EVALUATION OF IRON AND SULFUR SUPPLEMENTS TO PROMOTE REACTIVE MINERAL FORMATION IN IN SITU REACTIVE ZONES

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Overview

- Reactive Mineral Background
- Iron Supplement Pilot Study
- Sulfur Supplement Pilot Study
- Lessons Learned

What are reactive minerals?

- Iron containing minerals
- Form under iron-reducing and sulfate-reducing conditions
- Promote alternative degradation pathway for chlorinated solvents
- Active at low concentrations (<0.5%; He *et al.* 2015)

He, Y.T, J.T. Wilson, and R.T. Wilkin. 2015. Review of abiotic degradation of chlorinated solvents by reactive iron minerals in aquifers. Groundwater Monitoring & Remediation. 35 (3/Summer 2015): 57-75.

Abiotic Degradation

- Dechlorination takes place on reactive mineral surface
  – Rate $\propto$ exposed surface area
- No observable intermediates
- Signs of abiotic degradation
  – Decreases in parent compound
  – No formation of daughter products
  – Observable concentrations of end products

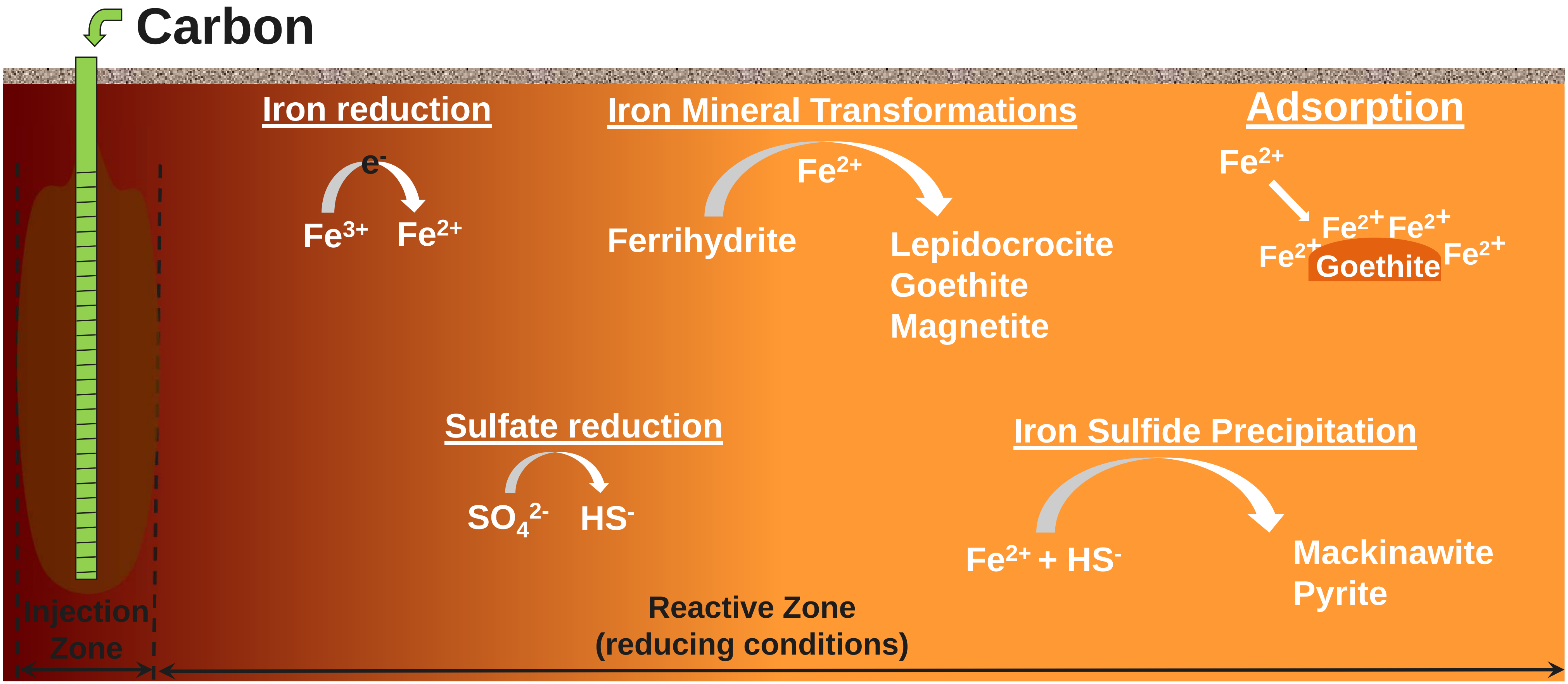
Types of Reactive Minerals

Iron Sulfides
- Mackinawite
- Pyrite

Iron oxides, hydroxides, and oxyhydroxides
- Goethite
- Lepidocrocite

Mixed Valence
- Magnetite
- Green rust

Reactive Mineral Formation in Reactive Zones



Reactive Mineral Engineering

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Iron reduction

e^-

Fe^{3+} → Fe^{2+}

Iron Mineral Transformations

Ferrihydrite → Fe^{2+} (11 – 56 mg/L) → Lepidocrocite, Goethite, Magnetite

Adsorption

Fe^{2+} → Fe^{2+} Fe^{2+} Fe^{2+} Goethite Fe^{2+}

Case Study 1: Iron Supplement

Sulfate reduction

SO_4^{2-} → HS^-

Iron Sulfide Precipitation

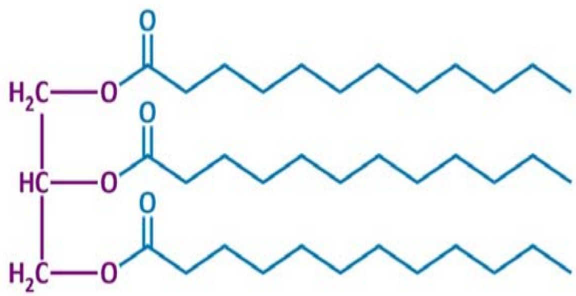
Fe^{2+} + HS^- → Mackinawite, Pyrite

Case Study 2: Sulfate Supplement

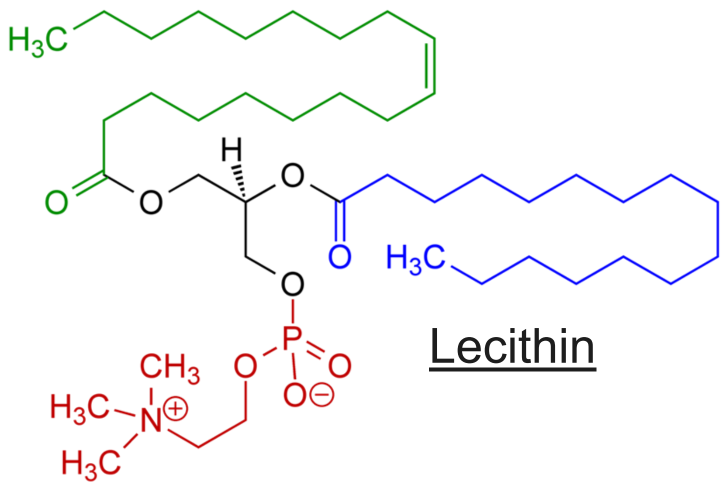
Case Study 1: Iron Supplement

Case Study 1: Fe^{2+} Supplement

- Client wanted to promote abiotic treatment
- Pilot study comparing two reagents *with same carbon loading*
  - 3% EVO
  - Lecithin with *ferrous iron supplement*
- Objective: evaluate reagents for abiotic treatment



Triglyceride (EVO)



Lecithin

Case Study 1: Background

- Located in the Northeast
- Cold weather application
- PCE plume (20 to 500 µg/L)
- Lithology
  - Sand and silt
  - Glacial till (silt/gravel/clay)
  - Bedrock (shale and siltstone)

Case Study 1: Potentiometric Map

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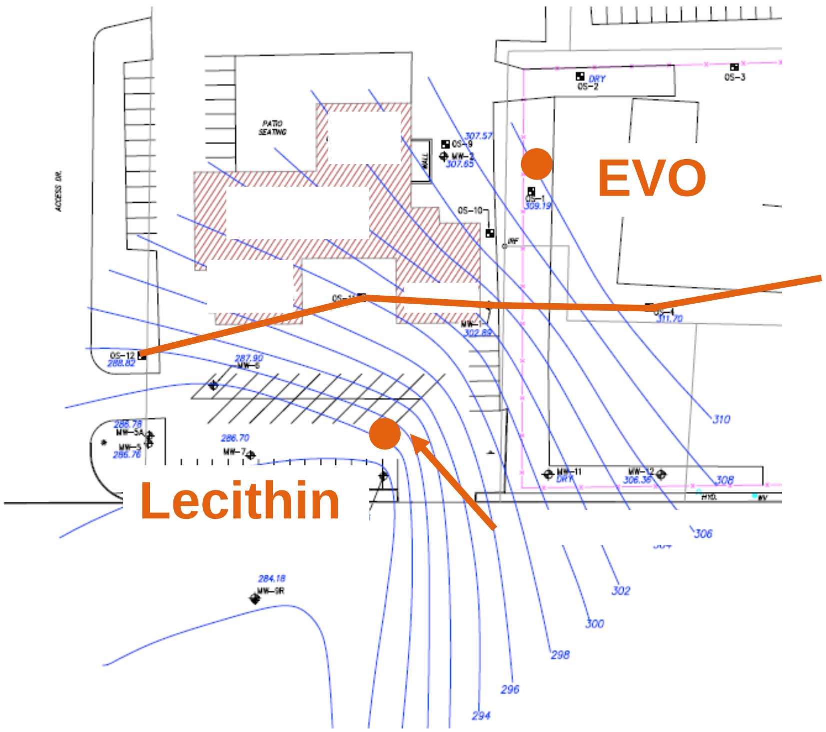

