

## THE NUCLEAR REGULATORY COMMISSION'S SORPTION-MODELING RESEARCH PROGRAM

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### ABSTRACT

This paper describes research supported by the Nuclear Regulatory Commission (NRC) to evaluate the use of surface-complexation models of sorption in radionuclide transport calculations as more realistic alternatives to transport models that use laboratory-measured constant distribution coefficients ( $K_d$ s). The uncertainties in surface-complexation model parameters result in lower uncertainties in  $K_d$  values than the uncertainties in the  $K_d$  values currently used in performance assessments (PAs) (when considered over a range of chemical conditions), and the surface-complexation uncertainties are more easily quantified. Generalized-composite surface-complexation models, which do not require detailed data on the composition of sorbing surfaces, give better results in most of the cases considered than component-additivity surface-complexation models, which do require detailed data on the composition of sorbing surfaces. The component-additive models often require more data than are currently available and the superposition assumption underlying these models may not be correct. The NRC is supporting work on the molecular aspects of sorption to determine how to get the data needed for component-additive models.

### INTRODUCTION

Operators and regulators of contaminated nuclear facilities, such as decommissioning facilities and nuclear waste sites, often use PA to evaluate the safety of the facilities and develop or evaluate strategies for monitoring the safety of the facilities. PA implements mathematical models of the mobilization of radionuclides, their release and transport through engineered barriers, their transport in the geosphere and/or the atmosphere, and their uptake by humans. In the geosphere, radionuclides may move with groundwater or may be kept from moving by one or more physical or chemical interactions with the soil or rock through which the groundwater is moving. One such interaction, the topic of this paper, is sorption, the chemical bonding of radionuclides to or release from soil or rock surfaces along the groundwater flow paths.

Laboratory-measured ratios (distribution coefficients or  $K_d$ s) of a radionuclide's concentration in the soil or solid to its concentration in the groundwater are traditionally used to represent sorption in the transport models implemented in PA. The  $K_d$ s are often treated as constants and applied to chemical conditions different from those under which they were measured. When  $K_d$ s are used in this way, the radionuclides' subsurface transport equations appear to have a "retarded" velocity (slower than the groundwater flow velocity) in their advective terms and reduced values of dispersion terms. The forms of the resulting transport equations are otherwise no different from their forms when  $K_d=0$ .

The use of  $K_d$  and the retardation factor to represent sorption is based on the use of a volumetric construct to represent a surficial phenomenon. There is no physical or chemical reason for one to expect that a radionuclide species moving in groundwater will move more slowly because some fraction of the species has adsorbed to a convenient surface, or to expect that dispersion coefficients would be diminished in any way because of adsorption. The modified transport equations described in the previous paragraph also do not account for the interactions between the sorption sites and the transport medium or solution. As radionuclides move into regions in the groundwater paths where they have not been before, there may be an abundance of sorption sites that could draw the radionuclides out of the groundwater. As

more radionuclides pass through the same regions, fewer sorption sites may be available to remove the radionuclides from the groundwater and radionuclides may move through these regions with less diminution of aqueous concentrations to new regions where there may be more available sorption sites, and so on. This process may lead to long "tails" of radionuclides left in the groundwater system. These tails have been observed at contaminated sites and their existence cannot be predicted with the modified transport equations described in the previous paragraph, which may predict that regions of a contaminated site are free of contaminants, or at least free enough to meet regulatory standards, when in fact they are not.

## **NRC SORPTION-MODELING RESEARCH**

As part of its research program on radionuclide transport in the environment [1], the NRC is supporting research at the United States Geological Survey (USGS) and Sandia National Laboratories (Sandia) to evaluate more realistic alternatives to the  $K_d$ -based models used in most performance assessments. The NRC also is participating in the NEA Sorption Project (Phase II) [2,3] coordinated by the Nuclear Energy Agency (NEA) of the Organisation for Economic Cooperation and Development. In a parallel effort, the Center for Nuclear Waste Regulatory Analyses is working for the NRC on more realistic approaches to modeling sorption processes in the high-level radioactive waste program, but that work is not addressed here.

With NRC support, the USGS has tested the use of surface-complexation models in uranium (U) transport calculations on samples taken from the Alligator Rivers Natural Analogue Project in Australia and on samples from and in the field at the site of the former uranium mill at Naturita, Colorado. Independently of NRC support, the USGS also has applied surface-complexation modeling to estimate the effects of sorption on the transport of non-radioactive contaminants.

In contrast to the USGS's macroscopic or continuum approach to sorption, Sandia has investigated, for the NRC, sorption on the molecular scale. Sandia has developed molecular models of the sorption of several radionuclides onto clays. The Sandia work provides data to support the continuum-scale component-additive surface-complexation modeling examined by the USGS and the NEA Sorption Project.

In the NEA Sorption Project, organizations from several countries have tested sorption models (surface-complexation models or ion-exchange models) that they have developed against seven test cases covering a wide degree of complexity. The NEA is currently preparing a final report on these tests.

## **USGS SORPTION-MODELING RESEARCH**

### **Application of Surface Complexation Modeling to Study Uranium(VI) Adsorption and Retardation at the Uranium Mill Tailings Site at Naturita, Colorado**

The formation of surface chemical species (or complexes) on minerals is well accepted in the geochemical literature, and the role of these species in various geochemical processes is considered very significant [4]. Despite the significance of these complexes, however, surface species are often not included yet in geochemical equilibrium or reactive solute transport models because of a poor understanding of the thermodynamics of surface complex formation in natural systems. There is considerable experimental data for metal ion adsorption (including radionuclides) in systems with one mineral phase, and surface complexation models (SCM) have been developed to describe these data [5-7] accurately. Nevertheless, the application of SCM to the mixtures of minerals in soils and sediments is difficult because of the presence of secondary mineral and organic coatings that affect the stoichiometry and coulombic correction factors of surface complexation reactions [8].

