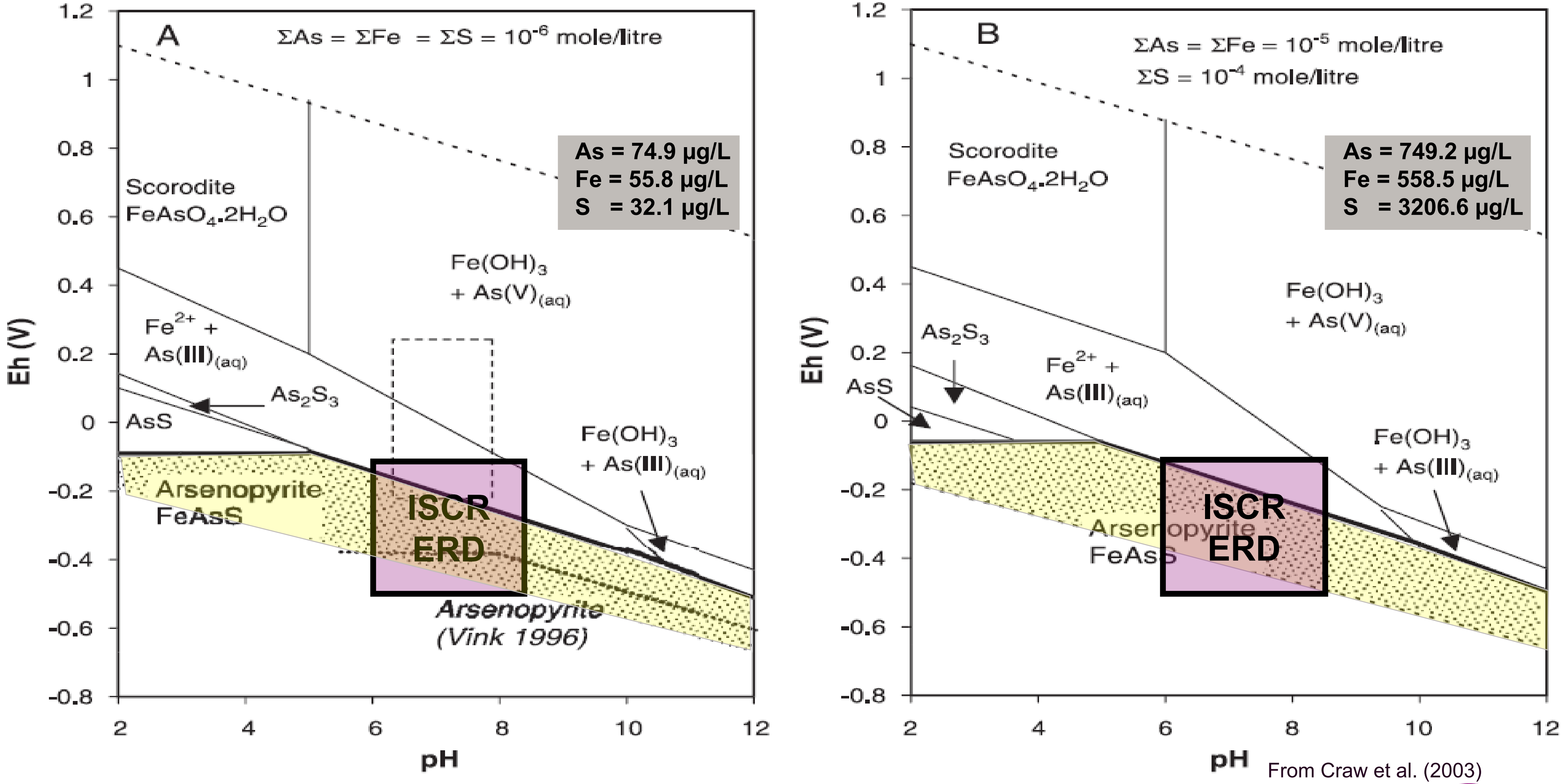
Arsenopyrite precipitates, and is stable at typical ERD/ISCR - Eh/pH conditions

As, Fe, S, Eh-pH Phase Diagrams



From Craw et al. (2003)

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:

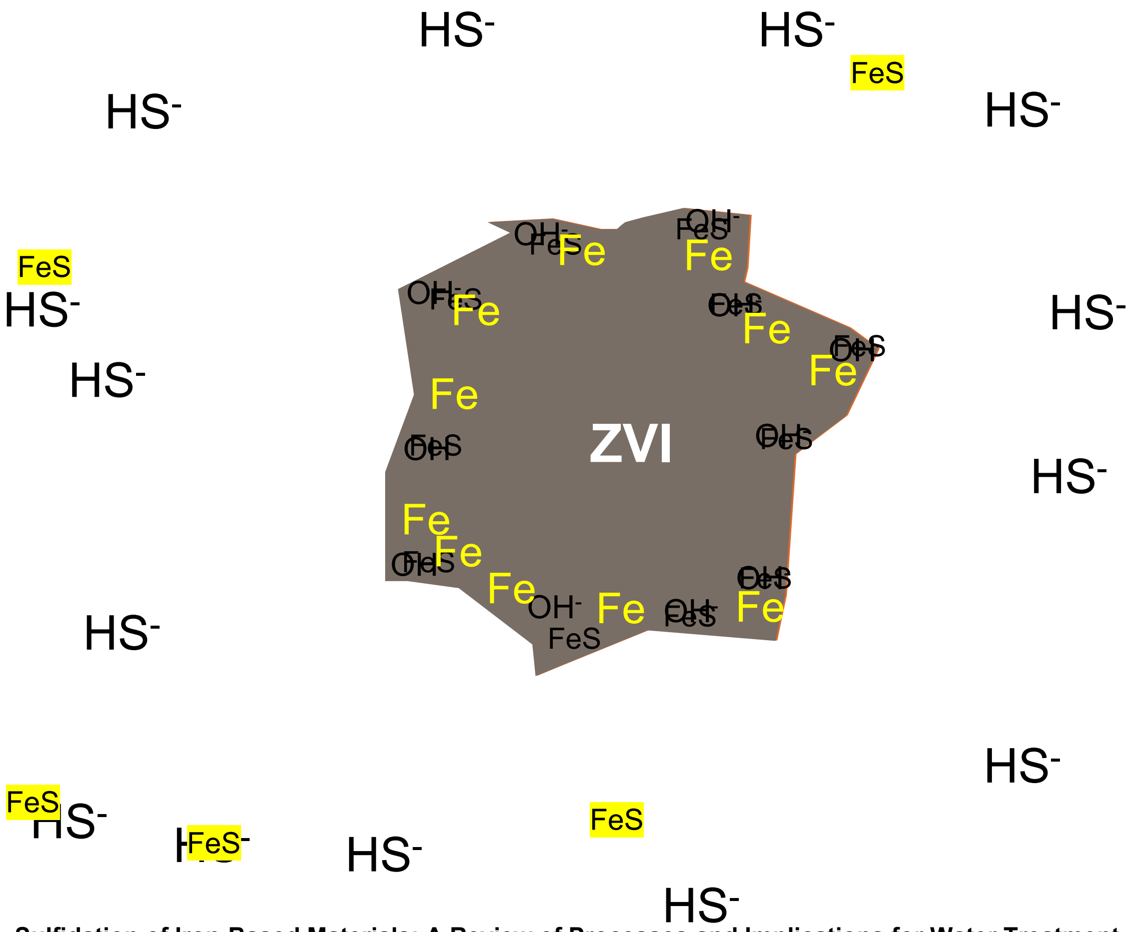
ZVI, sulfate (SO_4^{2-}), ferrous iron (Fe), and organic carbon (**OC**) are distributed in aquifer

