Geochemical Model, Model Uncertainty, and Pore Scale Insights for Uranyl Reactive Transport in Hanford 300A Smear Zone Sediments.

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This is a collaborative research to develop a consistent uranium geochemical model for Hanford 300A smear zone sediments, to assess model uncertainty for short- and long- term prediction of uranyl release from the sediments, and to provide pore-scale insights into the reactive transport in heterogeneous porous media. Experiments of batch, stirred flow-cell, and columns of variable sizes were performed to systematically investigate uranyl release from and reactive transport in different grain size fractions and their composites in a sediment composited from 300A smear zone sediments. A consistent geochemical model that integrates uranyl surface complexation reactions, aerobic denitrification, cation exchange, and calcite dissolution was developed to interpret the experimental results. A Bayesian-based Monte Carlo Markov Chain approach was developed to rigorously analyze the assumption and uncertainty of the rate parameters and their statistical distribution in the geochemical model and to assess the effect of the parameter uncertainty on the prediction of uranyl release from the sediment. X-ray computerized tomography (XCT), nuclear magnetic resonance relaxation (NMRR), and vacuum-drained pore water chemical analysis were used to provide insights into the pore-scale uranium distribution and release rates. Pore-scale micromodel and reactive transport simulations were used to investigate the coupling of advection and diffusion with surface reactions and to provide insights into the scale-dependent manifestation of the pore-scale geochemical reactions in both intragranular and inter-granular domains. The results showed that all grain size fractions ranging from clay/silt to gravel contributed to uranyl surface complexation reactions in the sediment. The desorption rates were similar in grains with <2mm sizes, but slower in the gravel fraction (2-8mm). The rate and extent of uranyl release was strongly affected by fluid chemical composition, which was collectively influenced by denitrification, calcite dissolution, and cation exchange. Uranyl release and reactive transport in the grain size composites (< 2mm and <8mm) were predictable from the linear addition of size-specific geochemical models, but were better simulated using a geochemical model for the composite. The results implied the importance of understanding microbial processes in the sediment that apparently led to the denitrification, which affected pH, calcite solubility, dissolved carbonate and calcium concentrations, which in turns affected uranyl surface complexation reactions. Besides the chemical composition effect, model simulations of the experimental results also indicated that uranyl release from individual grain size fractions and their composites was affected by diffusive mass transfer in intragranular and inter-granular domains, which was further confirmed by XCT and NMR tomographic analysis of sediment columns. Micromodel experiments and simulations revealed the importance of pore-scale coupling of geochemical reactions in controlling reaction rates at the Darcy scale. The coupling has a larger effect on faster reactions as they retarded the diffusion faster, which in turns affected more on surface reactions in interior diffusion domains. The developed uranium geochemical model contained uncertainty in its rate constants with slower rate constants having larger uncertainties. The uncertainty resulted from the assumption of the statistical distribution for the diffusive mass transfer rate constants in the model and from the time-scale limitation of laboratory experiments.