In contrast to the constant- $K_d$  modeling approach, SCM have the capability to describe changes in metal and radionuclide adsorption as chemical conditions and aqueous speciation vary [4-10]. Furthermore, SCM can be readily incorporated within solute transport models [11,12]. This modeling approach can predict the effects of variable chemical conditions on transport because, unlike the constant- $K_d$  approach, the linkage between surface and aqueous species is retained through the coupling of mass action equations [8]. Surface complexation modeling offers a scientifically defensible means of linking the selection of  $K_d$  values for (PA) modeling to existing knowledge of thermodynamic data for radionuclides and radionuclide speciation in aqueous systems.

There are two major approaches [8] for applying the SCM concept to model metal ion and radionuclide adsorption by soils and sediments: the Component Additivity (CA) and Generalized Composite (GC) approaches. 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 [5,14,15]. Then, based on a measurement of the relative amounts of 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 [8]. One sometimes makes CA model predictions by assuming that one mineral component dominates adsorption, allowing a straightforward equilibrium calculation if the exposed surface area of that mineral component in the soil or sediment can be quantified.

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. The complexity is, in part, an expression of the difficulties in quantifying the electrical field and proportions of surface functional groups at the mineral-water interface in the mixture of mineral phases and associated surface coatings. 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 [8,10].

The objective of the study at the Naturita mill tailings site was to demonstrate a surface complexation modeling approach *at the field scale*, for estimating  $K_d$  values and the retardation of a sorbing radionuclide with complex aqueous chemistry [11]. The site near Naturita, Colorado, was chosen for study, because it had a well-developed and definable U(VI) plume in a shallow alluvial aquifer and had spatially variant chemical conditions that were expected to be important in influencing U(VI) transport and retardation.

It was shown in laboratory batch and column experiments with uncontaminated Naturita sediments that the adsorption and retardation of U(VI) by the Naturita sediments was strongly influenced by the dissolved carbonate concentration (alkalinity) [11,13]. A Generalized Composite surface complexation model (GC-SCM) was developed for the Naturita aquifer background sediments (NABS) based on fitting batch U(VI) adsorption data. With only two surface reactions (four surface species), the GC-SCM, without electrical double layer terms, was able to simulate  $K_d$  values accurately for U(VI) adsorption on the Naturita aquifer sediments over the observed range of pH and dissolved carbonate and U(VI) concentrations (Fig. 1). For the range of Naturita aquifer chemical conditions, variable alkalinity was more important than either variable pH or U(VI) concentration in influencing U(VI) mobility [11].  $K_d$  values ranged from 0.29 to 22 mL/g when calculated for all Naturita groundwater analyses using the GC-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 [11,16].

In addition to the common experimental technique of batch adsorption studies, methods were also investigated to estimate U(VI)  $K_d$  values in the field [11]. Such methods are needed for: 1) validation of SCM model parameters for transport simulations within PA models, and 2) estimation of initial conditions for adsorbed radionuclides for transport simulations describing previously contaminated sites. It was shown that isotopic exchange and desorption extraction methods can be an important part of a field characterization and modeling program [11,17]. The GC-SCM predicted U(VI)  $K_d$  values generally agreed to within a factor of 2 to 3 with experimental estimates of the  $K_d$  values determined by isotopic exchange experiments with U-contaminated sediments. The 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 NABS samples in wells with U-contaminated groundwater for periods of time ranging from 3-15 months [11,16]. *In-situ* (field)  $K_d$  values were calculated from groundwater measurements of dissolved U(VI) and U 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 [11,16,17].