ZVI reacts with water to generate ferrous iron and OH^- on surface

Sulfate is biologically reduced to sulfide (HS^-)

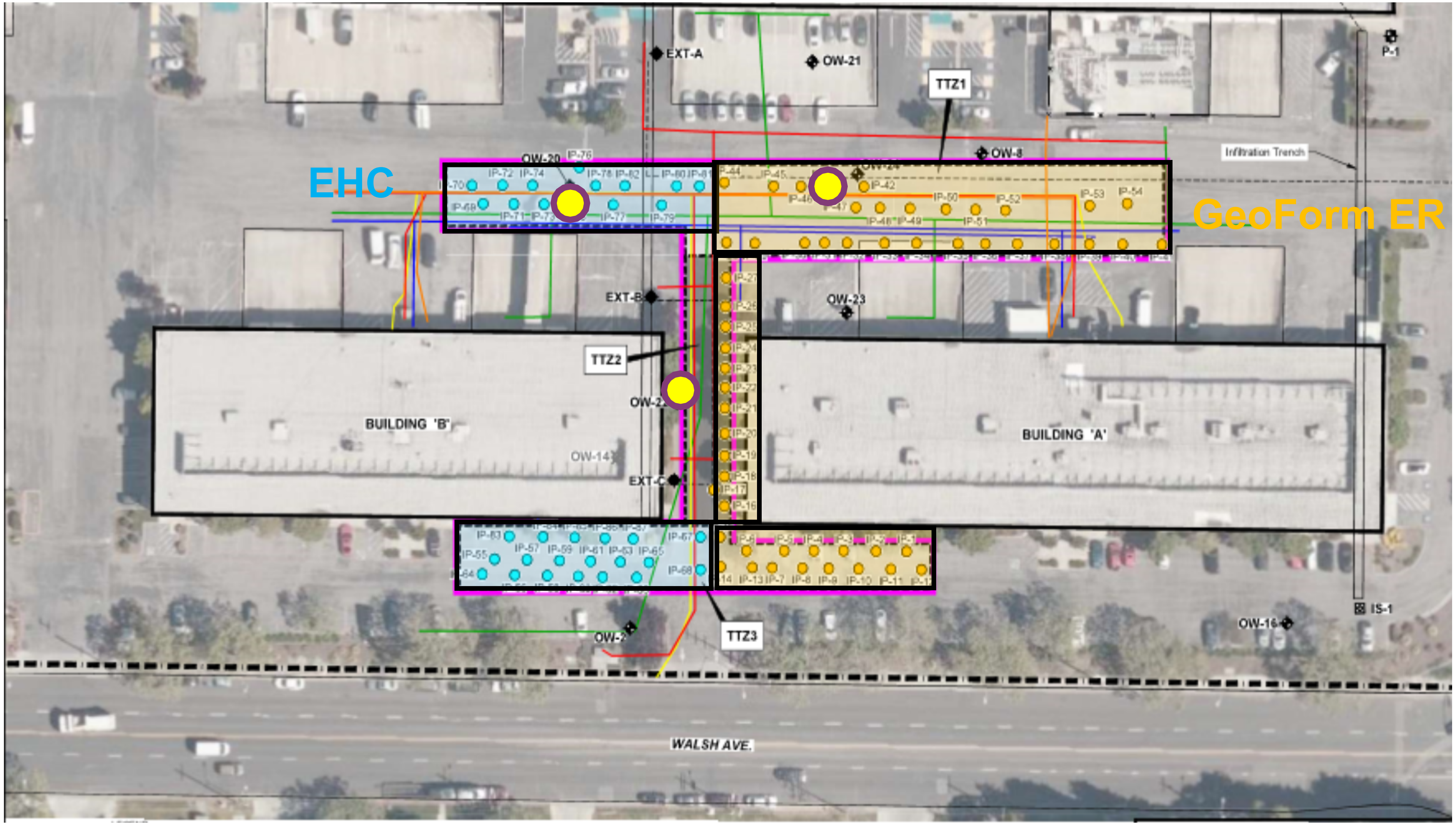
Sulfide replaces OH^- on ZVI

Fe^{2+} (ambient, supplied or from ZVI oxidation,) combines with HS^- to form FeS coating on ZVI and precipitate on aquifer matrix



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

EHC® and GeoForm™ ER Application



EHC Treatment Area

GeoForm ER Treatment Area

Mintrap Sample Location

Mintrap™ samples from
EHC® and GeoForm™ ER Application

Upgradient well
No Treatment

EHC®
(+ ambient sulfate)

