

# Application of Surface Complexation Modeling to Describe Uranium(VI) Adsorption and Retardation at the Field Scale

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## 1 INTRODUCTION

Uranium (U) is a contaminant of concern to the U. S. Federal Government at many sites where it has been released to the environment or where it remains in poorly designed storage facilities. At the U. S. Department of Energy facilities, U is the most common radionuclide contaminant in groundwater/sediment systems. Risk assessments must be conducted for many of these contaminated sites to evaluate remediation scenarios, and a significant component of such risk assessments includes predictions of U transport to drinking water supplies or biological receptors via a groundwater pathway.

In oxic environments, the most stable valence of uranium is U(VI) which forms moderately soluble solid phases. Thus, at concentrations less than approximately  $30\mu\text{M}$ , the mobility of U(VI) can be controlled by adsorption reactions at circumneutral pH values. In performance assessment model simulations, adsorption of U(VI) has been approximated by a single distribution coefficient,  $K_D$ , or a range of spatially and temporally uniform  $K_D$  values. If there is significant chemical variability, however, the  $K_D$  value may not be constant and therefore can introduce considerable uncertainty into the model simulations. This is particularly true for U(VI) which undergoes complex aqueous and surface speciation reactions. Alternatively, surface complexation models (SCMs) can be used to describe U(VI) adsorption for variable geochemical conditions. In this study, a semi-empirical SCM was calibrated to laboratory data for adsorption of U(VI) by aquifer sediments and then this SCM was tested in field studies and in reactive transport simulations.

## 2 SITE DESCRIPTION

A uranium mill that was located along the San Miguel River near the town of Naturita, CO processed uranium ores by salt roasting followed by both sodium carbonate and sulfuric acid extractions to produce uranium concentrates between 1939 and 1961. Processed mill tailings were removed from the site in 1979 and contaminated soils were removed from the site between 1996 and 1998. Figure 1 shows the locations of all of the active groundwater wells that were installed in the shallow, unconfined alluvial aquifer that consists of cobbles, gravels, sands and some fine material. The aqueous U(VI) concentrations observed in June 2000 are also shown. U(VI) varied from background concentrations of  $0.02$

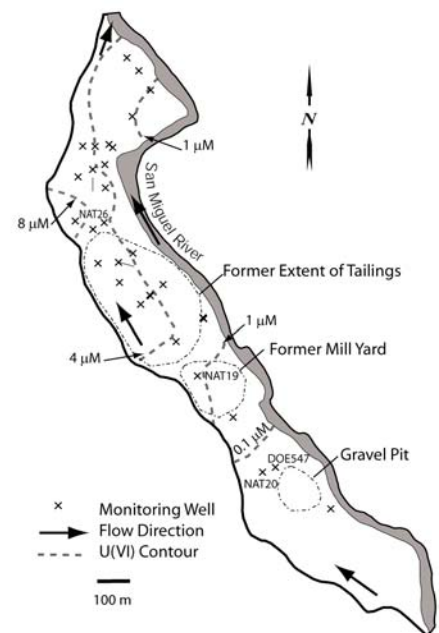


Figure 1. Naturita mill tailings site illustrating the monitoring wells, U(VI) concentrations, the extent of the former tailings piles and mill site, and the gravel pit.

$\mu\text{M}$  at DOE547 to maximum concentrations of  $10.2 \mu\text{M}$  at NAT26. The spatial distribution of alkalinity was similar in shape to that for dissolved U(VI) but the values ranged from 4 meq/L in background wells to 12 meq/L at NAT26. The pH values were typically between 6.8 and 7.2 and did not illustrate a discernable, persistent spatial pattern. The waters were generally close to saturation with calcite, which is present in the sediments.

### 3 APPROACHES TO ADSORPTION MODELING

Uranium(VI) adsorption onto Naturita aquifer background sediments (NABS) was studied in batch experiments as a function of pH, U(VI) and  $\text{CO}_2$  partial pressure in artificial ground-water solutions. The sediments were collected from the alluvial aquifer at a gravel pit located upgradient from the former uranium mill (Figure 1). The ranges of aqueous chemical conditions used in the U(VI) adsorption experiments (pH 6.9 to 7.9; U(VI) concentration 0.02 to  $10 \mu\text{M}$ ; partial pressure of carbon dioxide gas 0.05 to 6.8%) were based on chemical conditions observed in 1999-2000 in the Naturita alluvial aquifer. The major minerals in the sediments were quartz, feldspars, and calcite, with minor amounts of magnetite and clay minerals. Quartz grains commonly had coatings that were greater than 10 nm thick and composed of an illite-smectite clay with occluded ferrihydrite and goethite particles.