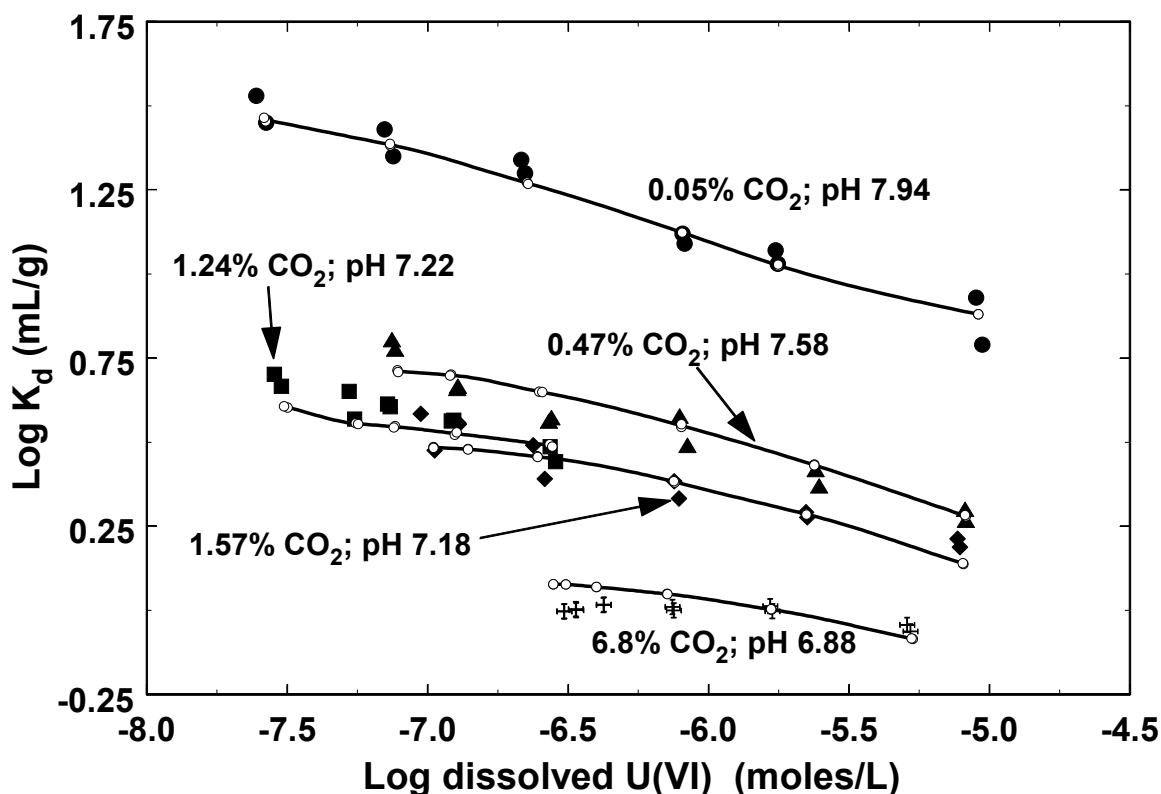


Fig. 1 U(VI) adsorption on the <3mm Naturita Aquifer background sediments composite sample as a function of the partial pressure of carbon dioxide, pH, and U(VI) concentration, expressed as log  $K_d$  values [11,13]. Experimental data points are shown as solid symbols. GC-SCM model simulations are shown as solid curves drawn through the small open symbols.

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 [11]. A major conclusion from the transport simulations was that PA 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 possesses significant spatial structure. Transport simulations with a rate-controlled U(VI) adsorption model agreed well with those that used the local chemical equilibrium approximation. The simulations also showed that predicted U(VI) transport was nearly identical whether or not surface charge was explicitly considered within the GC-SCM [11]. The linkage of traditional contaminant-transport models and reactive-contaminant-transport models to models for dose assessment in PA was also investigated in the project [11]. It was shown that a constant- $K_d$  modeling approach is not always conservative compared to using an SCM to describe radionuclide retardation in PA.

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 [8,10,11,13]. In order to be applied by solute transport modelers and within PA applications, the complexity of the adsorption model may need to be balanced with the goal of using the simplest model possible that is consistent with observed data and expected extremes of natural (or bounding) conditions. This can be achieved with the semi-empirical, site-binding GC modeling approach used for the Naturita site [11], as was also previously demonstrated for modeling zinc (Zn) retardation in a sand and gravel aquifer [12]. 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 at present.

Historically, solute transport modelers have lacked the necessary expertise to apply the SCM approach and many have

believed that the SCM approach was too complex to be applied. While it is true that the most complex SCM are difficult to apply at present, it has been demonstrated in the Naturita study that the GC modeling approach can be easily applied to simulations of radionuclide transport at the field scale and included within PA modeling [11]. 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 [10,13]. This linkage also provides a framework for conducting uncertainty analyses that are based on process level parameters rather than on ranges of  $K_d$  values that result from lumping together multiple processes. The current operational paradigm that employs constant- $K_d$  values to describe the retardation of radionuclides at the field scale can introduce more uncertainty than is necessary at sites with variable chemical conditions. This uncertainty could be reduced and more completely understood in the future with the use of the GC-SCM approach.

### **Application of Surface Complexation Modeling to Study Uranium(VI) Adsorption in Soils near the Koongarra Uranium Ore Deposit, Northern Territory, Australia**

This study preceded the research at the Naturita site, and its objective was to develop a general strategy and methodology for formulating an SCM to describe radionuclide adsorption for natural mineral assemblages in an aquifer. The strategy was developed and applied in a preliminary way to a shallow aquifer in the vicinity of the Koongarra U ore deposit in Australia [9]. The Koongarra U deposit lies 225 km east of the city of Darwin and 25 km south of the town of Jabiru in the Northern Territory of Australia. At the end of the project, the general strategy and methodology were applied in a more comprehensive manner to the Naturita site.

The general methodology can be considered as consisting of two major parts: 1) a field characterization phase, and 2) an SCM development phase. Characterization of the field site is required to: a) determine the porosity of an unconsolidated aquifer (in the case of fractured rock, the wetted mineral surface area per unit volume of groundwater), b) determine the reactive surface area of aquifer sediments, c) identify the bulk *and surficial* composition of solid phases present in the aquifer sediments, including both chemical and mineralogical data, and d) determine the chemical composition and aqueous speciation of groundwater solutes. It is important that the spatial variability of each of these properties of the aquifer be considered in the field characterization. The porosity value and reactive surface area are used to scale the SCM (calibrated with laboratory data) to the field conditions.

The mineral and solution phase composition data are used to develop a geochemical model of the aquifer. The initial objective of geochemical model development is to obtain coherence between groundwater chemical and aquifer mineralogical data, and values calculated using thermodynamic relations for mineral phase solubility and aqueous speciation equilibria [2]. Among the difficulties frequently encountered at this stage are large uncertainties in the solubilities of complex, heterogeneous solid phases, such as clay minerals.

The mineral and solution phase composition data and the geochemical model are used to propose hypotheses about which solid phases are likely to govern radionuclide transport and the range of system compositions over which  $K_d$  values will be needed. Generally, one or more minerals known to be capable of undergoing adsorption reactions with the radionuclides can be identified [2]. In this case, experimental results and existing databases for adsorption on reference solid phases can be used as the basis for formulating initial hypotheses regarding the stoichiometry of radionuclide adsorption reactions and the effects of the temporal or spatial variability of other solutes on radionuclide  $K_d$  values.

In the SCM development phase, the experimental and modeling approach to be used for each radionuclide of interest is defined based on the above information. The experimental approach typically commences with measurements designed to provide an initial estimate of the number and total concentration of adsorptive components [2,8,10,13]. This is followed by a stepwise, iterative modeling process of testing surface complexation reaction equations for the various adsorbing components, wherein potential stoichiometries and adsorbed radionuclide species formation constants are compared in their capability to represent experimental data [8,10,13] accurately.