GeoForm™ ER

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

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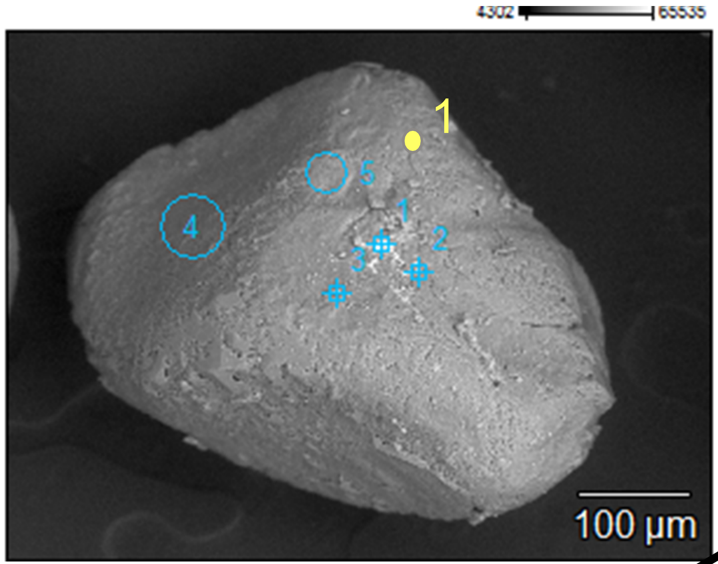
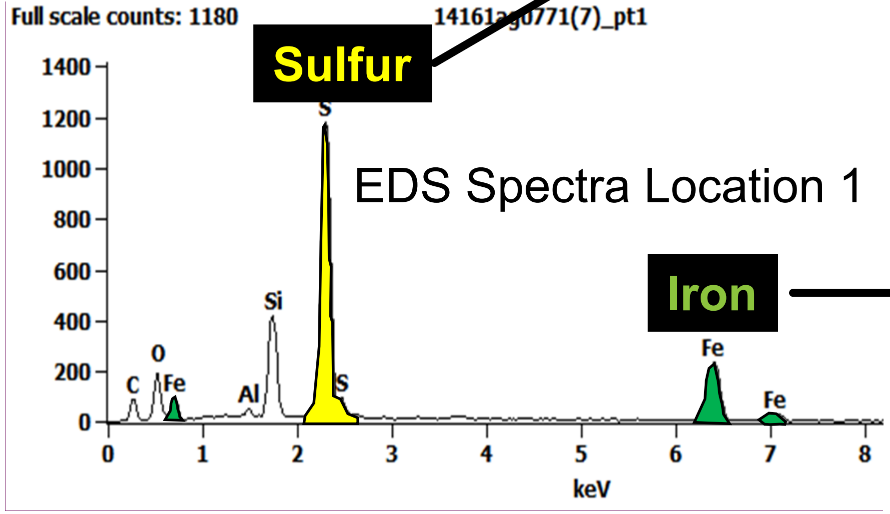
SEM-EDS Results
Following GeoForm™ ER Application

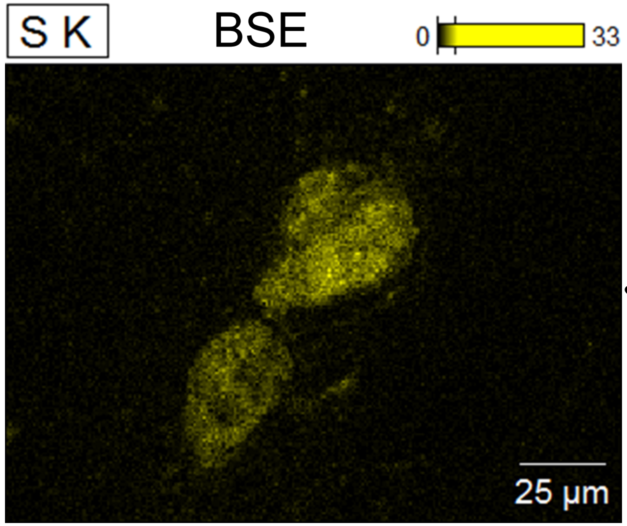
Scanning Electron Microscopy (SEM)-Energy Dispersive Spectroscopy (EDS)



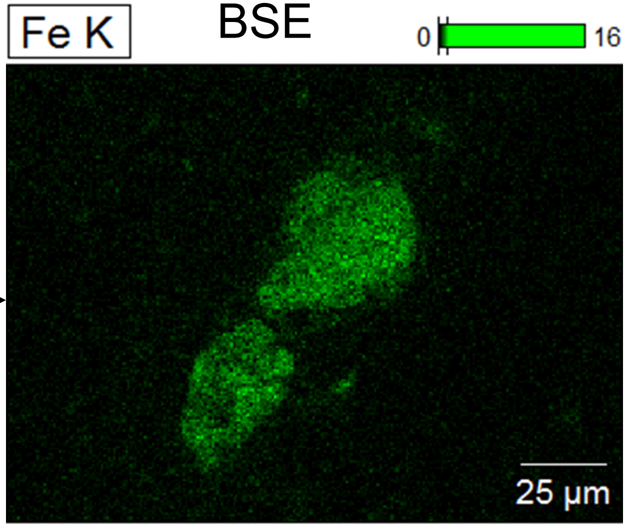
SE EDS Location map

(SE – Secondary Electrons – Show Morphology)





