Ferrous iron oxidation in hydrocarbon polluted groundwater for bioremediation

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Contamination

- Terrestrial oil spills
- Hydrocarbon compounds: BTEX
  - Soluble and mobile in groundwater
- Bioremediation

http://www.cged.org/Oil_Spill_4.jpg

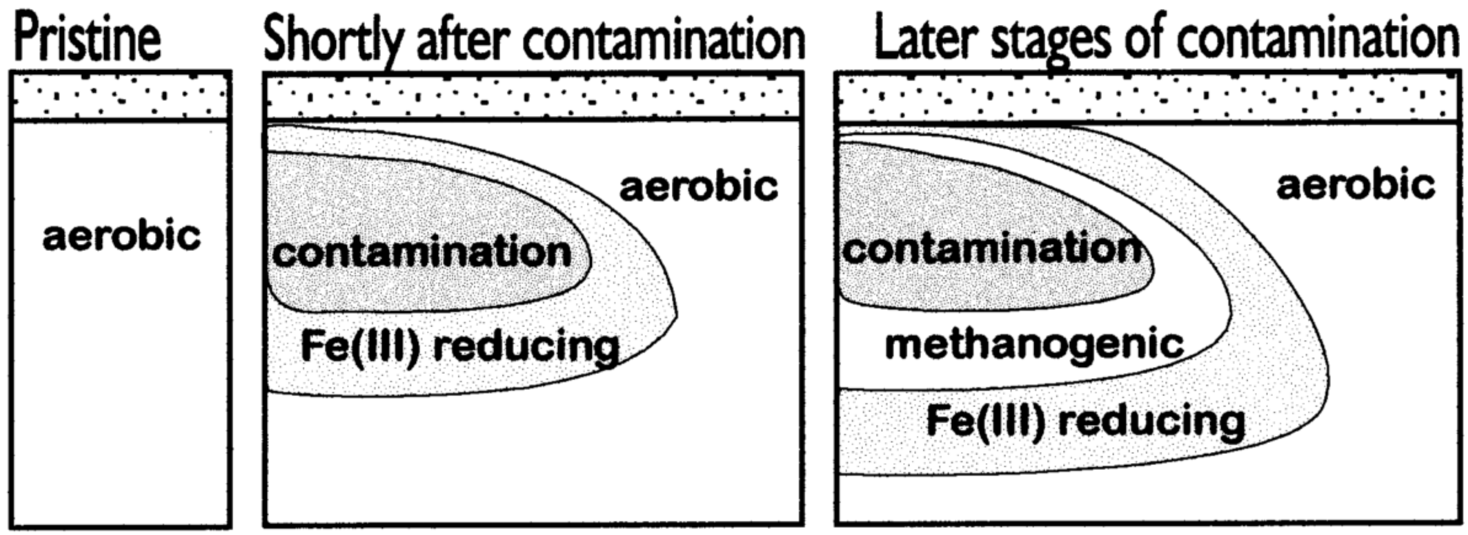
Bioremediation

- BTEX degradation
  - Common in aerobic environments
  - Also occurs in anaerobic conditions
- Anaerobic system occurs at slower rate
  - Includes most petroleum-contaminated aquifers

Electron acceptors

- Microbes consume most thermodynamically favorable electron acceptor
- Fe^{3+} provides greatest potential electron-accepting capacity
- Addition of electron acceptors to system

Anaerobic system



Anaerobic bioremediation of BTEX (Lovley, 1997)
DR Lovley

- Methanogens and nitrification limited pH <6

Study Site

Primary Literature

Prommer, H., Davis, G.B., and Barry, D.A. 1999. Geochemical changes during biodegradation of petroleum hydrocarbons: field investigations and biogeochemical modelling: Organic Geochemistry, v. 30, p. 423-435.

