Environmental Solutions

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Bench-Scale evaluation of FeS/CVOCs + Klozur® One

Mike SUMMERSGILL/PeroxyChem UK & Ireland

YCLF Sheffield – 27th February 2018

Environmental Solutions

PeroxyChem

Field-Proven Portfolio of Remediation Technologies Based on Sound Science

***In Situ* Chemical Oxidation**
- Klozur® SP
- Klozur® One
- Klozur® KP
- Klozur® CR

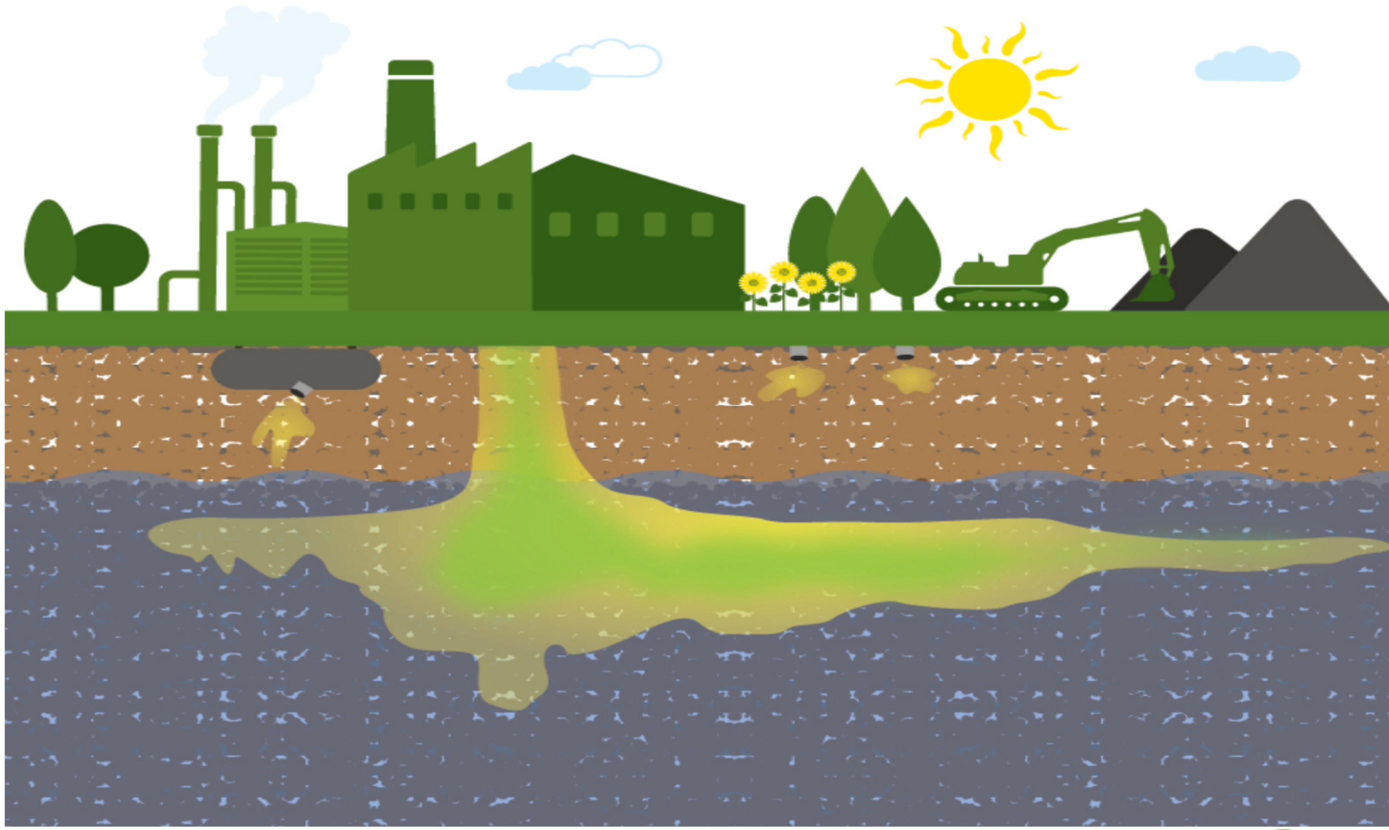
***In Situ* Chemical Reduction**
- EHC® Reagent
- EHC® Liquid
- Daramend® Reagent

Aerobic Bioremediation
- Terramend® Reagent
- PermeOx® Ultra & PermeOx® Ultra Granular

Metals Remediation
- MetaFix® Reagent

Enhanced Reductive Dechlorination
- ELS® Microemulsion & ELS® Concentrate

NAPL Stabilization/Mass Flux Reduction
- ISGS® Technology



Bench-Scale Evaluation of the Formation and Reactivity of Iron Sulfide Minerals for Treatment of CVOCs

AUTHORS - Josephine Molin, Dan Leigh, and Alan Seech
PeroxyChem, LLC, Philadelphia, PA

Background

- Reactive iron sulfide minerals may be formed *in situ* under sulfate reducing conditions in the presence of iron and a source of sulfur.
- This effect has been observed during the application of traditional ISCR at sites with naturally high sulfate concentrations in groundwater, but may also be engineered by directly applying the needed building blocks.
- High degradation rates and long lasting results have been observed at ISCR sites with background sulfate, but no controls to quantitatively measure the impact of sulfate.
- The objective of these bench tests was to evaluate the effectiveness of biogeochemical systems relative to traditional ISCR and anaerobic bioremediation for the removal of CVOCs.

ISCR and BioGeoChem Mechanisms

Mechanism	Component	Description
Direct Chemical Reduction	ZVI	• Redox reaction at iron surface where solvent gains electrons and iron donates electrons • Abiotic reaction via beta-elimination
Biological Reduction	Organic Carbon Substrate / H_2	• Anaerobic reductive dechlorination involving bacteria • Strongly influenced by the nutrient profile and the pH of the aquifer
Geochemical Reduction	SO_4 + Fe(II)	• Surface dechlorination by reactive iron sulfide minerals • Abiotic reaction via beta-elimination

Building Blocks for Engineering Iron Sulfide Minerals In Situ

Source of sulfate / sulfide
(gypsum, iron sulfate salts, Epsom salts etc)

Source of Fe(II)
(ZVI, soluble Fe(II) salts, Fe lactate etc)

H donor / reductants
(various organic carbon substrates available – ELS, fibrous organic carbon etc)

SULFATE REDUCING CONDITIONS

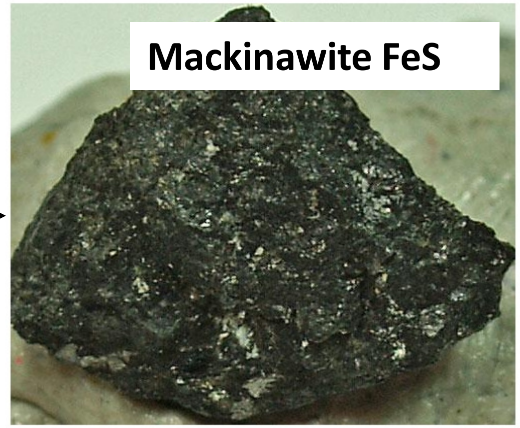
Sulfate reduction by SRBs:

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

Precipitation of Ferrous Iron with Sulfide:

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

where: CH_2O represents organic carbon



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Direct Dechlorination Reactions on ZVI Surfaces

