Reaction-Based Reactive Transport Modeling of Iron Reduction and Uranium Immobilization at Area 2 of the NABIR Field Research Center

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The proposed research is focused on developing mechanistic descriptions of important reactions and mathematical formulations for modeling the in situ immobilization of uranium promoted via microbial iron(III) reduction. Our goal is to develop and validate a mathematical model that can simulate all important chemical reactions and physical processes associated with in situ U(IV) immobilization. Experimental conditions will be designed to match those in saturated zone sediments at Area 2 of the DOE-NABIR Field Research Center (FRC).

The research will pursue three major objectives: (1) elucidate the mechanisms of reduction of solid-associated U(VI) in Area 2 sediment; (2) evaluate the potential for long-term sustained U(IV) reductive immobilization coupled to dissimilatory metal-reducing bacterial (DMRB) activity in Area 2 sediments; (3) numerically simulate the suite of hydrobiogeochemical processes occurring in experimental systems so as to facilitate modeling of in situ U(IV) immobilization at the field scale. The proposed research is based on the following five hypotheses: (1) the biological and chemical reduction of sediment-associated U(VI) is fundamentally controlled by its mineralogic and coordination environment; (2) the addition of humic substances can stimulate the reduction of solid-associated U(VI); (3) coupled Fe(III)/U(VI) reduction can be sustained in long-term flow-through reactor experiments with hydrologic residence times (week-to-month) comparable to those expected in pore domains likely to be colonized by DMRB in Area 2 sediments; (4) modest levels of nitrate input will not significantly inhibit coupled Fe(III)/U(VI) reduction in Area 2 sediments; and (5) the kinetics and thermodynamics of simultaneous biogeochemical reactions can be described by a series of reaction-based kinetic and equilibrium formulations derived independently from batch experiments.

To address the first hypothesis, we propose to use surface complexation modeling and spectroscopic techniques (XAS, LIFS) in a complementary fashion. Uranium(VI) sorption experiments will use Area 2 sediments and specimen minerals presumed to control U(VI) sorption and reducibility in these sediments (illite, goethite, and goethite-coated illite). The second hypothesis will be tested using a series of biotic (*Geobacter sulfurreducens*) and abiotic [excess Fe(II)] U(VI) reduction experiments with Area 2 sediments and specimen mineral assemblages in the presence/absence of FRC humic substances in batch reactors, semicontinuous culture reactors (SCRs), and constructed column reactors (CCRs). SCR experiments will provide suspension samples over time for solid-phase analyses (XAS, XPS, Mössbauer spectroscopy, ESEM, and wet chemistry). The third hypothesis will be tested in long-term SCR and CCR experiments containing Area 2 sediment inoculated with *Geobacter sulfurreducens*. The fourth hypothesis will be tested in long-term SCR and CCR experiments with *Geobacter metallireducens* (capable of both nitrate and metal reduction) and the presence/absence of 0.5 mM nitrate in the reactor feed solution. The fifth hypothesis will be addressed via continued development and calibration/validation of the BIOGEOCHEM–HYDROBIOGEOCHEM series of reaction-based computer models.