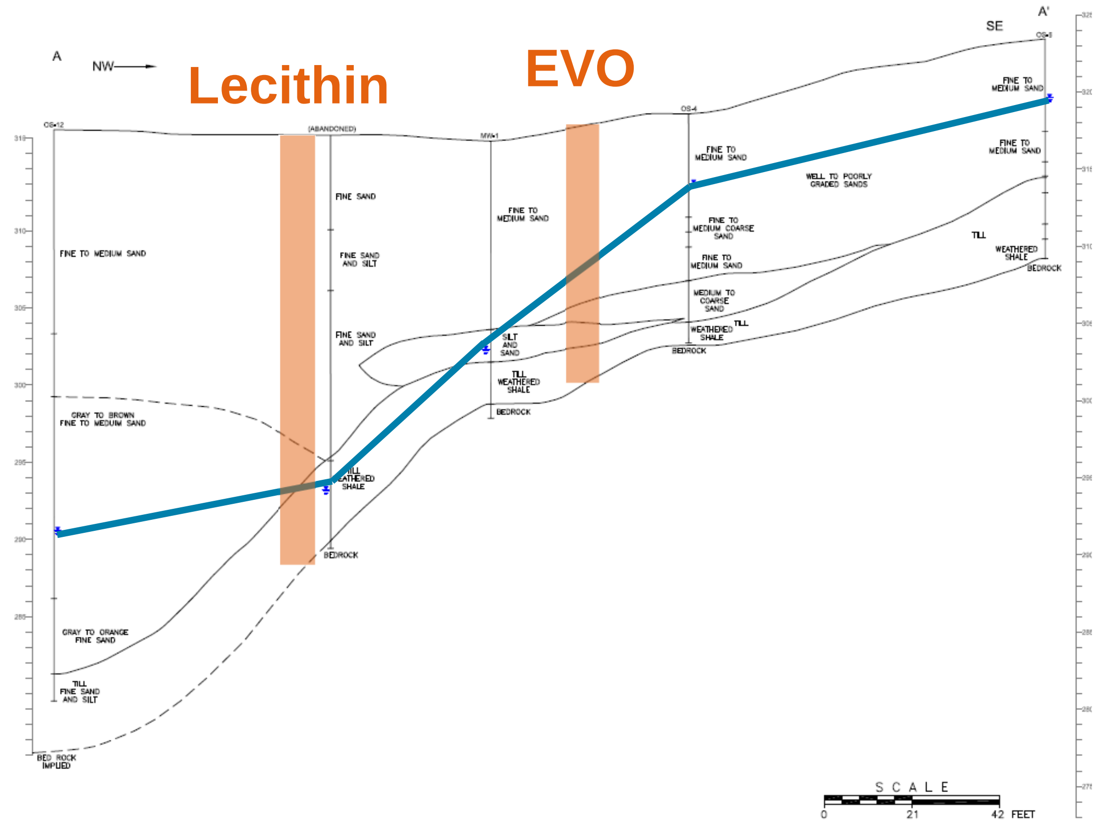

Lecithin selected for high flow rates/weathered rock application

Case Study 1: Injection Summary

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	EVO	Lecithin + Fe^{2+}
Injection Volume (gal)	1930	2700
TOC* (mg/L)	7800	7800
Iron (mg/L)	1.19	269

*Theoretical

EVO Injection Area

Lecithin Injection Area

Case 1: Remediation Performance

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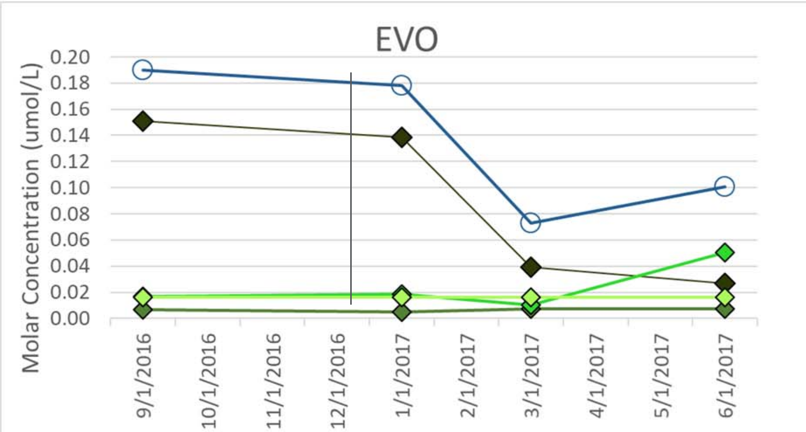

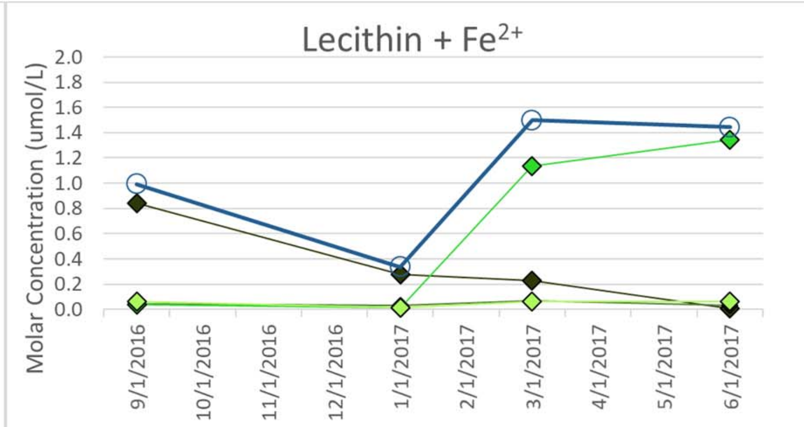

- PCE
- TCE
- cisDCE
- VC
- Total Molarity

EVO

- Consistent with abiotic degradation
  - Decrease in PCE
  - Limited increase in daughter products
  - Max Fe (80.6 mg/L)
  - Max methane (0.14 mg/L)

Lecithin + Fe^{2+}

- Consistent with biological degradation
  - Conversion to cisDCE
  - Max Fe (41.7 mg/L)
  - Max methane (5.4 mg/L)

- Total Iron
- TOC
- Methane

Case Study 1 Interpretation

- Ferrihydrite transforms to:
  - Lepidocrocite (11 mg/L Fe^{2+})
  - Goethite (56 mg/L Fe^{2+})
  - Magnetite (56+ mg/L Fe^{2+})
    - *Sources: Pedersen et al. 2005, Tamaura et al. 1983*
- Goethite and lepidocrocite not reactive with PCE
  - Reactive with CT when activated with adsorbed Fe^{2+}
- Magnetite reactive with PCE
  - Requires higher Fe^{2+} concentrations
  - Possible treatment mechanism

Pedersen *et al.* 2005. Fast transformation of iron oxyhydroxides by the catalytic action of aqueous Fe(II). Geochimica et Cosmochimica. 69 (16): 3967-3977.

Tamaura *et al.* 1983. Transformation of γ-FeO(OH) to Fe3O4 by adsorption of iron (II) on γ -FeO(OH). J. Chem. Soc. 1983: 189-194.

Case 1 Conclusions

- Abiotic degradation possible without iron addition
- Fe^{2+} concentration achieved in situ directly impacts minerology
- Important to determine whether an iron supplement is needed
  - Additional cost and time

Case Study 2: Sulfate Supplement

Case Study 2: Overview

- Client wanted to promote biological and abiotic treatment of PCE plume
- Pilot study comparing two reagents
  - Molasses (not discussed)
  - Molasses + Sulfate Supplement
- Objectives:
  - Evaluate iron sulfide formation and abiotic degradation
  - Limit offsite migration