- Perth, Australia
- 500 liters gasoline
- Background geochemistry is anaerobic
- pH is 5.0

Initial Study

- Focused on contribution of Fe^{3+} as electron acceptor
- Siderite and goethite assumed to be equilibrium
  - pH too low
- Modelled benzene, toluene, sulphate, Fe^{2+} with groundwater flow
- Concluded iron was not available for further reduction
  - Not a significant electron acceptor at this site
  - Reduced forms bound in formation of siderite, pyrite, and magnetite

Objective

- Addition of oxygen to system
  - Air sparging (Lee et al., 1988)
- Simulate ferrous iron oxidation
- Fe^{3+} as electron acceptor

Input

Four scenarios were simulated:

(1) oxidation of ferrous iron

(2) oxidation of ferrous iron with siderite in equilibrium

(3) oxidation of ferrous iron with an increase of initial Fe^{3+} input

(4) oxidation of ferrous iron with both siderite in equilibrium and an increase of initial Fe^{3+} input

*Increased Fe^{3+} concentration was 0.00005 mol L^{-1}

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Title Initial Concentrations
SOLUTION 1
    temp      27
    pH        5
    pe        1.21
    redox     pe
    units     mol/l
    density   1
    Alkalinity 0.000327
    Ca        0.000841
    Cl        0.00645
    Fe_di     6.65e-05
    Fe_tri    0
    K         0.000259
    Mg        0.000566
    Na        0.00524
    S(-2)     3e-06
    S(6)      0.000783
    -water    1 # kg
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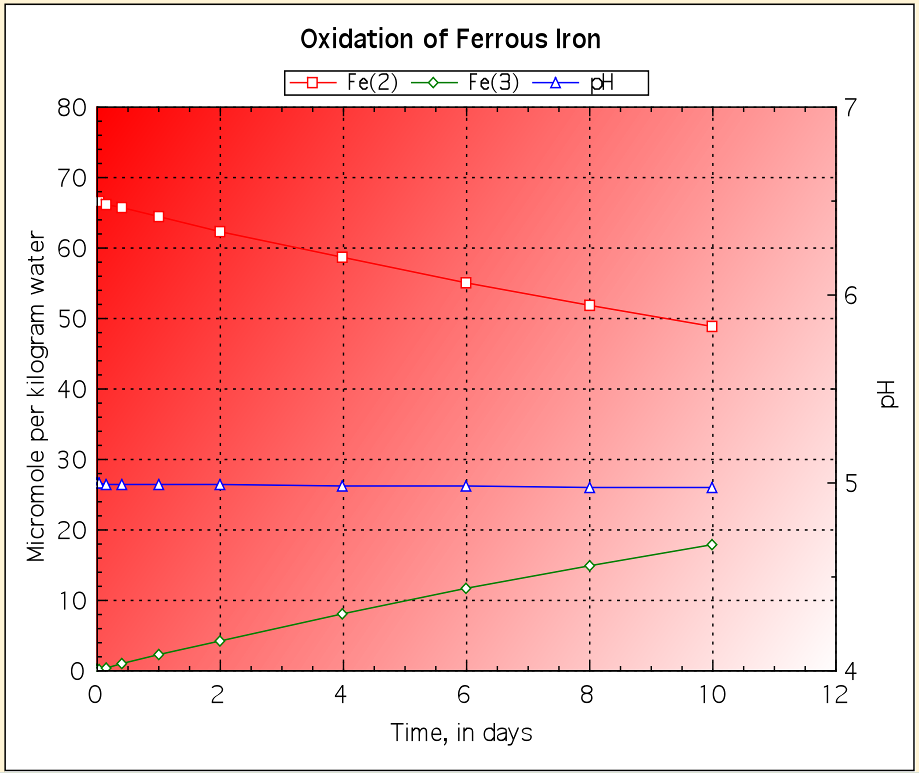
Saturation indices