A semi-empirical SCM was calibrated to laboratory adsorption data that used Naturita sediments and the observed ranges in geochemical conditions. In the modeling approach, adsorption was postulated to occur on generic surface sites that represent average properties of the surface rather than specific mineral surfaces. Model parameters were calibrated to adsorption data for postulated reaction stoichiometries and different model formulations are selected on the basis of simplicity and goodness of fit. Electrostatic terms were not included in the model because of the difficulties in quantifying the electrical field and charge at the mineral-water interface in the mixture of mineral phases and associated surface coatings. Figure 2 shows that the calibrated model reproduces measured U(VI)  $K_D$  values over the entire range of experimental (and field) conditions. The semi-empirical SCM approach is therefore a practical approach that allows the modeler to couple the effects of variable geochemical conditions on adsorption and retardation.

Published models for U(VI) adsorption on reference minerals were compared to the semi-empirical SCM in terms of the ability to describe the U(VI) experimental data based on assumptions about the sediment surface composition, surface area and electrical double layer properties. Predictions from these models were highly variable, with results over predicting or under predicting the experimental data, depending on the assumptions used to apply the model. Although the models for reference minerals are supported by detailed experimental studies (and in ideal cases, surface spectroscopy), the results suggest that errors in applying the models directly to the Naturita sediment result from uncertain knowledge of: (1) the proportion and types of surface functional groups available for adsorption in the inorganic surface coatings, (2) the electric field at the mineral-water interface, and (3) surface reactions of major ions in the aqueous phase, such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{H}_4\text{SiO}_4$ , and natural organic matter.

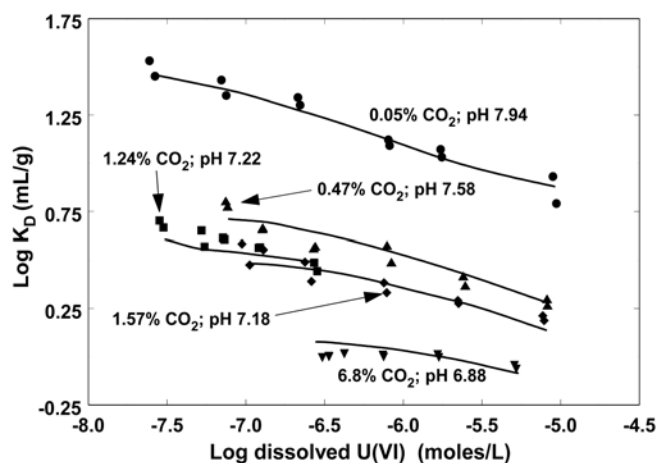


Figure 2. Fit of the semi empirical SCM to observed U(VI) adsorption data.

## 4 FIELD TESTS OF THE SCM

The SCM developed in laboratory studies was tested for its ability to describe U(VI) adsorption in the field using two different experimental approaches. In the first case, U(VI) adsorption onto contaminated sediments that were collected during well installation was measured using both isotopic exchange experiments and extractions with a  $\text{Na}_2\text{CO}_3$  solution that had a pH of 9.5 and an alkalinity of 20 meq/L. The two experimental methods gave nearly identical results. In the second case, U(VI) adsorbed by NABS samples that were suspended in wells that had contaminated groundwater was determined by extraction with the  $\text{Na}_2\text{CO}_3$  solution. Observed  $K_D$  values were calculated from adsorbed U(VI) measured in the extractions and the dissolved U(VI) measured in the wells. The observed  $K_D$  values are compared with model-predicted  $K_D$  values in Figure 3. The SCM gives model-predicted  $K_D$  values that agreed with measured  $K_D$  values within a factor of 2.2 on average. The contaminated sediments from MAU03 and MAU04 had measured  $K_D$  values that were significantly larger than the model-predicted  $K_D$  values and it is possible that these samples could have contained U(IV). The possible presence of U(IV) is consistent with the occurrence of Fe(II) in these wells; other chemical conditions at these wells are not likely explanations because measured  $K_D$  values for NABS samples in these wells agreed closely with model predictions. Overall, the agreement between model-calculated and measured  $K_D$  values increases the confidence in the applicability of the laboratory determined SCM to simulate U(VI) adsorption in the field.

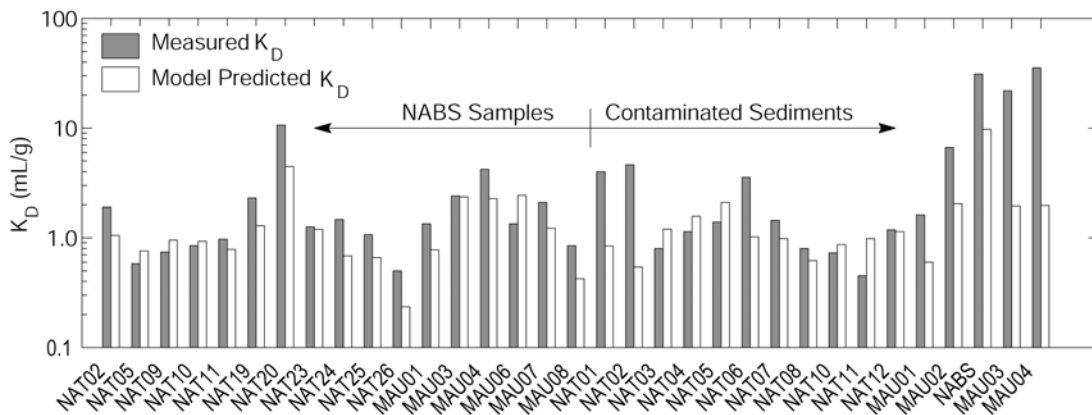


Figure 3. Comparison of measured and model-predicted  $K_D$  values for (a) uncontaminated NABS samples that were suspended in ground water wells and (b) contaminated sediments collected during well installation.

