Project Title: Characterization of U(VI) Sorption-Desorption Processes and Model Upscaling

Project Number: 86748

Science Category: Geochemistry

Principal Investigator: Peter C. Lichtner (LANL)

1 Research Objective

Uranium (VI) is a common subsurface contaminant on DOE lands because of its central role in the nuclear fuel cycle. U(VI) groundwater plumes exist at Hanford, Oak Ridge, Savannah River, and other DOE sites. At each of these locations, DOE, regulators, and stakeholders are attempting to identify the best corrective and remedial actions for these U(VI)-plumes to protect human health and valuable environmental resources. Typically, the credibility of such assessments has been low because of inability to forecast in-ground U(VI) migration rates and redistribution. An insufficient scientific understanding of U(VI) geochemistry, and lack of knowledge of the various mineralogic, geochemical, geophysical factors that control the rates and extent of U(VI) reactions in commonly heterogeneous subsurface environments are key impediments. In this proposal we plan to characterize sorption and desorption processes of U(VI) on pristine and contaminated Hanford sediments over a range of sediment facies and materials properties. The sediments will be obtained from vertical cores collected from outside and inside waste sites, and will include the important geologic formations and facies types in which U(VI) contaminant plumes exist. The physical and chemical properties of the sediments will be incrementally characterized with increasing sophistication until controlling properties are identified. Molecular speciation measurements of adsorbed and precipitated U(VI) will be made using X-ray absorption and laser induced fluorescence spectroscopy with the objective of developing speciation-based conceptual and numeric models of sorption/desorption. The implications of intragrain mass transfer and reaction will be investigated using U-spiked/contaminated materials varying in U-contact time up to 30 years or more. Geochemical and mass transfer model parameters will be correlated with sediment physical, chemical, and mineralogic properties in attempt to develop a site-wide model for U(VI) geochemical retardation. Simple, volume-based upscaling relationships will be established for both sorption and desorption processes. The developed models and upscaling relationships will be tested at a U(VI) vadose zone field injection experiment to be performed by others where sediment geochemical/geophysical properties and U-plume evolution can be sampled and studied at scales ranging from centimeters to tens of meters. The research will provide new insights on the mechanisms of U(VI) retardation at Hanford and approaches to upscale laboratory developed geochemical models for defensible field-scale predictions.

2 Research Progress and Implications

This report summarizes work done during year 2 of a three year project. This study focuses on understanding mobilization and transport of U(VI) in the Hanford 300 Area which involves multiscale processes in leaching U(VI) from the sediments. Earlier studies based on a constant K_d model, grossly overestimated the U(VI) plume migration rate which did not dissipate as rapidly as had been expected. Recently it has been recognized that because of long, in-ground, residence times (waste emplacement occurred since the 1940's), U(VI) is present in complex, microscopic intra-grain fractures, secondary grain coatings, and micro-porous aggregates.The constant K_d model does not account for the slow release of U(VI) from sediment grain interiors through

mineral dissolution and diffusion along tortuous pathways. In fact, the K_d approach implies a continuous displacement of the U(VI) plume along the direction of flow, including both sorbed and aqueous components, at a retarded rate. Quite the opposite behavior is suggested by observation, and, indeed, a solubility limited source term which communicates by diffusive mass transfer to the bulk fluid would not be expected to migrate at all—in contrast to predictions of a K_d model. Rather, it would persist at its original location until all of the U(VI) had been removed by dissolution of the U(VI)-bearing phase.

In this work a dual continuum formulation is used in an attempt to capture the interaction between bulk fluid flow and diffusional mass transfer from grain interiors. Processes accounted for in the model include bulk fluid flow, intra-granular diffusion between the bulk fluid and sediment grains, surface complexation, and dissolution of U(VI)-bearing minerals. One continuum is used to represent the bulk fluid, and the other porous U(VI)-bearing sediment grains. The model is applied to stop-flow column experiments conducted at PNNL using sediments from the North and South Process Ponds at the Hanford 300 Area. Only the NPP1-16 column experiment is analyzed here. Although tracer experiments were also performed, these data did not prove useful due to the insensitivity of the measured tracer concentration over time.

Model calculations are carried out using the dual continuum formulation in the computer code FLOTRAN. One hundred nodes with a spacing of 1.45 mm are used to represent the bulk column. A nested set of spheres is used to represent the matrix grains with an average radius of $R_m = 2$ mm. The matrix is assumed to have a porosity of $\phi_m = 0.05$. It is discretized into 10 nodes consisting of concentric spheres with equal volume. U(VI) is assumed to be leached from a fictitious U(VI)-bearing solid phase taken to have the same stoichiometric coefficients as weeksite. At the BX-102 tank farm it is thought that Na-boltwoodite is the primary U(VI)-bearing phase, whereas at the 300 Area, U(VI) is likely to have co-precipitated with calcite or aragonite. However, the exact form of the U(VI) source is still under investigation. The form for the U(VI) solid used in the model will likely lead to different fit parameters for the effective surface area and rate constant, but otherwise is not likely to be greatly significant. The phase must, however, be undersaturated so that it dissolves in the sediment pore water. To fit the data, the matrix diffusivity D_m, surface complex site concentration ω_m, and effective kinetic rate constant and initial amount of the U(VI) source present are varied. In addition, the total initial concentration of U(VI) including aqueous plus sorbed concentrations in the matrix is fit to the early UO_2^{2+} breakthrough concentration giving a value of 3×10^{-7} mol/L. Surface complexation reactions were assumed to take the form

$$>\mathrm{NPPSOUO_2^+} \rightleftharpoons \mathrm{UO_2^{++}} + >\mathrm{SOH} - \mathrm{H^+}, \quad \log\mathrm{K} = 2.880, \tag{1}$$

$$>\mathrm{NPPSOUO_2OH} \rightleftharpoons \mathrm{UO_2^{++}} + >\mathrm{SOH} - 2\,\mathrm{H^+} + \mathrm{H_2O}, \quad \log\mathrm{K} = -4.612. \tag{2}$$