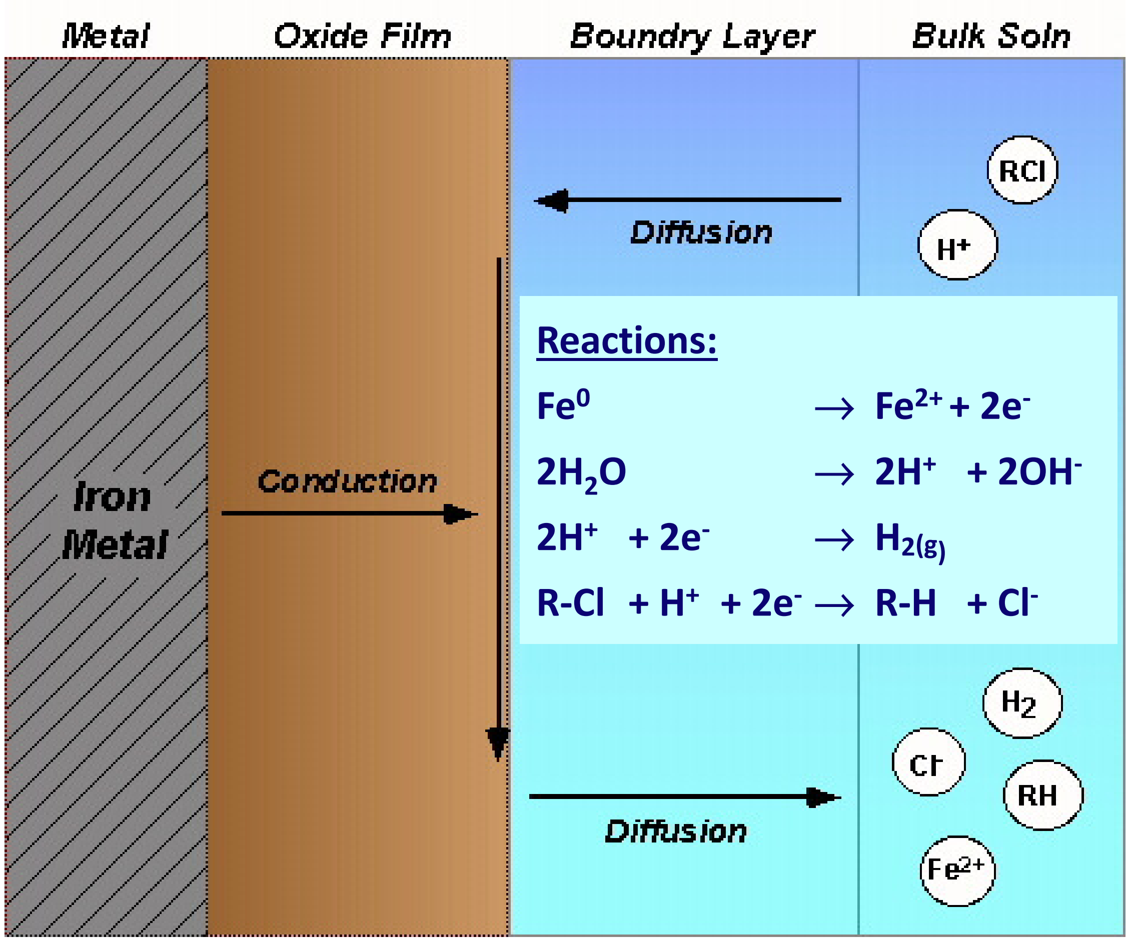

Figure Courtesy P. Tratnyek, Oregon Graduate Institute

- Abiotic dechlorination reactions occur in **direct contact** at the groundwater and ZVI particle / reactive mineral surface interface.
- Distribution critical to establish contact.
- Potential advantages of generating reactive minerals *in situ* compared to directly applying reductive minerals or ZVI as solid particles include:
  - Greater reactive surface area.
  - Improved subsurface distribution.

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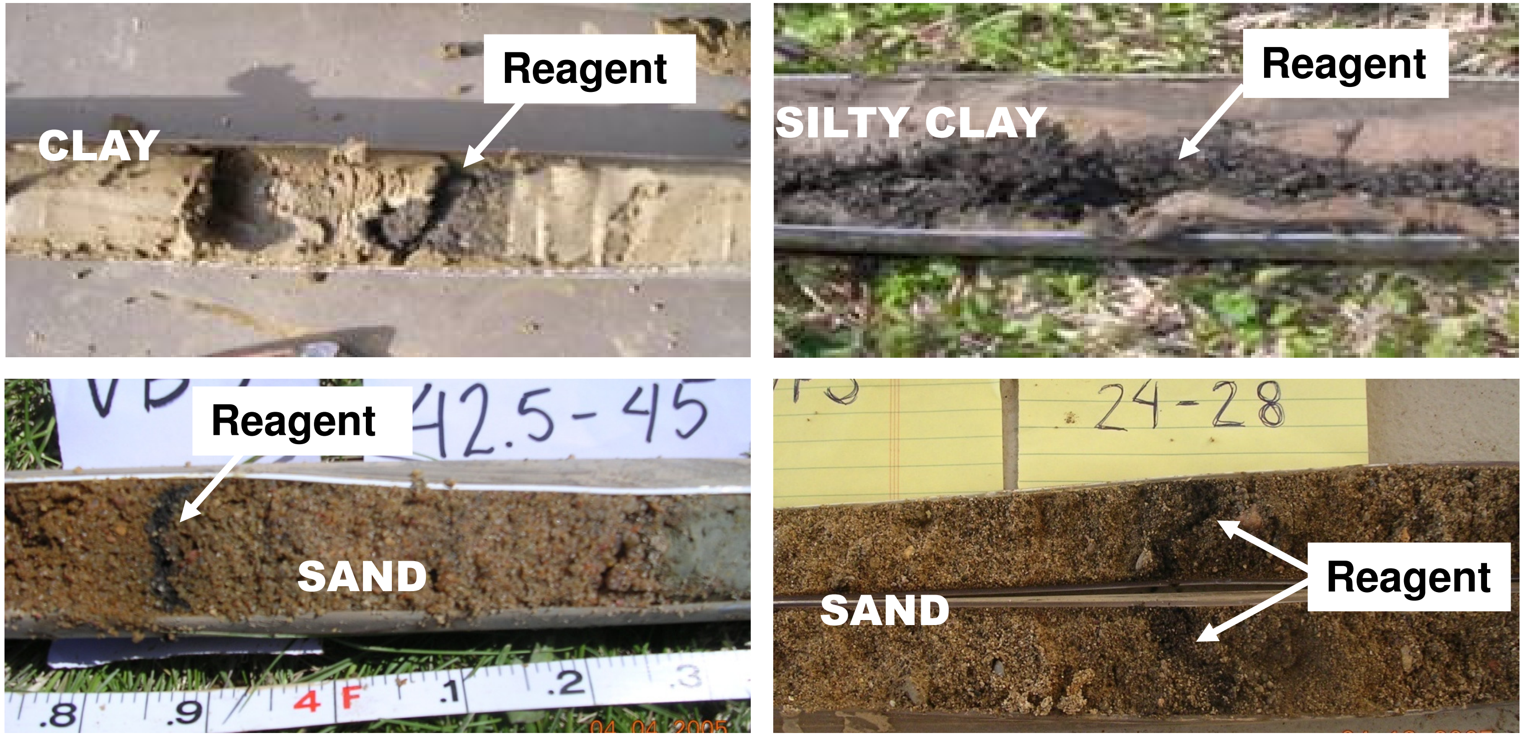
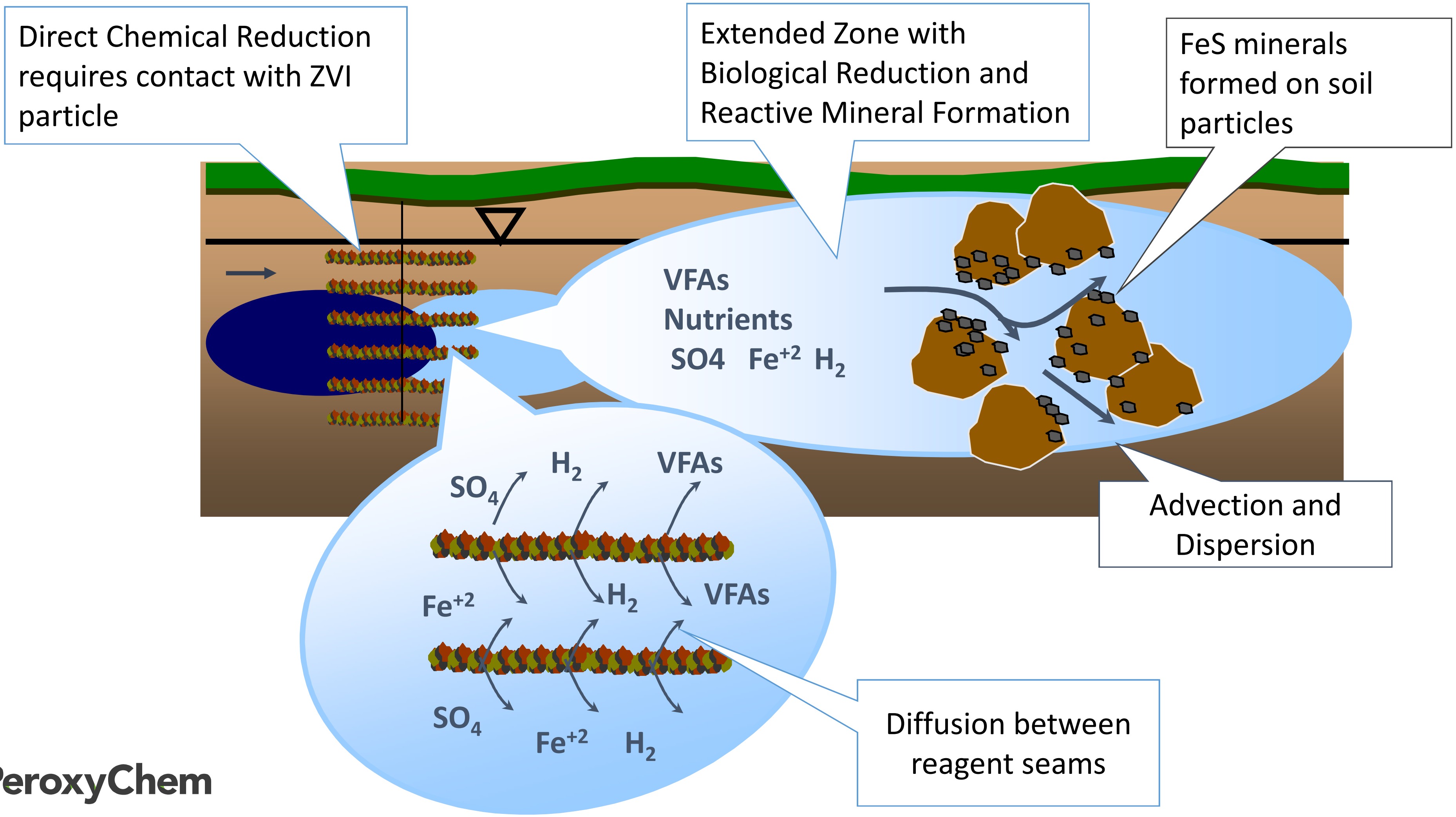
Typical Granular Reagent Distribution: Soil Cores with EHC Reagent Seams



- Granular reagents with ZVI has been observed to displace into discrete bands during injection.
- Direct chemical reduction with ZVI is limited to reagent distribution upon implementation.