In the Koongarra study, weathered schist materials were obtained in the vicinity of the Koongarra U ore deposit in Australia [9], and U(VI) adsorption was determined on several different samples as a function of chemical conditions. The ore deposit lies near land surface; the top 25-30 m of the subsurface consist of a highly weathered zone derived from the upper portion of the primary ore body. Deeper, within the unweathered zone of the primary ore body, the ore

consists of lenses containing coalescing veins of uraninite within steeply dipping host Cahill quartz-chlorite schists. Secondary mineralization is present in the weathered schists, from below a surficial sand cover to the base of weathering. Alteration of uraninite at the (hydrologic) upgradient edge of the primary ore zone has produced a variety of secondary minerals, particularly the uranyl silicates kasolite, sklodowskite, and uranophane. Above the ore body the secondary mineralization in the weathered schists is characterized by uranyl phosphates, particularly saleeite, metatorbernite, and renardite. Further away from the primary ore zone, U is dispersed in the weathered schists and adsorbed onto clays and iron oxides [18].

Cores were obtained from a number of locations in the weathered zone. The W1 core consisted of a highly weathered schist from above the upstream edge of the ore body, W2 was collected near the leading edge of the dispersion fan, approximately 50 m downgradient from the primary ore zone, and W7 was obtained about 100 m further downgradient. W7 had a U content that was only slightly elevated relative to background.

A fine fraction (approximately  $< 10 \mu\text{m}$ ) was obtained from each of these samples and used in the adsorption experiments. The samples were also studied by a sequential extraction scheme [9], and the  $^{234}\text{U}/^{238}\text{U}$  isotopic ratio in each extract was determined. For all samples, the leachable U(VI) in relatively weak extractions (acetate buffer and Tamm's acid oxalate) had a much lower  $^{234}\text{U}/^{238}\text{U}$  isotope ratio than was found in stronger extractions [9]. The  $^{234}\text{U}/^{238}\text{U}$  isotopic ratio in the weaker extractions was significantly below 1.0, and this ratio was very similar to the  $^{234}\text{U}/^{238}\text{U}$  isotope ratio observed in groundwater samples from the weathered zone. This provided significant evidence that the U(VI) released in weak extractions could be used as an estimate of adsorbed U(VI) on the samples. The quantification of adsorbed U(VI) in each of the samples by the weak extractions was also supported by excellent agreement with that determined by U(VI) isotopic exchange [9].

The experimental data for U(VI) adsorption on the soil samples are shown in Fig. 2. The decrease in adsorption at alkaline pH values is due to the formation of aqueous U(VI)-carbonate complexes [7,9]. The partial pressure of carbon dioxide ( $p\text{CO}_2$ ) in Koongarra ground waters ranges from 0.004 to 0.05 atm [9]. In experiments carried out with 1%  $\text{CO}_2$ , U(VI) adsorption was significantly reduced at  $\text{pH} > 6$ , relative to experiments carried out in air (Fig. 2). This is due to the greater dominance of aqueous U(VI)-carbonate complexes at higher  $p\text{CO}_2$  [7]. Adsorption of U(VI) at  $\text{pH} < 6$ , where aqueous U(VI)-carbonate complexes are not important, was not significantly affected by the higher  $p\text{CO}_2$ . The laboratory adsorption data have been shown to be very relevant to the *in-situ* partitioning of U(VI) in the shallow aquifer at Koongarra, particularly when laboratory experiments are conducted at the appropriate  $p\text{CO}_2$  [18].

A comparison of model calculations for the W1 sample is presented here, in order to discuss some modeling issues. High-resolution TEM studies indicate that the surficial U in the schist materials is principally associated with iron (Fe) oxide phases [19]. An acid oxalate extract of the W1 sample dissolved 0.88 mg Fe/g of sample [9]. Assuming that the Fe was derived from a poorly crystalline iron oxide phase similar to ferrihydrite, one can estimate a total surface site concentration for the sample from the relationship of 0.875 moles of sites per mole of Fe in ferrihydrite [7]. Using the model of Waite *et al.* [7], one can make predictive model calculations for U(VI) adsorption by ferrihydrite in the W1 sample (Fig. 3). The calculated U(VI) adsorption is considerably less than that observed experimentally for the W1 sample, although the predicted adsorption by ferrihydrite near pH 6 was significant. The calculations carry the assumption that the surface properties of the poorly crystalline iron oxide phases in the W1 sample are identical to ferrihydrite synthesized in the experiments of Waite *et al.* [7]. Perhaps the most important assumption of this modeling approach, though, is that the surface properties of the iron oxides are not changed by the adsorption of organic acids, silicate, and other solutes present in the groundwater. Adsorbed organic material and other surface coatings would be expected to alter significantly the electrical double layer on ferrihydrite, and thus, influence the adsorption of U(VI) [10].

In addition to adsorption of U(VI) by ferrihydrite in the W1 sample, other minerals would be expected to adsorb U(VI). If U(VI) adsorption models were available for each of the important minerals in the sample, and the surface areas of each mineral exposed to water could be determined, a true CA modeling calculation could be made. However, it is difficult to characterize the sample in sufficient detail to make such a calculation.

Given the difficulties and expense of following the CA modeling approach, the GC modeling approach represents a cost-effective tool for PA applications. It requires less data collection and can provide an excellent representation of the experimental data as a function of variable chemical conditions, as shown in Fig. 3.

