Biogeochemical Processes Enhance *In Situ* Treatment of Chlorinated Organics and Heavy Metals

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PeroxyChem

PeroxyChem is a company of Evonik Industries AG

Presentation Outline

- Conditions for Formation of Iron Sulfide Minerals
- Biogeochemical Degradation Processes
- Sulfidation of ZVI
- GeoForm™ Biogeochemical Reagent
- Case Studies
- Conclusions

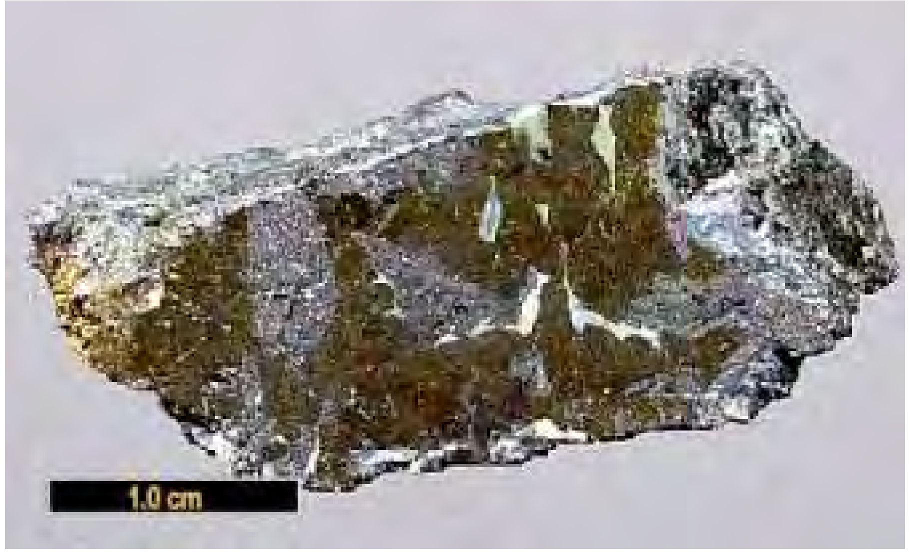
Biogeochemical Transformation

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

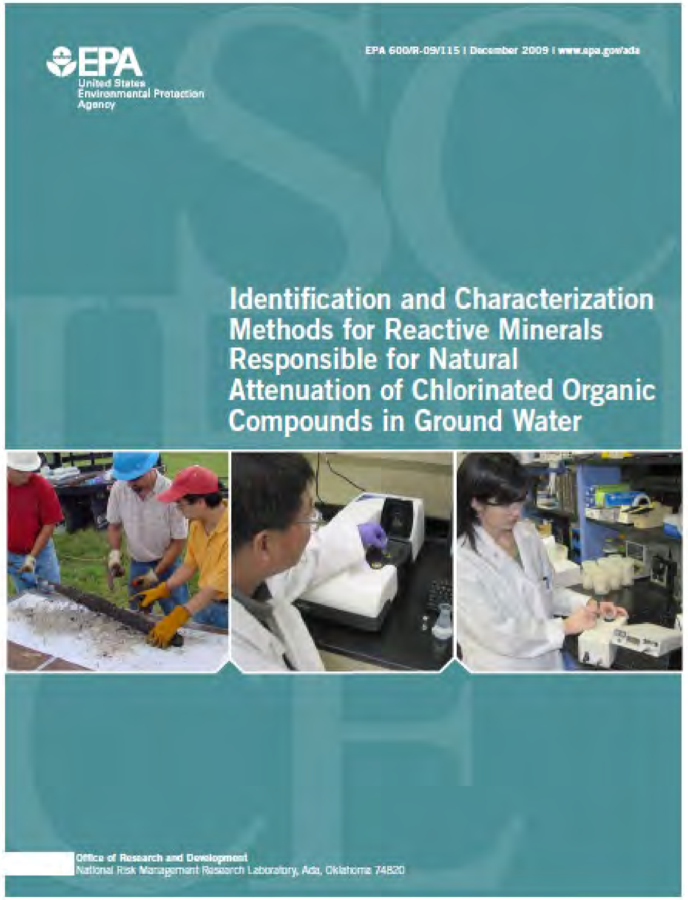
Reactive minerals include iron sulfides (e.g. pyrite, mackinawite, greigite) and oxides (e.g. magnetite)

Focus on Iron Sulfide Minerals

Pyrite (FeS_2)



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



Sources of Sulfate in Groundwater

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Sulfate is naturally occurring in most aquifers

Many aquifers exhibit high sulfate concentration (up to several thousand ppm)

Primary sources of sulfate in groundwater include:

- Seawater adjacent to coastal aquifers,

  Seawater sulfate concentration 2,700 mg/L

- Dissolution of sulfate containing minerals

  e.g., Gypsum ($CaSO_4$ – $2H_2O$), Anhydrite – ($CaSO_4$,), Barite – ($BaSO_4$)

- Dissolution and oxidation of sulfide containing minerals

  e.g., Pyrite (FeS_2),Sphalerite (ZnS), Galena (PbS)

- Evaporation and transpiration of surface water and shallow ground water

  Concentrates sulfate which migrates into aquifer

Concerns with Degradation of Chlorinated Organics in High Sulfate Groundwater

Sulfate is a competing electron acceptor to biological reductive dechlorination

Each mole of sulfate requires 9 H^+ equivalents to reduce to sulfide – more than PCE

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

Sulfate concentration often several orders of magnitude higher than CE concentration

Usually, most of electron donor (substrate) demand is for sulfate reduction

Hydrogen sulfide (HS^-) – toxic to microorganisms

Stops biological dechlorination (VC stall)

Sulfate has regulatory requirements (250 mg/L)

Based on aesthetics, not toxicity

Not typically enforced

Potential Benefits of Reductive Dechlorination in High Sulfate Aquifers

Most aquifers contain some solid iron (ferric) in/on the aquifer matrix

Under moderately reducing conditions solid ferric is reduced to soluble ferrous

Sulfide combines with ferrous iron to generate reactive iron sulfide minerals

Removes potential sulfide toxicity issues

Electrons are stored in aquifer as reactive iron sulfide

Iron sulfide minerals can abiotically degrade chlorinated organics

Sulfate is a preferential electron acceptor to CO_2, inhibiting methane generation

Iron sulfide minerals can sequester toxic metals (e.g., As)

Eh Range for Various Electron Acceptors

Decreasing Amount of Energy Released During Electron Transfer

Aerobic

Anaerobic

500

0

-250

Optimal range for dechlorination

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

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

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

Manganese (IV) $MnO_2(s) + HCO_3 + 3H^+ + 2e^- \longrightarrow MnCO_3(s) + 2H_20 \ (Eh^0 = {}^+520)$

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

Iron $FeOOH(s) + HCO_3 + 2H+ e^- \longrightarrow FeCO_3 + 2H_20 \ (Eh^0 = {}^-50)$

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

Methanogenesis $CO_2 + 8H^+ + 8e^- \longrightarrow CH_4 + 2H_20 \ (Eh^0 = {}^-240)$

AFCEE, NAVFAC, ESTCP, Principals and Practices, 2004

Iron Sulfide Stability Eh - pH

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

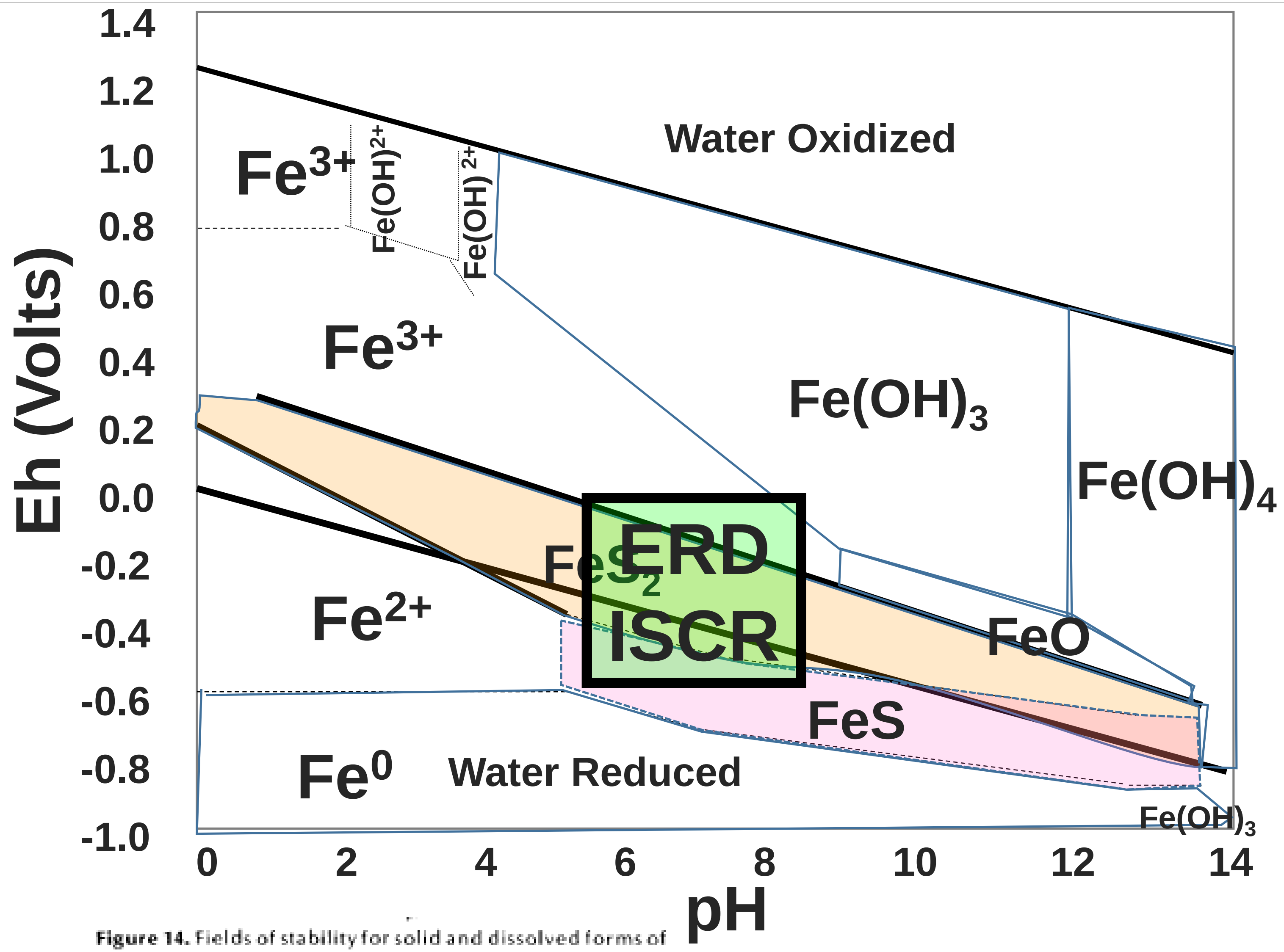

Figure 14. Fields of stability for solid and dissolved forms of iron as a function of Eh and pH at 25°C and 1 atmosphere pressure. Activity of sulfur species 96 mg/L as SO_4^{2-}, carbon dioxide species 61 mg/L as HCO_3^-, and dissolved iron 56 μg/L.

From USGS Water Supply Paper 2254

Ratio of Ferrous and Sulfate for FeS Generation

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Usually, sufficient iron is available to precipitate low to moderate levels of sulfide

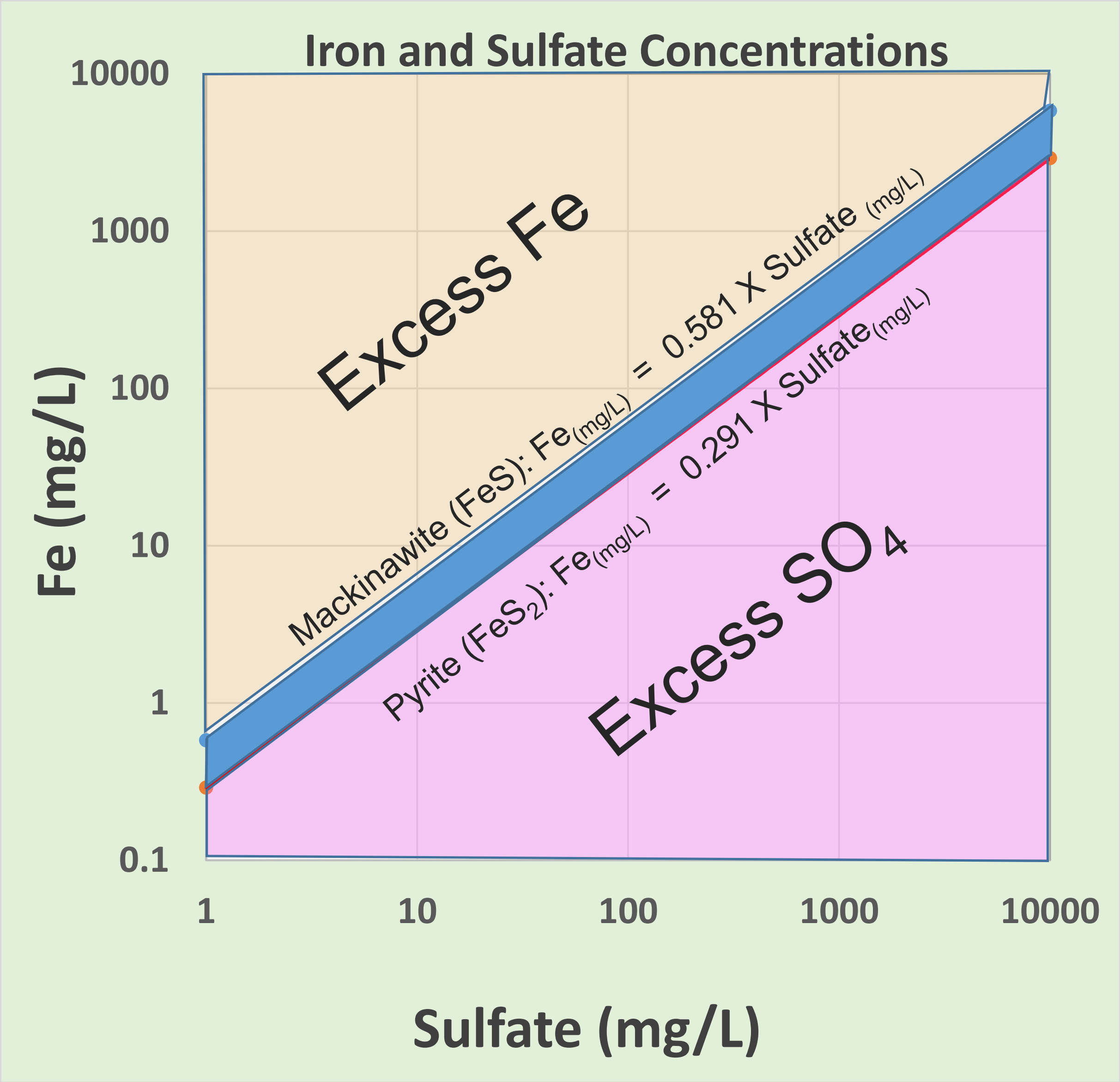
Iron content of aquifer matrices varies substantially:

- **Volcanic rock – high Fe**
- **Sandstones clay moderate to high Fe**
- **Limestone, Gypsum – Low to no Fe**

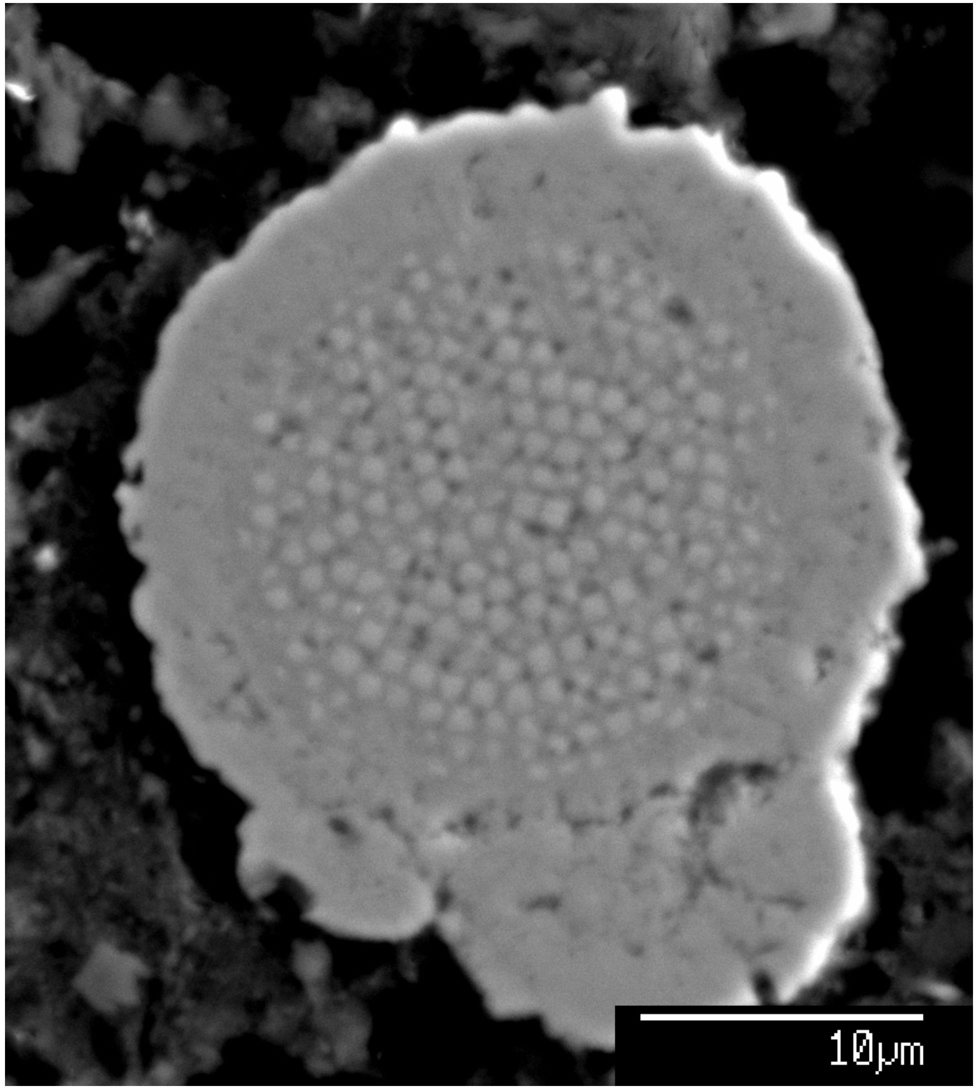
Difficult to determine available iron from GW concentrations alone

Sulfate mostly in solution however some may be in mineral form

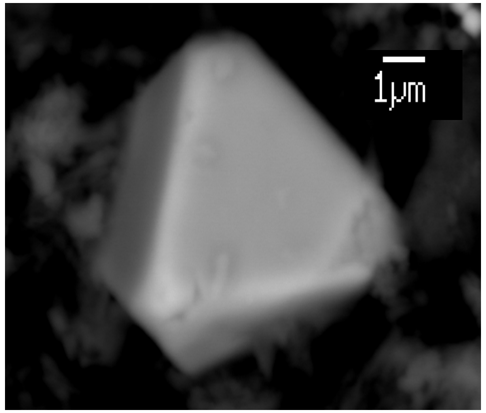
e.g., gypsum, anhydrite, barite



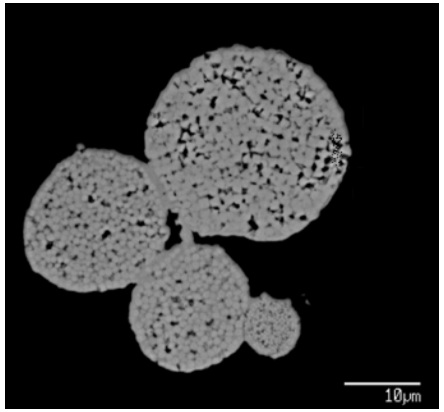
Form of FeS and FeS_2



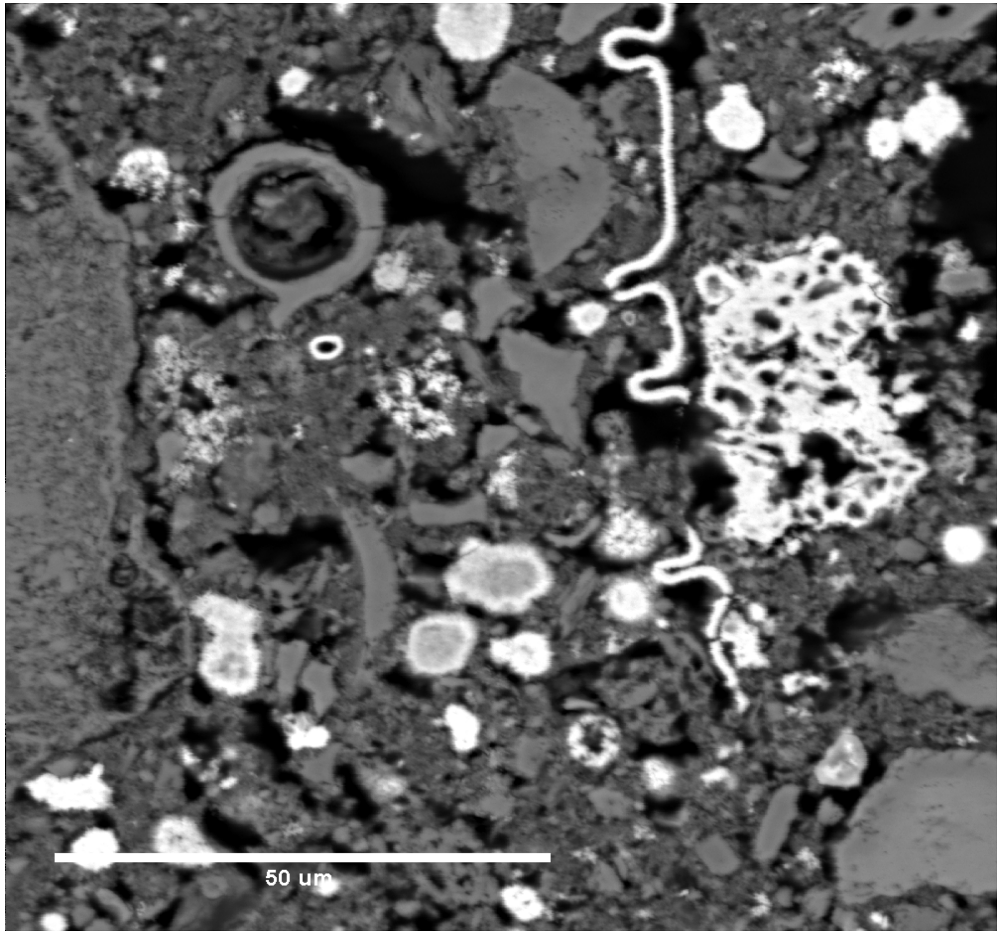
Framboidal FeS_2 and FeS Coating



Euhedral Pyrite (FeS_2)

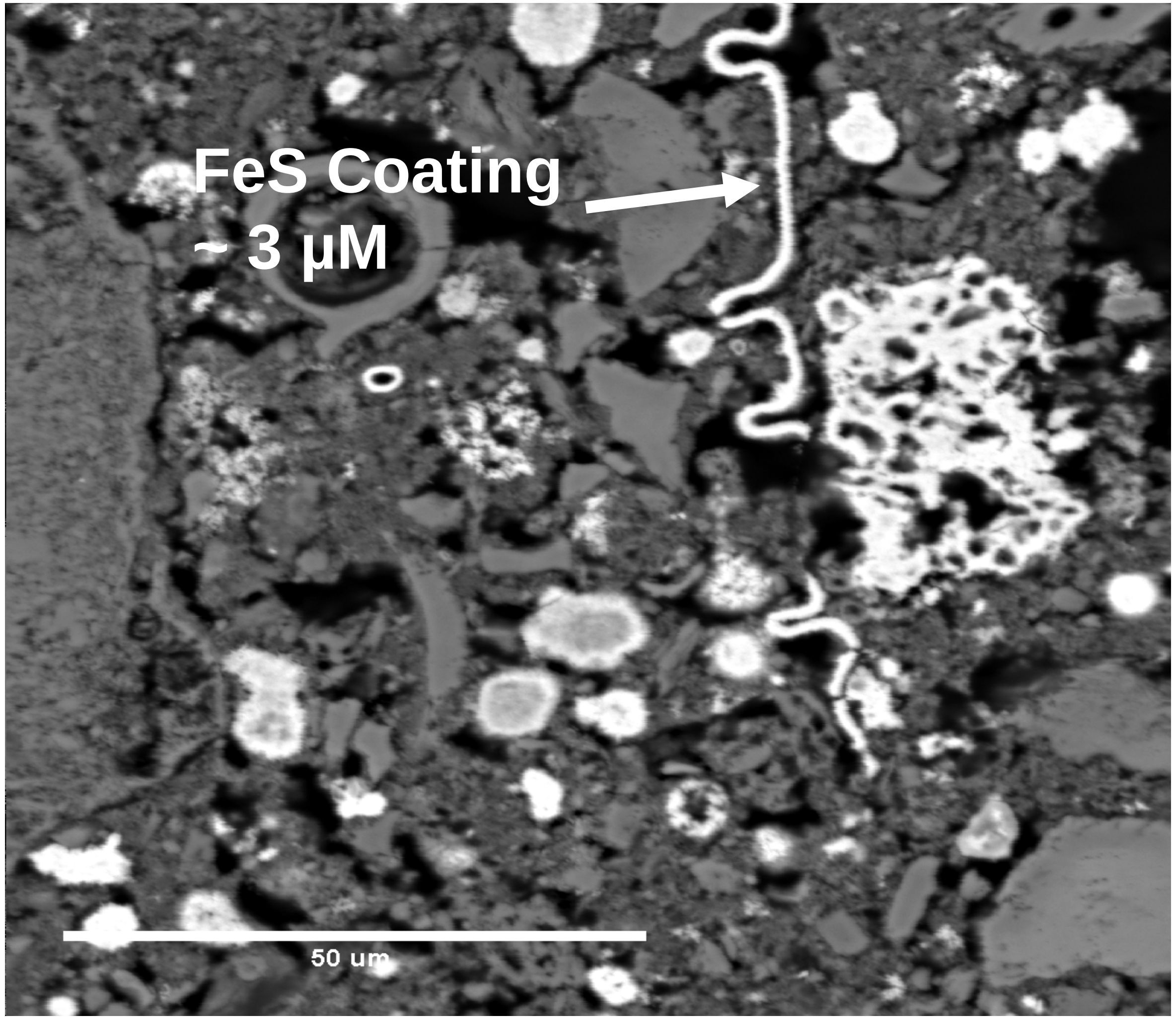


Framboidal Pyrite (FeS_2)



Fe replacement + FeS coating and nano scale FeS_2

Expanded Surface Area for Abiotic Pathway Without Aquifer Occlusion



3,000 mg/L SO_4 + Fe generates:

~2.7 g FeS per Liter

~3.7 g FeS_2 per Liter

Volume FeS_2 ~ 0.745 cm^3 per Liter

Volume FeS ~0.898 cm^3 per Liter

~ 0.09% of aquifer pore space

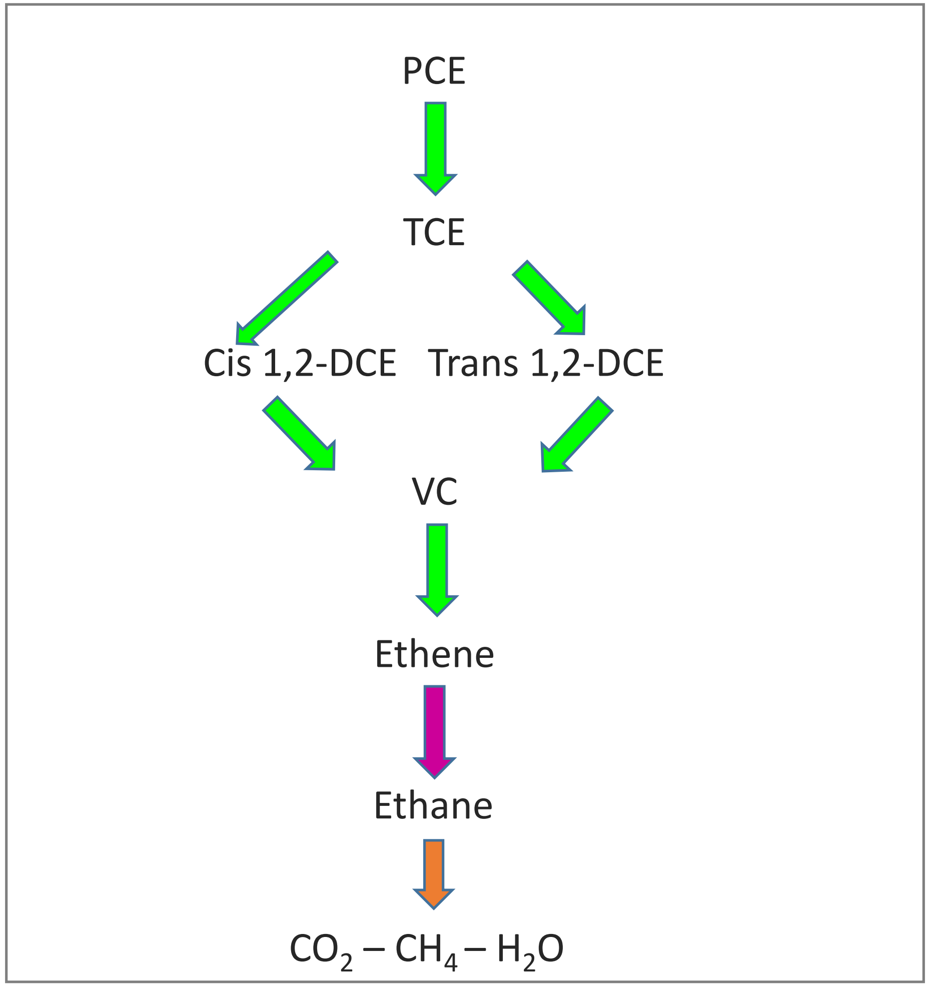
Produce a very large surface area:

3 µM coating ~ 3.2 ft^2

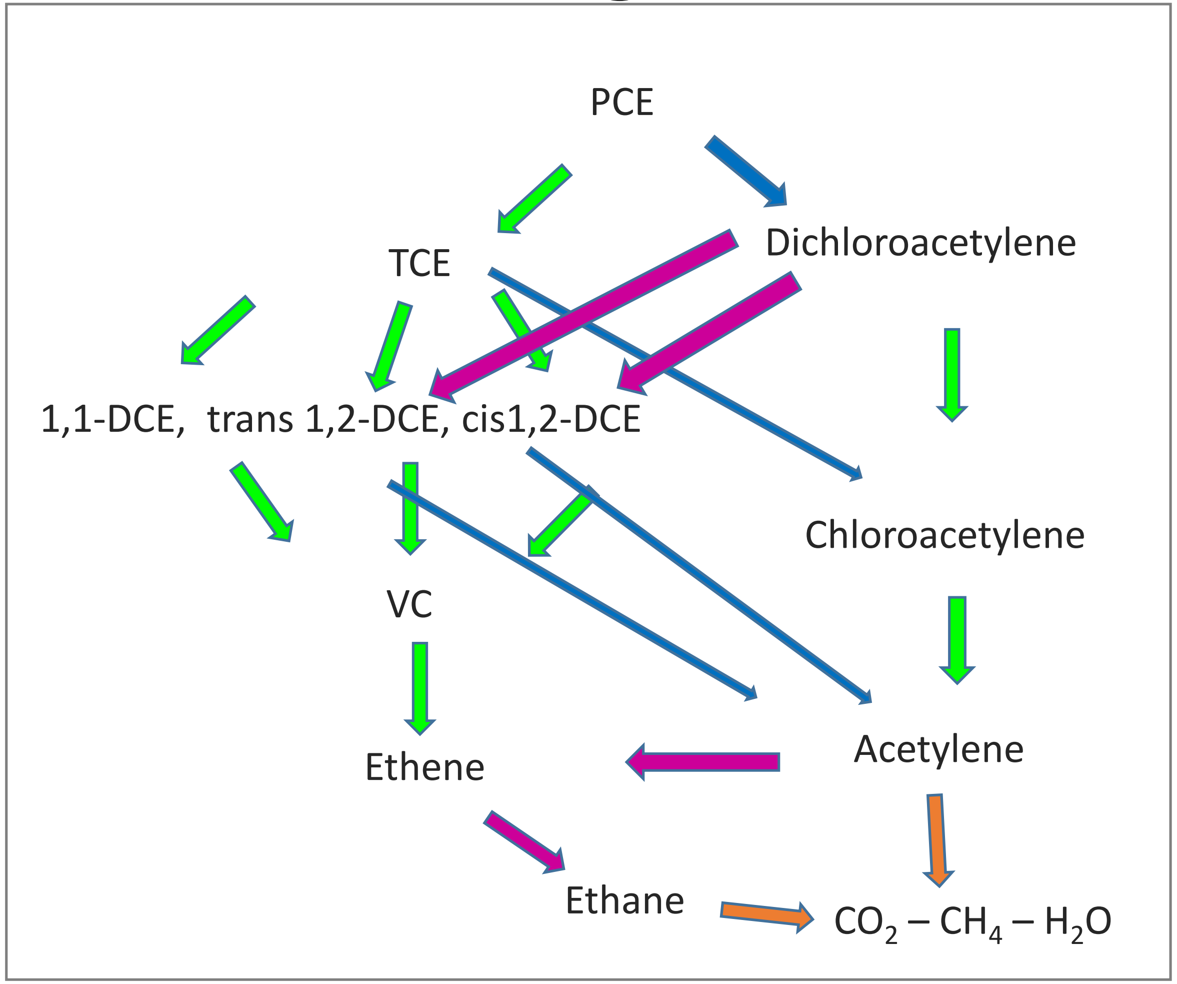
~ 30 ft^2 per ft^3

Biotic and Abiotic PCE Degradation Pathways

Biotic



Abiotic/ Biogeochemical



β-elimination

Hydrogenolysis

Hydrogenation

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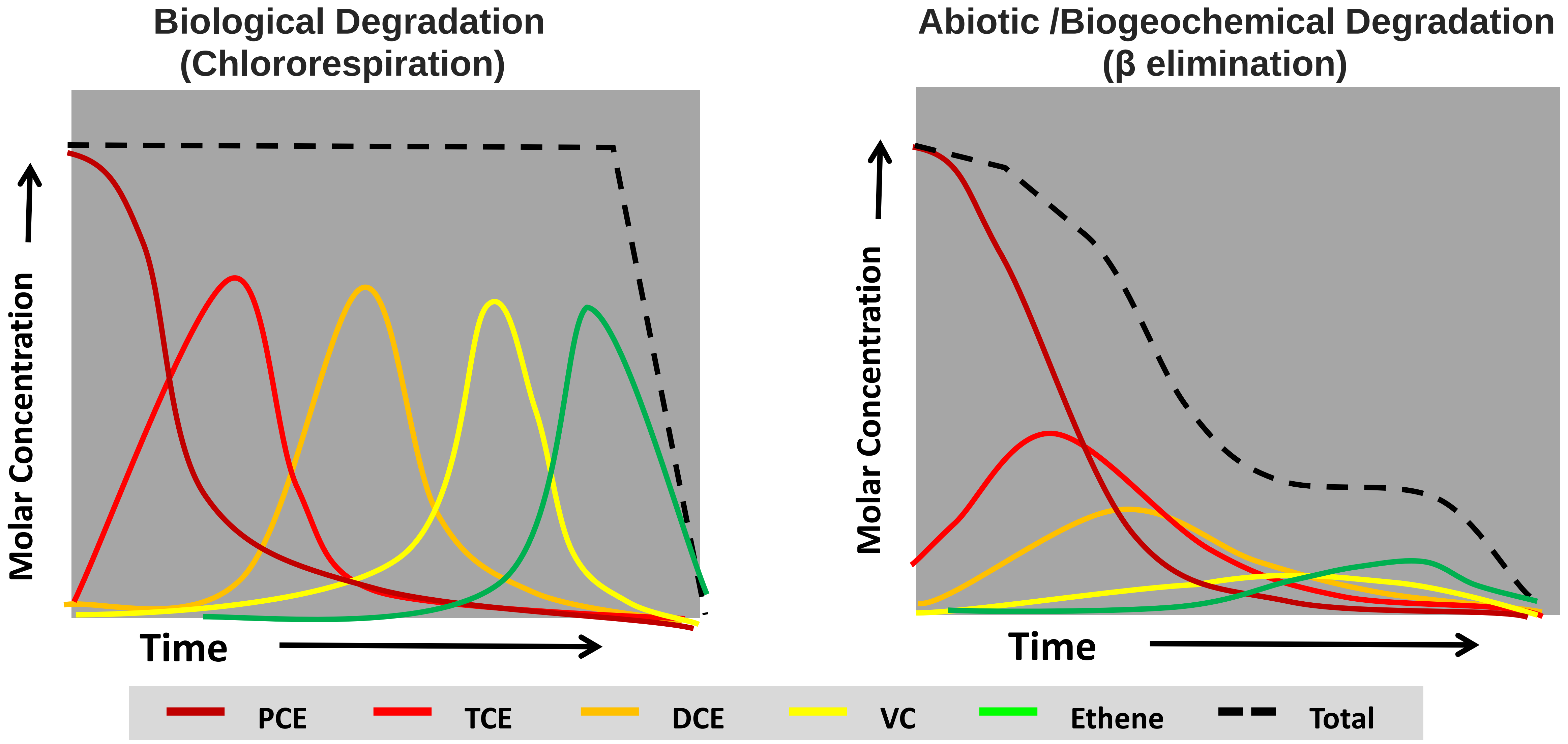
Anticipated Change in CE Molar Concentration



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GeoForm™ Reagents can be used for Treatment of Metals

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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.

Insoluble	**Arsenic As[V]**	→	**As[III]**	Soluble
Insoluble	**Manganese: Mns[V]**	→	**Mn[II]**	Soluble
Insoluble	**Iron Fe[III]**	→	**Fe[II]**	Soluble
Soluble	**Chromium Cr[VI]**	→	**Cr[III]**	Insoluble

Many metals can be precipitated as iron sulfides

As (Arsenopyrite), Zn (sphalerite), Fe (pyrite, mackinawite) Co (CoS), Lead (galena)

Biogeochemical process can be applied for treatment of many metals.

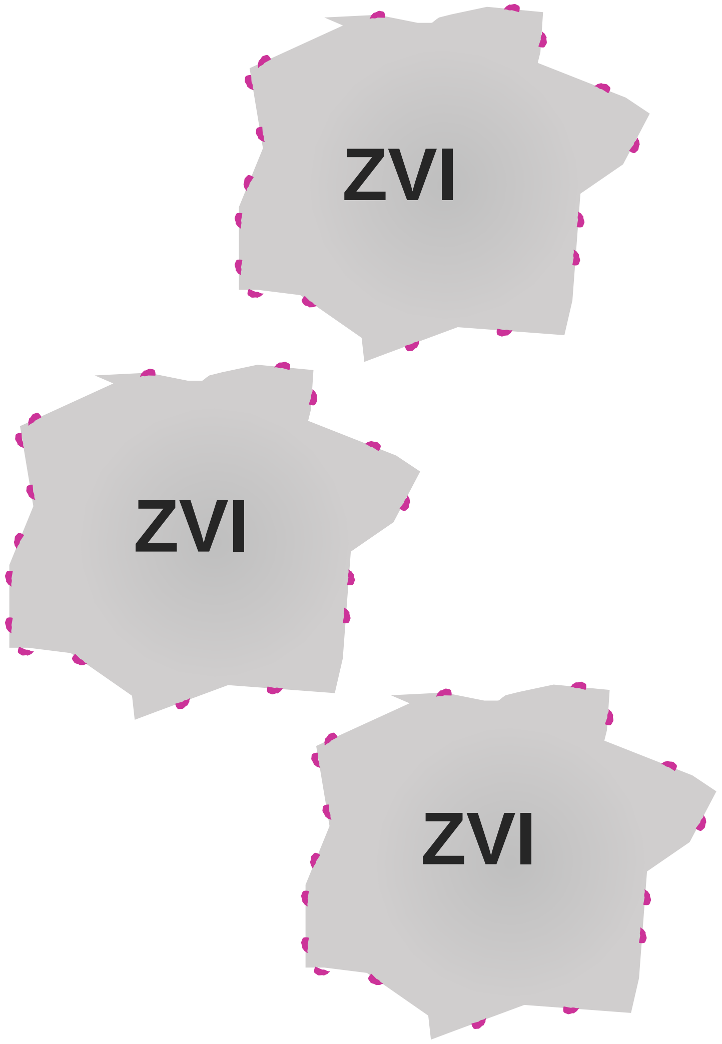
Sulfidation Increases ZVI reactivity

Biological reduction of supplied sulfate produces sulfide

Sulfide combines with ferrous iron on ZVI particles, or ZVI to form partial coating of FeS

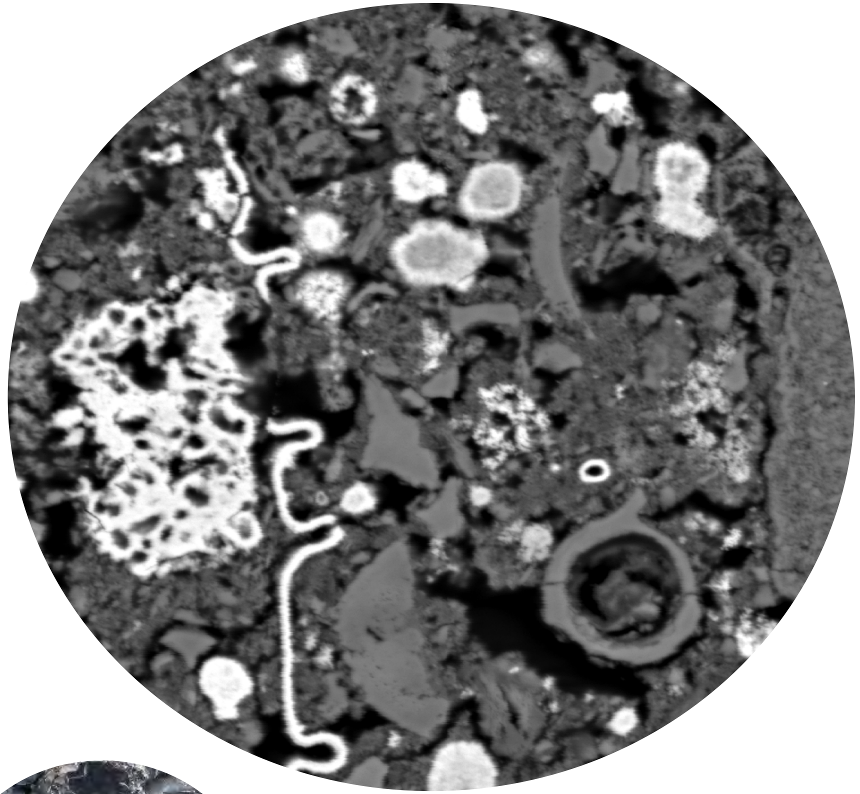
Partial coating of ZVI with sulfide reduces passivation and increases effectiveness of ZVI

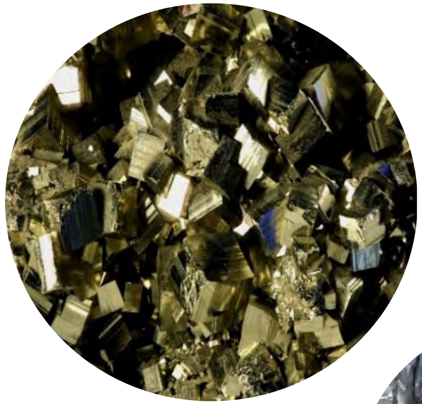
- Minimizes reaction with water while preferentially reacting with organics



GeoForm™
BIOGEOCHEMICAL REAGENTS

- All-In-One BioGeoChemical Reagent
- Provides All Building Blocks Needed for Reactive Mineral Formation
- Combines Sulfate, Ferrous Iron, Electron Donors, pH Buffer, and Nutrients
- Effective for Chlorinated Organics and Many Heavy Metals





