

## ABSTRACT

Surface complexation of U(VI) on mineral surfaces generally controls its transport in groundwater under oxic conditions. 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. (1) 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.

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 225 m 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 the 1990s at DOE monitoring wells and the equilibrium SCM. Based on the flow velocity of Fang et al. (2), 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 assumed 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 2007) 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>2</sub>. Assuming a porosity of 15% 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 35% or 27% sediment <2 mm decreases the natural attenuation time by 30% to 10.5 yr (until 2002). If one applies a rate-limited sorption model (3), 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 (well 310) 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 2003, but predicted a higher peak value (5 μmol/L) in 1995 when no monitoring wells were present. The higher values of U(VI) observed at present in comparison to the base case could be due to oxidation of U(VI) in the sediments, which has been found in the Rifle aquifer (4). Several simulations illustrate the potential impact of oxidation of U(VI) on the natural attenuation times for the aquifer and the sensitivity to various model parameter values.

## BACKGROUND, HYPOTHESIS & APPROACH



Figure 1. Rifle site, showing monitoring well locations, the direction of flow used for 1D transport modeling, and the U(VI) concentrations used for the initial conditions based on 1992 data.

The Old Rifle field site is a uranium mill tailings remediation (UMTRA) site located in Rifle, CO, on a floodplain of the Colorado River (Figure 1). From 1924-1958 uranium and vanadium ore processing facilities were located on the site and produced mill tailings that were originally disposed of on site. Remediation of the site was performed from 1992-1996, with removal of mill tailings and contaminated surface soils. Uranium-contaminated groundwater at the site flows through unconsolidated Quaternary floodplain deposits composed mainly of quartz and feldspar sands, plus silts, clays, pebbles, and cobbles. A U(VI) surface complexation model has been developed for the site that describes U(VI) sorption equilibrium as a function of pH, alkalinity, and Ca concentration (1). Historical head data suggest that the predominant groundwater flow direction is as shown in Figure 1, although there are seasonal changes. U(VI) concentrations in the middle of the modeling domain were much higher in 1992, prior to cleanout than later in 1998 (Figs. 2, 3, and 4), but are still persisting at well 310 in 2011.

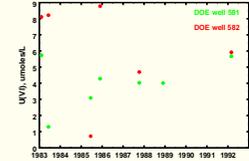


Figure 2. U(VI) concentrations at wells 581 and 582 in the years prior to site remediation, 1983-1992.

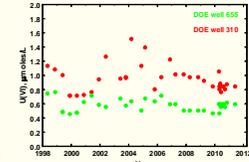


Figure 3. U(VI) concentrations at wells 310 and 655 in the years after site remediation, 1998-2011.

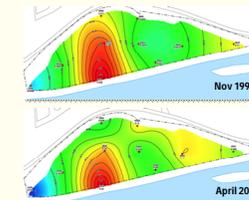


Figure 4. U(VI) concentration contours across the Rifle site at Nov. 1998 and April 2007.

## RESULTS

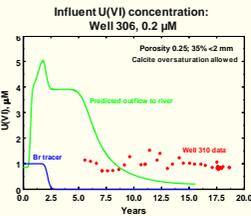


Figure 5. Predictions of U(VI) concentration elution from the Rifle aquifer with the following assumptions: 1) time zero is May 1992 with no U source terms other than background influent U(VI) of 0.2 μM, 2) groundwater velocity (0.28 m/day) from Fox et al. (2), 3) uniform porosity of 25% and sediment texture of 35% <2 mm in the 1D domain of 225m, 4) U(VI) sorption equilibrium as described by Hyun et al. (2009) only on sediments <2 mm, and 5) calcite oversaturation allowed, as it is observed at most wells in the Rifle alluvial aquifer. Note that breakthrough of a non-reactive tracer, Br<sup>-</sup>, occurs in 2.2 years and that U(VI) concentrations in well 310 persist beyond the predicted flushing of the aquifer at about 12 years (2004).

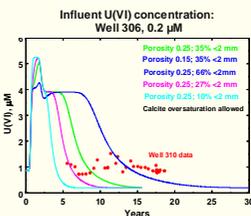


Figure 7. Comparison of the predicted U(VI) concentration elution from the Rifle aquifer as a function of porosity and sediment texture. Conditions were otherwise the same as in Figure 5. Mean groundwater velocity was kept at the same value despite the change in porosity. Note that lower porosity or greater % <2 mm increases sorption sites in the aquifer and the initial inventory of sorbed U(VI), which increases the time required to flush U(VI) out of the system.

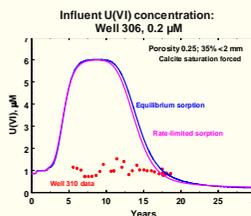


Figure 9. Comparison of the predicted U(VI) concentration elution from the Rifle aquifer using equilibrium versus rate-limited surface complexation modeling approaches under conditions that assume saturation with respect to calcite. The equilibrium model is the same as that shown in Figure 8. The rate-limited model predicts little difference compared to the equilibrium model.

