

A SURFACE COMPLEXATION MODELING APPROACH FOR URANIUM(VI) TRANSPORT IN GROUNDWATER

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ABSTRACT

Uranium(VI) adsorption by aquifer sediments was studied under oxic conditions as a function of pH, uranium(VI), calcium, and dissolved carbonate concentration. A surface complexation model was developed to describe uranium(VI) adsorption data; the model simulated uranium(VI) adsorption over the range of groundwater conditions at the field site, using a two-site, two-reaction model. The model is expected to contribute to the prediction of fate and transport of uranium in the alluvial aquifer at Rifle (Colorado, USA) and to assist in the modelling of natural attenuation of uranium transport at the site.

1. INTRODUCTION

Controlling uranium contamination in the subsurface is an important part of the uranium mining process and in closure planning for uranium mines. In-situ leach mining of uranium also presents specific problems in groundwater restoration and stabilization. Bioremediation is a promising strategy for the treatment of uranium-contaminated groundwater. In bioremediation schemes, dissolved uranium(VI) is reduced to insoluble uranium(IV) by stimulating indigenous metal-reducing bacteria *in situ* by the addition of low concentrations of an electron donor, such as acetate, lactate, or hydrogen gas. The use of active or passive remedial technologies for remediation of uranium plumes requires knowledge of the geochemical conditions in an aquifer, including its subsurface natural attenuation capacity. In general, reliable engineering of microbially-mediated uranium immobilization under site-specific subsurface conditions will require a predictive and quantitative understanding of the principal processes and properties controlling uranium biogeochemistry. Our research is focused on gaining a better mechanistic understanding of uranium mobility in the subsurface and the use of bioremediation to achieve groundwater uranium concentrations below desired water quality standards. The research is part of a larger project occurring at a former uranium mill tailings site, integrating biological, geochemical, and hydrological studies.

Under oxic conditions, uranium has a complex aqueous chemistry, with the hexavalent uranyl ion (UO_2^{2+}) predominant at low pH, and many hydrolysis and carbonate complexes predominant at neutral to alkaline pH values (Waite et al., 1994). Within the last several years, new uranium(VI) aqueous species (ternary calcium-uranyl-carbonate and magnesium-uranyl-carbonate complexes) have been discovered that are important in uranium(VI) speciation in groundwater (Dong and Brooks, 2006; Fox et al., 2006).

Uranium(VI) transport in aquifers is significantly slowed by adsorption and/or reduction, and strongly affected by the geochemical conditions (e.g., pH, $[\text{Ca}^{2+}]$, and P_{CO_2}) and their impacts on uranium(VI) aqueous speciation (Curtis et al., 2009; 2006; Jeon et al., 2005). For example, raising the partial pressure of carbon dioxide in equilibrium with water from its value in air to 1% decreases the distribution coefficient (K_d) value for uranium(VI) adsorption by ferrihydrite by four orders of magnitude at pH 8, as a result of the increasing importance of dissolved carbonate complexes (Davis et al., 2004). A significant range in the partial pressure of carbon dioxide is not uncommon in aquifers, especially those contaminated by uranium mill operations (Curtis et al., 2009; Curtis et al., 2006). Similarly, pH and calcium concentration have been shown to have an impact on K_d values (Fox et al., 2006; Waite et al., 1994).

Prediction of uranium transport at contaminated sites requires a reactive transport model capable of simulating uranium(VI) adsorption by aquifer sediments under a range of geochemical conditions relevant to the specific aquifer. In comparison to the use of a constant- K_d approach, surface complexation model approaches have the advantage of being able to capture spatially and temporally variable retardation as geochemical conditions change in an aquifer (Curtis et al., 2009). In contaminated aquifers, gradients in chemical concentrations can result in K_d values that range several orders of magnitude (Curtis et al., 2006; Kent et al., 2000; Kohler et al., 1996). When extensive sediment characterization is impractical or less model complexity is desired, a generalized composite modelling approach is often used (Davis et al., 2004; 1998), as is demonstrated here.