Engineering Reactive Iron Sulfide Minerals *In Situ*

Injection of GeoForm™

Sulfate
+
Fe(II)
+
Electron donor

REACTIONS PROMOTED

Organic Substrate Fermentation
→ Reduced RedOx Conditions

Sulfate reduction by SRBs:

$$2CH_2O_{(s)} + SO_4^{2-} + 2H^+_{(aq)} \rightarrow H_2S + 2CO_{2(aq)} + H_2O$$

Precipitation of Ferrous Iron with Sulfide:

$$Fe^{2+}_{(aq)} + H_2S_{(aq)} \rightarrow FeS_{(s)} + 2H^+_{(aq)}$$

GeoForm Formulations

GeoForm™ Soluble

- Injects as a solution forming long lasting solids.
- Proprietary blend of Soluble Organic Carbon, Sulfate, Ferrous Iron, pH buffer and nutrients.
- Delivered in 2 parts allowing for custom designs
- Longevity of 2-3 years or more

GeoForm™ Extended Release

- Provides a longer lasting source of electron donors for continued rejuvenation of reactive minerals.
- Extended Release Organic Carbon, Micro-Scale ZVI, Sulfate, Ferrous Iron, pH buffers and nutrients
- Longevity of 5-10 years

GeoForm™ Formulation	Treatment Mechanisms		
	Biotic Reduction	Abiotic Reduction	
		Reductive Minerals	ZVI
GeoForm™ Soluble	•	•	
GeoForm™ Extended Release	•	•	•

GeoForm™ Applicability Considerations

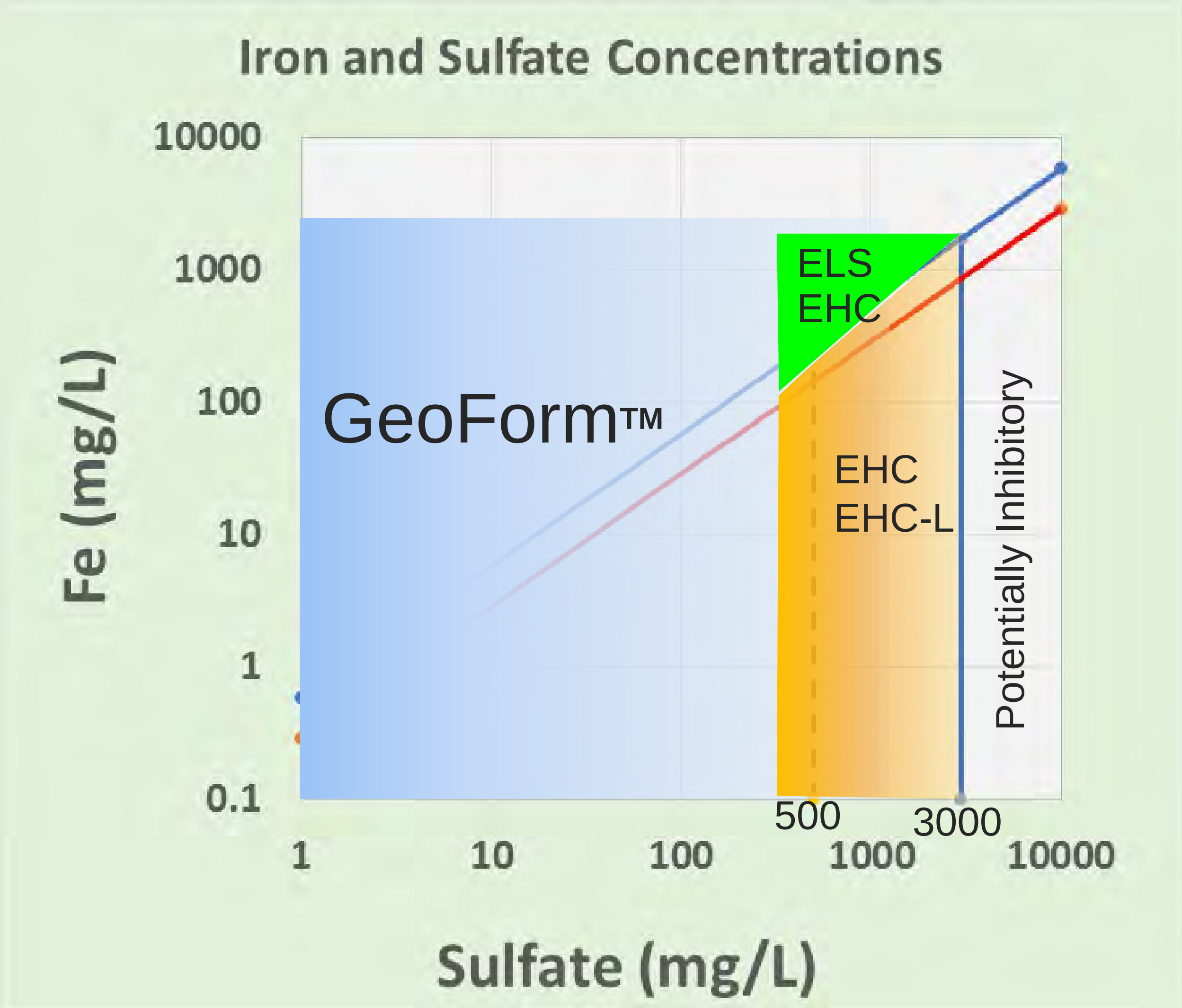
Sulfate in GeoForm™ Soluble calculated to achieve ~500 to 3,000 mg/L *In Situ* Target Concentration

ELS (organic component) exceeds demand from sulfate, contaminants and other acceptors

In high sulfate – low iron aquifers consider adding iron in form of EHC or EHC Liquid (EHC-L)

In high sulfate – high iron aquifers consider ELS or EHC.

Sulfate in excess of 3,000 mg/L may be inhibitory



Case Studies

1) Biogeochemical treatment in high sulfate aquifer

2) GeoForm™ for treatment of chlorinated ethenes (CEs)

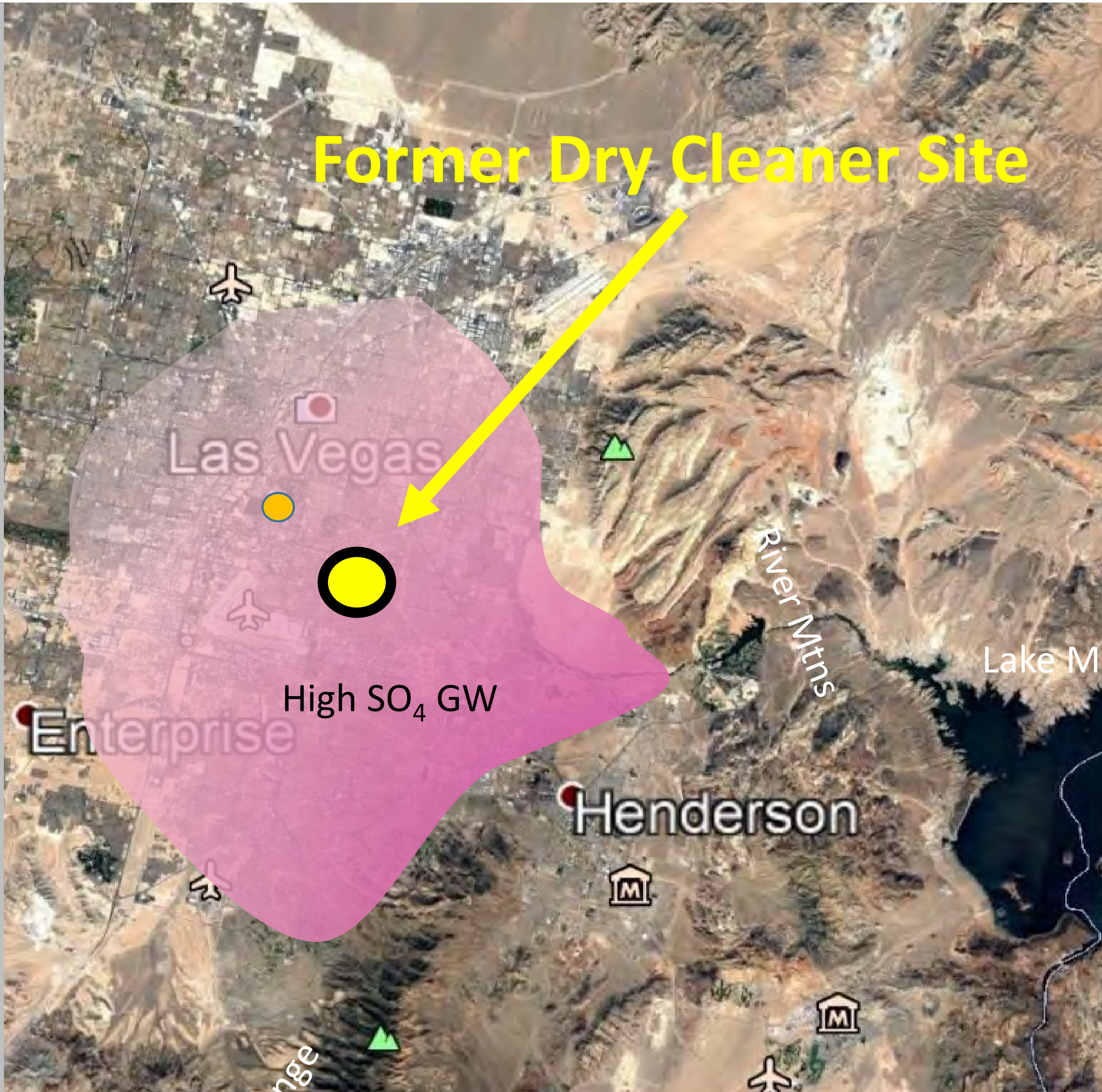
3) GeoForm™ for treatment of mixed CEs, CMs and DCA

4) GeoForm™ for treatment of Arsenic

Case Study 1: PCE Treatment in High Sulfate Aquifer

Site Conditions

- Elevated PCE >2 mg/L
- Aerobic aquifer (DO ~5.0 mg/L)
- Sulfate up to 3,000 mg/L
- Previous bio only pilot tests at similar sites unsuccessful
- Incomplete degradation of PCE
- Potential sulfide inhibition
- ERD considered not applicable



Case Study 1: PCE Treatment in High Sulfate Aquifer

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EHC® Liquid Components:

Part 1- ELS: Controlled-release emulsified organic carbon

Part 2- Organo-iron (ferrous) compound

Process:

Indigenous bacteria use ELS to reduce electron acceptors

Ferrous iron enhances biological activity by acting as an electron shuttle (more effective use of electrons)

Ambient sulfate reduced to sulfide

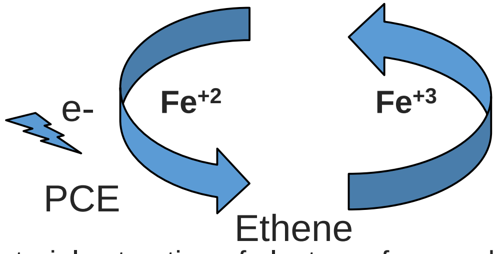
Added ferrous combines with sulfide to precipitate FeS minerals

Eliminates potential sulfide toxicity issues

Dechlorinating bacteria use H_2 from fermentation of ELS to degrade CEs

FeS minerals abiotically degrade CEs without toxic products

ISCR reactions of **Fe^{+2} with contaminants** and formation of Fe^{+3}



Bacterial extraction of electrons from carbon restores Ferric (Fe^{+3}) to Ferrous (Fe^{+2})

High Sulfate Aquifer Bench Test Setup

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Sediment and groundwater samples collected from source area wells

Some sediment in each of the microcosms

PCE – 170 µg/L - Spiked to 1,800 µg/L

Sulfate – 1,800 mg/L - Spiked to ~2,300 mg/L

SDC-9™ Dhc ~ 1X10^{8} cells/L

EHC Liquid 10 g/L + additional 14 g/L organo iron

EHC – 10 g/L

Visual changes in microcosms over time

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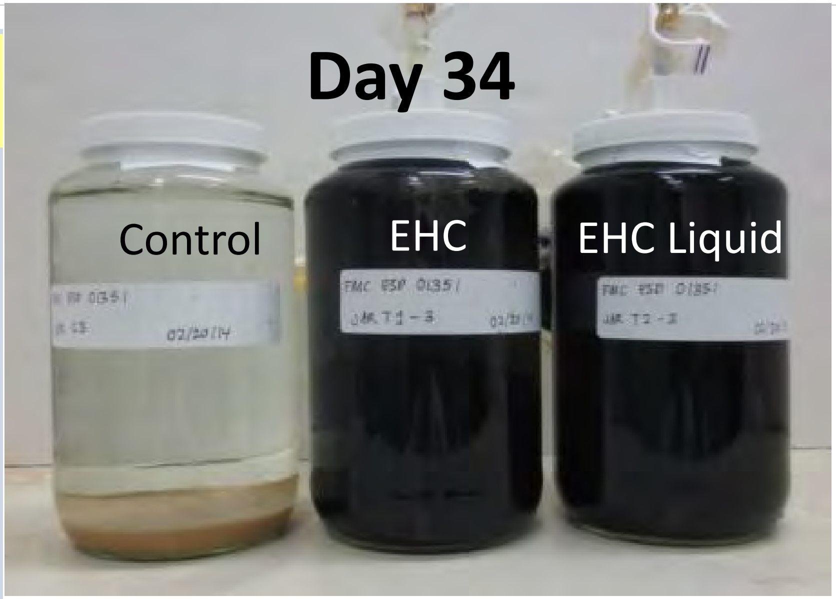
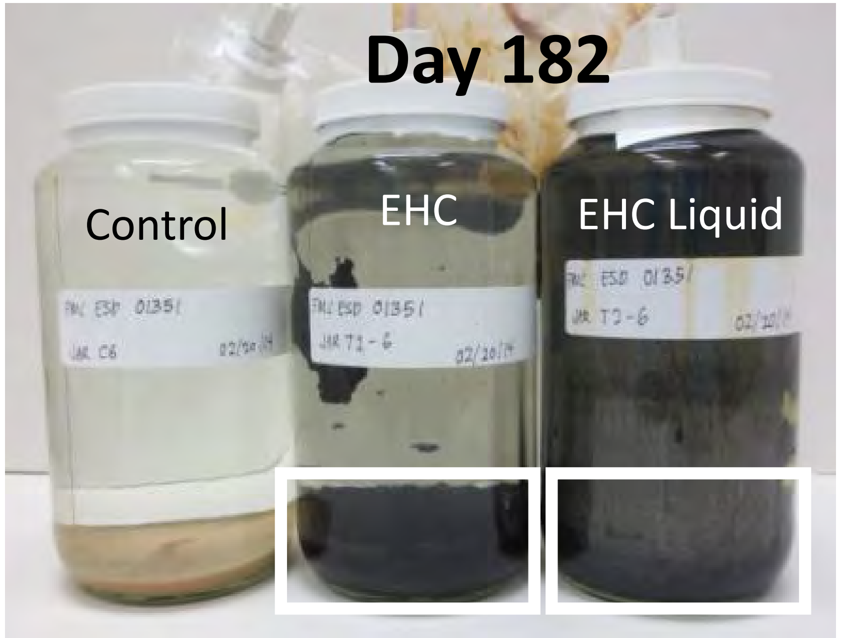
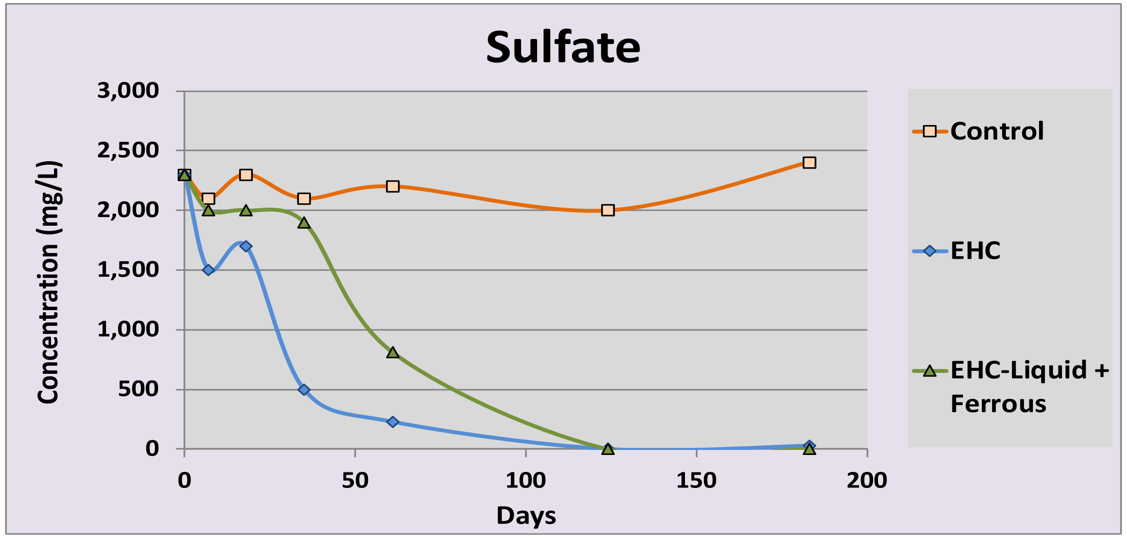
EHC Precipitate		
mg/Kg	Sulfide	31000
	Total Fe	210000
mMol/Kg	Sulfide	967
	Total Fe	3760