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



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

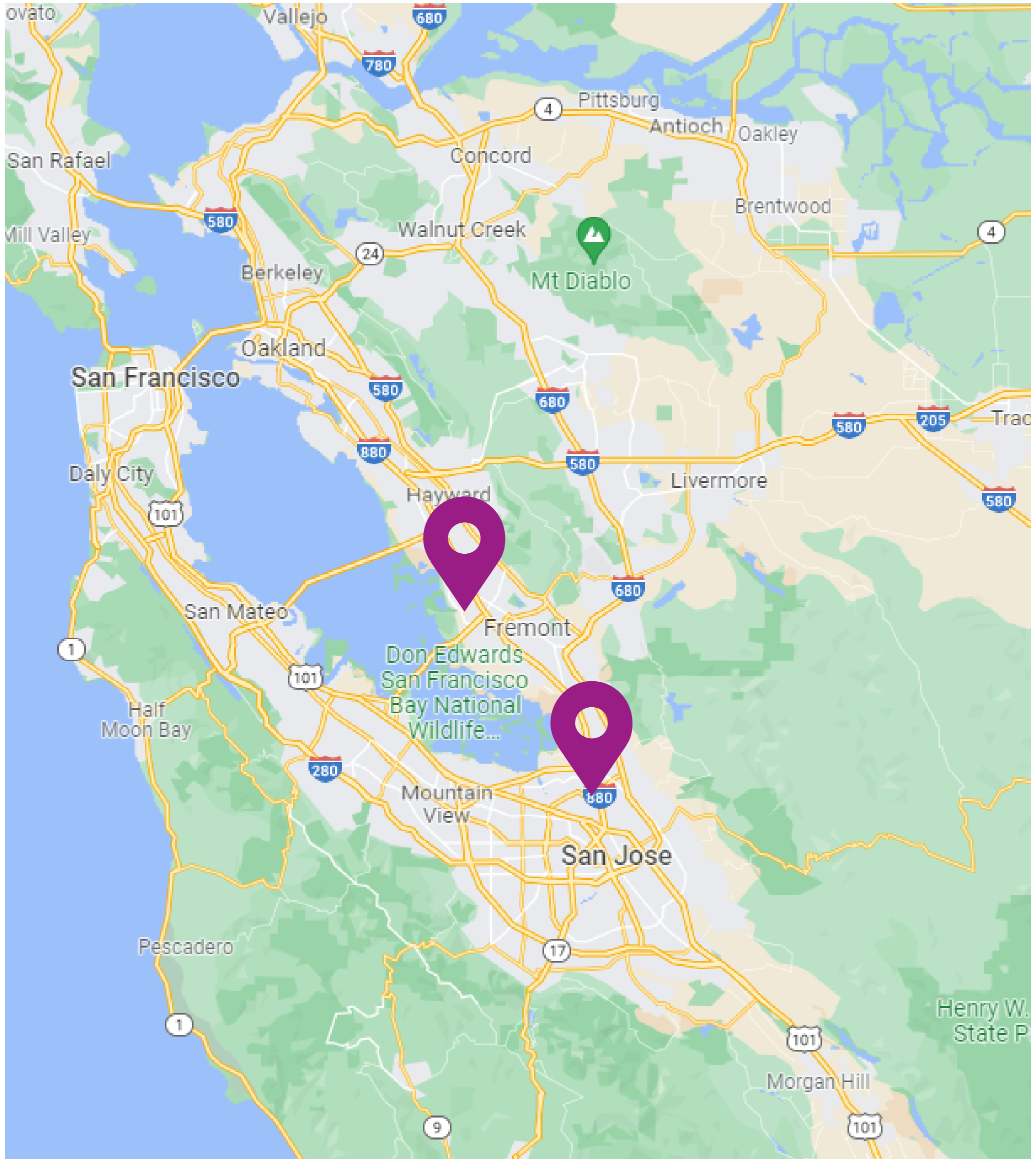
BSE

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



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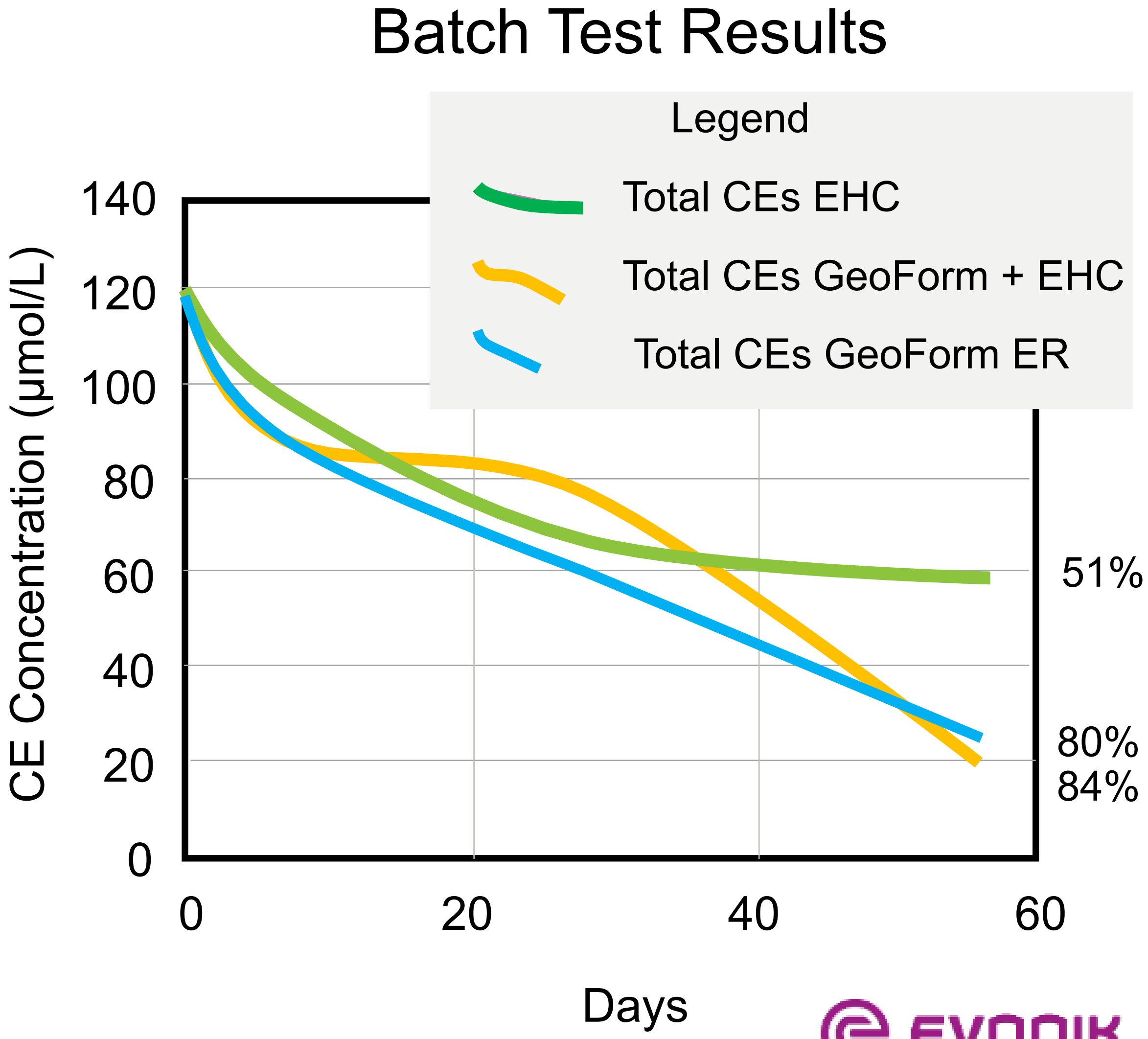
Case Study: Combined ISCR + BGCR for Treatment of High CE Concentration

