

Evaluation of Surface Complexation Models for Radionuclide Transport at the Nevada Test Site: Data Availability and Parameter Evaluation

prepared by

David Decker and Charalambos Papelis

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ABSTRACT

Models for radionuclide transport and migration at the Nevada Test Site were evaluated. Emphasis was placed on surface complexation models and, specifically, the more complex triple layer model. Sets of sorption data were identified and organized as a function of radionuclide and sorbent phase. An evaluation of model parameter estimation was also included. The literature review revealed that there are a number of reliable data sets for radionuclide sorption on several different mineral phases, but the set of surface complexation modeling data is substantially smaller. The two more important radionuclides for which surface complexation modeling appears to be essentially absent are cesium and plutonium. The difficulty of working with plutonium may explain this apparent data gap. Evaluation of model parameters related to the characteristics of mineral surfaces showed that for a number of these models, in a number of studies, parameters were either incorrectly derived or were inconsistent. In addition, the number of studies of surface characterization for each mineral was highly variable. A significant group of silicate minerals for which few surface chemistry data exist is the group of feldspars. The success or failure of a particular surface complexation model must be based on evaluation of modeling results from a data set as broad as possible. The test data set must include data of a range of concentrations, pH values, and background electrolyte type and concentration. Modeling of radionuclide sorption in complex mineral matrices must include a careful characterization of the components of the mineral assemblage thought to contribute to the observed sorption behavior.

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LIST OF ACRONYMS AND ABBREVIATIONS

BET	Brunauer Emmett Teller model
CC	constant capacitance model
CEC	cation exchange capacity
DLM	diffuse layer model
EXAFS	extended x-ray absorption fine structure
GW	groundwater
HFO	hydrrous ferric oxide
NEM	nonelectrostatic model
NR	not reported
NTS	Nevada Test Site
PZC	point of zero charge
REE	rare earth element
SCM	surface complexation model
TLM	triple layer model
YM	Yucca Mountain
XAS	x-ray absorption spectroscopy
XPS	x-ray photoelectron spectroscopy

INTRODUCTION

Scope of Work

The transport of radionuclides and other contaminants in the environment depends largely on the interaction of these contaminants with the mineral surfaces with which these compounds come into contact. The stronger the interactions between the contaminant of concern and the aquifer materials in a contaminated aquifer, the higher the retardation of the contaminant in the specific environment. Similarly, contaminants that interact weakly with rocks and minerals present in a specific environment tend to move much faster, sometimes without being retarded at all compared to the flow of the groundwater.

The importance of methods that can be used to evaluate and predict the degree of interactions with mineral surfaces should therefore be obvious. The affinity of specific radionuclides and other contaminants for specific mineral assemblages must be known or appropriate models must be used to incorporate contaminant-aquifer-material interactions into flow and transport models. Several models have been proposed during the last few decades in an attempt to model radionuclide sorption on mineral surfaces. These include, mainly, empirical and mechanistic models, semi-empirical and ion exchange models, as well as surface complexation models.

These models differ in their complexity, the number and type of parameters that need to be determined, their ability to model complex systems and, ultimately, their ability to predict contaminant interactions with mineral surfaces as a function of changing conditions. The choice of model is of significant importance for the overall prediction of radionuclide migration in the environment, in general, and the Nevada Test Site (NTS), in particular. Obviously, simpler models are easier to incorporate into flow and transport codes and require significantly less computational resources. Their applicability, however, may be substantially limited compared to their more complex counterparts. The major risk in using these simpler models is that if used outside their range of validity, errors of orders of magnitude are possible.