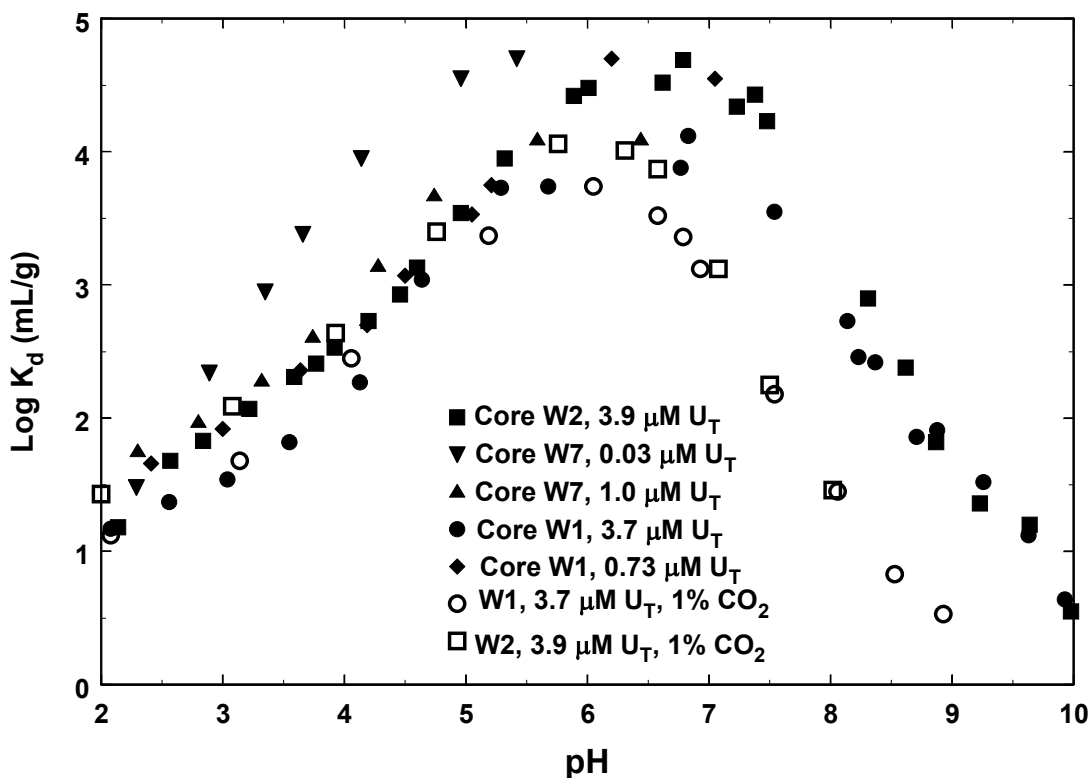


Fig. 2 U(VI) adsorption onto Koongarra soil samples expressed as  $K_d$  (mL/g) values as a function of pH, the partial pressure of  $\text{CO}_2$ , and the total U(VI) concentration involved in adsorption equilibria. Filled symbols are for systems equilibrated with air and open symbols are for systems equilibrated with a 1%  $\text{CO}_2$ /99%  $\text{N}_2$  gas mixture. Experimental details are given in reference [10].

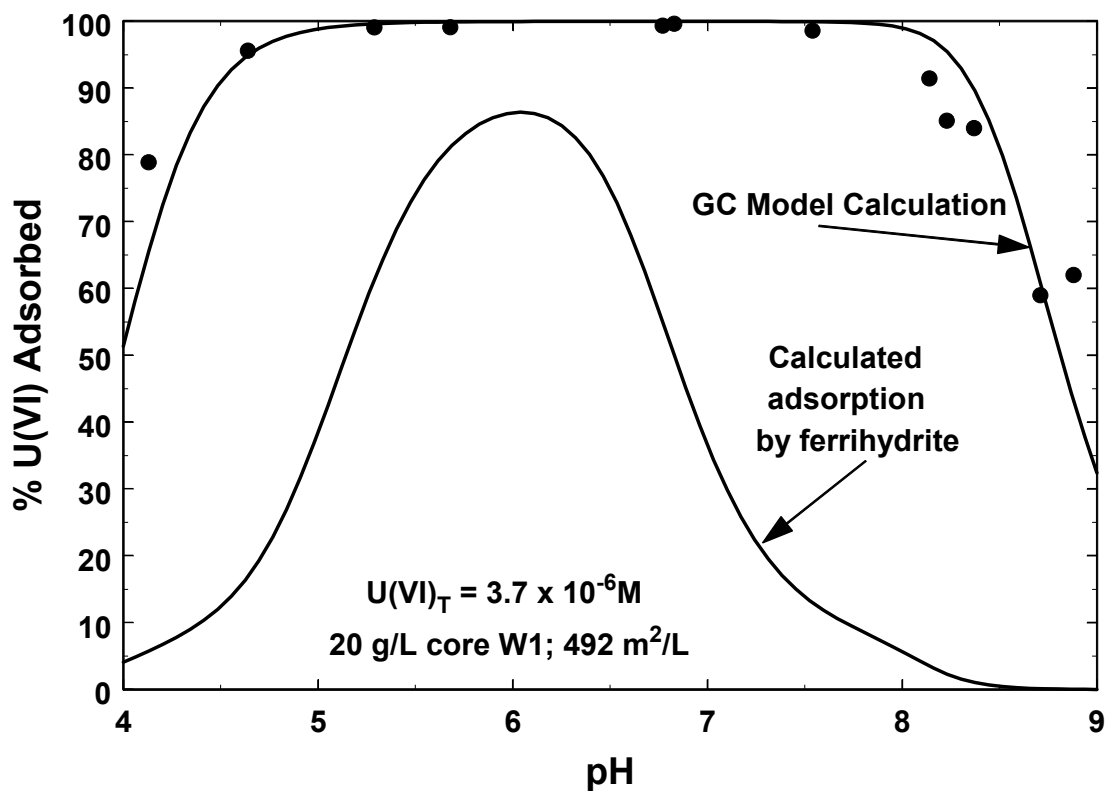


Fig. 3 Model calculations of U(VI) adsorption by ferrihydrite mineral present in the Koongarra W1 sample and the GC model calibrated with results from all 3 Koongarra samples (W1, W2, and W7) compared to experimental data (circles). More details are presented in reference [10].

