Reaction-Based Reactive Transport Modeling of Biological Iron(III) Reduction in Natural Sediments

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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 aim 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 Fe(III) reduction in natural sediments. All experiments were performed with a hematite-rich sand from Eatontown, NJ (366 μmol 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 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 (10^7–10^9 cells mL^{-1}), and variable lactate concentrations (1–50 mM). Reactors were incubated at 20°C on a shaker table for 7 days, and kinetic data were collected on a logarithmic scale. For each time point, soluble Fe(II) (0.2 μm), 0.5 N HCl Fe(II), lactate, acetate, and pH were measured. At the final 7 day point, iron mineralogy (by Mössbauer spectroscopy) was 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 0.993). The overall Fe(II) production rate was directly dependent on sediment concentration (e.g., proportional to reactive iron surface area) and not 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 nonlinear, suggesting a growth term may be required to accurately capture this effect. Future work includes using these data and reaction models to determine the most appropriate rate formulation/parameters for modeling the column bioreduction experiments.

Eatontown sand and the bacteria were carefully wet-packed into 1 cm diameter glass chromatography columns with a packed bed length of ca. 7.5 cm. All column experiments were conducted in triplicate or quadruplicate and run for 20 day. The only experimental variable was flow rate, which ranged from 1 to 12 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 20 day point, column sediment samples were used to measure cell concentration, iron mineralogy, and 0.5 N HCl Fe(II) as a function of column length. In most experiments, the effluent biogenic Fe(II) concentrations increased over the first 10 days and then remained relatively constant. From these pseudo-steady-state conditions, the biogenic flux of Fe(II) [μmol Fe(II) hr^{-1}] was calculated as the product of the "plateau" concentration (μmol L^{-1}) times the average flow rate (L hr^{-1}) and clearly demonstrates that hydrologic conditions affect biologic reactions. Based on calculations of the Peclet number for the various flow rates, a step-function 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 that we hope to quantitatively simulate using reactive transport reaction-based models.

Diversity of Uranium Reduction Processes in