A commonly used example is the widespread use of equilibrium distribution coefficients, usually referred to as K_d s. Such models are the easiest to incorporate in flow and transport codes; their applicability, however, depends on a number of factors and primarily the similarity between the conditions used to derive these parameters and the field conditions. Changes in conditions such as pH, and type and concentration of background electrolyte ions can have a dramatic effect on the predicted distribution coefficient. In addition, the K_d approach assumes that the sorption reaction is at equilibrium, i.e., that the reaction is reversible. This assumption is not always valid with respect to radionuclide sorption on mineral surfaces. Applying K_d models outside the range of concentrations used to obtain these values can lead to significant over- or underestimation of sorption. Finally, the K_d approach only provides a macroscopic description of the partitioning of an ion between the solid and liquid phases but does not provide any insight on the mechanism responsible for that partitioning. If, because of changing conditions, the controlling mechanism changes, K_d -based calculations may become irrelevant.

To address some of these issues, surface complexation models (SCMs), which treat surface functional groups as ligands in solution, have been developed. These models are more capable of incorporating solution chemistry and changing geochemical conditions. Even these models, however, differ in their ability to predict the effect of different conditions on ion sorption. A notable difference is in the ability of different models to incorporate changes in solution ionic strength. The simpler SCMs, both electrostatic and nonelectrostatic, have limited capabilities for treating competition between weakly binding cations and radionuclides. Although this aspect may or may not be significant, depending on the radionuclide considered, it is still not clear what the limitations of the different models are.

Objectives

To address some of these considerations, this report focuses on an evaluation of SCMs with specific emphasis on the reported use of these models to model the sorption behavior of radionuclides and other inorganic cations found at the NTS. Although other processes, such as ion exchange, may control the retardation of radionuclides and toxic metals in certain geologic environments, the focus of this study was to evaluate available surface complexation models. Models other than SCMs, therefore, are not considered further in this report. Specifically, the objectives of this study were to:

- Review the literature of sorption of radionuclides commonly found at the NTS on minerals that may control the migration of these radionuclides.
- In the case of lack of experimental work with such radionuclides, review experimental data with divalent and trivalent cations, such as rare earth elements (REEs), that may be used as surrogates for radionuclides or that may be present at nuclear test sites.
- Review studies that have used SCMs to model sorption of radionuclides and other trace metals on minerals of importance for radionuclide retardation. Emphasis was placed on the more complex SCM, the triple-layer model (TLM).
- Identify problems with SCM parameter estimation and model interpretation, again, placing special emphasis on the TLM.
- Identify gaps in parameters or methodology that prevent the application of a more robust SCM approach to modeling the migration of radionuclides and other contaminants at the NTS and other nuclear testing sites.

Approach

The above objectives were met by the following approach. A literature review was conducted to summarize data related to sorption of, primarily, radionuclides on minerals that might control their migration in aquifers. Whenever data on the more important radionuclides were apparently not available, data reporting the sorption of surrogates, such as REEs or other divalent and trivalent cations, were collected. Because the latter category of literature data is enormous, and certainly beyond the scope of this work, inclusion of the data was based on the relevance of the work to radionuclide migration. The data were evaluated based on soundness of experimental procedures, data interpretation, and justification of experimental parameters used.

A major focus of this project was the evaluation of radionuclide sorption models. Manuscripts, therefore, were categorized depending on whether a modeling attempt was made or raw sorption data were simply presented. When modeling of data was reported, the model was categorized as either an equilibrium model, most commonly evaluation of a K_d , or an SCM. In the case of K_d models, attention was focused on whether the studies were conducted as a function of pH and whether the pH was reported. Other important parameters included evaluation of the characterization of material properties, including mineralogy and surface area. Finally, the concentration range used was noted.

If an attempt was made to model the data using an SCM, additional parameters were included in the model evaluation. First, the type of model was noted, including whether it was an electrostatic or nonelectrostatic model. Whenever an electrostatic model was used, the main emphasis was placed on parameter estimation. The consistency and justification of the input parameters were evaluated. When literature values were adopted for one or more parameters, an attempt was made to clarify whether the rest of the parameters were obtained in a consistent way. Comments to that effect are included throughout the discussion. When the description of the modeling methodology revealed a problem with parameter estimation because of lack of data, the area of lack of data was identified and noted.

