Modeling Uranium(VI) Retardation in Groundwater

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Abstract

Remediation of groundwater contaminant plumes that result from mining activities requires a good understanding of sediment-water geochemical interactions, including processes such as precipitation and adsorption that immobilize or retard the transport of metal ions. Conceptual models for the description of retardation of metal ion transport include the constant K_d approach or a surface complexation modeling (SCM) approach. This paper describes a compromise between these two modeling approaches that is easier to apply to natural systems that more elaborate SCM applications.

Key words: Adsorption, retardation, groundwater, uranium, modeling

Introduction

Uranium (U) is a contaminant of concern at thousands of sites where it has been released to the environment or where it remains in storage in poorly designed facilities. Leaching of U mill tailings can cause the contamination of soils and aquifers, with the development of groundwater plumes with high concentrations of dissolved U and other metal ions (Abdelouas et al., 1999). Risk assessments must be conducted for many of these contaminated sites to evaluate remediation and cleanup 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.

Under oxidizing conditions, the most stable valence of U is U(VI), which is usually present as aqueous ternary complexes, e.g. $Ca_2UO_2(CO_3)_3$, in contaminated groundwaters (Dong and Brooks, 2006). U(VI)-bearing minerals are generally soluble, and U(VI) can be very mobile in aquifers (Abdelouas et al., 1999). At circumneutral pH and in the absence of strong complexing agents, U(VI) transport is generally limited by strong adsorption on mineral surfaces in soils and sediments (Kohler et al., 2004; Davis et al., 2004; Waite et al., 1994).

Although there is a general consensus that U(VI) transport in groundwater is generally controlled by adsorption, there is disagreement concerning the modeling approach that should be used to describe U(VI) adsorption in reactive transport models. For most metal and radionuclide risk assessments, reactive transport models utilize the distribution coefficient (constant-K_d) modeling approach to describe the retardation of metal and radionuclide contaminants in aquifers caused by adsorption reactions (Bethke and Brady, 2000). Significant uncertainty in the calculation of retardation may be introduced when the constant-K_d modeling approach is used, due to temporal or spatial variations in groundwater chemistry (Curtis et al., 2006; Glynn, 2003; Bethke and Brady, 2000). One reason this may occur is because K_d values are very sensitive to chemical conditions. For example, Figure 1 shows the dependence of K_d for U(VI) adsorption on the mineral, ferrihydrite, as a function of pH and the partial pressure of carbon dioxide gas (pCO_2). Note that the K_d value at pH 8 decreases by four orders of magnitude as the pCO_2 increases from its value in air to 1%. This is an important variation to understand because the pCO_2 in aquifers commonly reaches values of 1-5%, while most K_d values for U(VI) have been determined in laboratory experiments exposed to air. Moreover, pCO_2 often increases with transport after groundwater recharge, and such a spatial/temporal trend in chemical conditions can greatly affect U(VI) transport (Curtis et al., 2006).

In contrast to the constant-K_d modeling approach, surface complexation models (SCM) have the capability of describing changes in metal and radionuclide adsorption as chemical conditions and aqueous speciation vary (Davis et al., 2004; Waite et al., 1994). SCM describe the equilibria between aqueous chemical species and species formed at mineral surfaces (i.e., surface complexes) through mass action equations, and SCM can be readily incorporated within solute transport models (Curtis et al., 2006; Kent et al., 2000; Papini et al., 1999).