In this study, the generalized composite modelling approach was used to simulate uranium(VI) adsorption under oxic conditions on sediments collected at a former uranium mill site at Rifle, Colorado (USA). Groundwater samples from the site show spatial and seasonal variations in major element chemistry, especially calcium and magnesium concentrations and alkalinity. Batch experiments were previously conducted for uranium(VI) adsorption by two Rifle sediment samples over a range of dissolved uranium(VI), calcium, and bicarbonate concentration conditions that

spanned the range in groundwater chemistry at the site (Hyun et al., 2009).

Various uranium(VI) surface complexation reactions were evaluated to develop a surface complexation model that simulates uranium(VI) adsorption by the aquifer sediments as a function of aqueous chemical composition.

2. SITE DESCRIPTION

The Old Rifle uranium mill tailings site is located on a flood plain of the Colorado River in Rifle, Colorado (Figure 1). Groundwater at the site flows through unconsolidated Quaternary floodplain deposits composed mainly of quartz and feldspar sand plus silts, clays, pebbles, and cobbles, often coated with iron oxide minerals. A confining bedrock layer at a depth of approximately 8 m is a part of the Tertiary Wasatch Formation. From 1924-1958, the site hosted vanadium and uranium ore processing facilities and uranium mill tailings. Between 1992 and 1996, the site was remediated and restored by excavating and relocating contaminated materials. Nonetheless, groundwater and aquifer sediments beneath the site still have elevated concentrations of uranium.

A sediment sample was collected a mile upstream from the site (Figure 1) in October 2007 to ensure that the sediment was not contaminated from uranium ore processing or the mill tailings previously at the site. The sediment was air-dried and the <2 mm fraction was collected for uranium(VI) adsorption experiments. The sediment was mainly composed of quartz (56 %), plagioclase (20 %), and K-feldspar (15 %), with minor amounts of calcite, chlorite, kaolinite, and iron oxide minerals, magnetite, hematite, and goethite. Its BET specific surface area was 4.06 m²/g. Hydroxylamine hydrochloride extractions, using 0.5 h extraction with 0.25 M hydroxylamine hydrochloride/0.25 M hydrochloric acid at 50 °C, determined an iron oxide content of 4.70×10⁻⁶ mol/g.

To illustrate the ability of a set of surface complexation reactions to model the uranium(VI) uptake, a model was developed and simulations were compared with measured values of K_d. To determine K_d, it was necessary to measure the labile background uranium(VI) on the sediment samples. Details of the measured background uranium(VI), the kinetics of uranium(VI) adsorption/desorption, and the K_d values are presented in Hyun et al. (2009). A sodium (bi)carbonate extraction (Kohler et al., 2004) yielded a background labile sediment uranium(VI) concentration of 1.35×10⁻⁹ mol/g at 336 hr. To determine K_d values, the total uranium(VI) available for adsorption was calculated as the sum of the labile uranium(VI) initially present on the sediment samples plus uranium(VI) added to the artificial groundwater solution used in the batch experiments. When little or no uranium(VI) was added to an artificial groundwater solution (AGW), the background labile uranium(VI) strongly affected K_d values calculated from the adsorption data. Without consideration of the labile sediment uranium(VI), “negative” K_d values were calculated due to uranium(VI) desorption. In contrast, at high uranium(VI) concentrations, the background labile uranium(VI) had an insignificant effect on determined K_d values. It was important to take this effect into account in analyzing the data prior to development of the surface complexation model.