Case Study 2 Background

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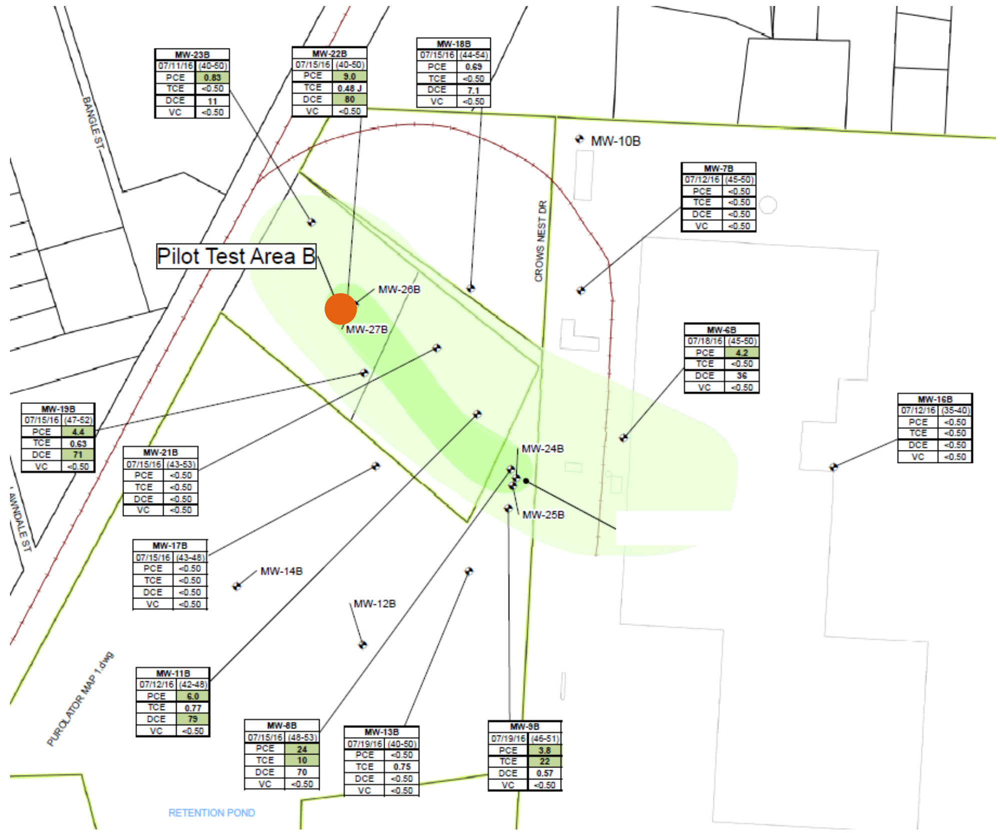
- Located in the Southeast
- Dilute PCE plume
  - PCE (8-10 µg/L)
  - cisDCE (92-97 µg/L)
- Lithology
  - Depositional
    - Sands
    - Silty sands
    - Silty clays



Case Study 2: Reagent

Reagent	Carbon + Sulfate
Molasses Strength	1%
Sulfate Loading	4.8 g/L $MgSO_4 \cdot 7H_2O$
NaOH	10 SU
Injection Volume	**3275 gal**
Resulting TOC	**3,400 - 3,800 mg/L**
Resulting Sulfate	**2,300 - 3,800 mg/L**

Case Study 2: Results

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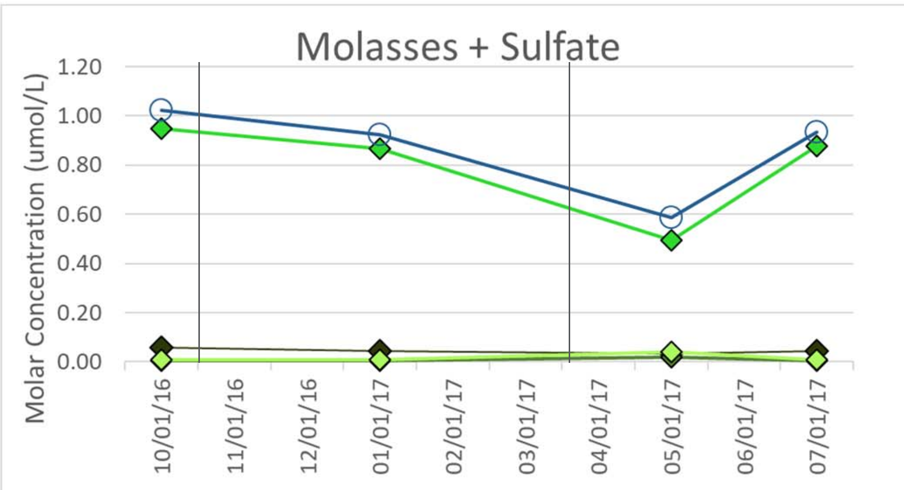