There are two major approaches for applying the SCM concept to soils and sediments: the Component Additivity (CA) and Generalized Composite (GC) approaches (Davis et al., 1998). In the CA
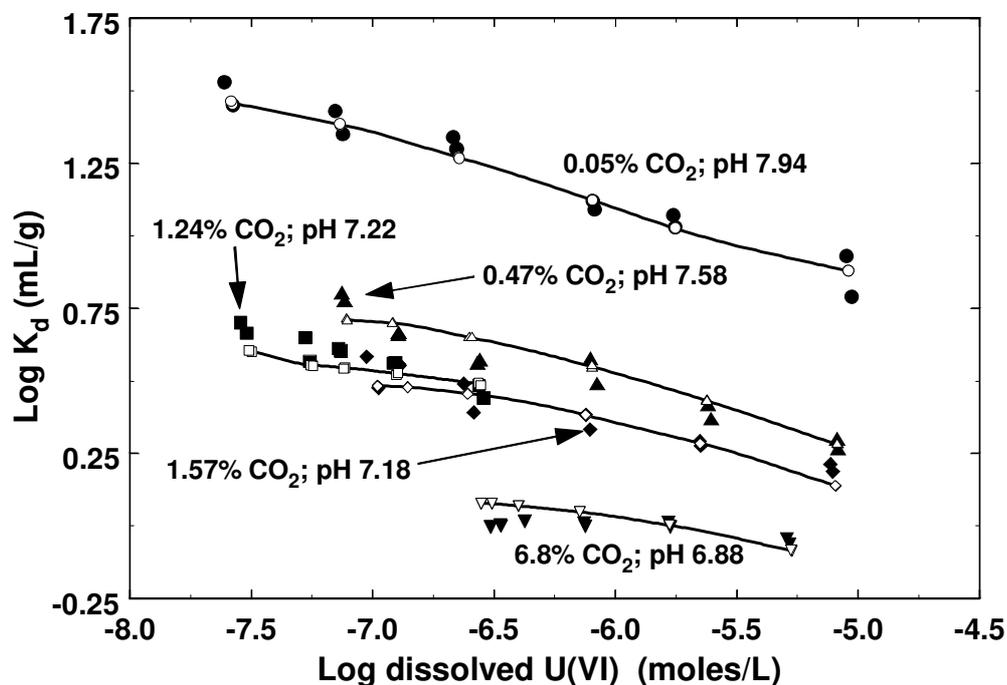
approach, it is assumed that a mineral assemblage is composed of a mixture of one or more reference phases, whose surface chemical reactions are known from independent studies of each phase. Then, based on a measurement of the relative amounts or surface areas of each mineral present in the soil or sediment, adsorption by the mixture of phases can be predicted by an equilibrium calculation, without any fitting of experimental data for the mixture. In the GC approach, the surface of the mineral assemblage is considered too complex to be quantified in terms of the contributions of individual phases to adsorption. In the GC approach it is assumed that adsorption can be described by mass laws written with "generic" surface functional groups, with the stoichiometry and formation constants for each mass law determined by fitting experimental data for the mineral assemblage as a whole (Davis et al., 2004). In this paper, I present GC model calculations to simulate U(VI) adsorption by subsurface sediments collected from the alluvial aquifer of a uranium mill tailings site near Naturita, Colorado, USA. It is shown that a simpler, semi-empirical model developed with the GC approach can be readily applied to predict *in-situ* K_d values or can be incorporated within a reactive transport model for U(VI). However, it is also shown that the simpler GC modeling approach can currently be utilized to great advantage in reactive transport modeling to describe adsorption and retardation in aquifers characterized by variable groundwater chemistry.

Results and Discussion

Uranium(VI) sorption on natural and uranium-contaminated sediments was studied using batch experiments and extractions in the laboratory and with samples of sediment suspended in wells in the field environment. The location of the study was a uranium mill tailings site near Naturita, Colorado, USA, which has a well characterized uranium(VI) contaminant plume in a shallow alluvial aquifer. It was shown in laboratory batch and column experiments with uncontaminated Naturita sediments that the sorption and retardation of U(VI) transport by the Naturita sediments was strongly influenced by the dissolved bicarbonate concentration (Figure 1). For the range of chemical conditions observed in the Naturita aquifer, variable bicarbonate was more important than either variable pH or U(VI) concentration in influencing U(VI) mobility. Methods were also investigated to measure U(VI) sorption on the sediments under field conditions. Such methods are needed for: 1) validation of SCM model parameters in transport simulations, and 2) estimation of initial conditions for sorbed metals at contaminated sites for predictive transport simulations. It was shown that isotopic exchange and desorption extraction methods can be an important part of a field characterization and modeling program. At the Naturita site, a pH 9.5 bicarbonate/carbonate solution was efficient at estimating adsorbed U(VI) and agreed well with the labile U(VI) determined in isotopic exchange studies.