GeoForm® Extended Release Increases EHC® Degradation Rates

Addition of GeoForm® Extended Release Increased degradation rate ~63% Relative to EHC® (ISCR) (with sulfate).

Results are similar with or without bioaugmentation.



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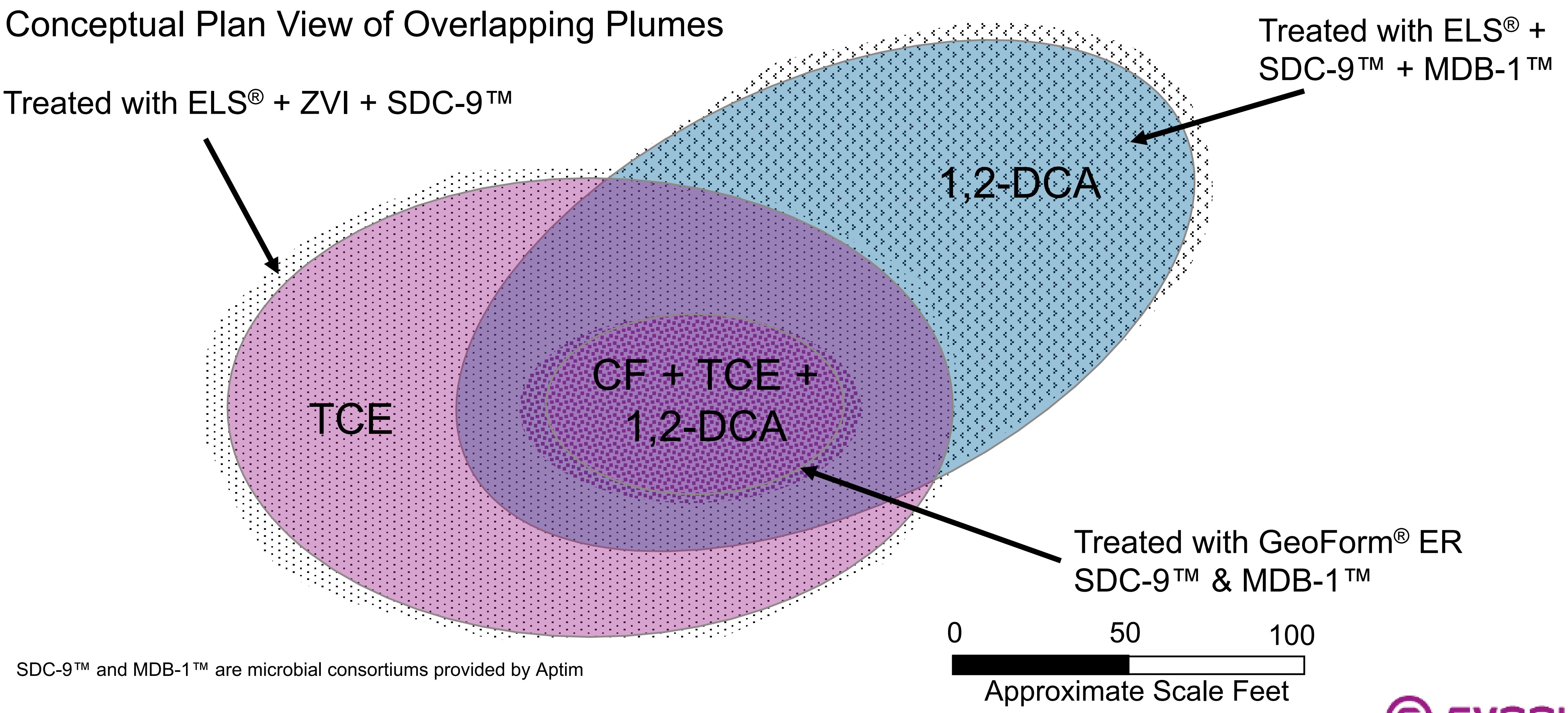
Case Study: BGCR Treatment of Mixed Chlorinated Organics