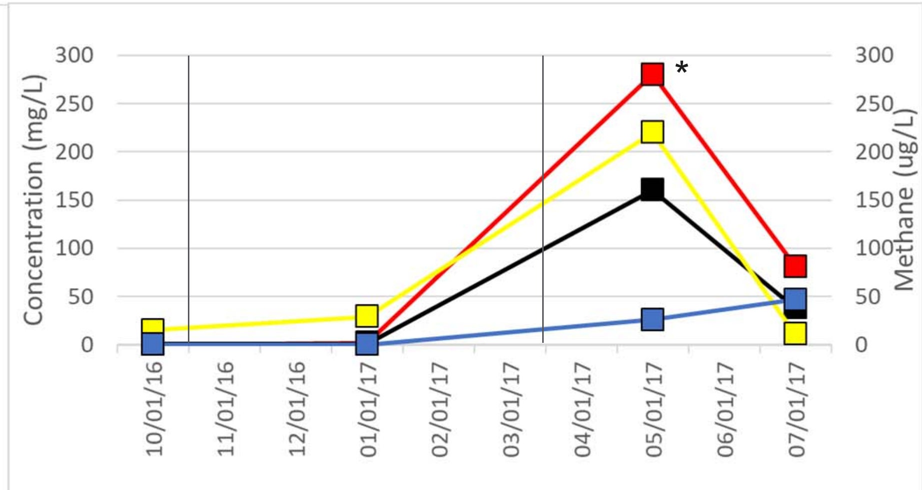

- PCE
- TCE
- cisDCE
- VC
- Total Molarity

- Dissolved Iron
- Sulfate
- TOC
- Methane

*Total Iron

Limited Treatment Observed

Case Study 2: Precipitate Formation

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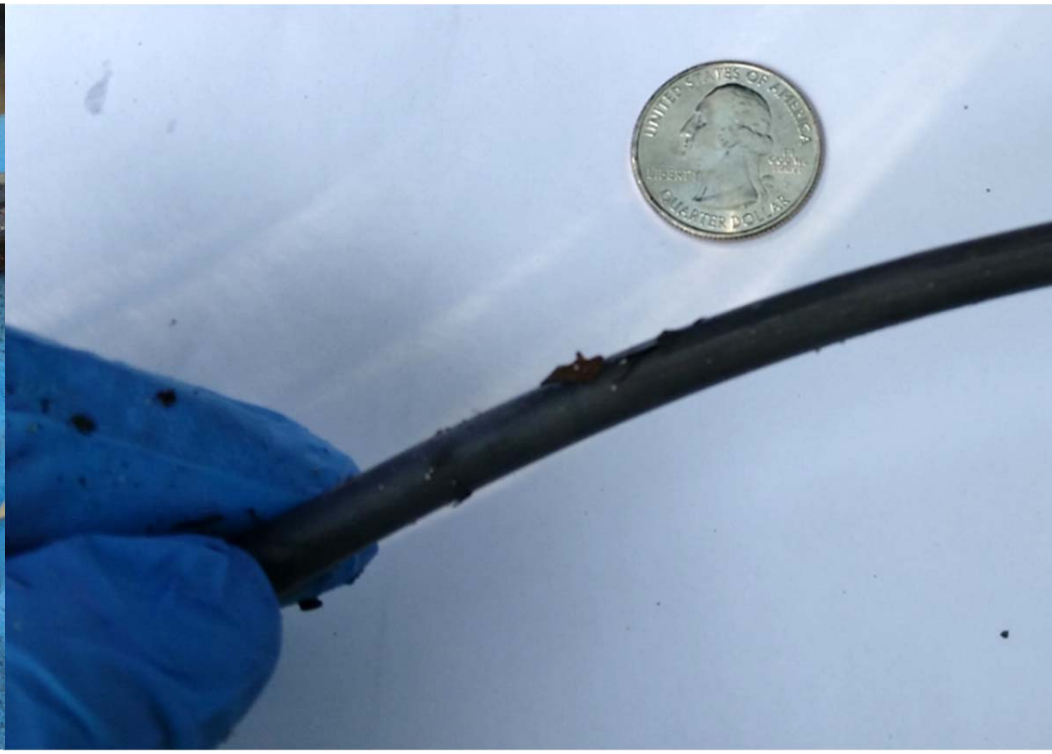