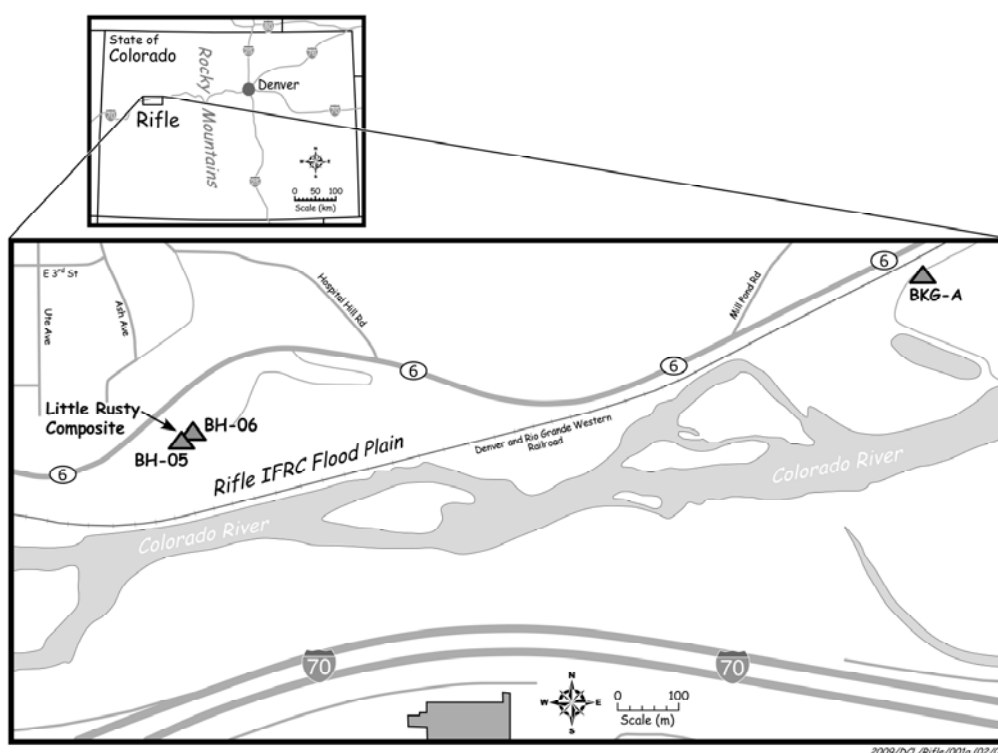


Figure 1. Site map and sampling location of the study site at Rifle, Colorado, USA. The Colorado River flows to the west, towards the left side of the diagram.

The kinetics of uranium(VI) adsorption was measured at a total uranium(VI) concentration of 2.12×10^{-7} M in equilibrium with air. The data showed that uranium(VI) adsorption is rapid, reaching completion within 24 h. However, uranium(VI) desorption was slower, as seen in the sodium (bi)carbonate extraction and in pre-equilibration of artificial groundwater solutions with the sediments (detailed results presented in Hyun et al., 2009).

Figure 2 shows the uranium(VI) adsorption data under variable uranium(VI) and dissolved carbonate concentrations, in terms of $\log K_d$ versus \log equilibrium dissolved uranium(VI) concentration. K_d values were dependent on the initial uranium(VI) concentration, pH, and P_{CO_2} . The measured K_d values show variation of almost 2 orders of magnitude, demonstrating the benefit of a surface complexation model rather than a constant- K_d model to describe uranium(VI) adsorption at the site. Groundwater chemistry at most wells at the site indicate that the partial pressure of CO_2 is in the range of 1-10% (based on the alkalinity and pH) (Yabusaki et al., 2007), indicating that the uranium(VI) K_d value should range from near zero up to about 7 ($\log K_d$ equal 0.5) (Figure 2).

3. SURFACE COMPLEXATION MODELING

An inverse modeling approach (Davis et al., 2004) was used to simulate the uranium(VI) adsorption data covering the range of chemical conditions encountered in the shallow aquifer at the site under suboxic conditions. First a one-site one-reaction approach was used to simulate the experimental data, with ionic strength, pH, alkalinity, total dissolved calcium, and total labile uranium(VI) concentrations as inputs to the speciation calculations. Table 1 lists the single surface reactions considered in the model, along with the corresponding equilibrium constants and goodness-of-the-fit (GOF) values obtained. Reaction 6, which represents the binding of a uranyl carbonate complex (UO_2CO_3) to the surface gave the best fitting result (GOF=7.41). Next, pairs of surface species binding to a single surface site were tested to see if having two surface reactions would improve the GOF. The combination of Reaction 2 and Reaction 10 gave the best fit (GOF=4.7). Next, a stronger bonding site was added to the single site model to test if the additional site could improve the GOF. To determine the appropriate number of strong sites, the set of single reactions were tested with this two-site model by varying the value of the strong binding site density. The results indicated that adding the strong site significantly improved the fitting. Ultimately, the final result (Figure 2) was found using two sites with a strong site density of 0.01 % of the total site density and Reactions 2 and 10 (GOF=1.17; Table 2).