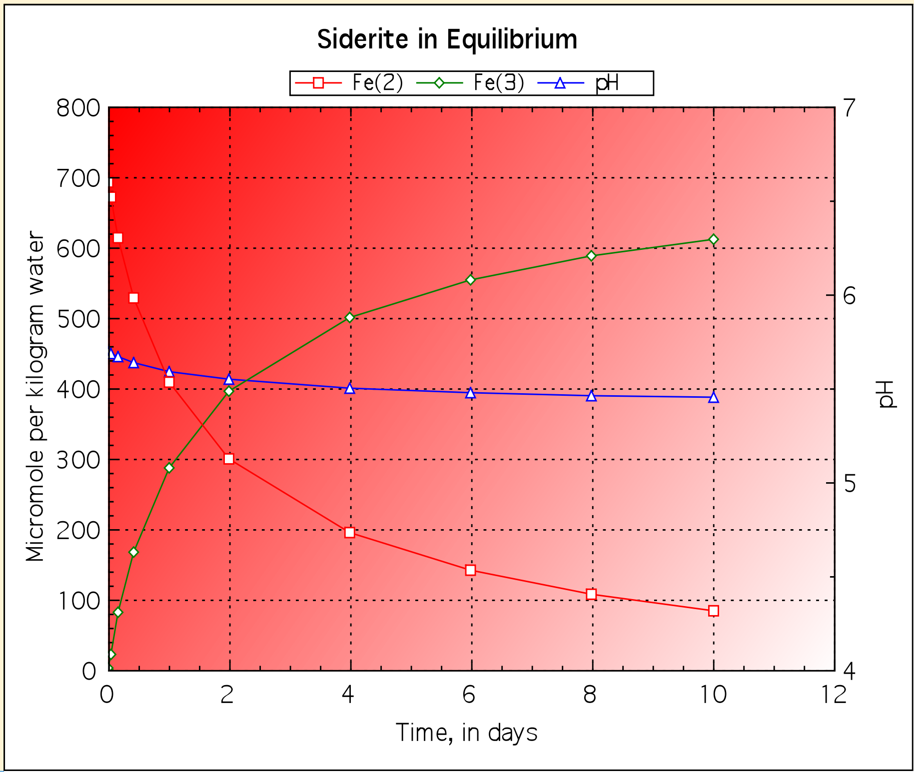
Phase	**Formula**	**SI Values**			
		Equilibrium Phase			
		Initial	Siderite in equilibrium	Increase in initial Fe^{3+}	Siderite in equilibrium & increase in initial Fe^{3+}
Goethite	$Fe^{3+}OOH$	6.8	8.8	7.4	8.9
Hematite	$Fe^{3+}{}_2O_3$	15.6	19.7	16.8	19.8
Jarosite-K	$KFe^{3+}(SO_4)_2(OH)_6$	1.4	6.0	3.1	6.0
Melanterite	$Fe^{2+}SO_4{:}7H_2O$	-5.7	-5.5	-5.7	-5.7
Pyrite	$Fe^{2+}S$	-222.4	-221.9	-222.4	-222.3
Siderite	$Fe^{2+}CO_3$	-2.5	-1.3	-2.7	-1.7

Oxidation of Ferrous Iron



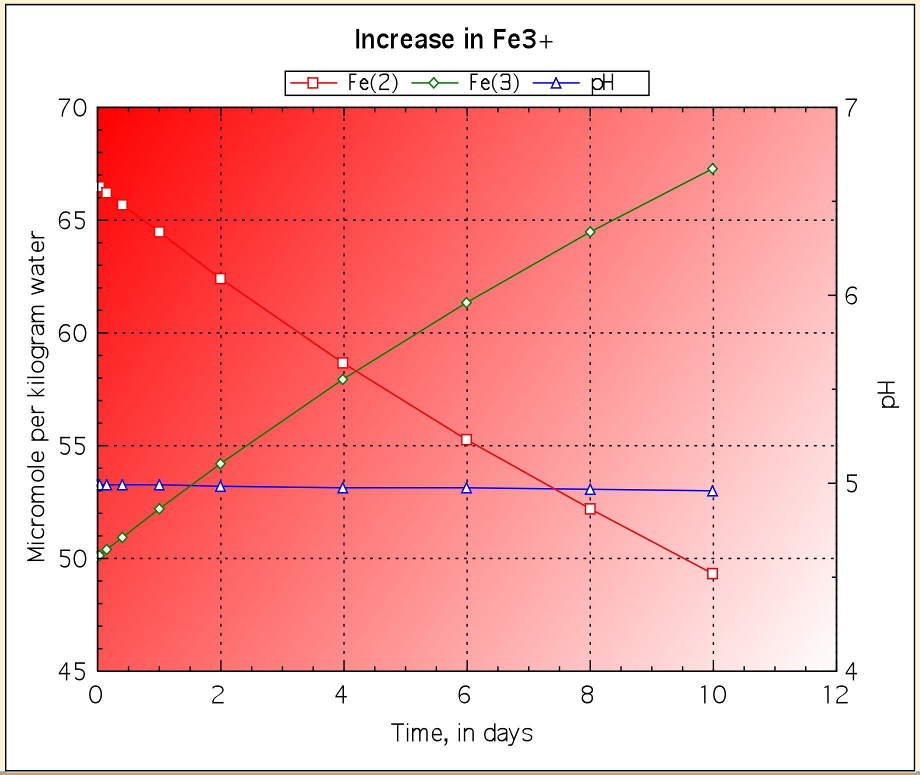
- As expected Fe^{3+} increased
- Fe^{2+} decreased
- pH did not change, 5.0