Reductive Mechanisms Zone of Influence



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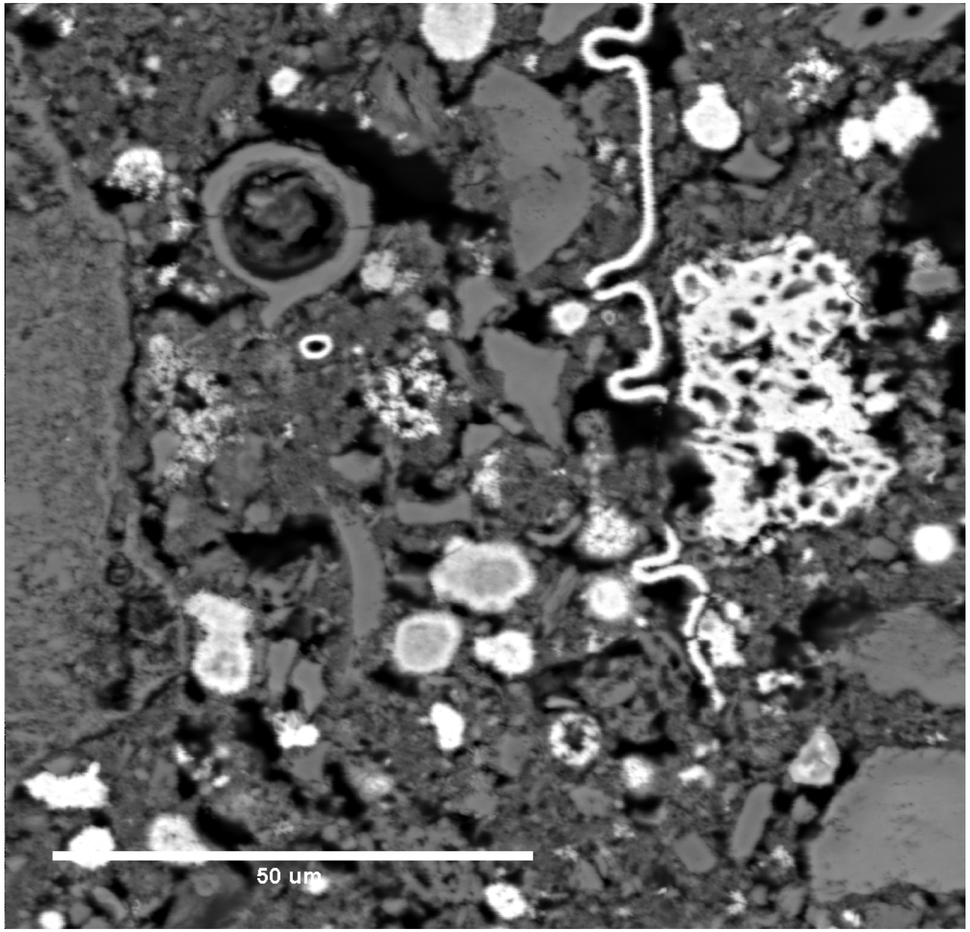
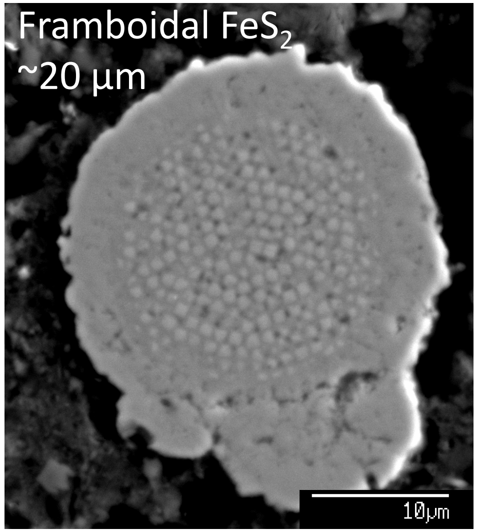
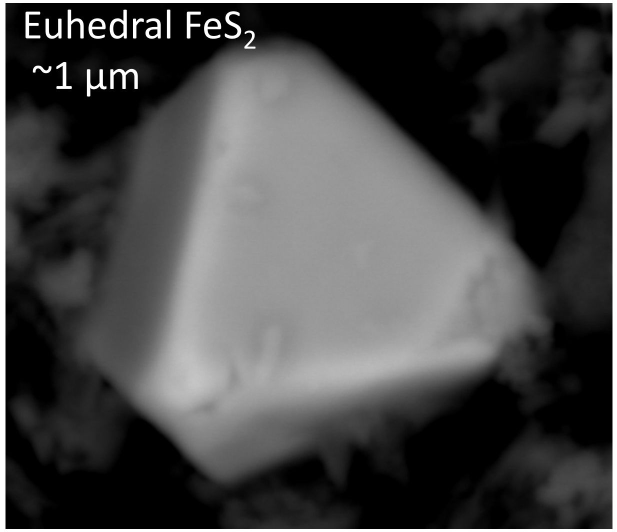
Electron Microprobe Analyses of FeS Precipitates







- Electron microprobe analyses of the precipitates 1 year after application of organic substrate (lactate) and ferrous iron to high sulfate aquifer (3,000 mg/L SO_4)
- Estimate: each 1.0 L of groundwater with sulfate at 3,000 mg/L reduced to 3.0 µm thick FeS precipitates will yield about 4.7 ft^2 of very reactive surface

Reference: Leigh et al, 2012

Smaller Grain Size = Larger Surface Area

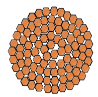
Euhedral Pyrite
~1 µM

~200 m²/Kg

FeS Coatings
~3 µM

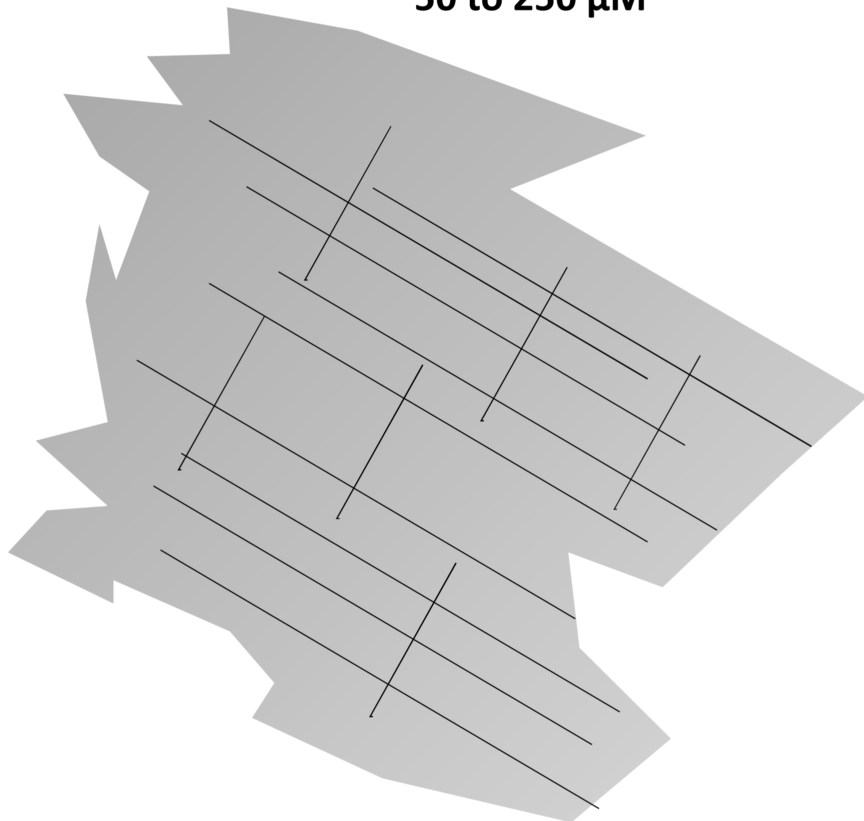
~80 m²/Kg

Framboidal Pyrite
~20 µM



~20 to 50 m²/Kg

Microscale ZVI
~50 to 250 µM



~5 to 20 m²/Kg

Reference: Leigh et al, 2012

Engineering BioGeoChemical Remediation Systems at the Bench Scale

- Objective:
  - Evaluate the effectiveness of biogeochemical systems relative to traditional ISCR and bioremediation for the removal of CVOCs.
- Bench studies:
  - Microcosm Study #1: EHC vs. EHC Liquid for treatment of PCE in high sulfate aquifer
  - Microcosm Study #2: ISCR vs. Bio vs. BioGeoChem for treatment of CVOCs in high sulfate aquifer
  - Microcosm Study #3: ISCR vs. BioGeoChem for treatment of CVOCs in low pH aquifer
  - Microcosm Study #4: BioGeoChem vs. Bio for treatment of CVOCs and Heavy Metals in low pH aquifer

Microcosm Study #1
(Data courtesy of SCS Engineers)

Site Conditions:

- Elevated PCE >2000 µg/L
- Sulfate up to 3,000 mg/L
- Aerobic Aquifer (DO ~5.0 mg/L)
- Previous bio only pilot tests unsuccessful - Potential sulfide inhibition