Case Study 2: SEM-EDS

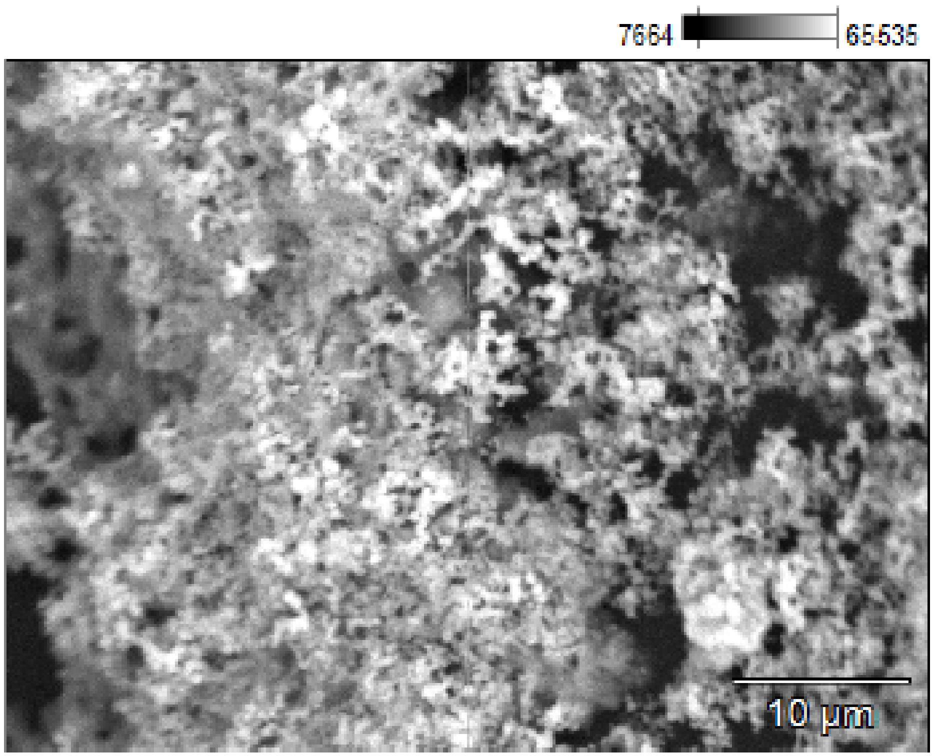
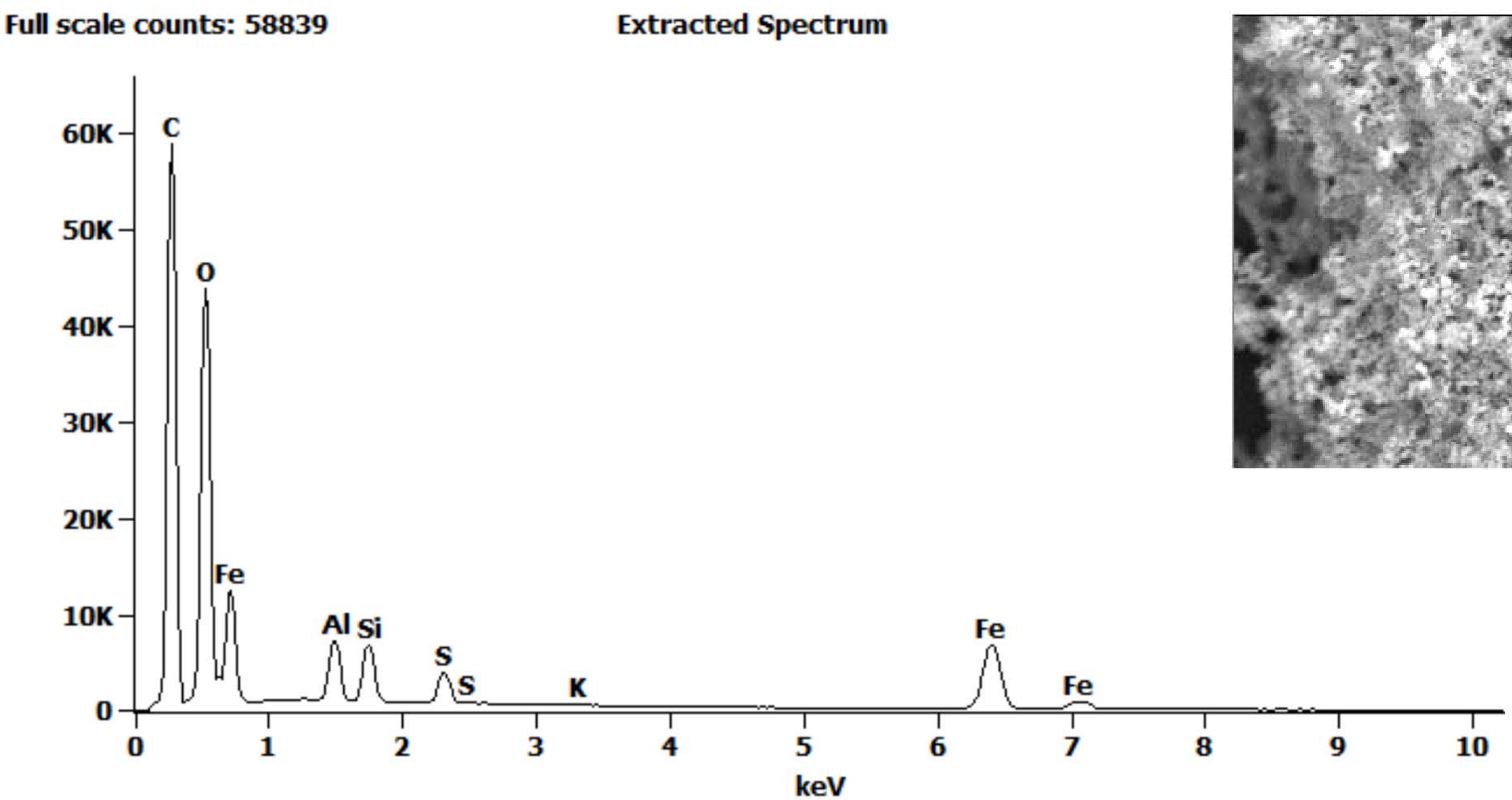
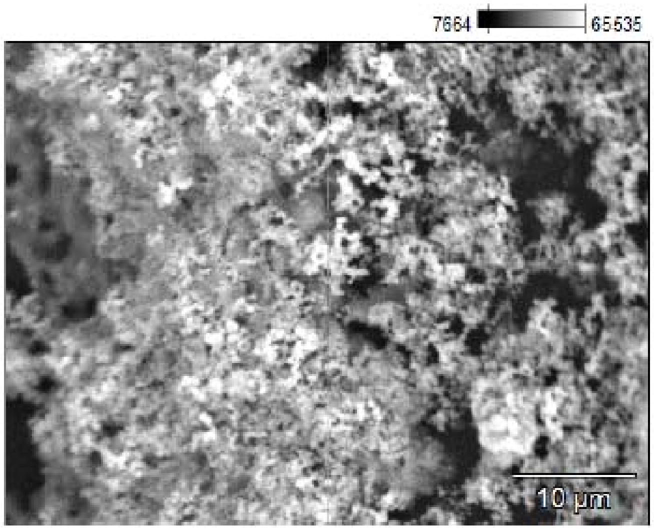