The abovementioned results were all incorporated in the discussion and they are also included in the tables at the end of the report. These tables are organized by element and by rock type or mineral surface. The element tables include information regarding experimental conditions and modeling procedure, if any. The final table presents the results in terms of the mineral phases used. Data that were used to model sorption reactions on these minerals were summarized. This table provides an overview of the origin of the parameters that were used to model sorption reactions on the different minerals and points out data gaps in these parameters.

Geochemical Mineral-water Interface Modeling – Overview of Existing Models

As mentioned above, the importance of methods that can be used to evaluate and predict the degree of interactions with mineral surfaces should be obvious. The affinity of specific radionuclides and other contaminants for specific mineral assemblages must be known or appropriate models must be used to incorporate contaminant-aquifer-material interactions into flow and transport models. Several models have been proposed during the last few decades in an attempt to model radionuclide sorption on mineral surfaces. These include, mainly, empirical and mechanistic models, semi-empirical and ion exchange models, as well as surface complexation models. A brief overview of some of these models will be given here.

Empirical models include conditional distribution coefficients and several different isotherms (see below for more details). Semi-empirical models include mass-action models and ion exchange models. Finally, SCMs treat surface functional groups as analogs of complexing ligands in solution. These models are distinguished based on assumptions about the structure of the mineral-water interface. A more detailed description of these models will be given below. The SCMs can be further subdivided into electrostatic and nonelectrostatic models, depending on whether the specific

electrostatic interaction between a charged surface and a charged ion is considered. The basic principles of nonelectrostatic models will also be outlined below.

Equilibrium Sorption Isotherms

Although SCMs can be used to account for solution geochemistry and changing conditions in an aquifer and have therefore an advantage over empirical models in terms of predicting ion transport in a natural system, empirical isotherm models are still widely used in flow and transport codes. The reason for using empirical isotherms is that isotherm models are very easy to incorporate into large transport codes. These isotherms are either linear or nonlinear empirical expressions describing the sorption of any sorbate on any sorbent. Although the isotherms are empirical, several of their parameters have a physical, thermodynamic significance. The most commonly used isotherms are briefly described below.

Linear Isotherm

Plotting of sorption data as a linear isotherm results in estimation of a conditional distribution coefficient, K_d ($L^3 M^{-1}$), a ratio of the mass of sorbate sorbed per mass of sorbent, S ($M M^{-1}$), to the aqueous concentration of sorbate in equilibrium with the sorbed contaminant, C_{eq} ($M L^{-3}$), as shown in Equation (1):

$$K_d = \frac{S}{C_{eq}} \quad (1)$$

Distribution coefficients have been used extensively to model organic contaminant sorption on aquifer materials. For inorganic contaminants, however, K_d is frequently a strong function of pH, temperature, and other geochemical conditions (i.e., solution composition, resulting from aqueous reactions and redox potential) (Stumm, 1992). Use of distribution coefficients to model contaminant partitioning at the mineral-water interface assumes that the isotherm is linear and that sorption is controlled by equilibrium (usually referred to as the local equilibrium approach), as opposed to kinetics. Sorption of inorganic contaminants on mineral surfaces is frequently nonlinear. The degree of nonlinearity may be a complex function of the dominant sorption process and other experimental conditions. For example, as the metal ion concentration increases, the onset of surface precipitation may result in increasingly nonlinear isotherms. In addition, distribution coefficients can result in severe errors when used without reference to the specific experimental conditions under which they were determined.