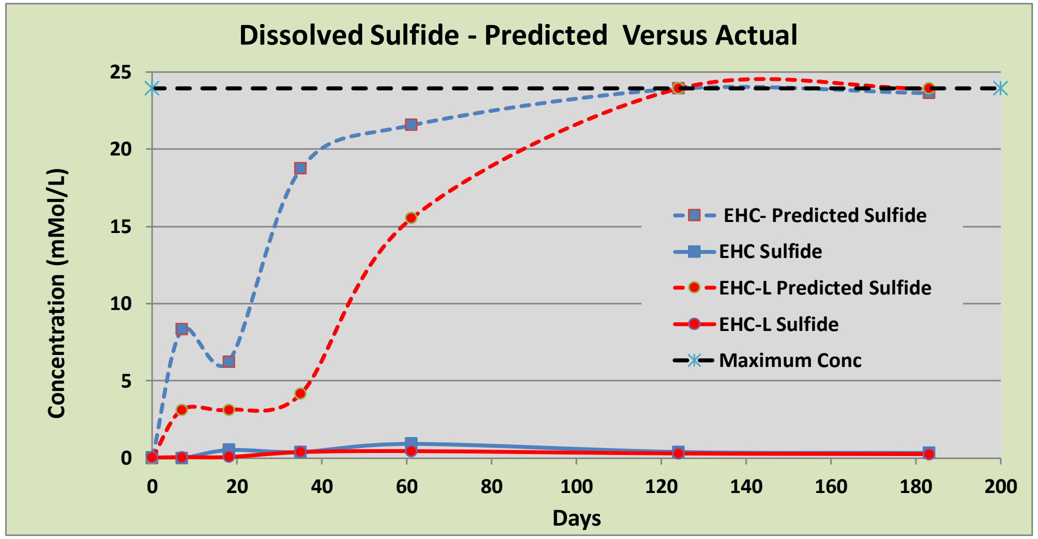


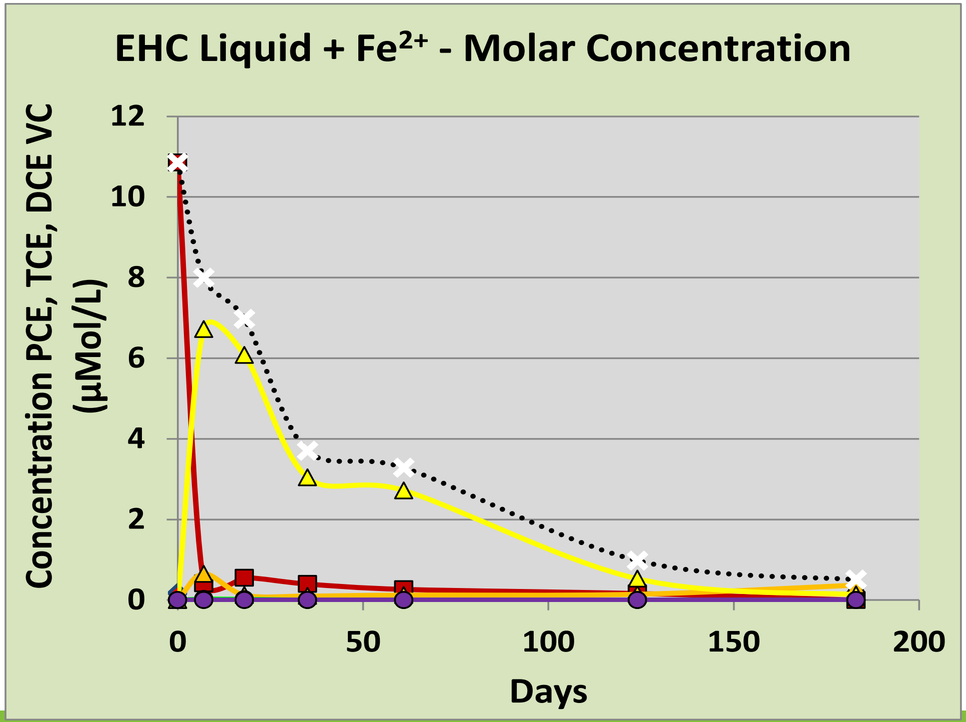
EHC-L + Iron Precipitate		
mg/Kg	Sulfide	42000
	Total Fe	130000
Mmol/Kg	Sulfide	1310
	Total Fe	2328

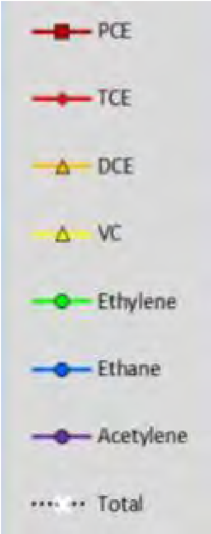


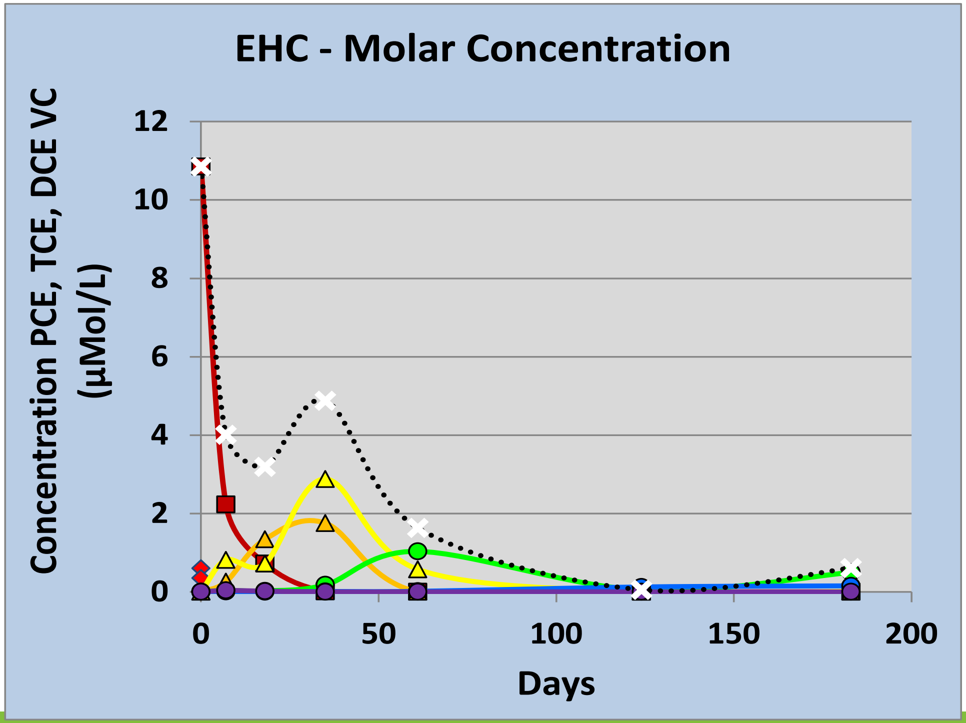
PCE Degraded both Biotically and Abiotically











Case Study 2:

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GeoForm™ Soluble & Extended Release For Treatment of CEs

- San Francisco Bay area
- Very high concentration chlorinated ethenes (CEs) (10s mg/L)
- Moderate sulfate groundwater (~ 400 mg/L)
- Low DO, slightly reducing
- GW flow rate ~ 50 feet per year

Client wanted very aggressive approach

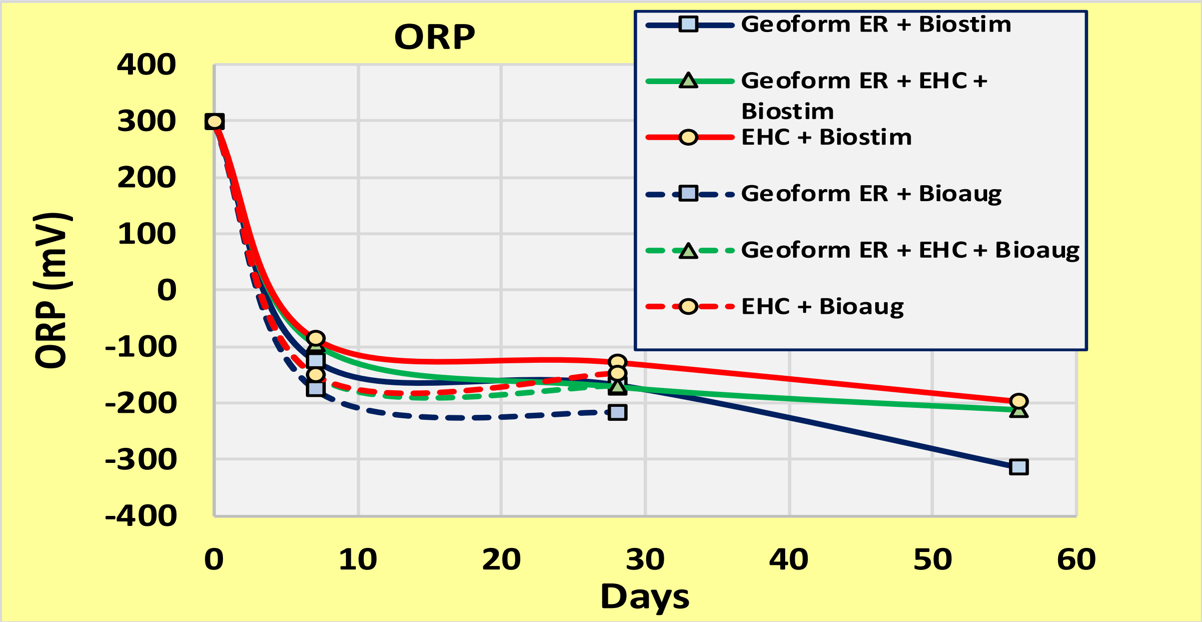
Evaluated BGCR, ERD, and ISCR

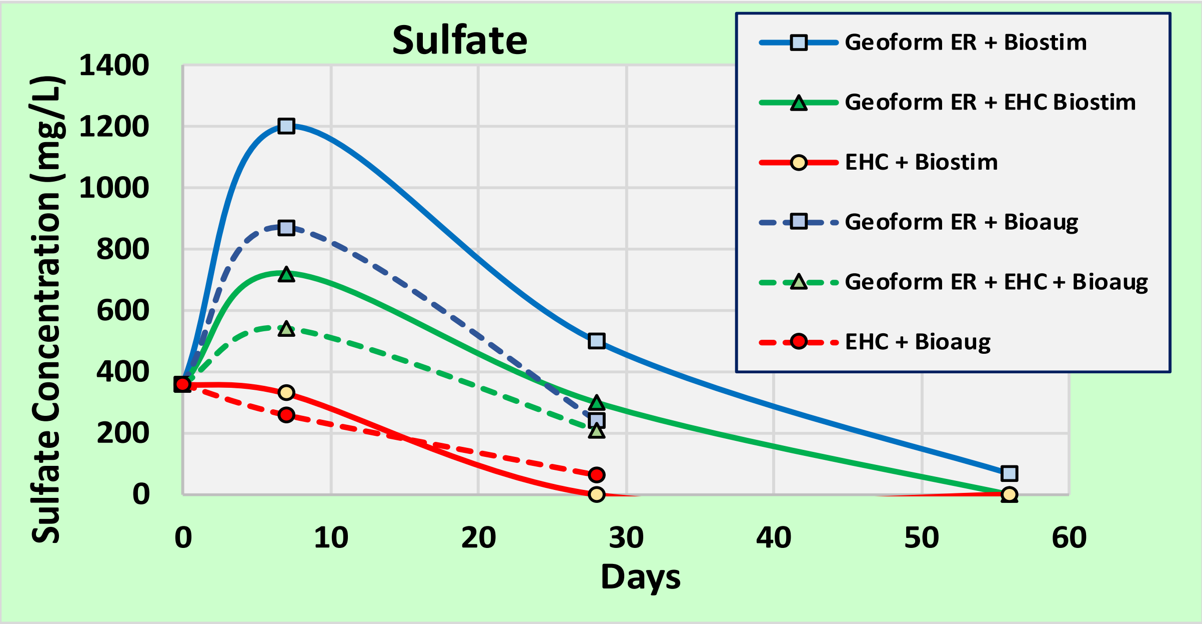
Simultaneous Laboratory Batch, Column Tests and Field Pilot Test

Subsequent Full-Scale Field Application

Case Study 2: Batch Test Results

PeroxyChem





Bench Test compared:

- **EHC® Reagent**
- **GeoForm™ Extended Release + EHC**
- **GeoForm™ Extended Release**

With ambient sulfate (~ 400 mg/L)