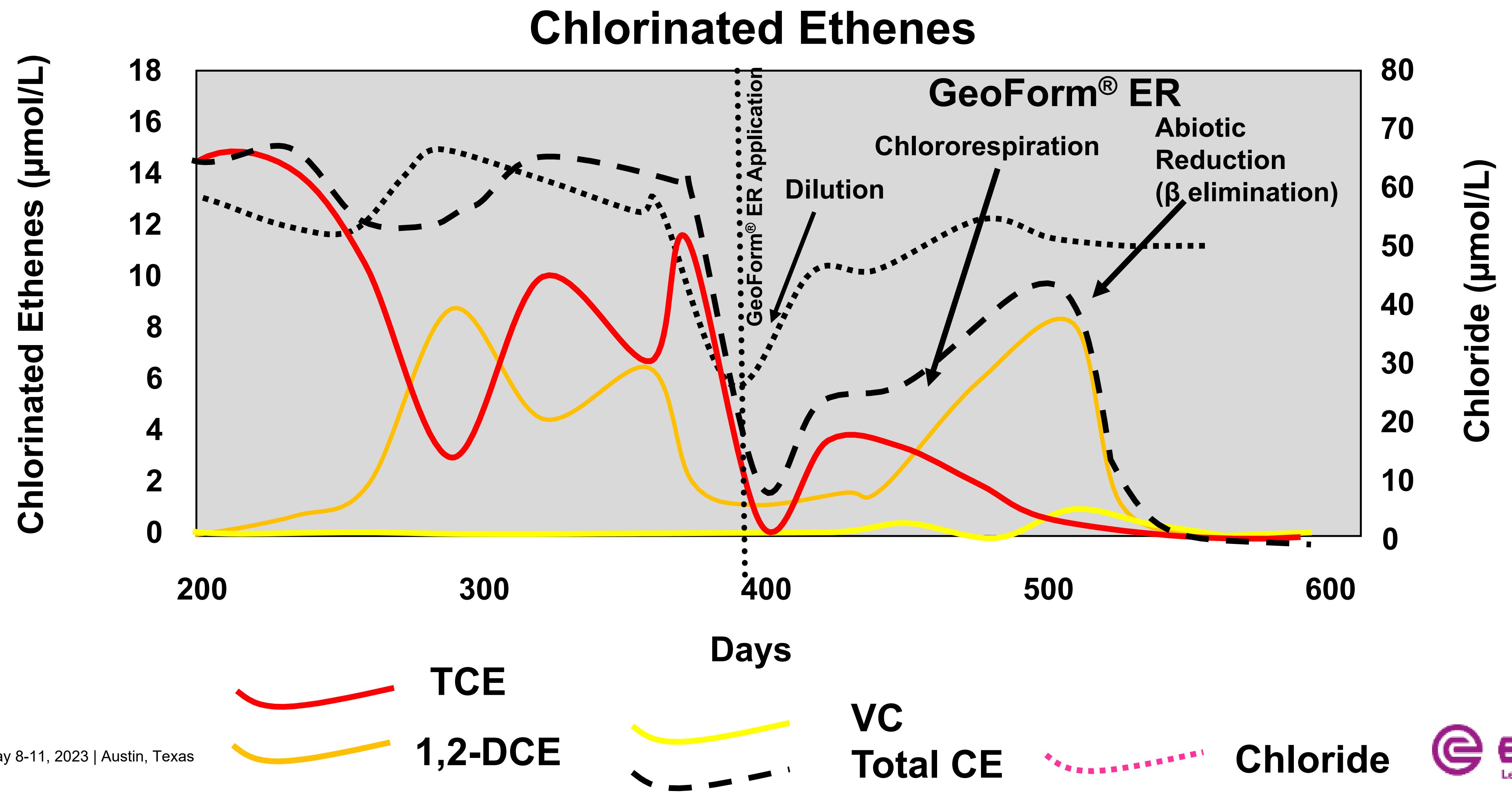
Sequential Treatment of Mixed Plume



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

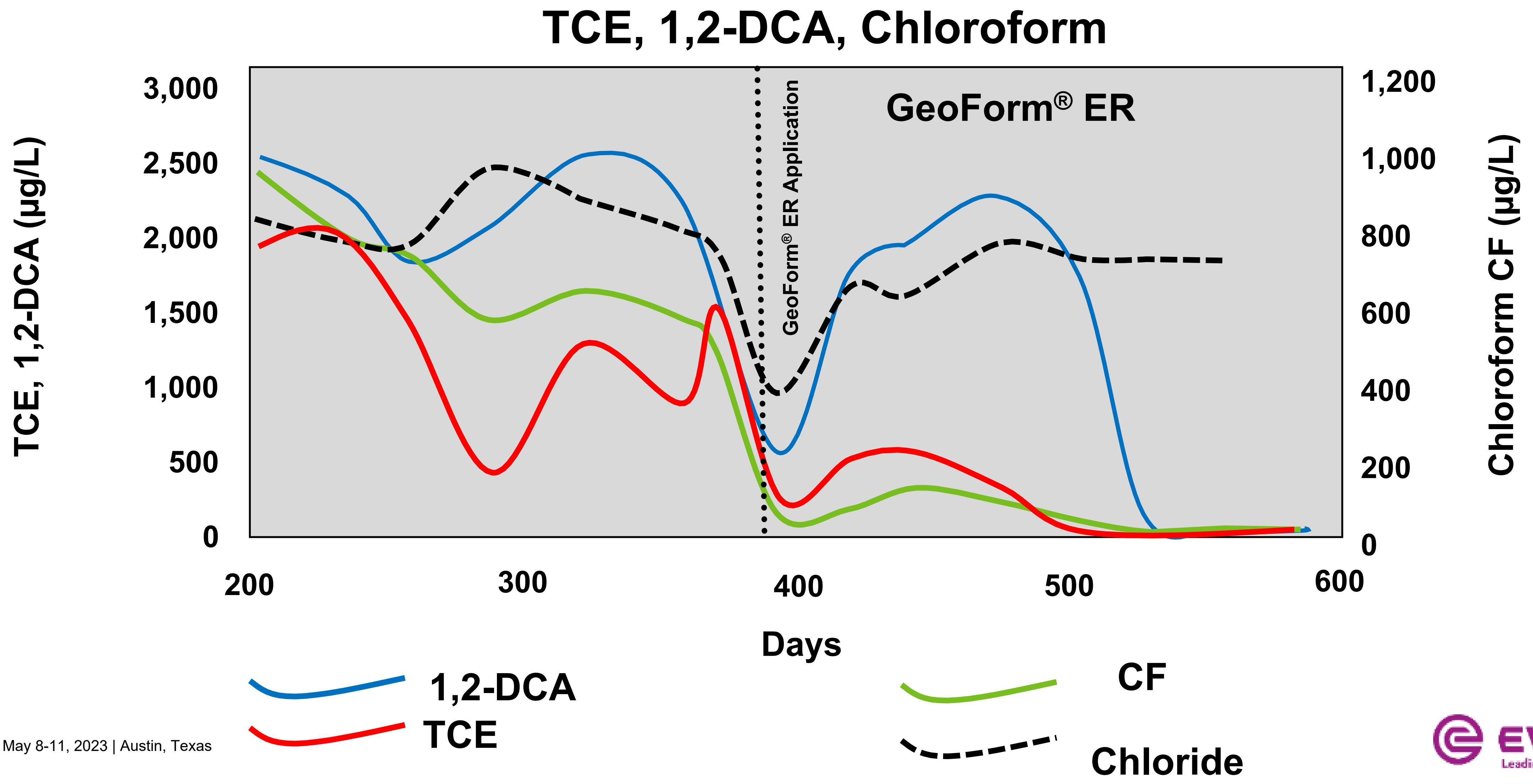
Case Study: BGCR Treatment of Mixed Chlorinated Organics