## SANDIA SORPTION-MODELING RESEARCH

Sandia supports the NRC in providing a defensible, science-based understanding of radionuclide migration and retardation for assessing contaminant transport in the environment. Several tasks contribute to this effort with particular emphasis in determining the mechanisms and controls of radionuclide sorption onto ferrihydrite and related clay minerals. The research involves the generalization of the simplified  $K_d$  approach that incorporates localized properties and is sometimes not applicable over time and at other contaminated sites considering the range of nonlinear geochemical phenomena and chemical conditions that can significantly affect radionuclide transport. Sandia combines various state-of-the-art theoretical and analytical methods to evaluate these sorption mechanisms. The research includes the identification of sorption-controlling soil minerals for selected radioactive waste sites, determination of the extent of radionuclide retention on the sorption-controlling minerals, derivation of the theoretical limits on the range of  $K_d$  values for selected radionuclide-mineral pairs through molecular simulation, and the probabilistic analysis of sorption parameter uncertainty and the influence on radionuclide migration.

## Molecular Modeling of Radionuclides on Clay Minerals

The theoretical effort includes the molecular modeling of radionuclides on clay minerals by using molecular dynamics simulations to evaluate the sorption of the selected radionuclide species onto the basal surfaces of clay phases commonly found in soil. The simulations provide an opportunity to identify sorption complex geometries and derive relative binding energies for the radionuclide species. Ultimately, the molecular dynamics simulations offer an opportunity to derive theoretical  $K_d$  values for the equilibrated systems. The simulations can be used to develop



models of sorption processes that can be compared with experimental results and used to test surface complexation models. Chemical systems that have been investigated to date include  $\text{Na}^+$ ,  $\text{Cs}^+$ ,  $\text{Sr}^{2+}$ , and  $\text{UO}_2^{2+}$  cations sorbing onto various kaolinite and montmorillonite surfaces.

As part of this effort, Sandia initially developed, CLAYFF, a model of a general force field suitable for the simulation of hydrated and multicomponent mineral systems and their interfaces with aqueous solutions [20]. Interatomic potentials were derived from parameterizations incorporating structural and spectroscopic data for a variety of simple hydrated compounds. A flexible simple-point-charge-based water model is used to describe the water and hydroxyl behavior. Metal-oxygen interactions are described by a Lennard-Jones function and a Coulombic term with partial charges derived by Mulliken and electrostatic potential analysis. Bulk structures, relaxed surface structures, and intercalation processes are evaluated and compared to experimental and spectroscopic findings for validation. Sandia's approach differs from others in that Sandia treats most interatomic interactions as non-bonded, allowing Sandia to use the force field effectively for a wide variety of phases and to account properly for energy and momentum transfer between the fluid phase and the solid, while keeping the number of parameters small enough to allow modeling of relatively large and highly disordered systems. Simulations of clay, hydroxide, and oxyhydroxide phases and their interfaces with aqueous solutions combine energy minimization and molecular dynamics methods to describe the structure and behavior of water, hydroxyl, surface species, and intercalates in these systems. The results obtained to date demonstrate that CLAYFF shows good promise to evolve into a widely adaptable and broadly effective force field model for molecular simulations of fluid interfaces with clays and other clay-related phases, as well as other inorganic materials characterized by complex, disordered, and often ill-determined structure and composition.

Large-scale molecular dynamics computer simulations have been completed to evaluate the sorption of  $\text{Cs}^+$ ,  $\text{Sr}^{2+}$ , and other related ions onto the (001) basal planes of kaolinite and montmorillonite [21]. Simulations were undertaken as a function of metal ion concentration to evaluate sorption mechanisms and to determine distribution coefficients ( $K_d$ s). The simulations show that  $\text{Cs}^+$  ions bind to both kaolinite and montmorillonite, while  $\text{Sr}^{2+}$  ions tend to remain in solution. At high ionic strengths (greater than 0.5 M), the fundamental mechanism for  $\text{Cs}^+$  sorption to the aluminol plane of kaolinite is through the formation of  $\text{CsCl}$  complexes where the  $\text{Cl}^-$  ion is loosely bound to the outer hydroxyl groups (Fig. 4). At lower concentrations (0.1 M and 0.01 M), the  $\text{Cs}^+$  ions do not sorb to the aluminol plane, but prefer to bind adjacent to the center of the six-membered ring silica tetrahedral sheet as an inner-sphere complex. Sandia has determined a  $K_d$  of  $10 \pm 4$  ml/g for kaolinite to sorb  $\text{Cs}^+$  ions from a 0.01M  $\text{CsCl}$  solution, and a  $K_d$  of 0 for kaolinite to sorb  $\text{Sr}^{2+}$  ions from a 0.01M  $\text{SrCl}_2$  solution. For the case of montmorillonite, Sandia has determined a  $K_d$  of  $293 \pm 30$  ml/g to sorb  $\text{Cs}^+$  ions from a 0.1M  $\text{CsCl}$  solution, and a  $K_d$  of  $11 \pm 4$  ml/g to sorb  $\text{Sr}^{2+}$  ions from a 0.1M  $\text{SrCl}_2$  solution. The montmorillonite sorbs the cations more effectively than kaolinite because it has negatively charged sorption sites that are created by isomorphic substitutions on both tetrahedral and octahedral sites. Calculations show that the  $\text{Sr}^{2+}$  ion is solvated more strongly than  $\text{Cs}^+$  and is not sorbed by the kaolinite or montmorillonite surfaces.