The objective of this study was to demonstrate a surface complexation modeling approach at the field scale for estimating K_d values and the retardation of U(VI). An SCM was developed from the batch experiments to describe U(VI) sorption measured in the laboratory on the uncontaminated sediments. With only two surface reactions (six surface species), the GC-SCM without electrical double layer terms was able to accurately simulate K_d values for U(VI) adsorption on the Naturita aquifer sediments over the observed range of pH and dissolved carbonate and U(VI) concentrations (Figure 1). For the range of Naturita aquifer chemical conditions, alkalinity was more important than either variable pH or U(VI) concentration in influencing U(VI) mobility. K_d values ranged from 0.29 to 22 mL/g when calculated for all Naturita groundwater analyses using the SCM. Low K_d values were associated with portions of the U(VI) groundwater plume containing high concentrations of dissolved U(VI) and alkalinity. Higher K_d values were associated with low concentrations of dissolved U(VI) and alkalinity.

Figure 1 *U(VI) adsorption on a <3mm uncontaminated sediment composite sample from the Naturita aquifer, as a function of the partial pressure of carbon dioxide, pH, and solid/liquid ratio and expressed as log K_d values. Experimental data points are shown as solid symbols and the Generalized Composite SCM calculations are shown as smoothed solid curves drawn through the open symbols.*

Model-predicted U(VI) K_d values generally agreed to within a factor of 2 to 3 with experimental estimates of the K_d values of the U-contaminated sediments based on isotopic exchange measurements. This agreement with the experimental determinations of sorbed U(VI) in the contaminated portion of the Naturita alluvial aquifer provides confidence in the predictive capability of the GC-SCM, which was developed from data with uncontaminated Naturita sediments. Another approach used to validate the GC-SCM was the determination of *in-situ* K_d values by suspending uncontaminated sediment samples in wells with U-contaminated groundwater for periods of time ranging from 3-15 months. *In-situ* (field) K_d values were calculated from groundwater measurements of dissolved U(VI) and U(VI) extracted from the suspended sediment samples. The *in-situ* K_d values in 17 wells ranged from 0.5 to 12 mL/g, with the K_d values decreasing with increasing alkalinity. There was close agreement between these measured *in-situ* K_d values and model-predicted K_d values using the GC-SCM.

Transport simulations conducted for the field scale demonstrated the importance of using the SCM to describe U(VI) adsorption rather than a constant-K_d modeling approach. A major conclusion from the transport simulations was that modelers must recognize not only that variable chemical conditions can cause a range of K_d values to be observed, but also that the spatial distribution of K_d values within that range is not likely to be a random function or a normal distribution. In plumes with chemical gradients, the spatial distribution of K_d values can be quite complex and be characterized by significant spatial character. Transport simulations with a rate-controlled U(VI) adsorption model agreed well with those that used the local chemical equilibrium approximation.

Conclusions
The challenge in applying the surface complexation concept in the environment is to simplify the SCM, such that predicted adsorption is still calculated with mass laws that are coupled with aqueous speciation, while lumping parameters that are difficult to characterize in the environment in with other parameters. In order to be applied by solute transport modelers, the complexity of the adsorption model needs to be balanced with the goal of using the simplest model possible that is consistent with observed data. This can be achieved with the semi-empirical GC-SCM approach described here and in

applications from our research group (Curtis et al., 2006; Kent et al., 2000). The GC-SCM is a compromise between the simple constant-K_d approach and more complex SCM that are difficult to apply to the environment. The GC modeling approach is preferable to completely empirical approaches, such as the constant-K_d model or adsorption isotherms, because the important linkage between surface and aqueous species (and associated thermodynamic data) is retained in the modeling through the coupling of mass action equations.

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