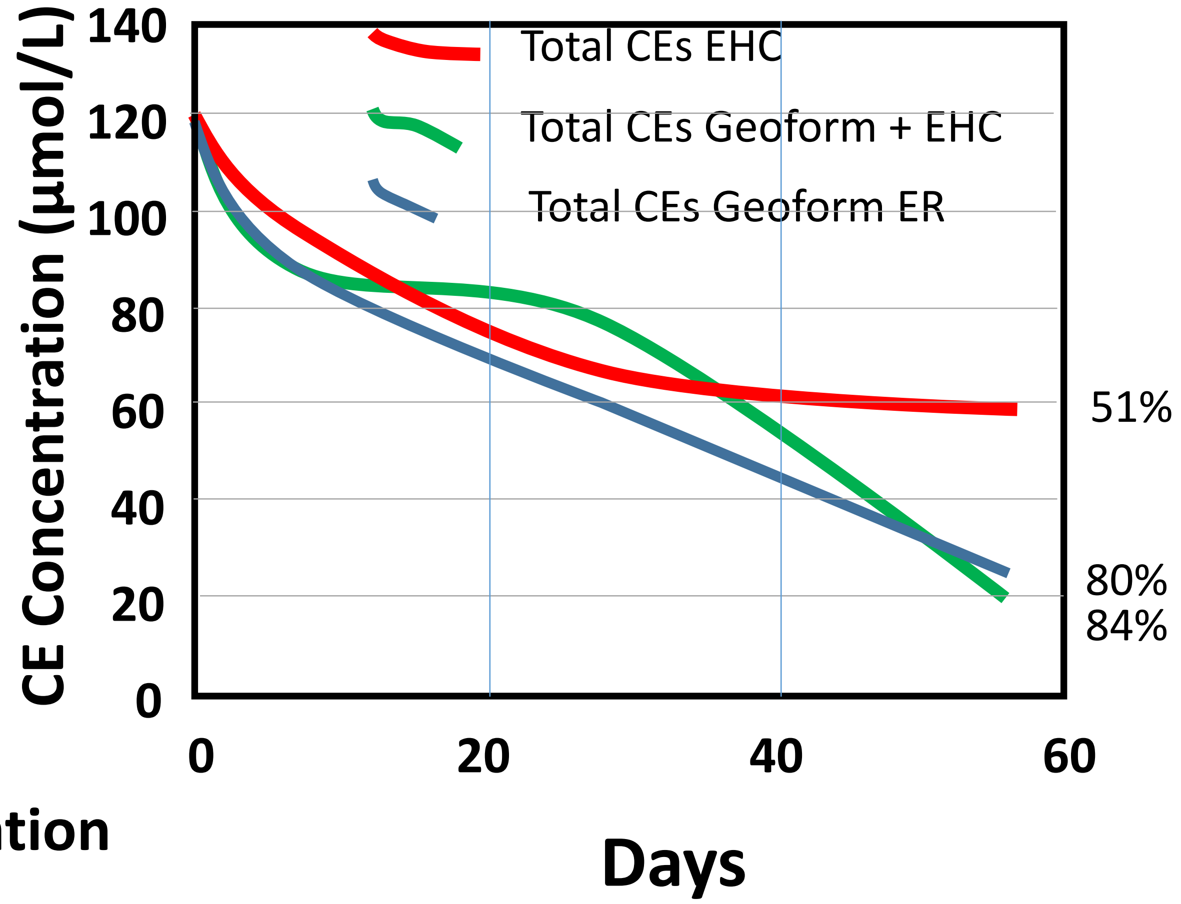
With and without bioaugmentation (SDC-9™)

Case Study 2:

GeoForm™ Extended Release Increases EHC Degradation Rates

GeoForm™ Extended Release + EHC® Reagent
+ 67% Increase

GeoForm™ Extended Release
+ 58% increase



Results are similar with or without bioaugmentation

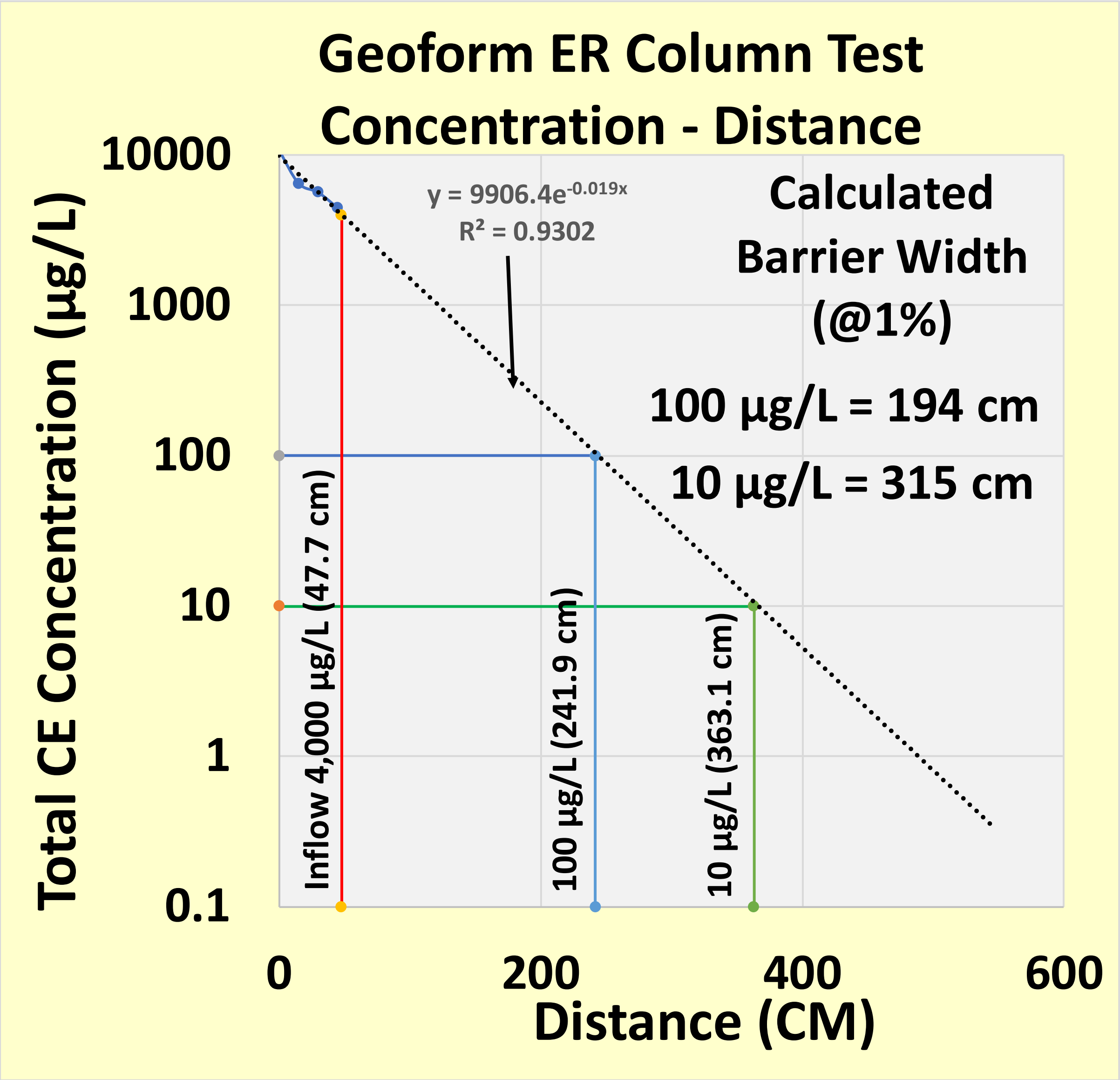
Case Study 2: Column Studies

Determine TCE Degradation rates

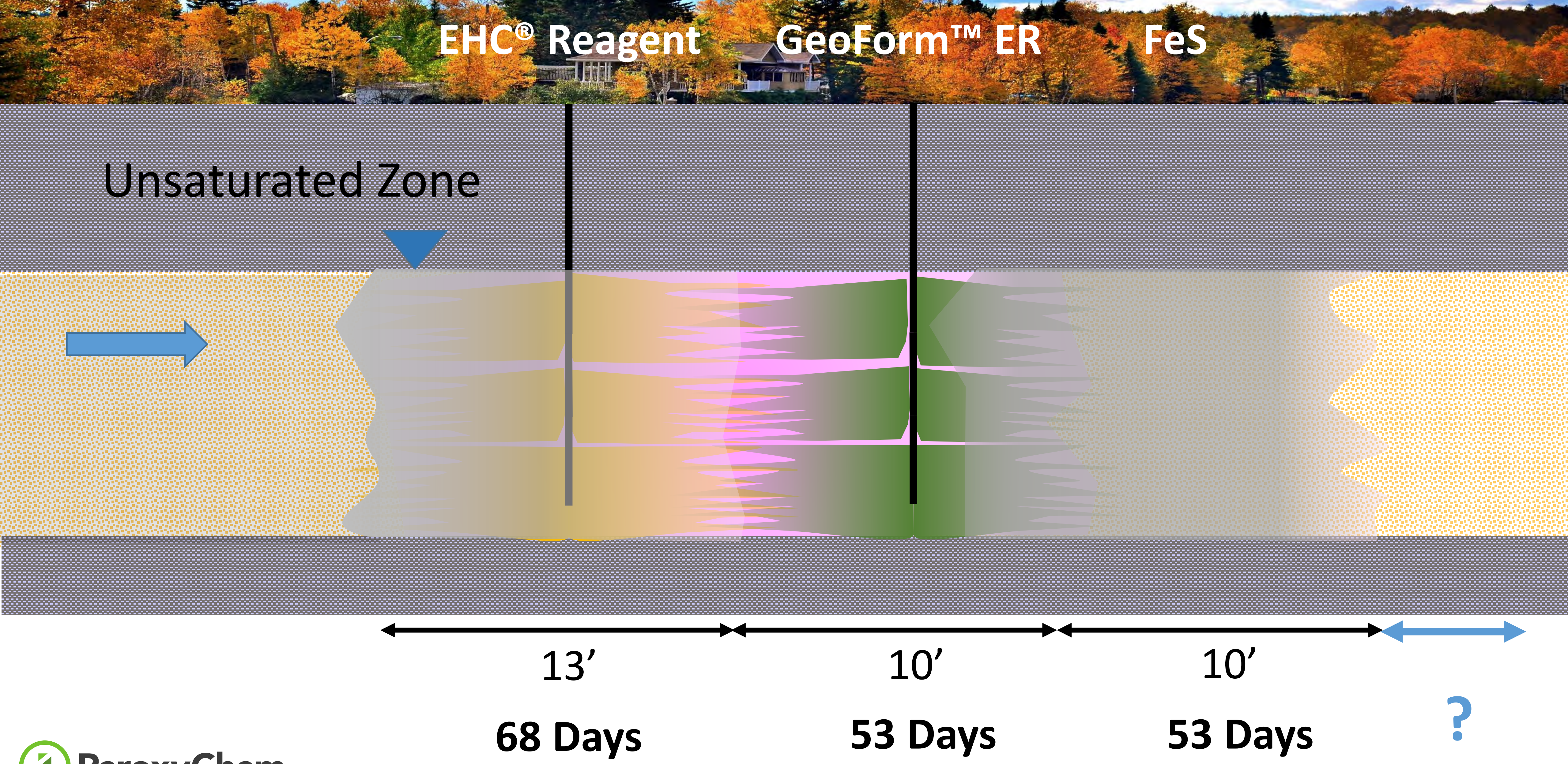
Determine PRB Width & Residence Time

Site Soil and Groundwater

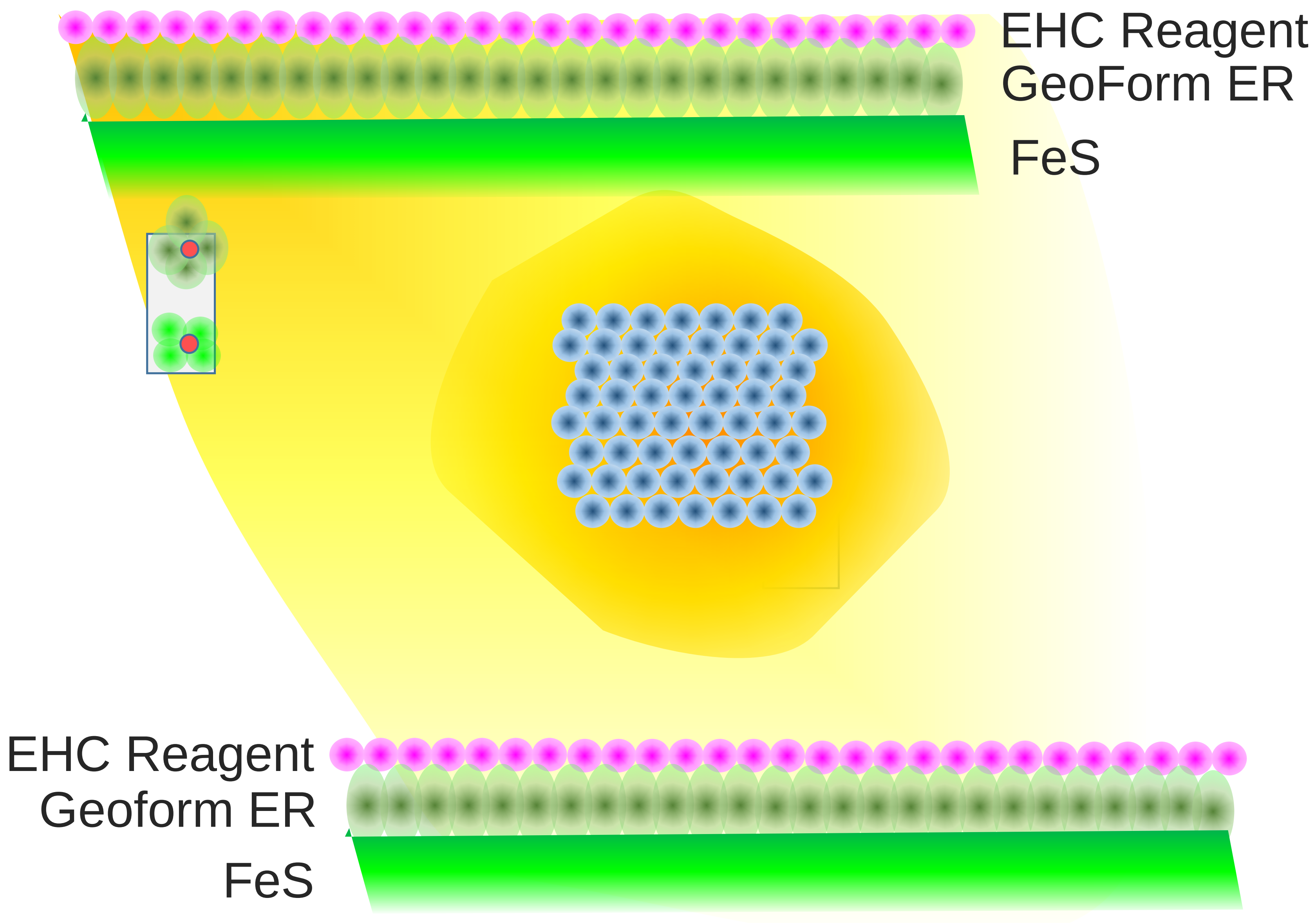
1X and 2X GW flow rate



PRB Construction



Case Study 2: Full Scale



Pilot Test Area

GeoForm Soluble

GeoForm Extended Release (ER)