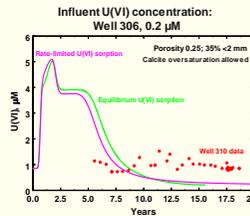


Figure 6. Comparison of the predicted U(VI) concentration elution from the Rifle aquifer using equilibrium versus rate-limited surface complexation modeling approaches. The equilibrium model is the same as that shown in Figure 5. The rate-limited model is that of Fox et al. (3), based on a tracer test conducted at the site with a spatial domain on the order of 5 m. The rate-limited model predicts little difference compared to the equilibrium model, but the rate limitation is likely scale-dependent, and thus may be more significant than shown over the 225 m domain.

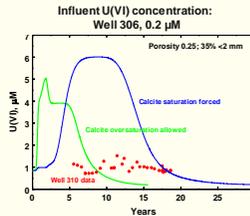


Figure 8. Comparison of the predicted U(VI) concentration elution from the Rifle aquifer as a function of calcite saturation. The green curve is the same as in Figure 5. The model shown as the blue curve changed the groundwater chemistry of the initial conditions and that of influent groundwater such that it was in equilibrium with calcite, which slightly lowered dissolved Ca, alkalinity, and pH. These changes had a very significant effect on U(VI) flushing because of the large sensitivity of U(VI) sorption to these variables.

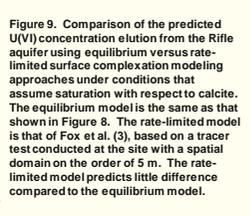


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## RESULTS

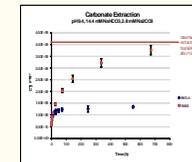


Figure 10. Aerobic carbonate extractions of U from two Rifle sediment samples: a background sample used for the U(VI) surface complexation model (1), and the RABS sample, collected from a contaminated portion of the aquifer. RABS had more extractable U that was more slowly released than from the background sample.

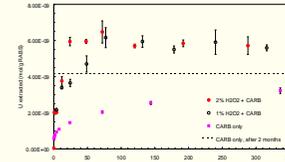


Figure 11. Carbonate extractions of U from the RABS sample, which show a very large increase in the extractable U in the presence of the oxidant, H<sub>2</sub>O<sub>2</sub>, suggesting the presence of U(IV) in the sample.

**Unknown subsurface inventory of U(IV).** Wet chemical extractions of the RABS sample (Figs. 10 and 11) suggest that U(IV) is present in some Rifle aquifer sediment samples at low concentrations. U(IV) has been observed directly in one subsurface sample where the U concentration was high enough to use XANES spectroscopy (4). Natural reducing zones (with sulfidic minerals) have been observed in a few locations in the aquifer, but the amounts of U(IV) in the aquifer are not known. Figures 12 and 13 illustrate predictions of U flushing from the aquifer at various initial concentrations of U(IV) in the modeling domain and with varying rates of oxidation by ferrihydrite under anoxic conditions, based on the laboratory rate measured by Ginder-Vogel et al. (5).

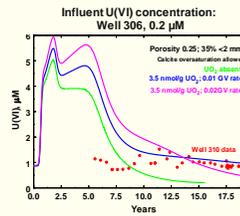


Figure 12. Comparison of predicted U(VI) concentration elutions from the Rifle aquifer as a function of the rate of oxidation by ferrihydrite with an initial U(VI) concentration of 3.5 nmol/g sediment. The blue and magenta curves compare the U(VI) elution rate with U(VI) oxidation rates at 0.01 and 0.02 times the laboratory rate measured by Ginder-Vogel et al. (5). The green curve is from Figure 5 with zero U(IV) present. The presence of U(IV) may explain the persistence of measurable U(VI) concentrations at well 310.

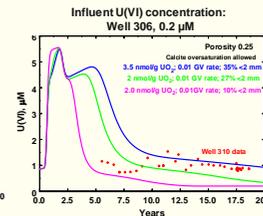


Figure 13. Comparison of predicted U(VI) concentration elutions from the Rifle aquifer at selected initial U(IV) concentrations and sediment textures at 0.01 times the rate measured by Ginder-Vogel (5). The blue curve is the same as Fig. 12. Green and magenta curves show U(VI) flushing with an initial U(IV) concentration of 2 nmol/g sediment with either 27 or 10% <2 mm sediment. As shown in Fig. 7, the % <2 mm affects the initial U(VI) inventory in the subsurface. The initial U(IV) concentration in the subsurface may explain the persistence of measurable U(VI) concentrations at well 310.

## SUMMARY

Simple 1D reactive transport predictions suggest that flushing of U from the Rifle site to achieve background U concentrations in groundwater should have been complete by 2007 if only sorbed U(VI) was present. Initial chemical conditions in the model were based on data collected in the 1992 and an equilibrium SCM for U(VI). The simulations are sensitive to several parameters or assumptions, including the porosity and sediment texture. Current field observations of U(VI) concentration near the river outlet are 0.84 μmol/L, which has decreased from a peak value of 1.5 μmol/L in 2004. The persistence of a U(VI) plume in the Rifle aquifer may be caused in part by the presence of a low concentration of U(IV) in the sediments that is only slowly oxidized by iron oxides.

## REFERENCES

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