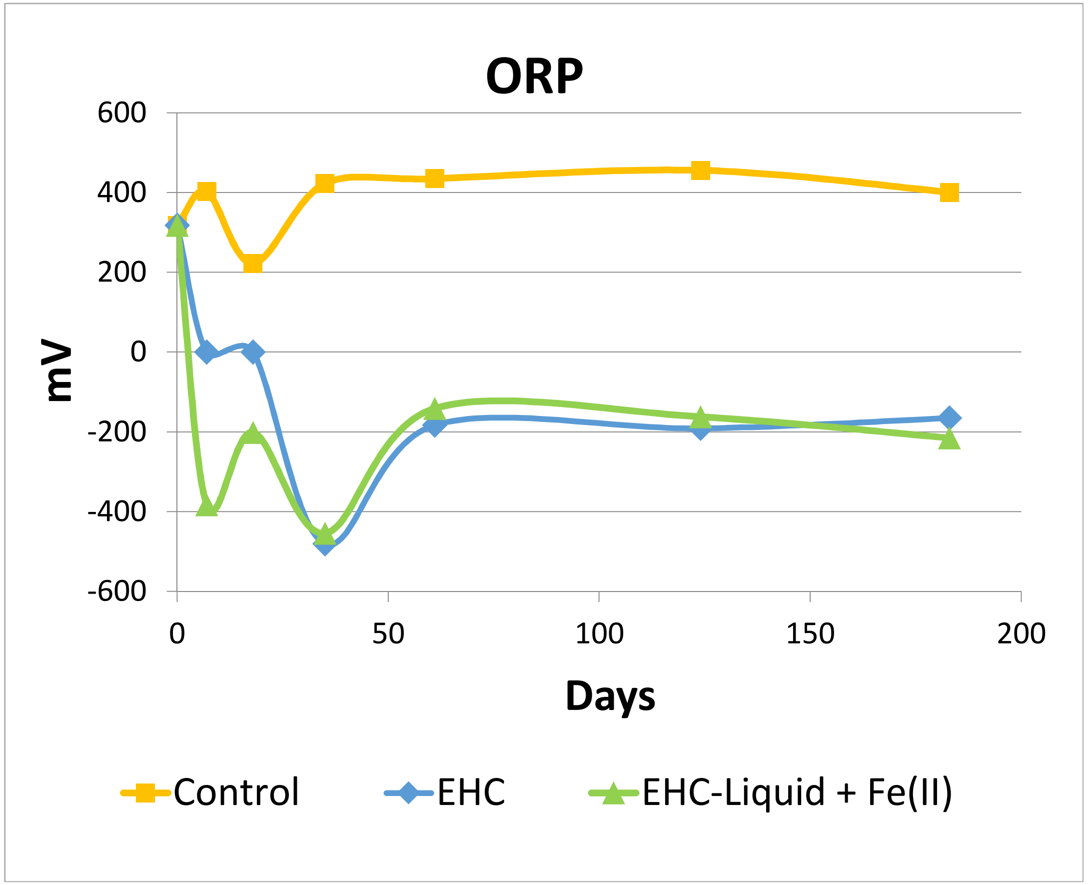
Bench Set-Up:

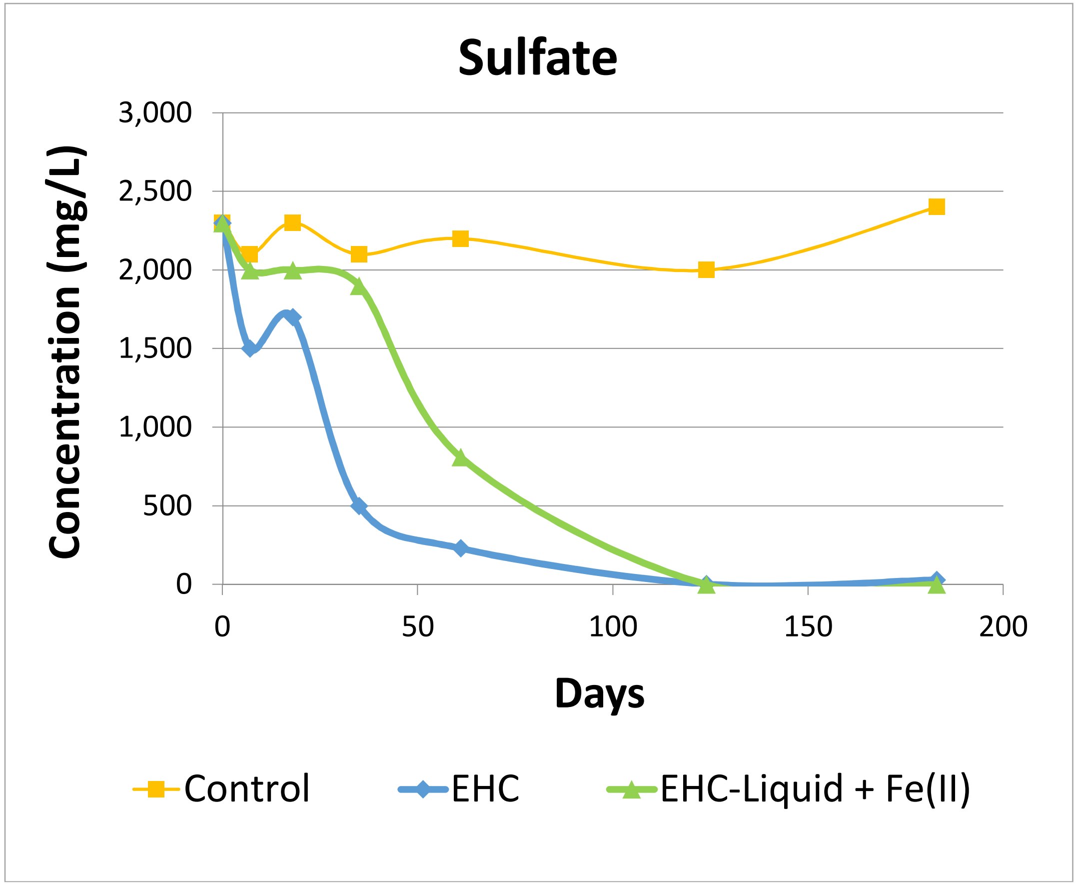
Microcosms set up with GW and sediment from the site:

- Control
- EHC: 10 g/L (60% organic carbon + 40% ZVI)
- EHC Liquid: 10 g/L ELS + 14 g/L ferrous gluconate

Treatment systems inoculated with DHC ~ $1X10^8$ Cells/L

Sulfate Reduction





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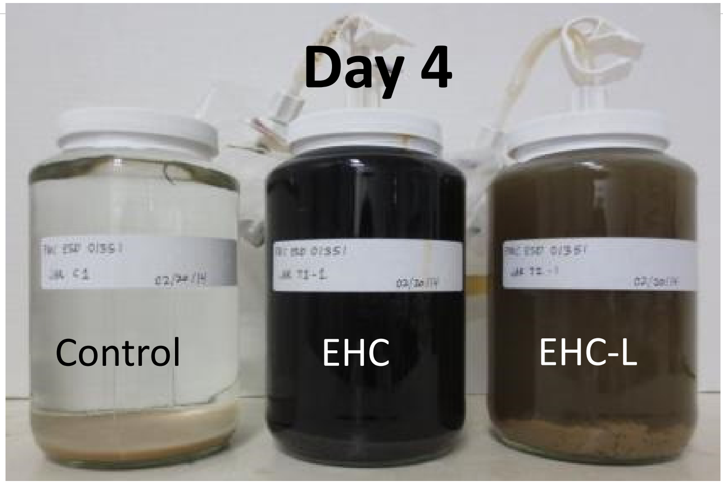
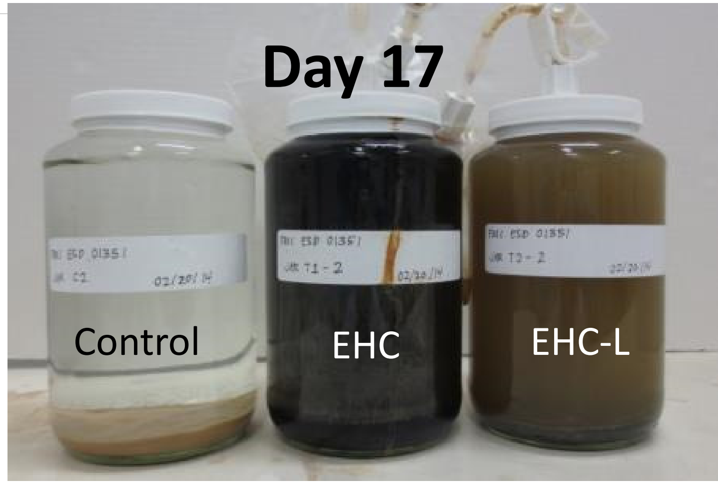
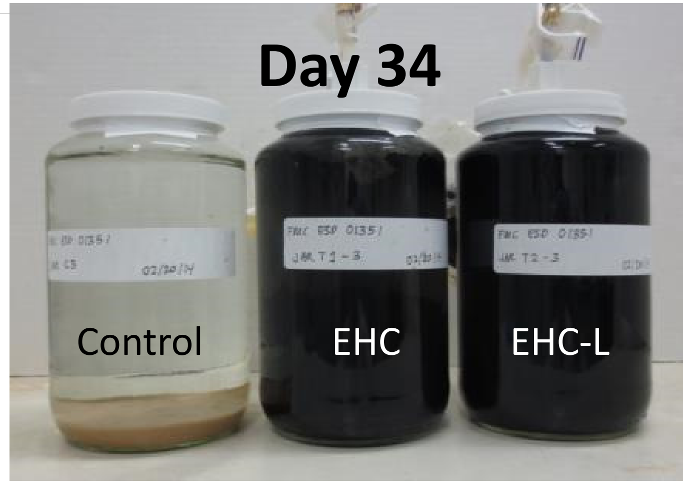
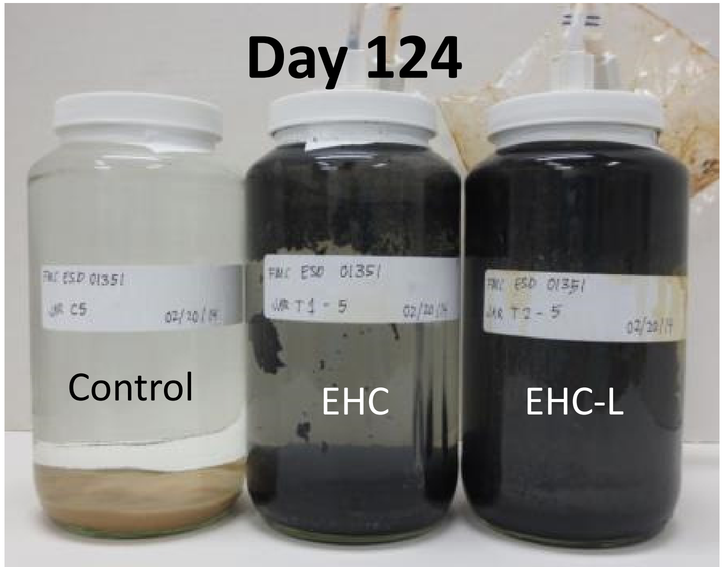
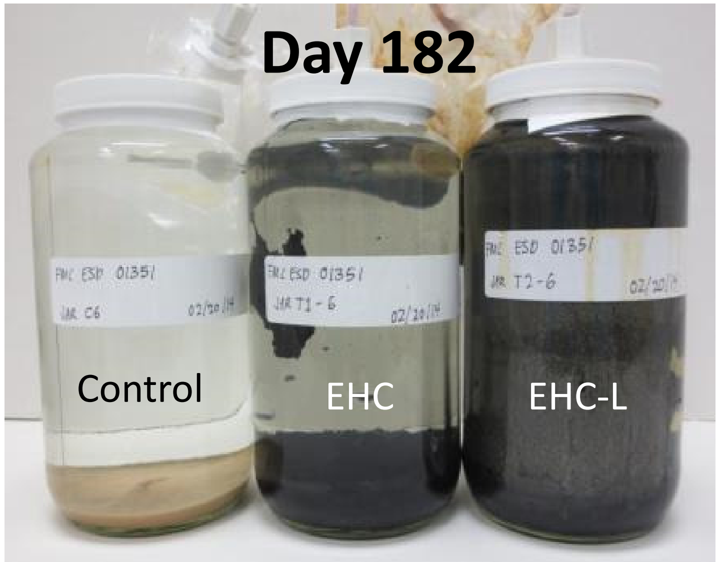
Visual Evidence of FeS Generation