Hot Spot – EHC Liquid

Permeable Reactive Barriers

EHC 13’ dia

Geoform ER 10’ dia

FeS ~ 10’ downgradient

Treatment zone ~32.5’

Residence time – 173 days

SF = ~3

Case Study 3:

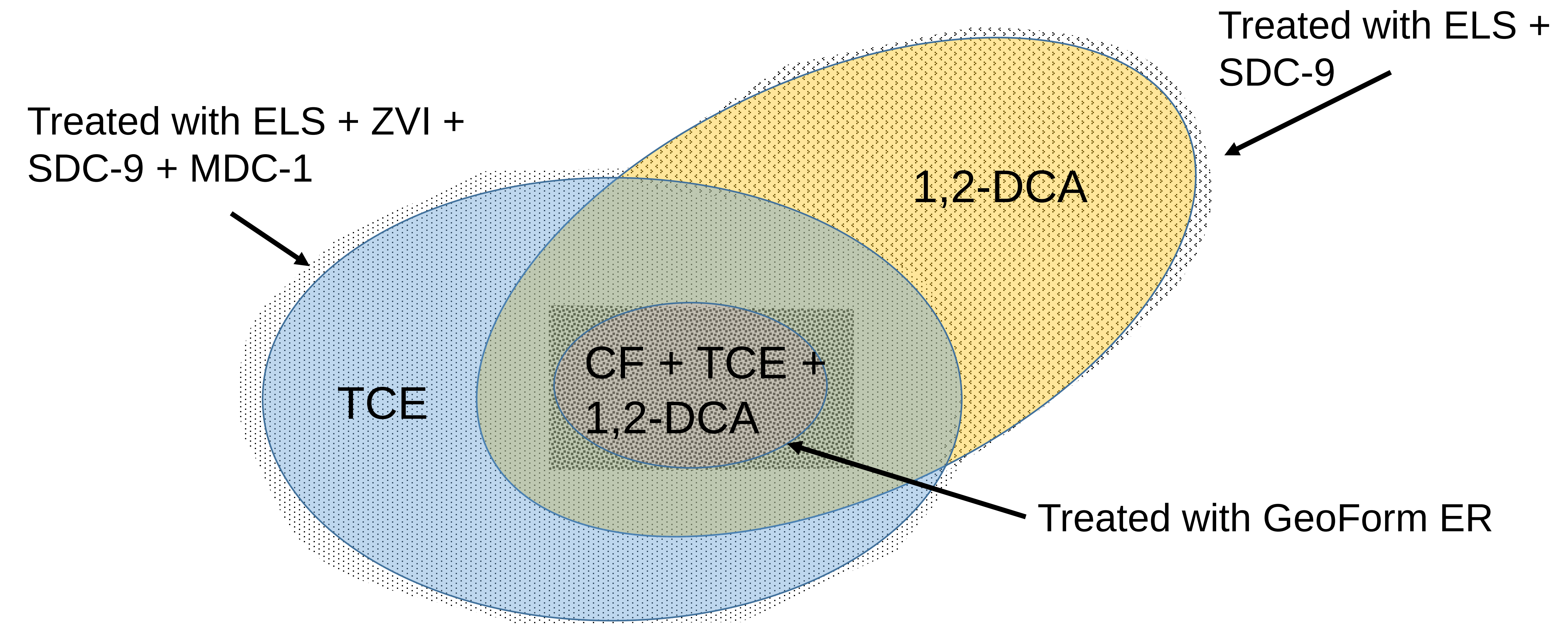
Nearby Site GeoForm™ ER Application

- San Francisco Bay area
- High sulfate (~700 mg/L)
- Mixed plume (TCE, 1,2-DCA, CF)
- 1 Recalcitrant area

- Property being developed
- Client wanted aggressive approach
- Sequentially applied reagents appropriate for contaminants

Case Study 3:

Treatment of Mixed Plume



Case Study 3:

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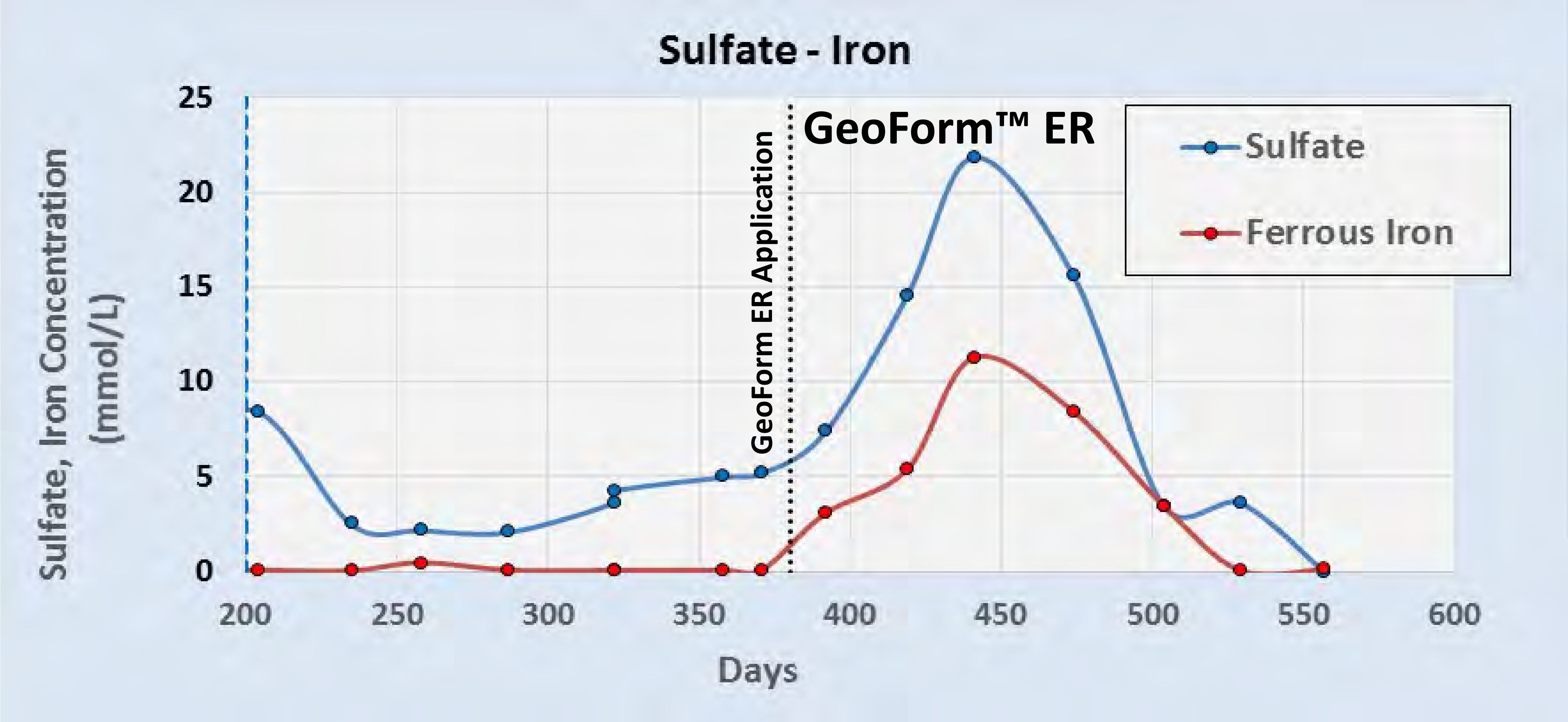
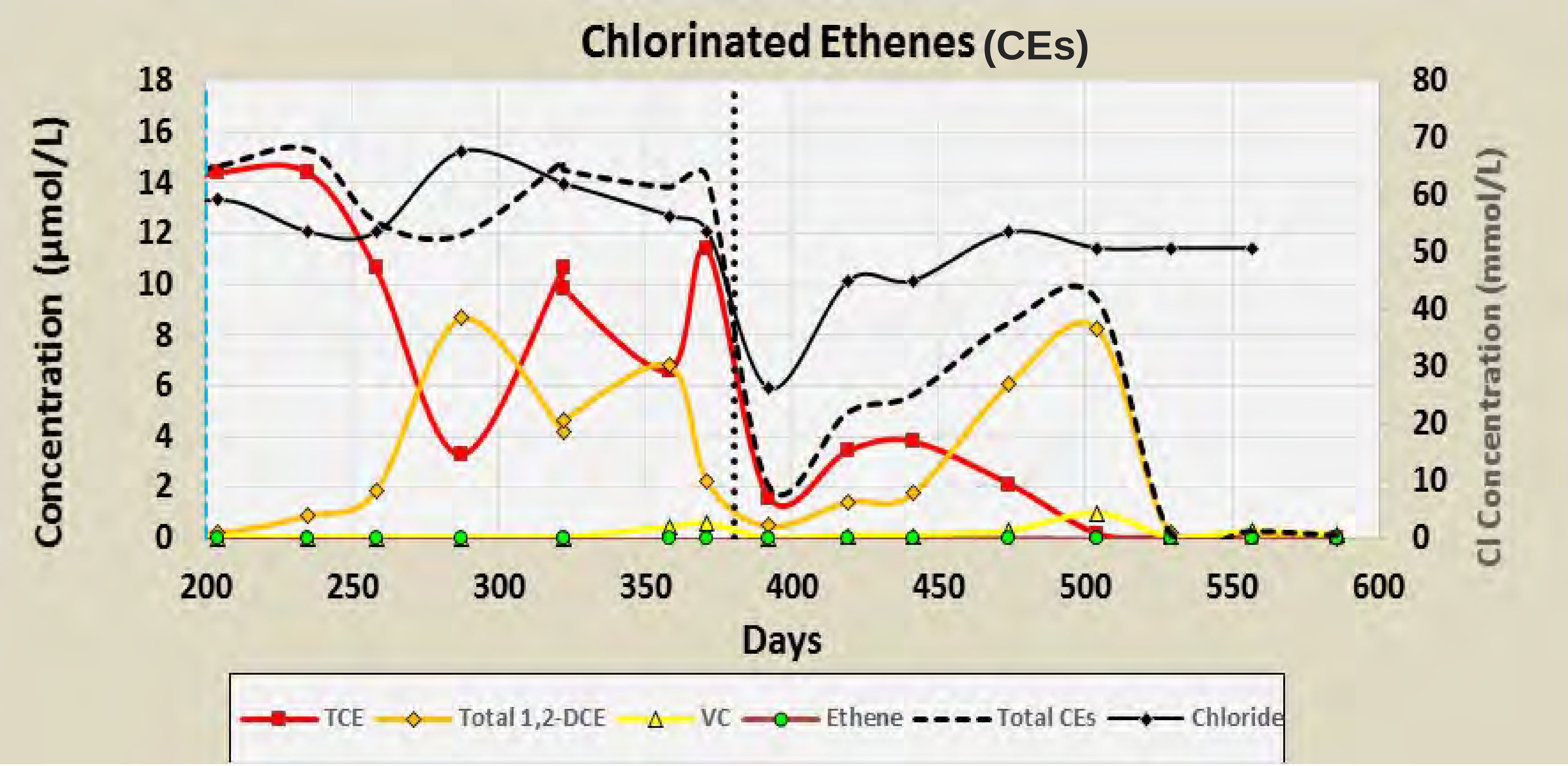
Sulfate & Iron Increase following GeoForm™ ER Application



Case Study 3:



Chlorinated Ethenes (CEs)
Concentration (µmol/L)
18
16
14
12
10
8
6
4
2
0
200
250
300
350
400
450
500
550
600
Days
80
70
60
50
40
30
20
10
0
Cl Concentration (mmol/L)
TCE
Total 1,2-DCE
VC
Ethene
Total CEs
Chloride

Case Study 3:

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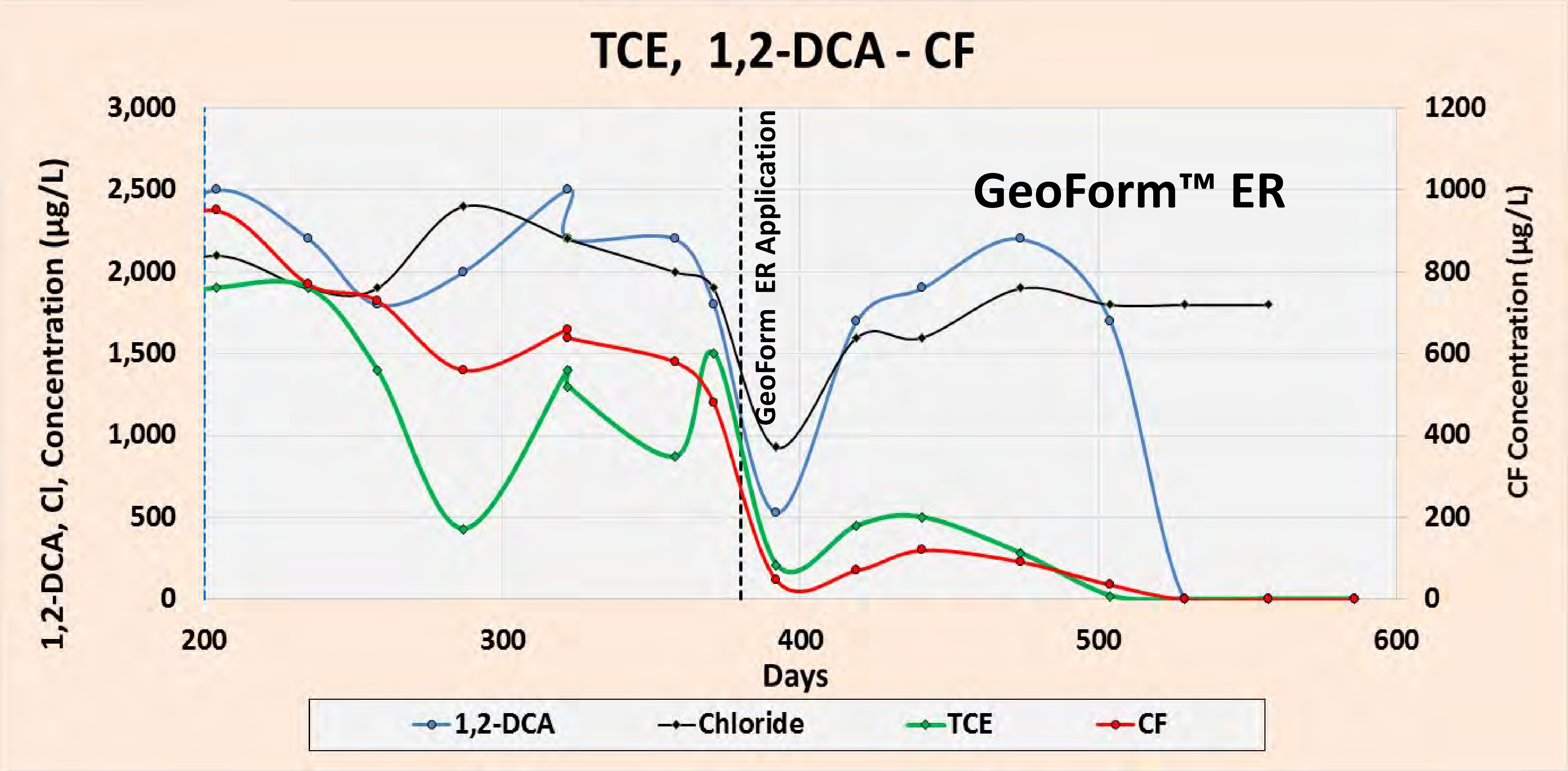
GeoForm ER treats mixed CEs, CA and CMs