GeoForm® ER Treats Mixed CEs, CA and CMs



Case Study: BGCR Treatment of Mixed Chlorinated Organics

Applied Geoform ER + SDC-9 + MDB-1



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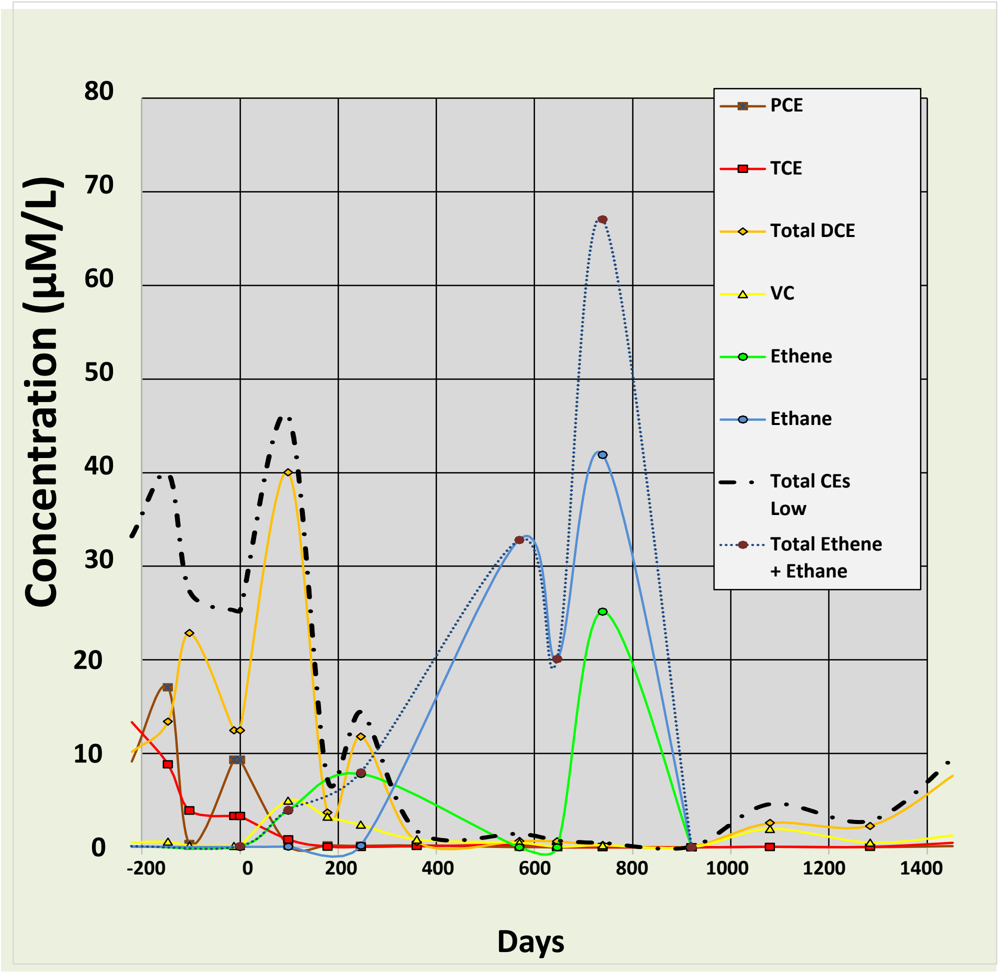
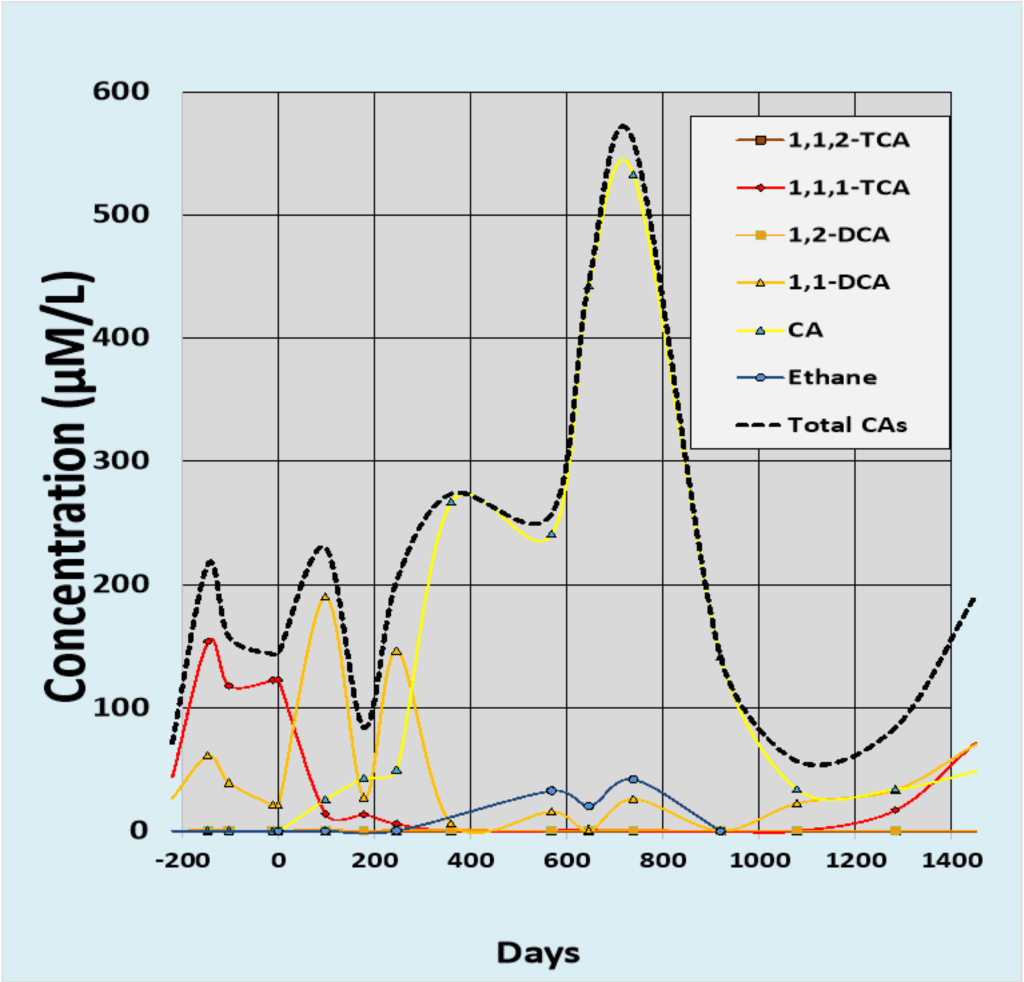
Degradation of Combined Chlorinated Ethenes and Ethanes

