

## Sensitivity of Predictions of Uranium Plume Persistence at the Rifle IFRC Site to Reactive Transport Geochemical Parameters and Initial Conditions

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Surface complexation of U(VI) on mineral surfaces generally controls its transport in groundwater under oxic conditions. The degree of surface complexation is affected by several aqueous chemical variables, including pH and Ca, U(VI), and HCO<sub>3</sub><sup>-</sup> concentrations. Sorption of U(VI) on Rifle sediments as a function of these variables has been studied in batch experiments and used to develop a surface complexation model (SCM) for the Rifle site (1). Hyun et al. also tested the ability of the SCM to predict field-measured U(VI) sorption on Rifle sediments collected by coring and found the model performed successfully. In a further test of the model, Fox et al. (2) observed in a field experiment that an abrupt increase in HCO<sub>3</sub><sup>-</sup> concentration in Rifle groundwater required a kinetic sorption model to describe U(VI) desorption and transport, because groundwater velocity is fast relative to the time to reach sorptive equilibrium. A multi-rate, mass transfer model was applied to describe these data, using the SCM to describe equilibrium U(VI) conditions.

We have conducted 1-D reactive transport predictions for a likely groundwater flow path along a transect of the Old Rifle site. The model domain is 225m long, with input of relatively uncontaminated groundwater; the outlet is at the Colorado River near DOE well 310. Initial chemical conditions in the model were based on data collected in 1998 at DOE monitoring wells and the equilibrium SCM. Based on the flow velocity of (3), one pore volume passes through the domain in 2.2 yr. For a base case, the following assumptions were made: a) porosity = 25%, b) 35% of subsurface sediment mass is <2 mm with a surface area of 3.5 m<sup>2</sup>/g (sediments >2 mm are inert), and c) slight calcite oversaturation was allowed, based on field observations. Using the equilibrium SCM, it is predicted that it would take approximately 15 yr (i.e., until 2013) for U(VI) concentrations to decrease to near the upgradient value of 0.2 µmol/L at the model outlet.

The simulations are sensitive to several parameters or assumptions of the base case. For example, assuming calcite equilibrium with groundwater increases the time to reach 0.2 µmol/L U(VI) at the river by 60% to 24 yr. The reason for this effect is that U(VI) sorption is very sensitive to the Ca<sup>2+</sup> concentration because the major aqueous U(VI) species is Ca<sub>2</sub>UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub><sup>o</sup>. Assuming a porosity of 35% or that 61% of the sediment mass is <2 mm has a similar impact, because of the increase in surface area in the aquifer. Assuming a porosity of 15% (or 27% sediment <2 mm) decreases the natural attenuation time by 30% to 10.5 yr (until 2009). If one applies the multi-rate kinetic rate model (2), U(VI) concentrations fall faster at first at the end of the domain but are then followed by a much longer tail, increasing the cleanout time by 40% to 21 yr.

Current (2011) field observations of U(VI) concentration near the river outlet for this flowpath are 0.84 µmol/L, which has decreased from a peak value of 1.5 µmol/L in 2004. The base case predicted the 2011 value would be achieved by 2007, but predicted a higher peak value (5 µmol/L) in 2000 that was not observed. The higher values of U(VI) observed at present in comparison to the base case could be due to oxidation of U(IV) in the sediments, which has been found in the Rifle aquifer. Several simulations illustrate the potential impact of oxidation of U(IV) on the natural attenuation times for the aquifer and the sensitivity to various model parameter values.

1. Hyun, S.P., Fox, P.M., et al., 2009, Surface complexation modeling of U(VI) adsorption by aquifer sediments from a former mill tailings site at Rifle, Colorado, *Environ. Sci. Tech.*, 43, 9368-9373.
2. Fox, P.M., Davis, J.A., et al., 2012, Rate-Limited U(VI) desorption during a small-scale tracer test in a heterogeneous uranium contaminated aquifer, *Water Resources Res.*, in press.
3. Yabusaki, S. B., Fang, Y. et al., 2007, Uranium removal from groundwater via in situ biostimulation: Field-scale modeling of transport and biological processes, *J. Contam. Hydrol.*, 93, 216-235.