The fit to the NPP1-16 breakthrough data for UO_2^{2+} with and without surface complexation is shown in Figure 1 which gives the bulk (red curve), matrix (blue curve), and experimental data (points) as listed in the figure. Matrix effective diffusivity of $D_{\mathrm{eff}} = 10^{-6}$ cm^2 s^{-1} is used in the simulations. An effective rate constant of 3×10^{-15} mol cm^{-3} s^{-1} is used for the U(VI) source. In order to obtain the observed drop in UO_2^{2+} concentration with time, it was necessary to use a small volume fraction of 10^{-5} for the U(VI) source and allow the surface area to vary according to the relation

$$a_s = a_s^0 \left(\frac{\varphi_s}{\varphi_s^0} \right)^{2/3}, \tag{3}$$

where subscript s refers to the U(VI) solid source. The same sorption surface site concentration ω of 2.46×10^{-4} mol dm^{-3} is used for both the bulk and matrix continua.

It was found that surface complexation of U(VI) played only a minor role in the simulation as shown in the right panel of Figure 1 in which surface complexation is turned off. Only a slight shift occurs in the breakthrough points at stop-start events due to surface complexation.

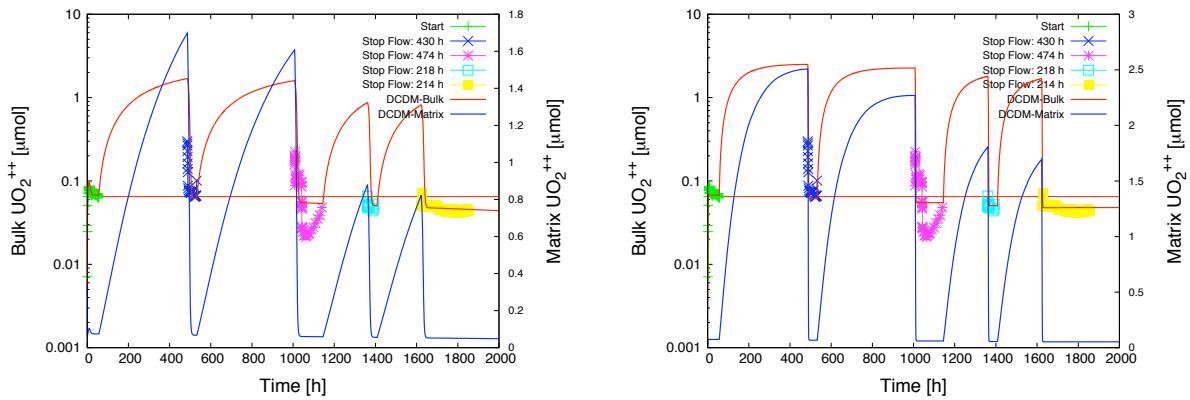

Figure 1: Breakthrough curves for UO_2^{2+} corresponding to bulk and matrix continua with (left) and without (right) surface complexation reactions. Data points refer to column experiment NPP1-16, column 19. Parameters used in the fit are given in the text. The thin horizontal red line is to aid the eye in showing the drop in UO_2^{2+} concentration as the U(VI) source becomes gradually depleted over time.

Future work will involve larger scale column experiments including cobbles and field applications. A new numerical approach for incorporating multi-scale processes into multicomponent reactive transport equations will be incorporated into FLOTRAN. The approach currently used in FLOTRAN, which is based on a brute force method that incorporates all subdomains together with the primary continuum within the Jacobian matrix, is too time consuming for anything more than a one-dimensional problem. With the new approach, multi-scale processes will be incorporated through a source/sink term added to the primary continuum equations that may be placed at any nodes within the problem domain. This versatility is essential at the Hanford 300 Area site where only the U(VI) source requires a multi-scale description. The multi-scale continuum model will be applied to larger scale column experiments conducted at PNNL containing cobbles in addition to Hanford sediment. The model will attempt to account for diffusion of U(VI) from surface regions of the cobbles to the bulk flow domain. Once it is demonstrated that the model can adequately explain leaching of U(VI) from column experiments including cobbles, it will be applied to a field-scale simulation of the 300 Area employing the massively parallel computer code PFLOTRAN. Varying stage of the Columbia River will be incorporated as a boundary condition on the field-scale model.

3 Information Access

Lichtner, P.C. (2006) Modeling U(VI) Transport at the Hanford 300 Area: Generalized Multiple Interacting Continuum (GMINC) Model, Los Alamos National Laboratory report, LA-UR-05-7754.