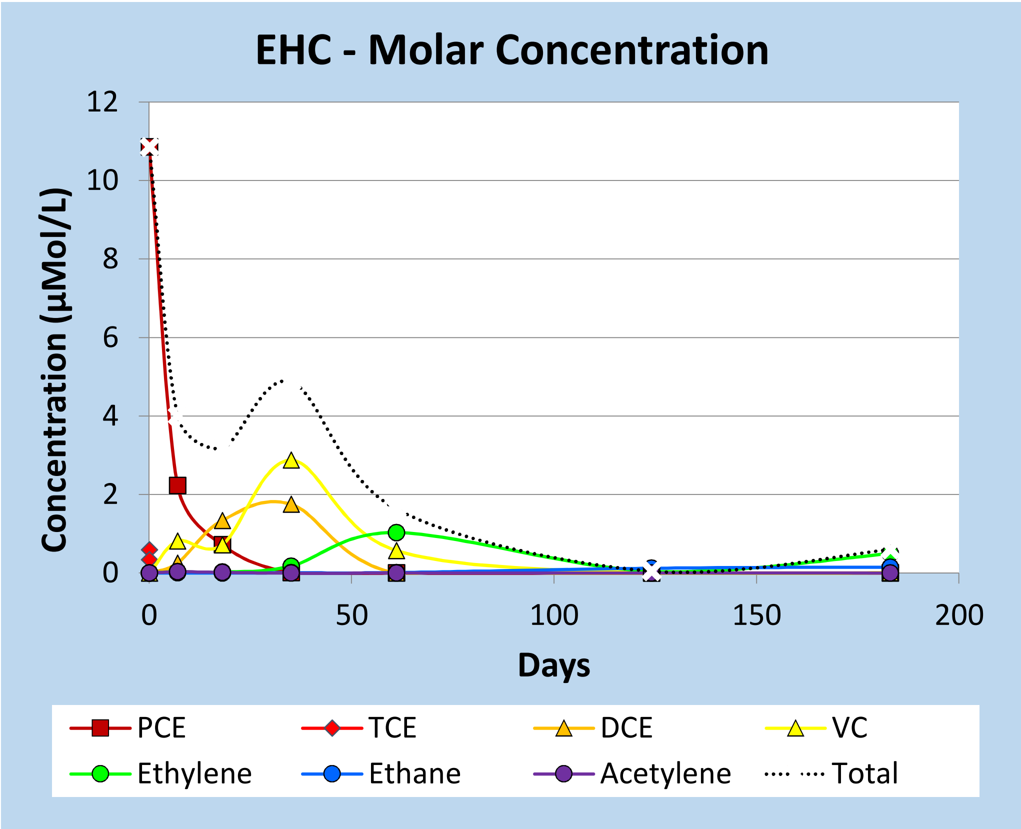


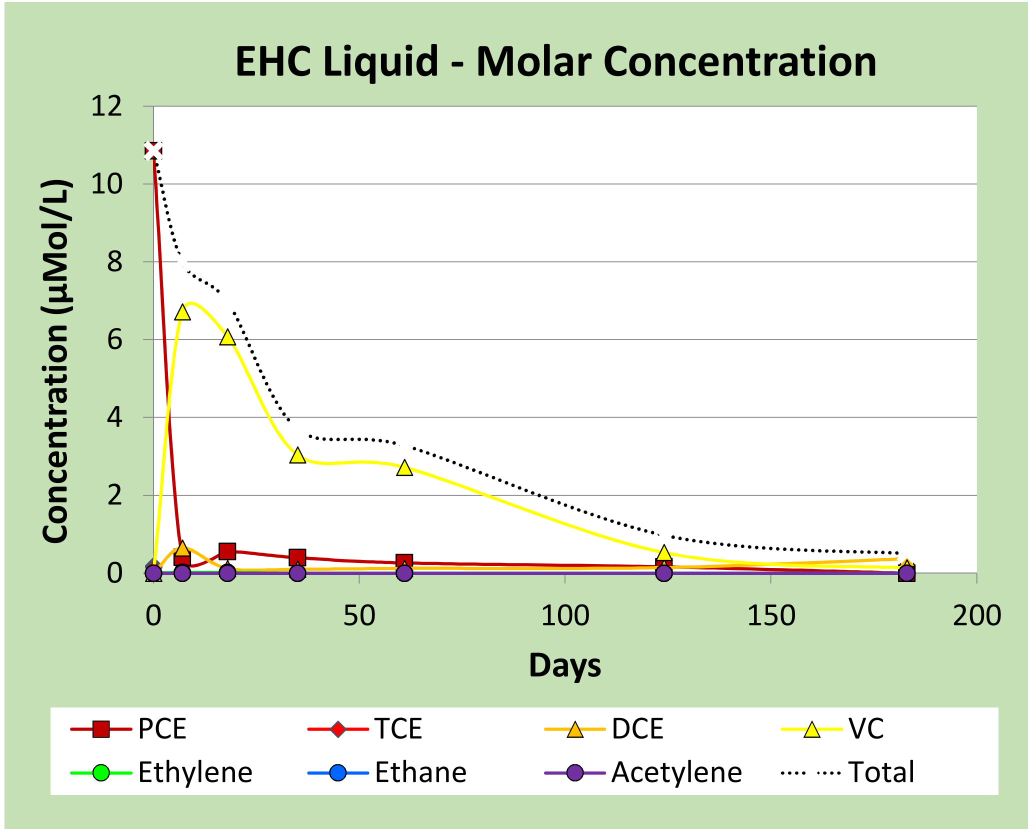


EHC Precipitate		
g/kg	Sulfide	31
	Total Fe	210
mMol/kg	Sulfide	967
	Total Fe	3,760

EHC Liquid Precipitate		
g/kg	Sulfide	42
	Total Fe	130
mMol/kg	Sulfide	1,310
	Total Fe	2,328

VOC Analytical Results





Less than Stoichiometric conversion to daughter products → Abiotic degradation pathway promoted in both systems

