Reactive Transport Modeling of Biologic Iron(III) Reduction Under Varied Hydrologic Conditions

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1 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 (Burgos et al., 2003). 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 in natural sediments. All experiments were performed with a hematite-rich sand from Eatontown, NJ (366 umol DCB-extractable Fe g^{-1} sediment), and the dissimilatory metal-reducing bacterium (DMRB) *Shewanella putrefaciens* CN32 with lactate as the sole electron donor in a buffered (pH = 6.8) background electrolyte (BE) containing 45 mM PIPES, 1 mM $CaCl_2$, 0.1 mM NH_4Cl, 0.01 K_2HPO_4, 0.01 mM $MgSO_4$, and 0.1 g L^{-1} yeast extract (growth conditions). A series of batch kinetic experiments were performed to systematically measure iron reduction as a function of iron oxide surface area, cell density, and electron donor concentration in order to independently formulate a kinetic rate expression for the biological iron reduction. Batch experiments were conducted with variable sediment concentrations (0.007 – 2.0 g mL^{-1}), variable initial DMRB concentrations (10^6 – 10^9 cells mL^{-1}), and variable lactate concentrations (1 – 50 mM). Reactors were incubated at 20°C on a shaker table for 7 d, and kinetic data were collected on a logarithmic scale. For each time point, soluble Fe(II) (0.2 um), 0.5 N HCl Fe(II), lactate, acetate, and pH were measured. At the final 7 d point, cell concentration (by AODC following 24 h 20 mM Na_2HPO_4 pH 7.4 extraction) and iron mineralogy (by Mössbauer spectroscopy) were also measured. For all batch experiments the overall reaction rate of Fe(II) production was zero-order (R^2 values for [0.5 N HCl Fe(II)]-vs-time ranged from 0.905 to 0.999). The overall Fe(II) production rate was directly dependent on sediment concentration (e.g., proportional to reactive iron surface area) and not dependent on lactate concentration (i.e., system was never electron donor limited). The effect of DMRB concentration on the overall Fe(II) production rate was complex and non-linear, suggesting a growth term may be required to accurately capture this effect.

Eatontown sand was carefully wet-packed into 1-cm diameter glass chromatography columns with a packed bed length of ca. 7.5 cm. Dry sand was added in 1.0 g lifts into BE containing the 10^8 cells mL^{-1} DMRB, and the overlying water height was maintained at 1.0 cm. All column experiments were conducted in triplicate or quadruplicate and run for 21 d. The only experimental variable was flow rate, which ranged from 0.4 to 10 pore volumes day^{-1}, corresponding to Darcy velocities of 7.5 to 90 cm day^{-1}. Column effluent samples were collected daily and used to measure soluble Fe(II), lactate, and acetate. At the final 21 d point, columns were deconstructed in an anaerobic chamber to collect sediment samples as

a function of column length. These samples were used to measure 0.5 N HCl Fe(II), cell concentration, and iron mineralogy by Mossbauer spectroscopy. In most experiments, the effluent biogenic Fe(II) concentrations increased over the first 10 days and then remained relatively constant (Figure 1). From these pseudo steady state conditions the biogenic flux of Fe(II) (umol Fe(II) d^{-1}) was calculated as the product of the "plateau" concentration (umol L^{-1}) times the average flow rate (L d^{-1}). These flux results clearly demonstrate that hydrologic conditions effect biologic reactions (Figure 2). Based on calculations of the Peclet number for the various flow rates, the increase in biogenic flux occurs when transport processes switch from diffusion-controlled to advective-controlled. These results highlight the intriguing linkages between hydrology and biogeochemistry.

A simple reaction network was proposed to describe these systems and included four reactions: 1 – biological reduction of hematite coupled to lactate oxidation; 2 – sorption of biogenic Fe(II) to hematite; 3 – surface "hydration" of hematite to produce and account for "free" surface sites; and, 4 – organic Pipes buffering of the solution. The batch reaction-based model BIOGEOCHEM (Fang et al., 2003) was used to simulate all batch experiments and formulate and parameterize the hematite bioreduction reaction. An empirical rate formulation that was first-order with respect to free surface sites was selected for this reaction. Fe(II) sorption was modeled using a Freundlich isotherm. Surface hydration was modeled based on measured surface area and assumed site density. Pipes buffering was modeled based on the pKa value provided by the chemical manufacturer. With no further modifications, these rate formulations/parameters and equilibrium constants were used to model the constructed column results. The reaction-based reactive transport model HYDROGEOCHEM version 5.0 (Yeh et al., 2004) was used for these simulations. These column simulations revealed that the independently obtained reaction-based parameters could only accurately capture some of the experimental results. Therefore, our current effort is to re-examine and possibly expand the reaction network to include an appropriate term for DMRB growth.