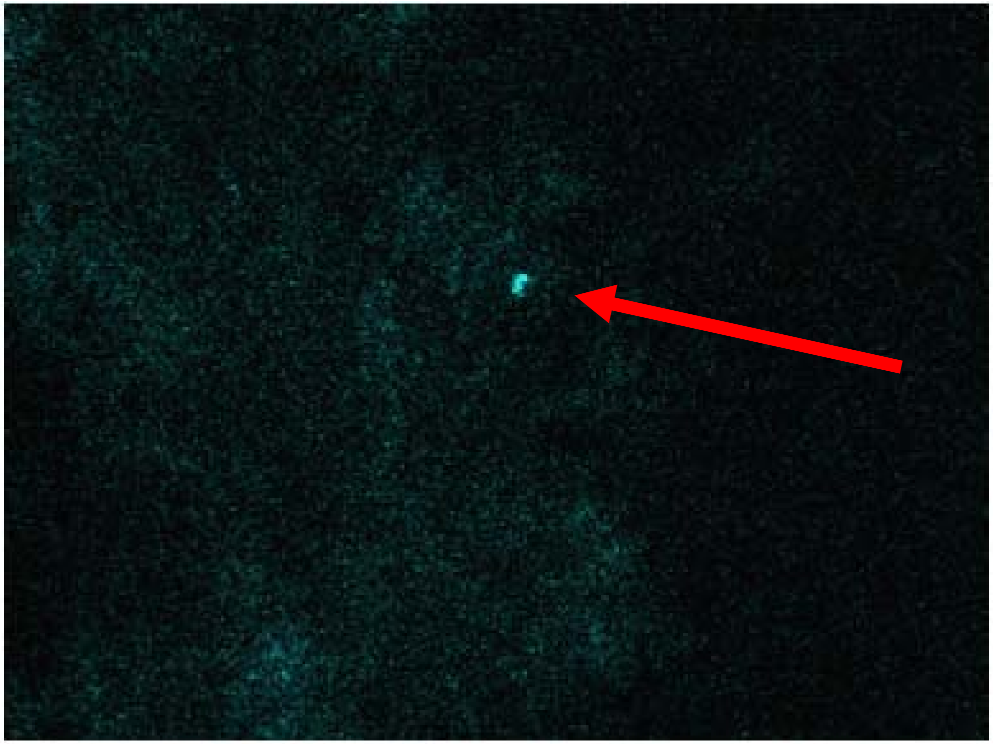
Figure 1. SEM image (above) and EDS spectrum (below) obtained from a portion of the material on the ID of sample MW-27B.