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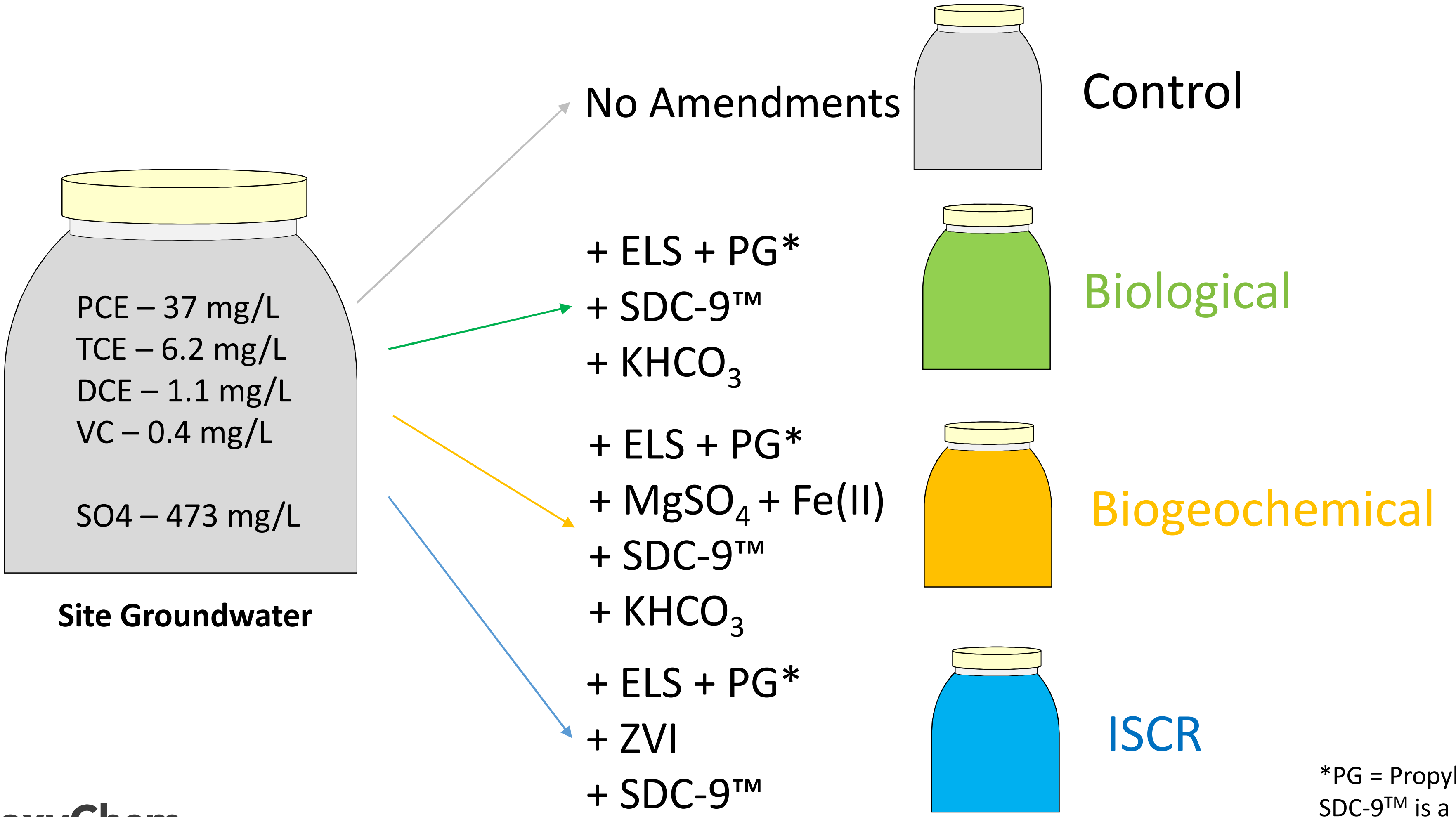
Microcosm Study #2

(Data courtesy of TEA Consultants)



*PG = Propylene Glycol
SDC-9™ is a trademark of CB&I

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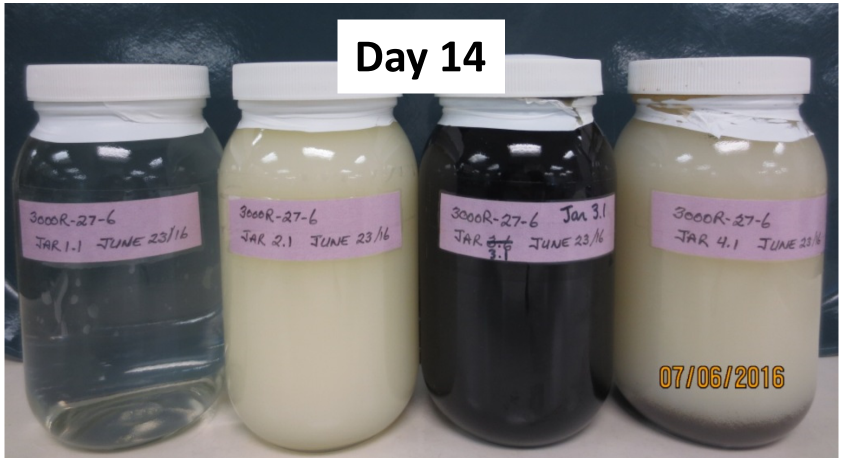
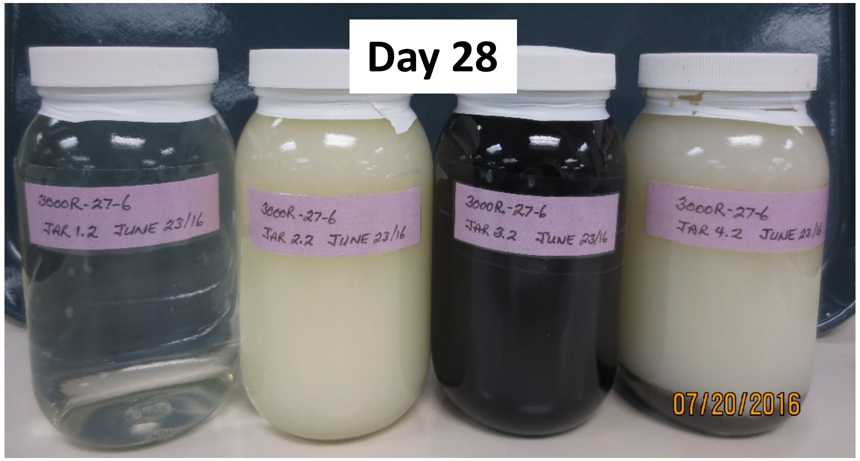
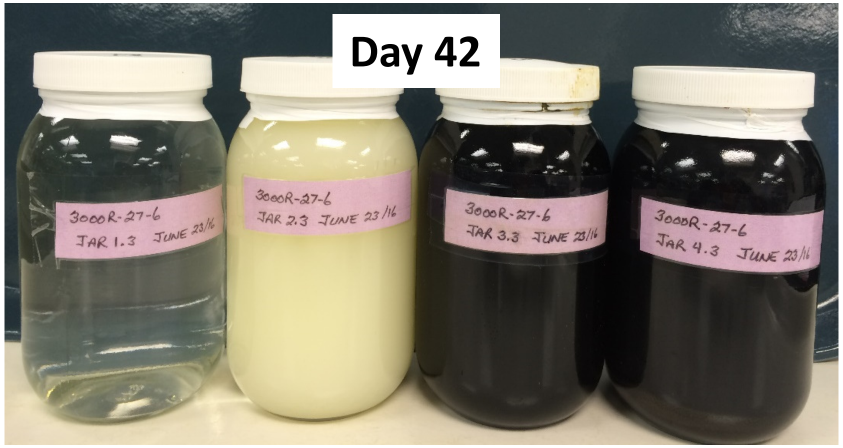
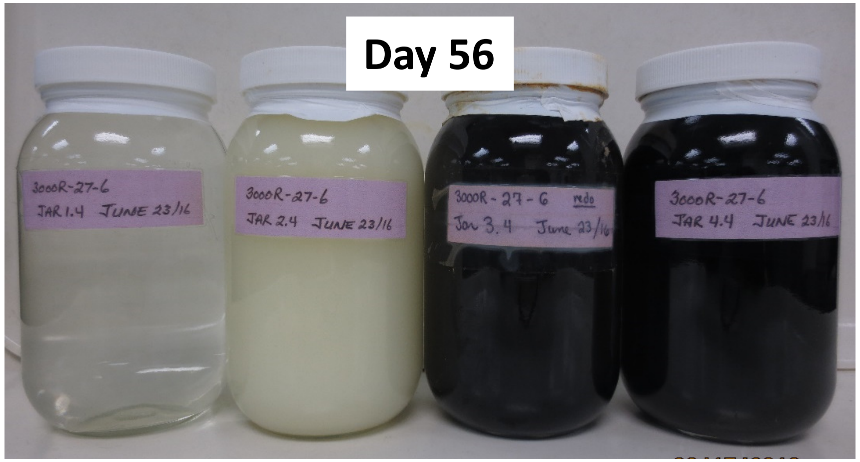
Visual Bench Test Results