### **Probabilistic Analysis of Sorption Parameters and Hydrologic Flow**

Sandia has applied probabilistic techniques to recent investigations of uranium mill tailings sites where U(VI) has leached into the surrounding soil for many years. One site under investigation is at Naturita, Colorado where the NRC is working cooperatively with the USGS (see above) to investigate both hydrological and geochemical conditions as a function of time, and to assess the ability of surface complexation models coupled with hydrologic models to predict radionuclide migration through the soil. Naturita is one of several UMTRA (Uranium Mill Tailings Remedial Action) Title 1 sites where the mine tailings have been removed by the U.S. Government to reduce contaminant levels. However, lingering uranium dissolved in groundwater and adsorbed in shallow alluvium still remains, creating some concerns regarding the extent of contaminant transport within the site.

This is one of the first studies to investigate the effects of uncertainty in adsorption constants in an electrostatic surface complexation model on calculated contaminant plume migration using simple one- and two-dimensional reactive-transport models [22]. Sandia's investigation focused on examining uranium adsorption onto clay surfaces, one of several possible retardation mechanisms at the Naturita site, and on the influence of the adsorption constants on calculated uranium concentration versus distance profiles and plume migration. For the uncertainty analysis presented here, the model only considers uranyl and proton adsorption to two active adsorption sites, one each on the basal and edge surfaces of smectite clay. This simple model for uranyl adsorption is sufficient to demonstrate that uncertainties in adsorption constants can lead to widely differing predictions of uranium migration in the subsurface environment;

differences that are sufficiently large that they can pose a problem when one assesses the risk associated with contaminant migration from mill tailings.

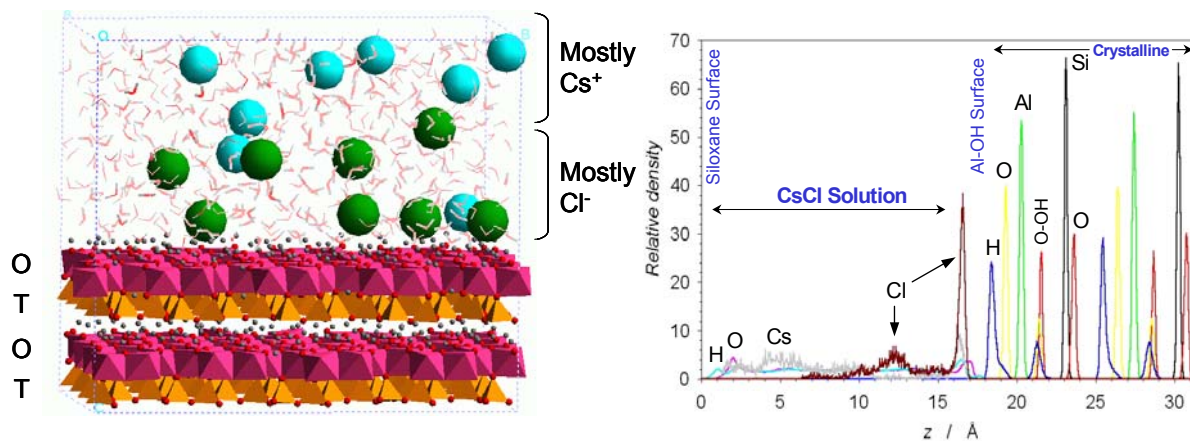


Fig. 4. Equilibrated configuration (left) and atomic density profile (right) derived from molecular dynamics simulation of aqueous CsCl sorption onto the (001) basal surfaces of kaolinite. The smaller  $\text{Cs}^+$  spheres sorb primarily to the tetrahedral siloxane surface while the larger  $\text{Cl}^-$  spheres coordinate to the aluminol surface. Note that the simulation is periodic in three dimensions and that both basal surfaces of kaolinite are available to the CsCl solution. The very small spheres immediately above the kaolinite surface are the hydrogen atoms associated with the aluminol groups. The atomic density profile exhibits the inner and outer sphere complexes of  $\text{Cl}^-$  and the more diffuse behavior of  $\text{Cs}^+$  in solution, and the relatively rigid structure of the kaolinite substrate.

The probabilistic investigation demonstrates that the uncertainty in two thermodynamic values for describing adsorption in reaction-transport models ( $\log K_{>(\text{e})\text{AlO}^-}$  and  $\log K_{>(\text{e})\text{AlOUO}_2^+}$ ) can dramatically change both the shape of calculated contaminant concentration profiles in one-dimensional simulations and the extent of calculated contaminant migration in two-dimensional simulations. Different  $\log K$  pairs selected for the simulations resulted in initial aqueous uranium concentrations that varied over seven orders of magnitude, from approximately 0.0001 to 1000 ppm. In the one-dimensional simulations, two different groups of concentration profiles are exhibited. In one group the concentration profiles exhibit a classical sigmoidal shape while in the second group the concentration profiles display greater changes in aqueous uranium concentration over smaller distances and times than in the first group. These two groups of concentration profiles differ because of the values chosen for  $\log K_{>(\text{e})\text{AlO}^-}$  (that is, 7 to 10 versus 10.5 to 13).

In the two dimensional simulations, the spread of the uranyl plume in both the downfield and transverse directions is primarily influenced by variations in  $\log K_{>(\text{e})\text{AlOUO}_2^+}$ . The difference in the relative significance of the two  $\log K$  parameters in the one- and two-dimensional simulations may be due to the different scenarios posed for these two sets of simulations (that is, rainwater entering an already contaminated aquifer versus a point source of contamination entering a pristine aquifer). The differences found in these two sets of simulations suggest that further investigation into the relative significance of different input parameters on calculated output from reactive-transport models is warranted.