Case Study 2: SEM-EDS



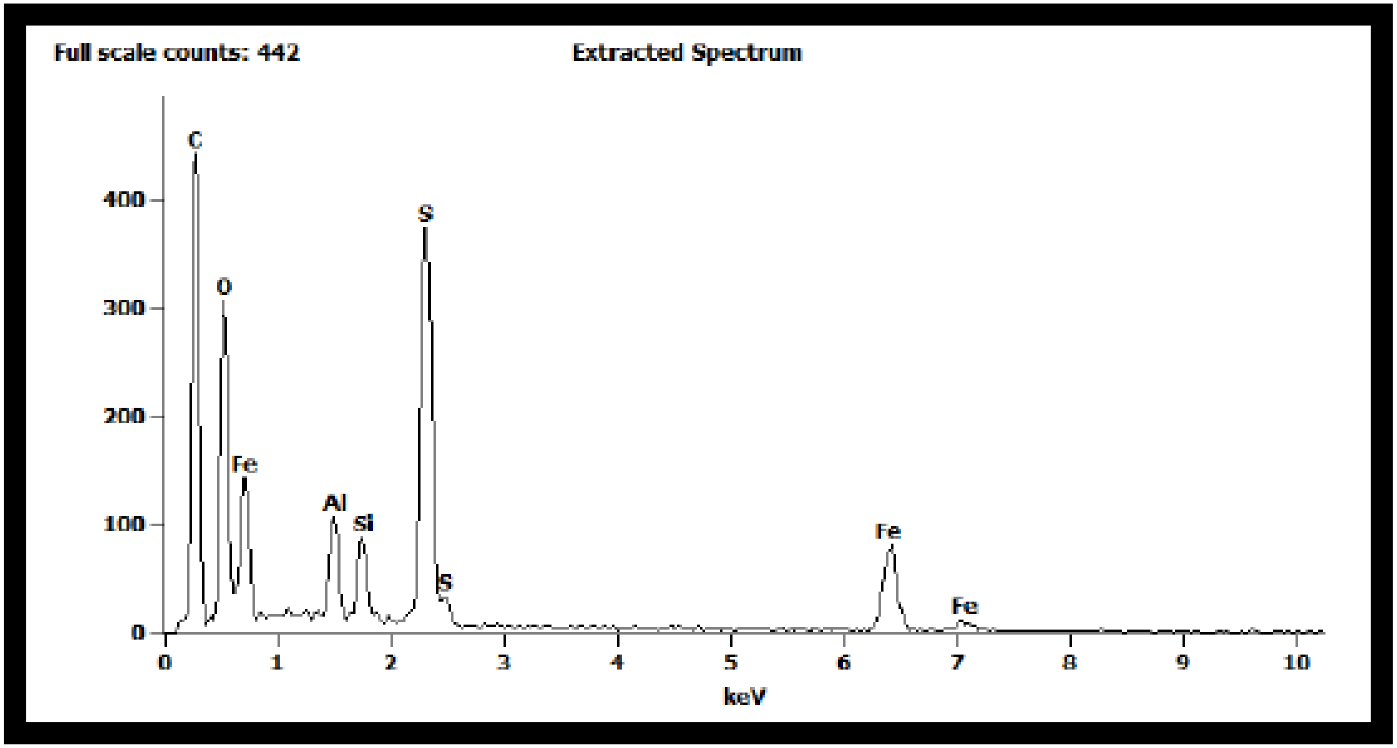


Case Study 2: SEM-EDS

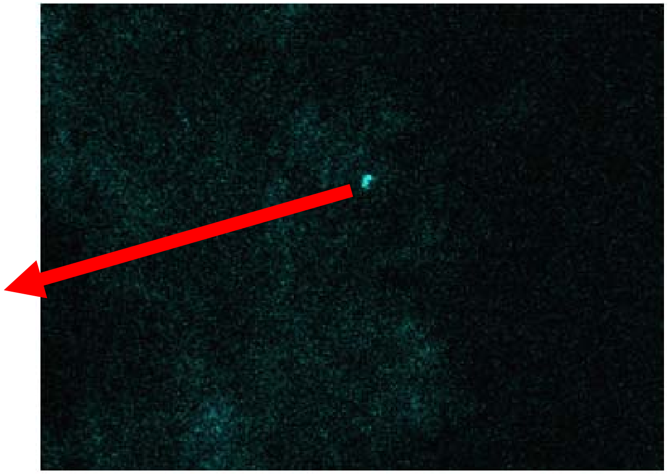


Sulfur Distribution Map

Case Study 2: Sulfur Addition



EDS Spectrum from sulfur-rich area



Sulfur Distribution Map

Iron sulfide precipitate identified by SEM-EDS

Case Study 2 Conclusions

- Iron sulfides formed in situ
- No strong evidence of abiotic degradation
- Biofilm may be inhibiting adsorption of CVOCs onto mineral surface