2 REFERENCES

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3 FIGURES

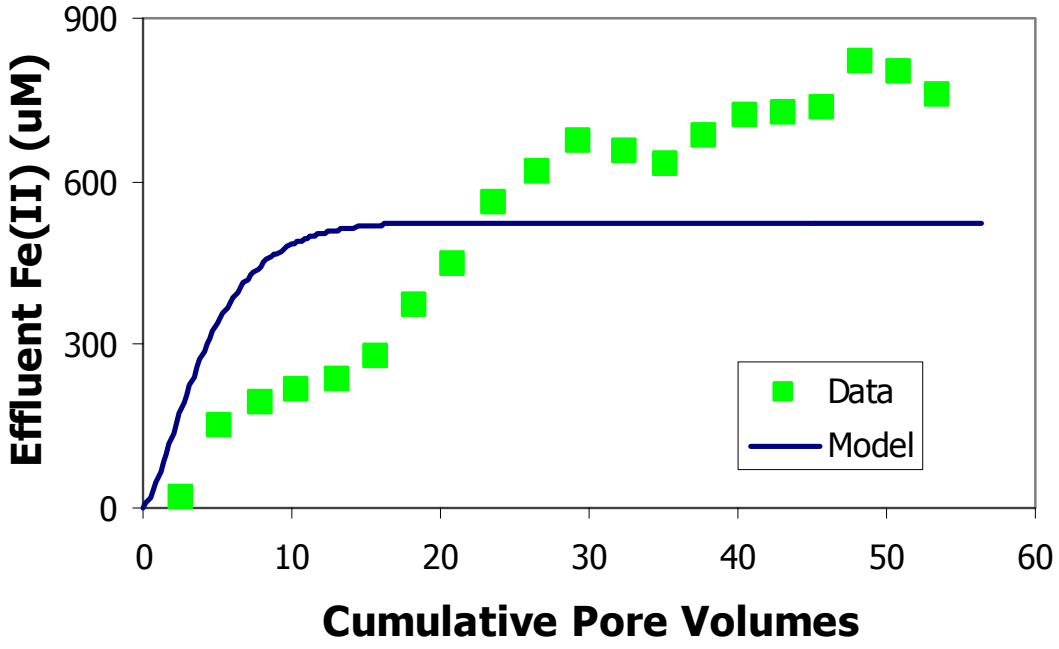

Figure 1. Effluent biogenic Fe(II) versus cumulative pore volumes from constructed columns of Eatontown hematite. Columns were 1-cm dia, 7.5-cm bed length, contained 9.0 g dry sediment, and were wet-packed with 10^8 cells/mL *Shewanella putrefaciens* CN32. Data shown is for a flow rate of 2.6 pore volumes per day.

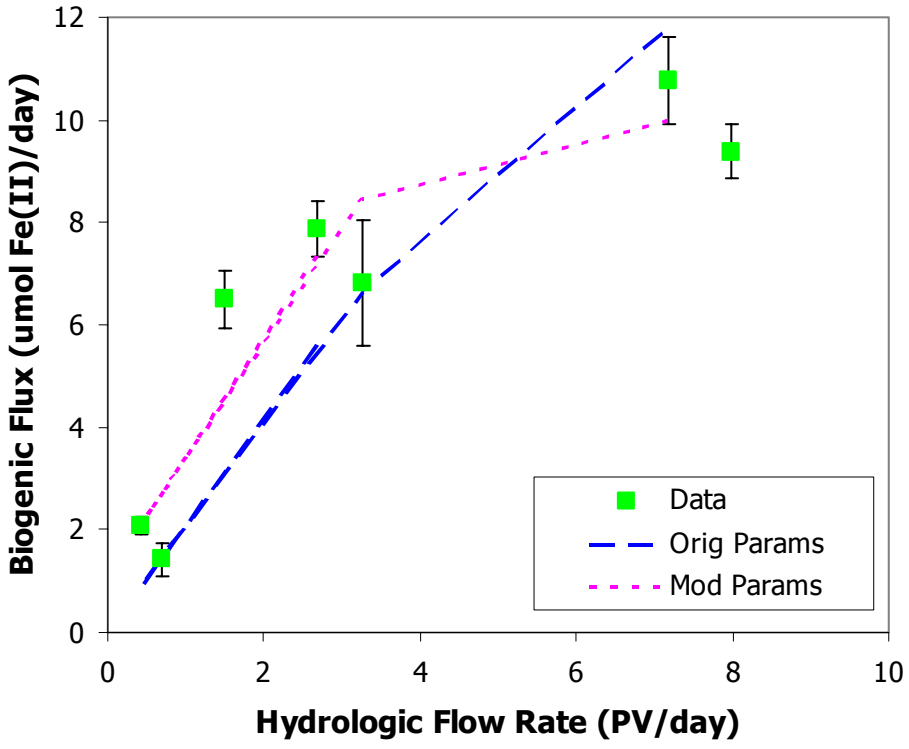

Figure 2. Psuedo-state biologic flux as a function of hydrologic flow rate.