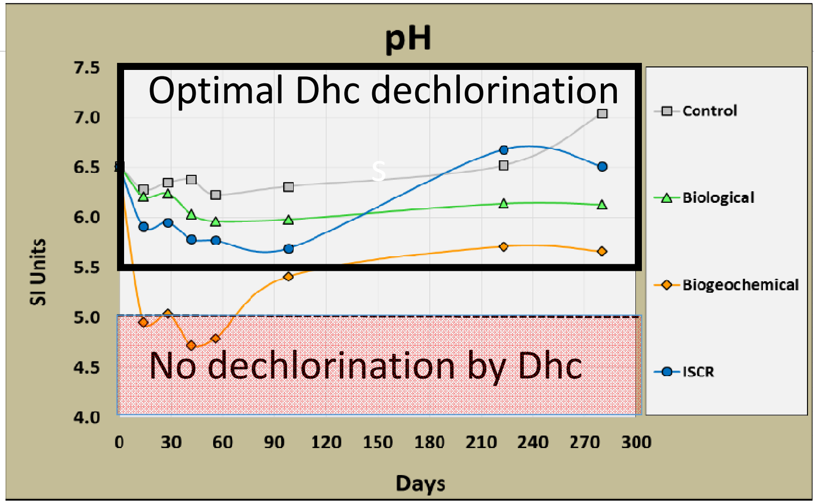


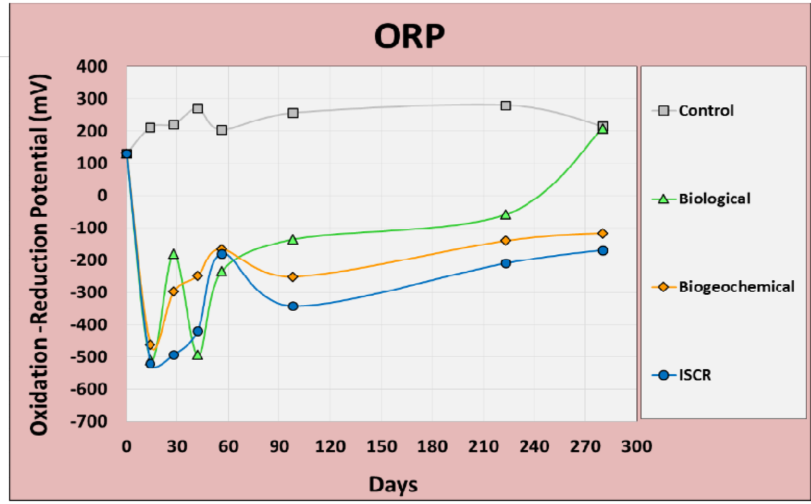


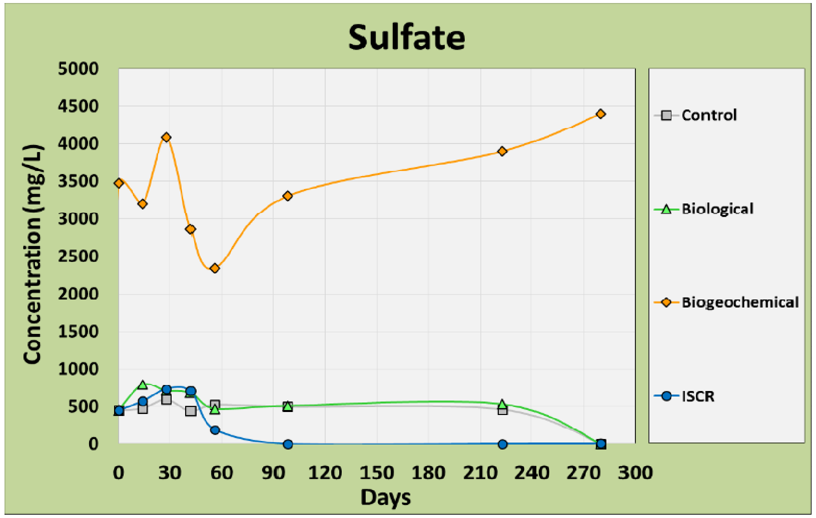


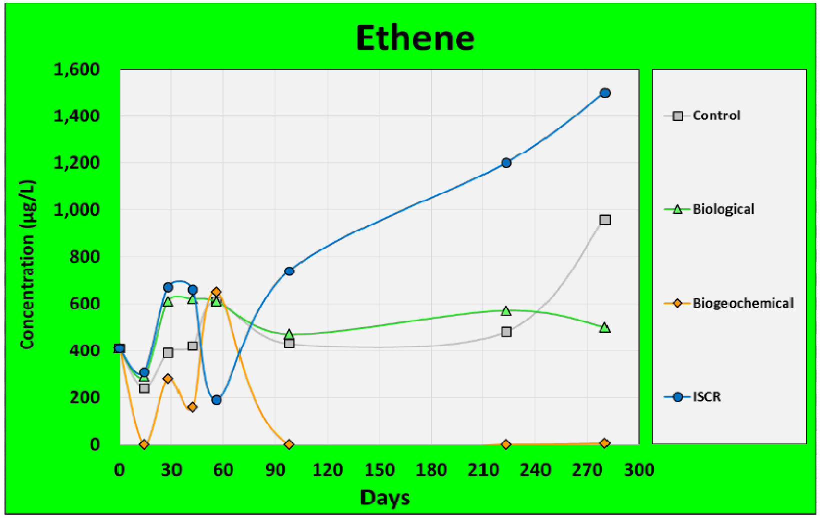


Geochemical Data









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Microcosm Study #3

(Data courtesy of Golder)

Site Conditions:

- CVOCs ~4,200 µg/L (mainly 1,1-DCE); Cr(VI) ~11 µg/L
- pH = 4.7; ORP = 342 mV; Sulfate = 2 mg/L
- Little evidence of ongoing natural attenuation

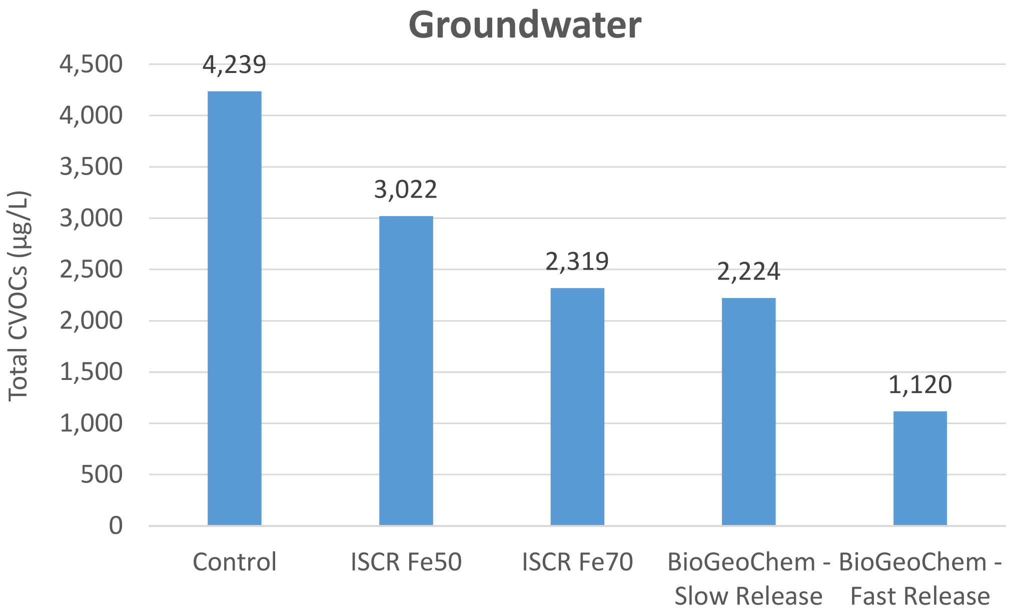
Bench Set-Up:

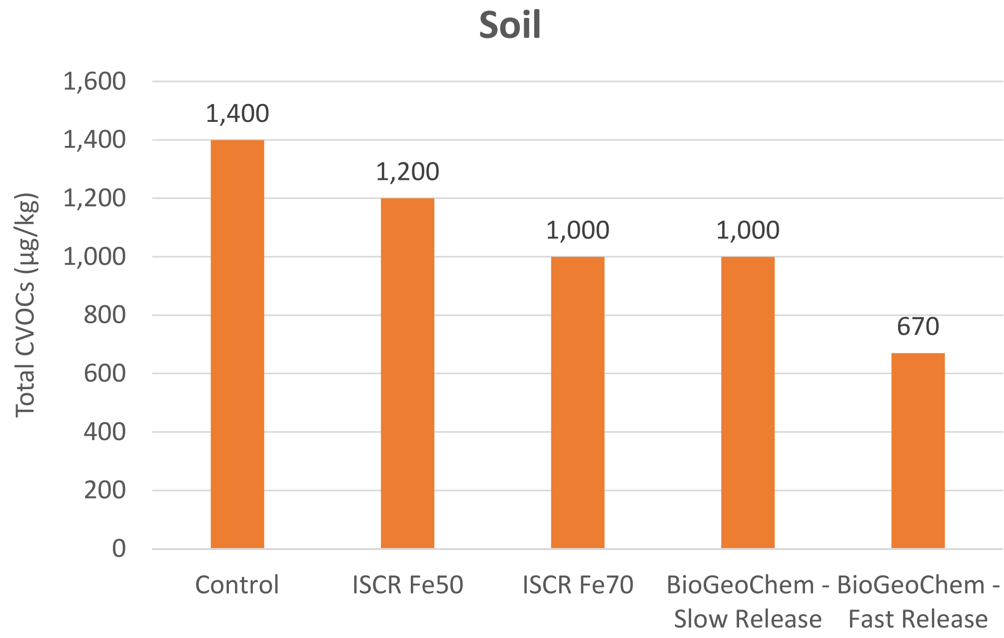
Microcosms set up with groundwater and sediment from the site (1:3 ratio):

- Control
- ISCR Fe50 (50% ZVI, 50% organic carbon)
- ISCR Fe70 (70% ZVI, 30% organic carbon)
- BioGeoChem – slow release (FOM + ZVI + slow release SO4)
- BioGeoChem – fast release (ELS + ZVI + Fe(II) + SO4)

- Dose rate: All systems amended with 1.7 g/L total reagents + pH buffer on Day 0
Reamended with an additional 3.3 g/L for a total of 5 g/L on Day 80

Treatment Results after 96 Days





- Higher removal rates in biogeochemical systems with sulfate relative to traditional ISCR
- Minimal generation of daughter products in all systems (<15 µg/L)
- Chromium non-detect in all amended systems
- Elevated levels of sulfide and iron measured in soil from both biogeochem systems relative to control

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Conclusions

- The combination of sulfate, iron and organic carbon was found to support higher CVOC degradation rates compared to organic carbon substrate or ISCR alone.
- A potential key benefit of forming reactive minerals in situ is increased distribution and surface area relative to directly adding solid reductants.
- The generation of daughter products was in less than Stoichiometric amounts for the BioGeoChemical systems indicating an abiotic degradation pathway.
- Iron (ZVI / Fe(II)) can help prevent sulfide inhibition during ERD at high sulfate sites.
- BioGeoChemical systems can also serve to immobilize many heavy metals.