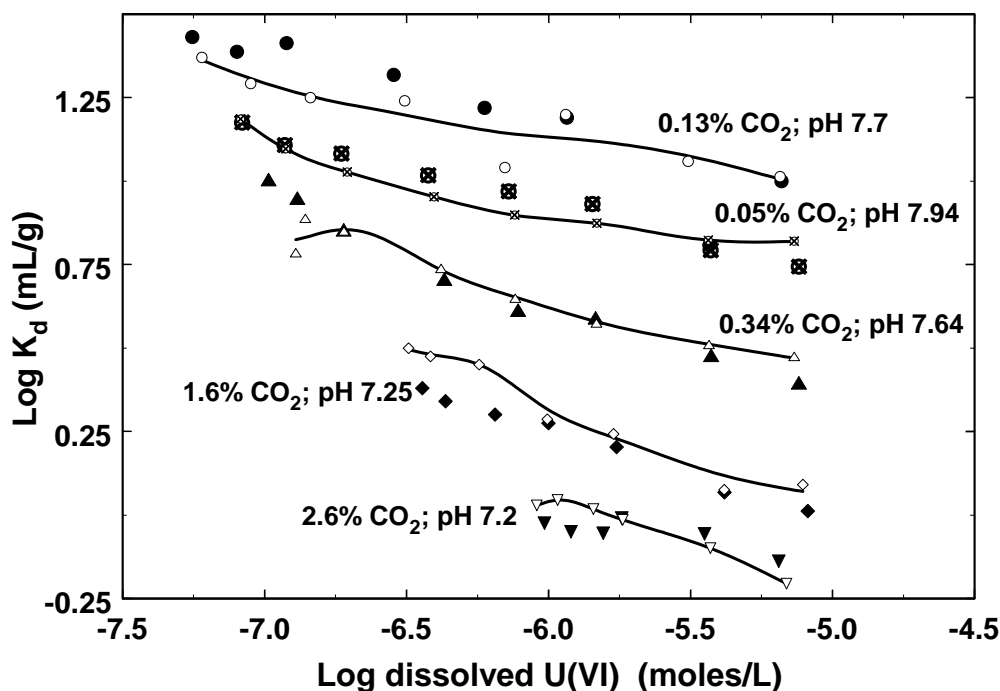


Figure 2. Generalized composite model simulation of uranium(VI) adsorption on Rifle aquifer sediments. Filled symbols represent experimental data points. Corresponding open symbols represent model simulations for the conditions of each experimental point. The solid curves are splines drawn to represent the trends of the modeling calculations.

The value of the formation constants for calcium-uranyl-carbonate solution complexes (Dong and Brooks, 2006) had significant impact on the values of the surface complexation constants. For all solution conditions, the model predicted $Ca_2UO_2(CO_3)_3(aq)$ as the dominant aqueous species. This observation illustrates the importance of obtaining experimental data over a sufficiently wide range of chemical conditions when developing a surface complexation model. The conditions should span the range that is expected in field applications (Curtis et al., 2006; Davis et al., 1998) so that the model will be sufficiently robust for simulating adsorption as a function of conditions that vary temporally and spatially within a transport modeling domain.

The surface complexation model developed here contributes to our understanding of uranium fate and transport at the Rifle site, but needs to be expanded further to consider coupled uranium redox reactions that occur at the field site under ambient and biostimulated conditions (Yabusaki et al., 2007). One feature of the field site is naturally occurring zones of bioreduction. The effect of these zones on the fate and transport of uranium in the subsurface is likely very important in making an accurate prediction of natural attenuation of uranium in alluvial aquifers with high organic matter. Sediment samples from a transect of cores were analyzed for uranium and iron content and oxidation state, reduced sulfur phases, and solid phase organic carbon content. Solid-phase uranium concentrations were higher in the naturally bioreduced zone by more than two orders of magnitude (up to 500 ppm), with evidence for significant amounts of uranium(IV) present. The sediments were also elevated in reduced sulfur phases and iron(II), indicating that uranium, iron, and sulfate reduction had occurred in the sediment.