## 5 REACTIVE TRANSPORT MODELING

A groundwater flow and transport model was developed for the site using tritium-helium age dating results and a Cl plume that originated from residues from the salt roasting of the U ore. A reactive transport model was calibrated to the existing site data by varying the U(VI) and alkalinity concentrations in the recharge water to give a best fit to the observed values. The contaminated recharge was assumed to extend from the upgradient boundary of the former mill yard to the downstream boundary of the former tailings pile. The contaminated recharge was assumed to be present until the contaminated soils were removed from the site in 1998. The calibration of the reactive transport model did not vary the SCM parameters or the hydraulic conductivity ( $K_H$ ), which were determined independently.

Figure 4 shows the simulated and observed distributions of U(VI) and alkalinity. The simulated U(VI) and alkalinity plumes generally match the observed spatial distribution in that the locations and values of the highest concentrations are similar and there are lower observed and simulated values near the river.

The log  $K_D$  values shown in Figure 5 were calculated from the simulated adsorbed and dissolved U(VI) concentrations. The simulated  $K_D$  values vary by approximately a factor of 10 and the simulated values are not distributed randomly but have significant spatial structure. The groundwater with the largest dissolved U(VI) and alkalinity is transported with the smallest  $K_D$  values. Therefore the spatial distribution of  $K_D$  values is also expected to vary temporally.

A simple sensitivity analysis was conducted to evaluate the influence of hydraulic conductivity ( $K_H$ ) and SCM model parameters on the simulated U(VI) concentration. The model was most sensitive to  $K_H$ . The sum of sensitivity of the model to the SCM site concentrations was about 40% of the  $K_H$  value.

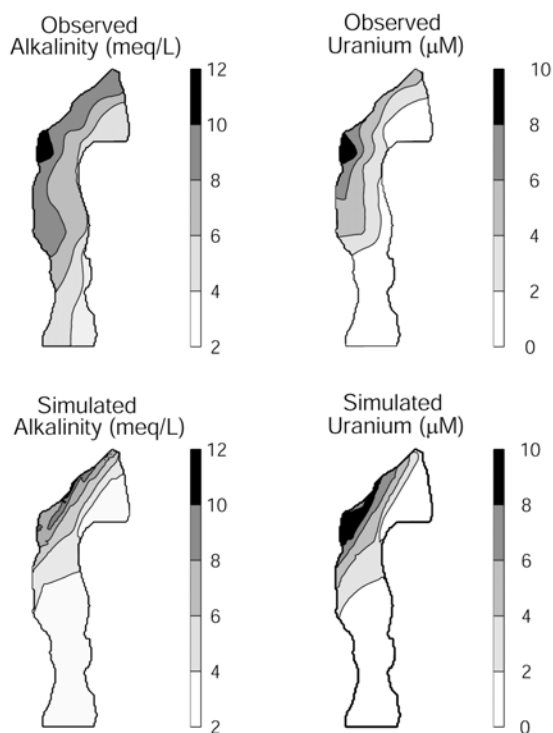


Figure 4. Comparison of observed and simulated distributions of dissolved U(VI) concentration and alkalinity in 2000.

## 6 SUMMARY AND CONCLUSIONS

The reactive transport model that includes the semi-empirical SCM is a useful tool for simulating the transport of U(VI) at the field scale with chemically variable conditions. This modeling approach is a compromise modeling approach between the simple constant  $K_D$  approach and the most complex of SCM modeling approaches that attempt to account for sorption on each of the many minerals present in most sediments and possibly the electrical double layer properties of each mineral phase. The semi-empirical SCM approach is based on the premise that coatings dominate the surface chemistry of most of the mineral grains, and as a consequence, adsorption can be described with a relatively small set of reactions and mass action expressions. The semi-empirical SCM modeling approach can be relatively easily applied, and it does not require a burdensome program of data collection. The model is capable of accounting for the effects of variable chemical conditions on U(VI) adsorption and transport. In the Naturita case, the most important variable chemical condition was the alkalinity, but at other sites, pH or the concentrations of other complexing ligands could be important.

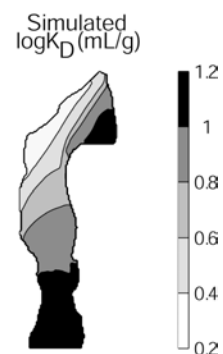


Figure 5. Simulated  $K_D$  values for the year 2000.