Abstract

Previously we demonstrated that diagonalized reaction-based models could be applied to batch systems in which parallel kinetic reactions were operative if separate experiments were used to independently formulate and parameterize kinetic rate expressions. Currently our objective is to demonstrate that reaction-based models can accurately simulate complex biogeochemical systems under advective flow conditions using rate formulations/parameters obtained from independent batch experiments. For demonstration purposes we selected biological iron(III) reduction by the bacterium *Shewanella putrefaciens* CN32 in natural sediments, Eatontown sand from Eatontown, NJ. A series of batch kinetic experiments were performed in order to independently formulate a kinetic rate expression for the biological iron reduction. From the column data, flux results clearly demonstrate that hydrologic conditions effect biologic reactions. The results highlight the intriguing linkages between hydrology and biogeochemistry that we hope to quantitatively simulate using reactive transport reaction-based models.

Background

- Studies suggest advective transport plays role in the rate and extent of microbial Fe(III) oxide reduction in subsurface sedimentary environments (Roden 1999)
- Bioreduction of hematite in batch kinetic experiments produced reaction-based biogeochemical models (Burgos 2002)
- We hope to demonstrate that reaction based models can accurately simulate complex biogeochemical systems under advective flow conditions using rate formulations/parameters obtained from independent batch experiments using *Shewanella putrefaciens* CN32 and the hematite rich Eatontown sand (demonstrated high concentrations of evolved Fe(II) (Zachara 1998)),

Methods

Batch

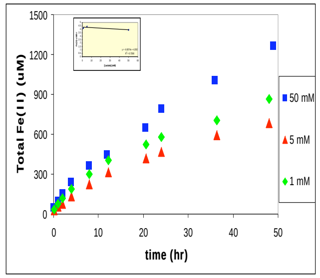
- All batch experiments done in triplicate
- Experiments conducted with variable sediment concentrations (0.007 – 2.0 g mL-1), variable initial DMRB concentrations (10^7 – 10^9 cells mL-1), and variable lactate concentrations (1 – 50 mM)
- Suspension sample collected on logarithmic timescale and analyzed for Fe(II) (aq), 0.5 N HCl Fe(II), lactate, acetate, and pH
- Fe(II) measured by Ferrozine and Lactate measured by HPLC

Column

- Columns: 1 cm diameter, 7.5 cm bed length, 9 grams of sand and porosity of 0.69
- Feed solution: 45 mM PIPES, 1 mM CaCl2, 0.1 mM NH4Cl, 0.01 K2HPO4, 0.01 mM MgSO4, and growth conditions (0.1 g L-1 yeast extract and 5 mM lactate)
- Wet pack column using method below:
  1) Bring liquid height upto 1 cm in glass column
  2) Add first 1 gram lift of sand to liquid
  3) Tap column 3 times of 4 sides, then increase liquid height to 1.5 cm
  4) Drain 0.5 cm from liquid height and add next lift

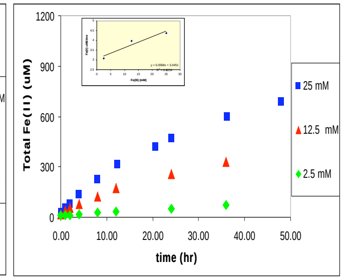
- Varying flow rate of: 1.6 mL/day, 5.6 mL/day, 11 mL/day, 29.7 mL/day
- Samples analyzed daily for 20 days. Measured effluent Fe(II), lactate, and acetate.
- Column deconstruction: analyzed Fe(II), cell count, and Mössbauer

Batch Experiments



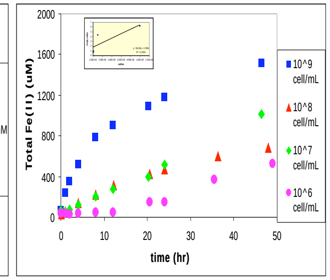
Effect of Lactate

- Initial rates not dependent on lactate (never electron donor limited)
- Increased Fe(II) production with 50 mM could be caused by DMRB growth.



Effect of [Fe(III)]

- Initial rate linearly dependent on Fe(II) (See inserted graph)
- Results consistent with "free surface site" rate formulation

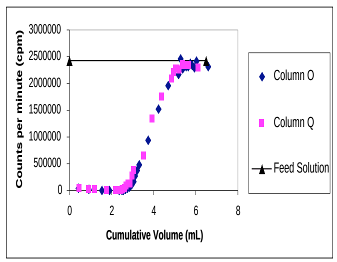


Effect of DMRB

- Initial rates non-linearly dependent on DMRB concentration
- Demonstrates importance of measuring DMRB as a function of time

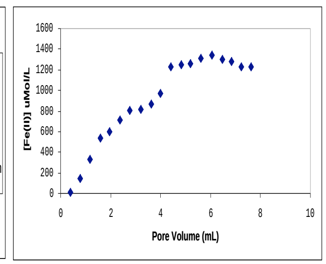
- Overall Fe(II) reaction rate was first order
- Growth term will be required to accurately describe non-linear effect of DMRB
- Future work: use data and reaction models to refine rate formulation/parameters for modeling column bioreduction experiments

Column Experiments



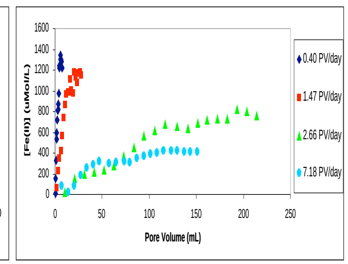
Tritium break-through curves for two columns

- Non-reactive tracer, tritium, break-through curves reveal reproducible hydrologic conditions
- Used to determine porosity and dispersivity



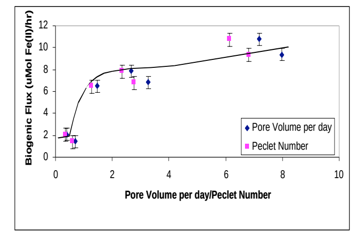
Effluent Fe(II) for 0.40 pore volumes per day columns

- Effluent Fe(II) increases to pseudo steady state value used to calculate biogenic flux
- All columns reached pseudo steady state around day 10 of experiment



Effluent Fe(II) for columns with varyable flow rates

- Time dependent nature of Fe(II) generation similar with all flow rates
- Pseudo steady state effluent Fe(II) concentrations dependent on flow rate



- Peclet number from various flow rates demonstrates biogenic flux occurs when transport process switch from diffusion to advective control
- Future work: Simulate linkage quantitatively using reactive transport reaction-based model

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References Burgos, W. D. et. al. Theoretical and Experimenntal Considerations Related to Reaction-Based Modeling: A Case Study Using Iron(III) Oxode Bioreduction. *Geomicrobiology Journal.* **19**. 253-287. Roden E.E. and Urrutia M. M. (1999) Ferrous iron removal promotes microbial reduction of crystalline iron(III) oxides. *Environ. Sci. Technol.* **33**, 1847-1853.