Case Study 4:

Treatment of Arsenic with GeoForm™ Biogeochemical Reagents

Site in Florida

Carbonate aquifer

Soil and groundwater impacted with arsenic (As)

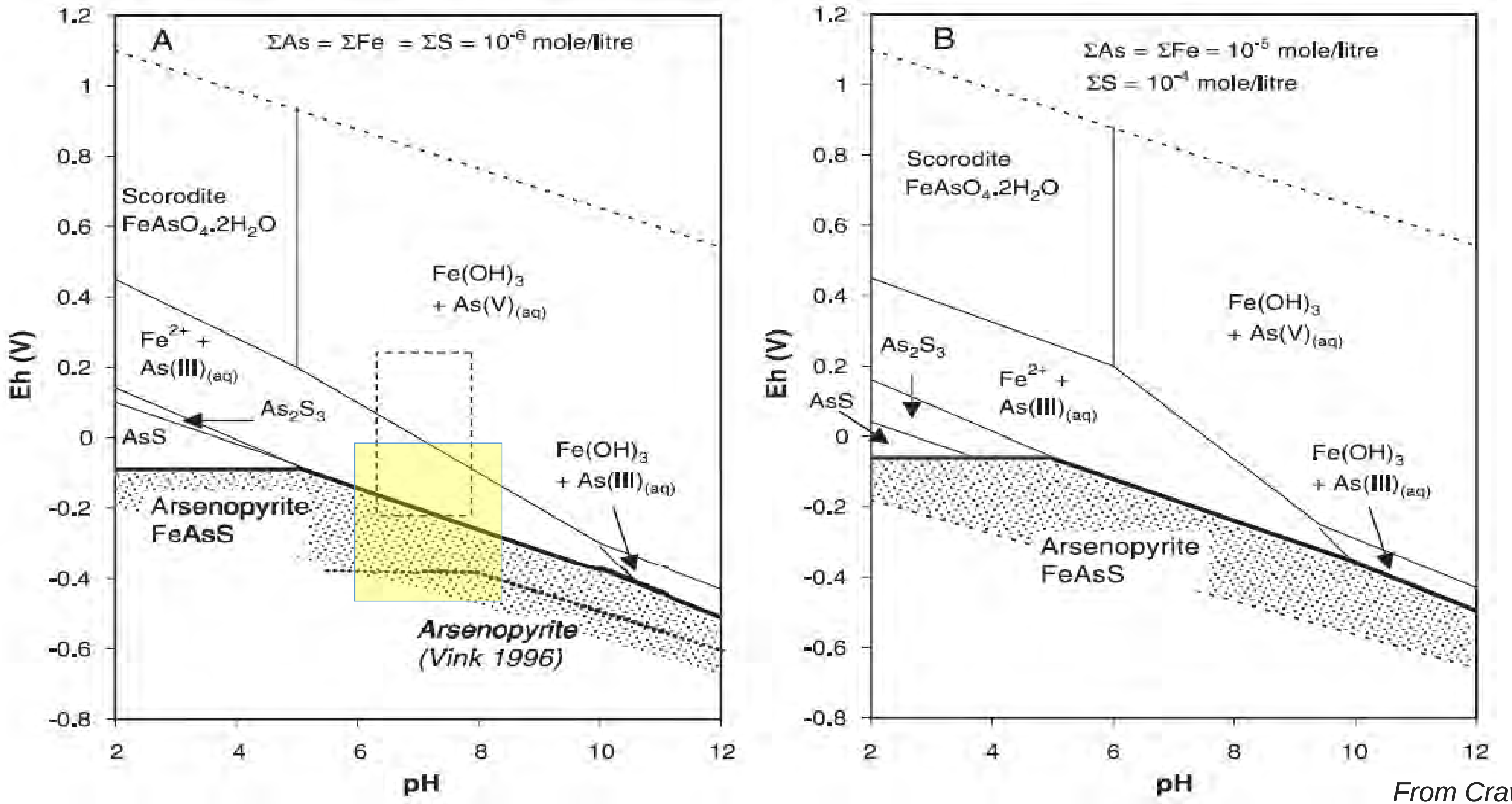
Cattle Dip?

Several hundred µg/L

Bench tests conducted to evaluate GeoForm™ ER for treatment of As.

Case Study 4:

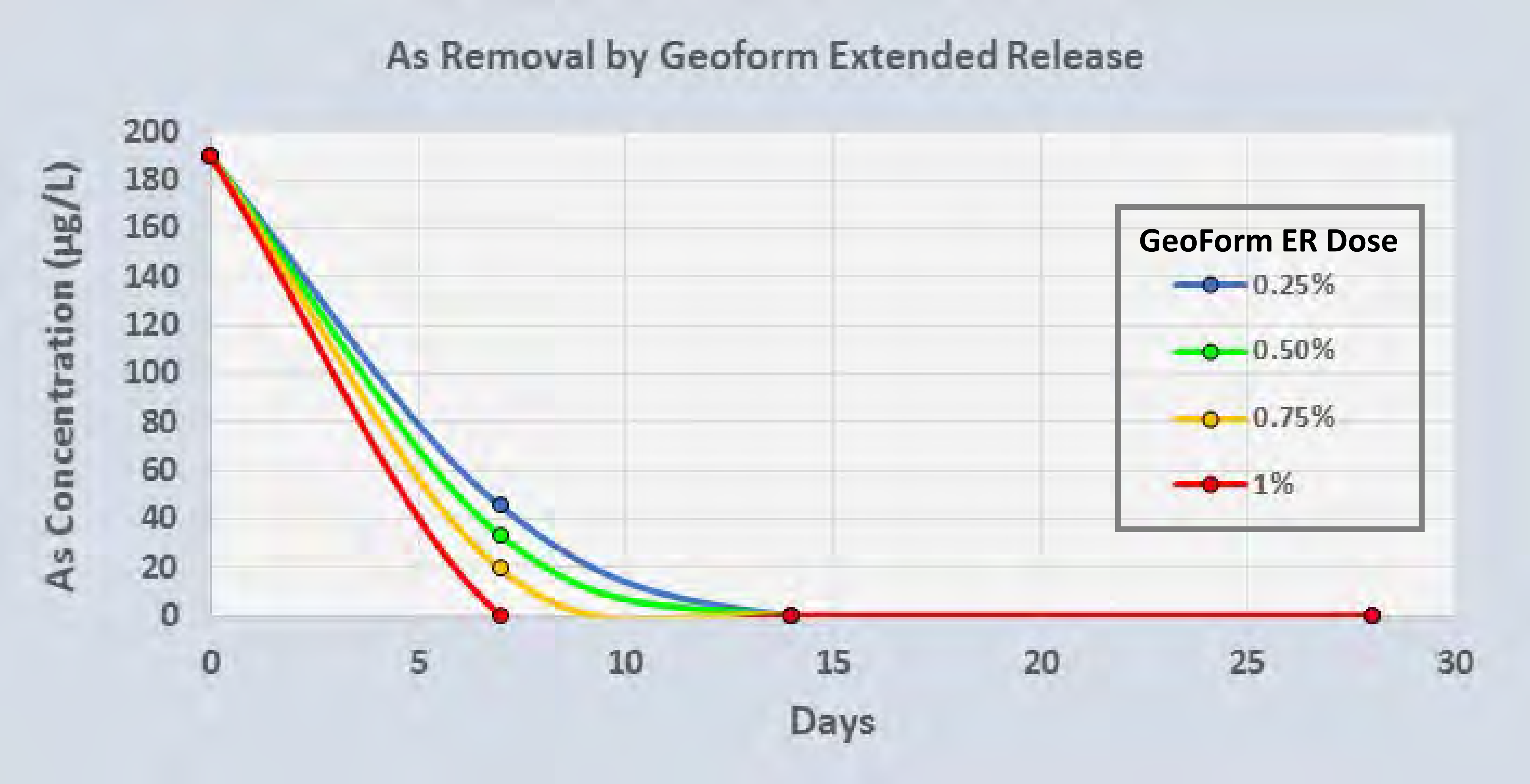
Co-precipitation/adsorption of Arsenic in the presence of dissolved Fe and S



From Craw et al. (2003)

Case Study 4:

GeoForm™ ER Treats As



Arsenic Stabilization in a Column Test
Influence of changing DO and pH

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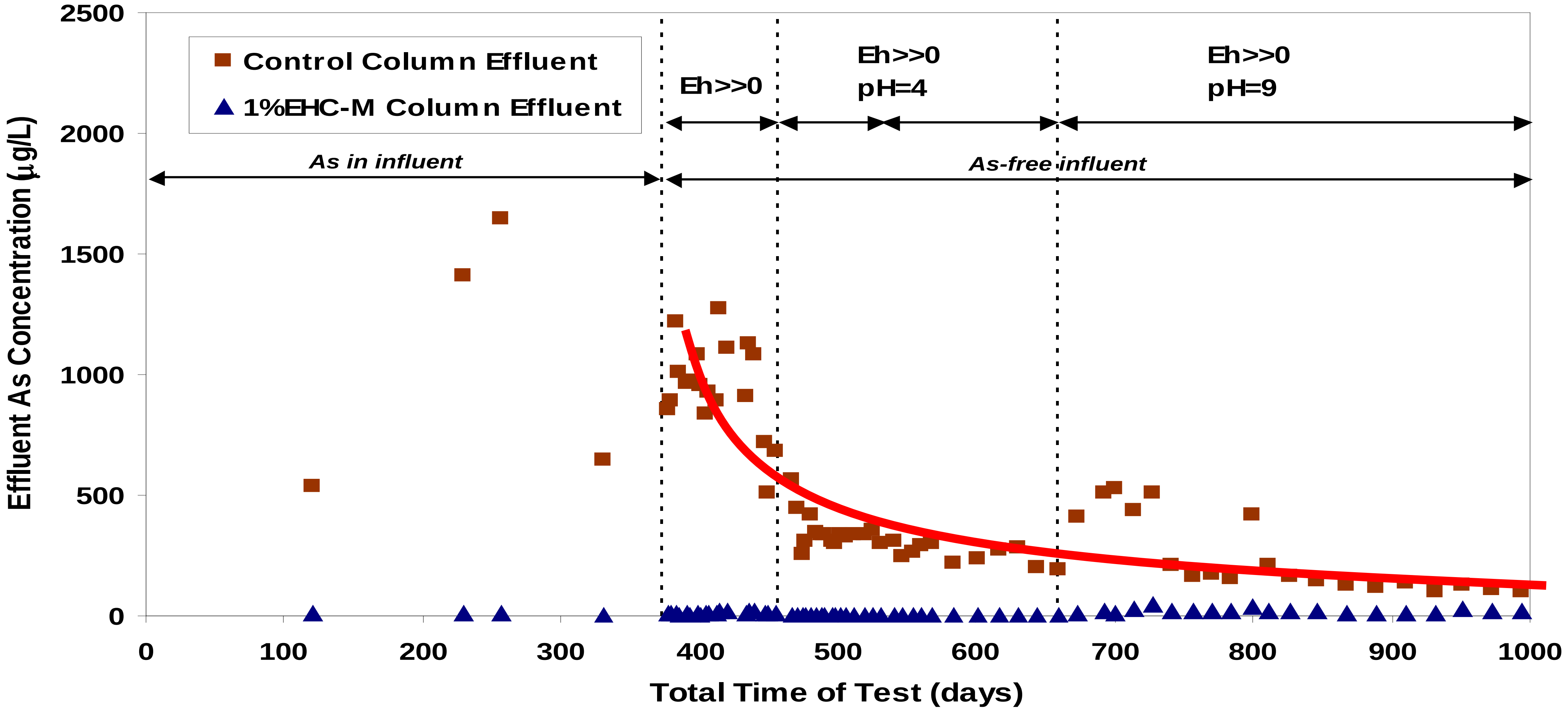
Column: 13 cm long and 5 cm Ø, Flow rate = 50 mL/d, Residence time = 2 days



By Andrzej Przepiora

Conclusions

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Biogeochemical Reduction (BGCR) is a naturally occurring process.

BGCR processes occur with and 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)

GeoForm™ extends the size and longevity of treatment zones

GeoForm™ sequesters toxic metals from groundwater for extended periods of time

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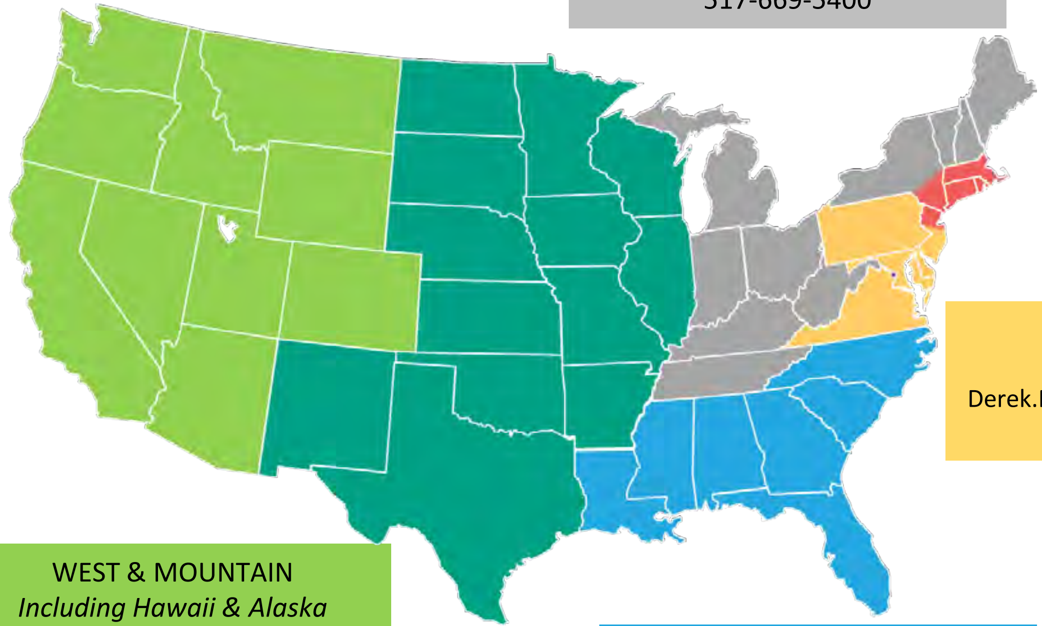

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Questions ????

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