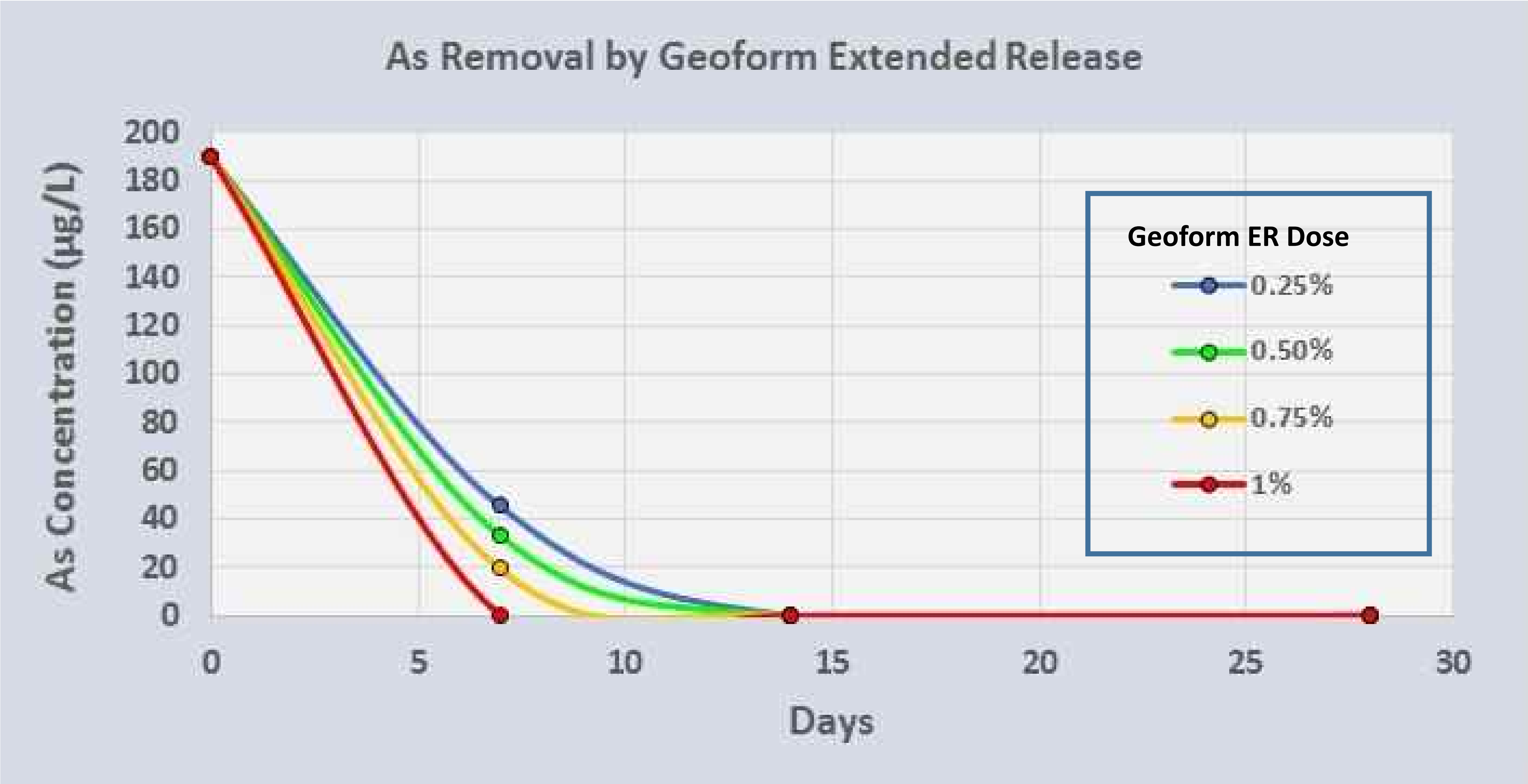
Geoform ® Soluble Application + SDC-9





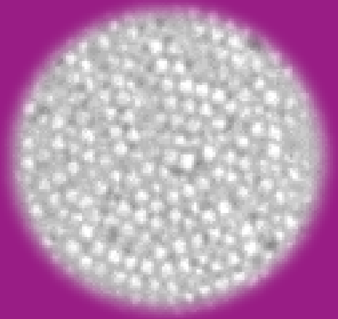
GeoForm™ ER Treats As

PeroxyChem



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 toxic metals from groundwater.

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Questions?

Or stop by our booth #300

Panel Discussion:
Science, Application and Monitoring and illustrative Case Studies of Biogeochemical Remediation.
Thursday, 10:30 E Session Walter A-B Level 3.

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