KLOZUR® ONE

- Responding to Market Demand for simpler site use
- Activator and Klozur® SP in a single product
  - 95% Klozur SP
  - 5% Activator Blend
- Convenience and easier use version of Klozur SP

What is Klozur One?

- 5% Activator Blend
  - Includes trace potassium permanganate (less than 1%) that gives Klozur One its distinctive colour once dissolved
    - Colour is intended to change as permanganate changes its oxidation states
  - Dry phase is off-white colour with purple/black and brown specks

What Activates Klozur One?

- Activation mechanisms:
  - Iron-chelate
  - Manganese

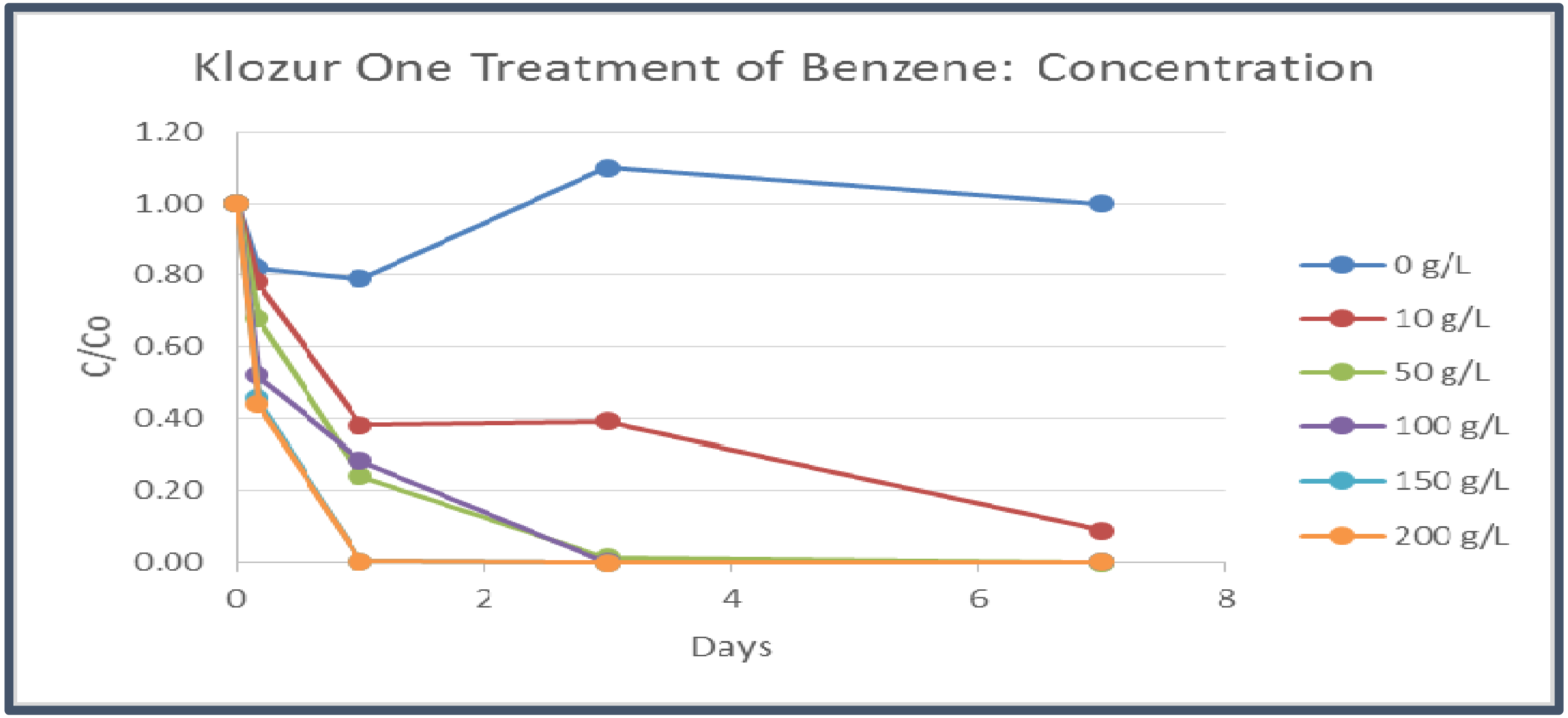
- Built in redundancy to account for natural site variability

Compounds Treated

- Klozur One primarily benefits from the **oxidative pathway**
  - Total petroleum hydrocarbons (BTEX, PAHs, GRO and DRO)
  - Chlorinated ethenes (PCE, TCE, DCE, and VC)
  - Chlorobenzenes
  - 1,4-Dioxane

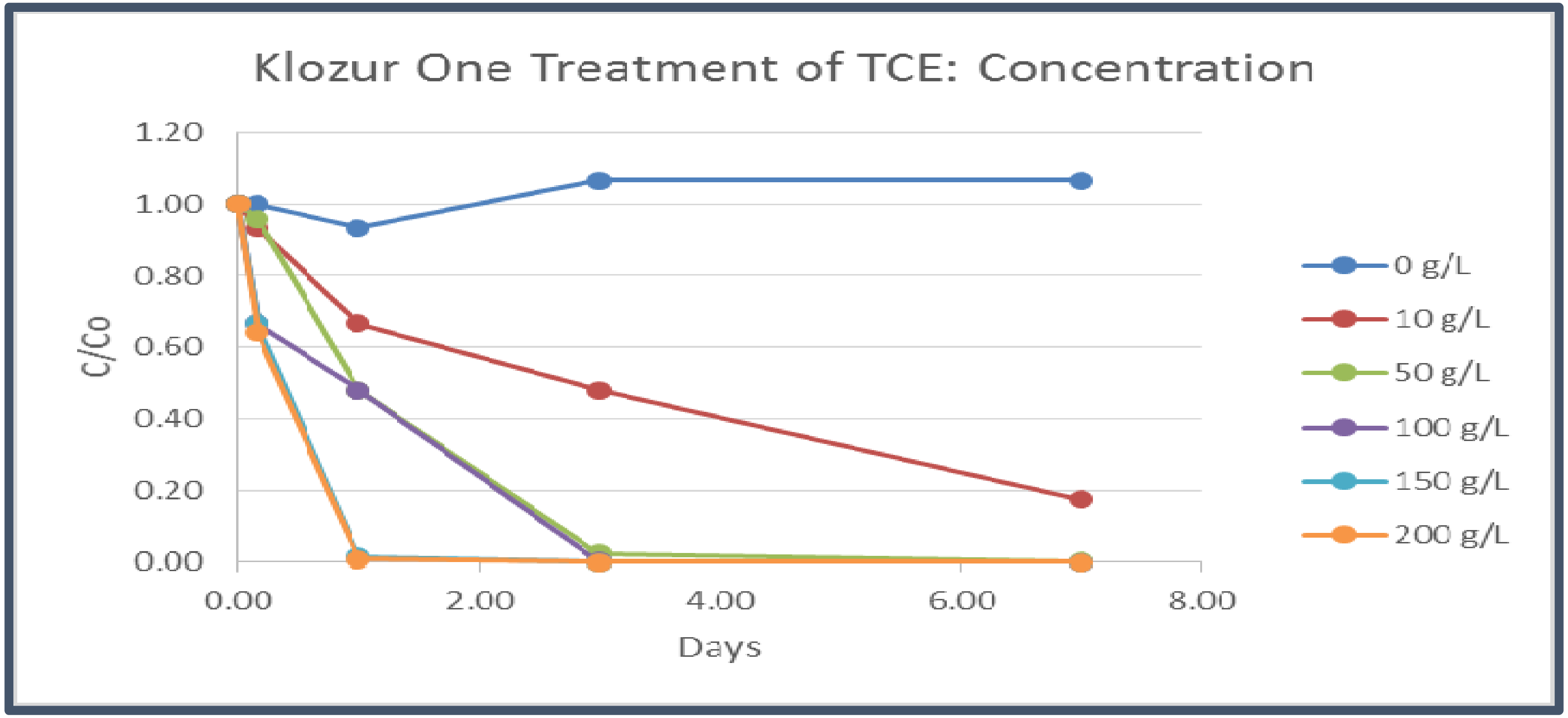
Concentration Based Kinetics

- Varied conc of Klozur One
- 20°C
- 10 mg/L Benzene



Concentration Based Kinetics

- Varied conc of Klozur One
- 20°C
- 15 mg/L TCE



Transportation

- Availability
  - 55.1 lb bags (25 Kg)
  - 2,204 lb supersacks (1,000 Kg)

- UN 1505 - shipping name (hazard basis)

- Same oxidizer classification as Klozur SP and Klozur KP (UN Class 5.1 Packing Group III)

Recommendations: Injection

- Injection concentrations of between 50 g/L and 200 g/L
- Inject through constructed wells
  - Stainless steel or PVC
  - Corrosive nature will require precautions with carbon steel
- Contaminants:
  - Chlorinated ethenes
  - BTEX
  - PAHs
  - DRO/GRO
  - Chlorobenzenes
  - 1,4-Dioxane

Klozur One Summary

- Activation methods coupled with Klozur SP:
  <u>STILL WORK!!!</u>

- Klozur One is a new All-in-One product
  - Combining activator in the same product as Klozur SP
  - Ease of use and convenience

- Reacts with most common oxidizable contaminants of concern

ONE Product

ONE Tank

ONE Injection System

ONE Design

KLOZUR® ONE

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Environmental Solutions

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Bench-Scale evaluation of FeS/CVOCs + Klozur® One

Mike SUMMERSGILL/PeroxyChem UK & Ireland

Email: mike.summersgill@peroxychem.com. Mob: 07779-367412

YCLF Sheffield – 27th February 2018