Table 1. Surface complexation reactions considered in the Rifle generalized composite model

#	Reaction	Log <i>K</i>	*GOF
1	$T_x(OH)_2 + UO_2^{2+} = T_x(OH)_2UO_2$	11.7	36.1
2	$T_x(OH)_2 + UO_2^{2+} = T_x(OH,O)UO_2^+ + H^+$	4.05	38.4
3	$T_x(OH)_2 + UO_2^{2+} = T_xO_2UO_2 + 2H^+$	-3.59	55.3
4	$T_x(OH)_2 + UO_2^{2+} + H_2CO_3 = T_x(OH)_2UO_2HCO_3^+ + H^+$	7.89	42.2
5	$T_x(OH)_2 + UO_2^{2+} + H_2CO_3 = T_x(OH)_2UO_2CO_3 + 2H^+$	0.241	14.1
6	$T_x(OH)_2 + UO_2^{2+} + H_2CO_3 = T_x(OH,O)UO_2CO_3^- + 3H^+$	-7.38	7.41
7	$T_x(OH)_2 + UO_2^{2+} + H_2CO_3 = T_xO_2UO_2CO_3^{2-} + 4H^+$	-15.0	25.4
8	$T_x(OH)_2 + UO_2^{2+} + 2H_2CO_3 = T_x(OH)_2UO_2CO_3HCO_3^- + 3H^+$	-3.50	87.3
9	$T_x(OH)_2 + UO_2^{2+} + 2H_2CO_3 = T_x(OH)_2UO_2(CO_3)_2^{2-} + 4H^+$	-11.2	47.2
10	$T_x(OH)_2 + UO_2^{2+} + 2H_2CO_3 = T_x(OH,O)UO_2(CO_3)_2^{3-} + 5H^+$	-18.8	30.6
11	$T_x(OH)_2 + UO_2^{2+} + 2H_2CO_3 = T_xO_2UO_2(CO_3)_2^{4-} + 6H^+$	-26.4	63.7

*GOF: Goodness-of-the-Fit

Table 2. Surface complex formation constants of Rifle uranium(VI) adsorption model

Reaction ^a	Log <i>K</i>
$S_x(OH)_2 + UO_2^{2+} = S_x(OH,O)UO_2^+ + H^+$	7.92
$T_x(OH)_2 + UO_2^{2+} = T_x(OH,O)UO_2^+ + H^+$	3.52
$S_x(OH)_2 + UO_2^{2+} + 2H_2CO_3 = S_x(OH,O)UO_2(CO_3)_2^{3-} + 5H^+$	-15.2
$T_x(OH)_2 + UO_2^{2+} + 2H_2CO_3 = T_x(OH,O)UO_2(CO_3)_2^{3-} + 5H^+$	-20.0

^a *S_x* and *T_x* stand for strong and weak site, respectively.

Increased concentration of solid phase organic carbon and biomass in the naturally reduced sediment suggest that natural bioreduction is stimulated by zones of high organic carbon content. Seasonal fluctuations in the water table occur on the order of 2 meters due to the effect of snow melt on the Colorado River stage. These fluctuations deliver pulses of entrained oxygen to the top of the aquifer, resulting in vertical gradients in the concentration of uranium(VI) in the groundwater as uranium(IV) gets oxidized. After oxidation to uranium(VI), the transport is controlled by the adsorption process described above.

4. CONCLUDING REMARKS

A semi-empirical surface complexation model was developed to describe uranium(VI) adsorption. The non-electrostatic, generalized composite surface complexation model successfully simulated uranium(VI) adsorption over the range of groundwater conditions at the Rifle site, using a two-site, two-reaction fitting scheme. Despite the low retardation of uranium(VI) in the aquifer caused by high groundwater bicarbonate concentrations, cleanup of the aquifer by natural attenuation appears to be greatly slowed by the presence of zones in which uranium is naturally bioreduced to uranium(IV).

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