## Characterization of Soil Minerals at a Contaminated Site

Sandia used synchrotron-source X-ray computerized microtomography (CMT) to evaluate the iron content of intergranular material in soil aggregates samples. The soil samples were collected from the Naturita UMTRA site in collaboration with the USGS. Iron content is important because of the evidence that it is correlated to the sorption of uranium in soils. CMT can be used to distinguish whether the intergranular material is composed of iron oxide minerals (e.g., goethite and ferrihydrite) and/or iron-bearing clay minerals. Ultimately, Sandia hopes that this work will contribute to the predictive modeling for uranium transport in reactive transport simulations. As uranium will sorb to clays and iron oxide minerals by different mechanisms, determining the amount of different iron-bearing

minerals in a sample can be an important input to a predictive model. CMT could provide a relatively easy, nondestructive method for making these determinations.

The following three types of samples were imaged at the Advanced Photon Source of the Argonne National Laboratory: 1) mineral standards of known composition and iron content at two different energies (18 and 26 keV); 2) soil aggregate samples imaged dry at two different energies (18 and 26 keV); and 3) soil aggregates that were saturated in CsCl solution and then rinsed with deionized water. The mineral standards were used to determine a relationship between measured linear absorption coefficient and iron content. The soil aggregates were imaged to characterize the intergranular material composition. Finally, the CsCl-treated soil aggregates were imaged to visualize Cs sorption sites on the aggregate samples. Eight mineral standards were imaged: four clay samples of varying iron content (kaolinite, montmorillonite, corrensite and ferruginous smectite), siderite, ferrihydrite, hematite, and quartz. An energy of 26 keV was used to ensure X-ray transmission through some of the higher iron-content minerals. An energy of 18 keV was used because it appeared to be the optimal energy to view iron in the soil aggregate samples. Five soil aggregates were imaged. Some were imaged multiple times. Of these five samples, four were re-imaged after undergoing the CsCl treatment.

Histogram data of measured linear absorption coefficients of an aggregate sample show clear peaks differentiating the air and epoxy surrounding the sample, the quartz grains in the sample, and the intergranular material. Three different populations can define the intergranular material for the soil samples. Using the average linear absorption coefficient for the sample presented and the relationship between linear absorption coefficient and the iron content, the weight percent iron in the intergranular material is estimated to be between 15% and 25%. These values are in the range of the higher iron clays (ferruginous smectite with ~22% and corrensite with ~14%). They are significantly lower than ferrihydrite (~58%). These preliminary results indicate that the intergranular material is predominantly a high-iron-content clay with a possible small fraction of a iron-oxide mineral. The lower the iron content of the clay, the greater the fraction of the iron oxide. Sandia has also attained evidence that Cs, which can be thought of as a surrogate for uranium, sorbs on to the intergranular material in the aggregates. Future work will focus on analyzing images of additional aggregates and attaining more quantitative clay to iron oxide ratios.

## CONCLUSIONS

Advanced PA modeling of nuclear waste disposal sites often includes an estimation of the geochemical evolution of the entire repository system for various time-dependent scenarios. This is normally done by simulating the variation of key chemical parameters (pH, Eh, major ion groundwater composition) in the various parts of the system with geochemical modeling. The variability in the geochemical composition of the system influences the adsorption reactivity of radionuclides along a migration path. If the thermodynamic models include SCM, then the adsorption modeling can be integrated within a common framework, allowing simultaneous consideration of both the geochemical variability of the system and its influence on radionuclide adsorption, thereby providing support for the selection and uncertainty estimation of radionuclide  $K_d$  values.

From a practical standpoint, SCM offers the following advantages to the PA modeling effort: 1) the SCM approach is based on fundamental chemical principles, and therefore can be defended in terms of its scientific rationale; and 2) SCM modeling can be cost effective to the NRC and its licensees over the long term, in comparison to the large number of measured  $K_d$  values that would be necessary for advanced PA modeling. A great deal of effort has been invested in experimentally determining  $K_d$  values for a relatively small number of radionuclides on a wide variety of geological solids [2]. However, it is now recognized that a  $K_d$  measured for a given radionuclide/solid phase combination under one set of conditions cannot generally be used to predict a  $K_d$  accurately for another set of conditions. In contrast, an SCM modeling approach allows predictions of radionuclide partitioning over a wider range of system conditions because it quantifies the fundamental parameters responsible for radionuclide partitioning and couples adsorption calculations with aqueous speciation [8,10,13].

In addition, an SCM distinguishes between the chemical processes of adsorption and precipitation, each of which may contribute to radionuclide partitioning during a PA calculation. As a result, the PA modeler will have a better understanding of the nature and reactivity of the radionuclide, and predictions of its transport under hypothetical scenarios of changing chemical conditions, either spatially or temporally, will be more accurate. Thus, the long-term fate of the radionuclide can be predicted with greater confidence.

Given the relative success of SCM models in describing the adsorption of U(VI) to sediments in the laboratory in the two investigations described above and the apparent equivalence of partitioning of U(VI) to laboratory suspensions and sediments in the field [16-18], the SCM modeling approach can provide a tool of considerable benefit to PA modeling.

It is necessary for PA and SCM modelers to work more closely together in order to build confidence and provide technical support for the efforts being pursued in each of these scientific communities. SCM modelers need to support PA transport modelers, by providing an understanding of the SCM modeling approach and an appreciation of the importance of knowing how and why  $K_d$  values may vary with geochemical conditions. These collaborative efforts could reduce the uncertainties of quantifying adsorption and retardation in PA transport modeling and increase its scientific defensibility.

In summary, SCM can be of significant value to PA if it is used to provide a scientific basis for the range of  $K_d$  values chosen and their variation with environmental conditions. The uncertainties in SCM parameters are less than the uncertainties in  $K_d$  values (when considered over a range of chemical conditions), and the uncertainties are more easily quantified. If used properly, SCM for radionuclide adsorption has the potential to increase the confidence and scientific credibility of PA transport modeling by reducing the uncertainty in quantifying adsorption and by providing a means of better quantifying that uncertainty.

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