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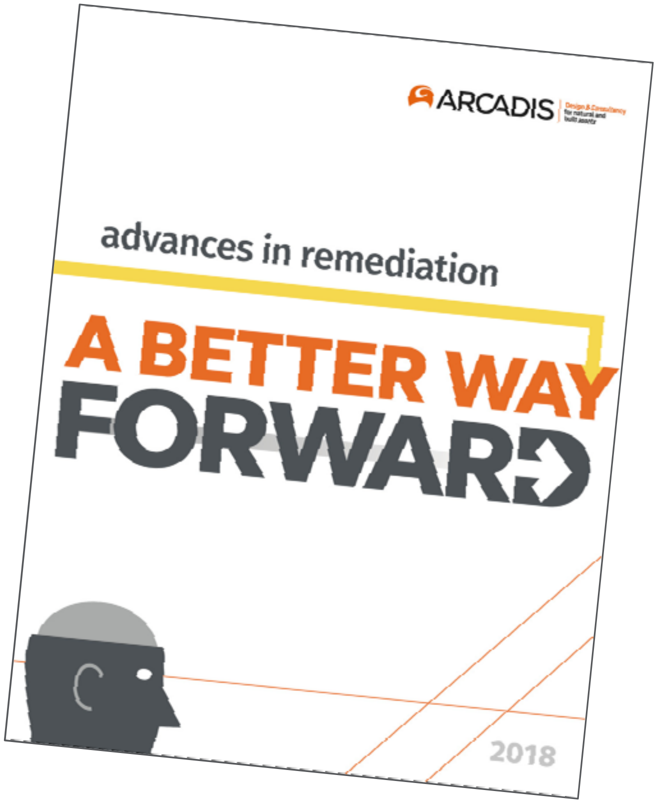

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Resources

Iron Shifting

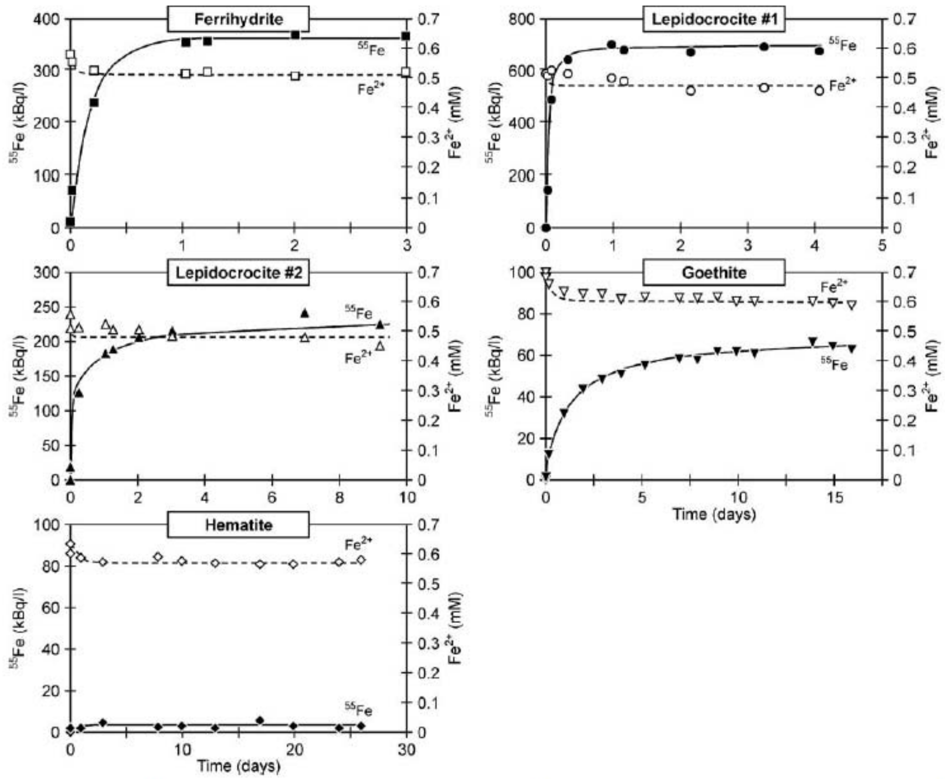

Fig. 4. Aqueous Fe^{2+} concentration (open symbols) and release of ^{55}Fe (filled symbols) from ferrihydrite (860 kBq ^{55}Fe/L added), lepidocrocite #1 (2400 kBq ^{55}Fe/L added) and #2 (1400 kBq ^{55}Fe/L added), goethite (1270 kBq ^{55}Fe/L added), and hematite (860 kBq ^{55}Fe/L added). Initial solutions contained 0.6 mM Fe^{2+}. Lines are provided for visual aid.

Pedersen *et al.* 2005. Fast transformation of iron oxyhydroxides by the catalytic action of aqueous Fe(II). Geochimica et Cosmochimica. 69 (16): 3967-3977.

Ferrous Iron Release from Ferrihydrite

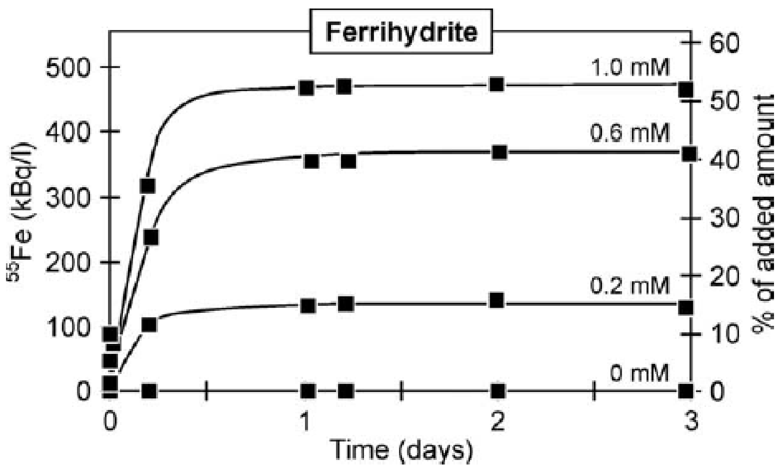

Fig. 3. The release of ^{55}Fe into solution in experiments with ^{55}Fe-labelled ferrihydrite dispersed in solutions containing 0, 0.2, 0.6, and 1.0 mM Fe^{2+}. Lines are provided for visual aid.

Pedersen *et al.* 2005. Fast transformation of iron oxyhydroxides by the catalytic action of aqueous Fe(II). Geochimica et Cosmochimica. 69 (16): 3967-3977.