Siderite in Equilibrium



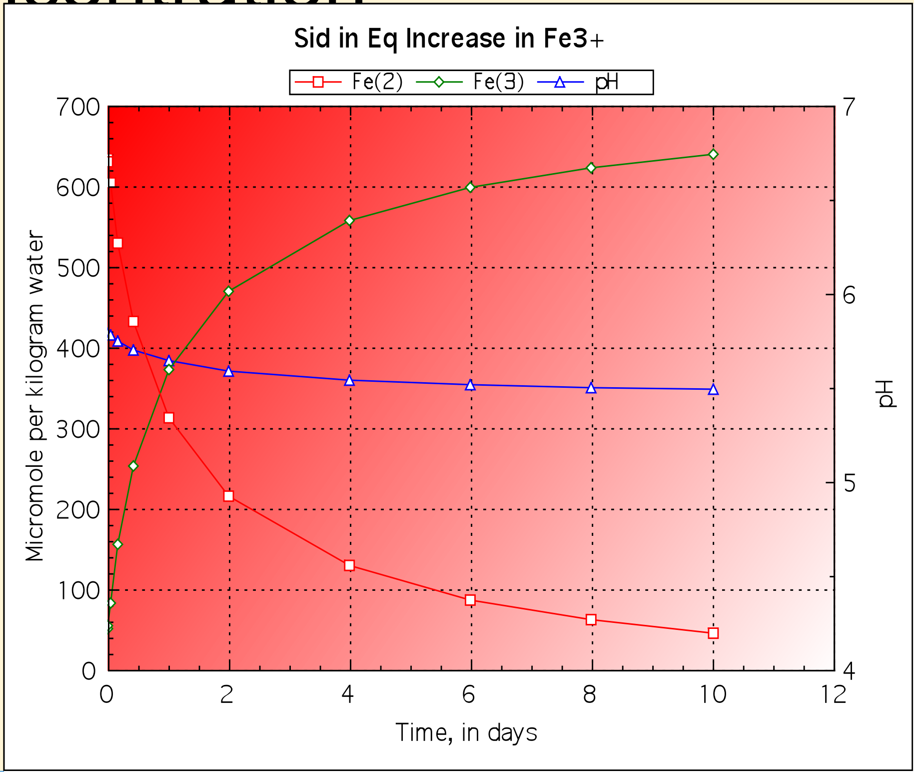
- Fe^{3+} increased much more dramatically
- Fe^{2+} decreased
- pH ending 5.5

Initial increase in Fe^{3+} concentration



- Steady increase in Fe^{3+}
- Steady decrease in Fe^{2+}
- pH constant at 5.0

Siderite in Equilibrium, Initial Fe^{3+} concentration



- Greatest increase in Fe^{3+} (6.40×10^{-4} mol/kg)
- Greatest decrease in Fe^{2+} (4.60×10^{-5} mol/kg)
- pH ending at 5.5

Discussion

- Longer time period
- An aerobic phase would have to occur for ferric iron reduction by microbes
- Theoretically, this is creating an aerobic system that does not use ferric iron

Conclusion

- Results are assuming the program was used correctly
- Theory to promote Fe^{3+} abundance to stimulate degradation of hydrocarbons
    - Other electron acceptors are available
- Remediation by addition of oxygen includes many benefits (Lovley, 1997)
    - Does not produce waste products
    - Generally fast, safe, and economical

References

- Lee, M.D., Thomas, J.M., Borden, R.C., Bedient, P.B., Ward, C.H., Wilson, J.T., and Conway, R.A., 1988, Biorestoration of aquifers contaminated with organic compounds: Critical Reviews in Environmental Control, v. 18, p. 29–89.
- Lovley, D.R., 1997, Potential for anaerobic bioremediation of BTEX in petroleum- contaminated aquifers: Journal of Industrial Microbiology & Biotechnology, v. 18, p. 75–81.
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