Nonlinear Isotherms - Langmuir Isotherm

The Langmuir isotherm is linear at low surface coverages of the adsorbent but becomes nonlinear at higher surface coverages. The theoretical assumptions behind the Langmuir isotherm are that adsorption occurs only at independent, localized sites with constant sorption energy, independent of surface coverage and that adsorption is limited by the formation of a monolayer (Weber and DiGiano, 1996). The Langmuir isotherm is typically represented by Equation (2):

$$S = \frac{Q_a \beta C_{eq}}{1 + \beta C_{eq}} \quad (2)$$

where Q_a corresponds to the maximum sorption capacity of the sorbent ($M M^{-1}$) and β is related primarily to the net enthalpy of adsorption.

Nonlinear Isotherms- Freundlich Isotherm

The Freundlich isotherm is usually represented by Equation (3):

$$S = K_F C_{eq}^{1/n} \quad (3)$$

where K_F ($(M M^{-1})/(M L^{-3})^{1/n}$) and $1/n$ (–) represent the equivalent of K_d and the exponent of the equilibrium concentration, respectively ($1/n$ is assumed to be 1, by definition, for linear isotherms). The parameter $1/n$ is a function of both the cumulative magnitude and diversity of energies associated with a particular sorption reaction (Weber and DiGianno, 1996). It can also be shown that $1/n$ is related to the enthalpy of adsorption.

Surface Complexation Models

Surface complexation models (SCMs) have been used extensively during the last 20 years to model sorption of inorganic ions on mineral surfaces, primarily oxides. The major advantage of SCMs over empirical isotherms is that solution speciation can be incorporated in the model, thereby allowing a more realistic representation of sorption reactions and accounting for changing geochemical parameters, such as pH. Several different SCMs have been developed over the years; the most commonly used ones will be briefly described below. Several aspects, however, are common in all SCMs.

The main assumption of all SCMs is that mineral surfaces are composed of functional groups that can form complexes with ions in solution. In other words, sorption of ions is analogous to formation of complexes, except that the ligands are surface functional groups and therefore the resulting complexes are surface complexes, as opposed to aqueous complexes, hence the term surface complexation models. Other assumptions common to all SCMs include that mass law expressions apply to both aqueous and surface species, and that electroneutrality must be satisfied overall for the entire system. The mass law equations and electroneutrality condition result in a set of equations that can be solved simultaneously while satisfying mass-balance conditions (Papelis *et al.*, 1988).

The main difference between the different SCMs is in the assumptions regarding the structure of the mineral-water interfacial region. Specifically, the location of sorbed ions at the mineral-water interface and the number of sorption planes available primarily distinguish the different models. Most of the models account for the accumulation of surface charge due to sorption of charged species, whereas the nonelectrostatic model (NEM) ignores the effects of that charge. A brief description of the more common electrostatic models and the nonelectrostatic model is given below.

Electrostatic Models

The more commonly used electrostatic SCMs are the constant capacitance model (CCM), the diffuse layer model (DLM), and the triple layer model (TLM). These models differ in their representation of the interfacial region and, therefore, in the number of model parameters that need to be determined. Generally, models that are more complex allow greater flexibility of modeling sorption reactions; this greater power, however,

comes at the price of a more complex parameter estimation procedure. The three electrostatic SCMs will be described below briefly. The TLM will be described in more detail in the next section.

Constant Capacitance Model

The CCM assumes that all reactions occur at the surface, also referred to as the o-plane (Hayes *et al.*, 1991; Goldberg, 1992). These reactions include protonation-deprotonation of amphoteric surface hydroxyl sites on oxide minerals, as well as surface complexation reactions. Overall surface charge is a function of pH and determined based on Equations (4) and (5):



that result in the intrinsic equilibrium constants given by Equations (6) and (7):

$$K^+ = \frac{(\text{SOH}_2^+)}{(\text{SOH})(\text{H}^+)} \exp\left(\frac{F\Psi_o}{RT}\right) \quad (6)$$

$$K^- = \frac{(\text{SO}^-)(\text{H}^+)}{(\text{SOH})} \exp\left(-\frac{F\Psi_o}{RT}\right) \quad (7)$$

where K^+ and K^- are the acidity constants of the mineral considered and SOH, SOH_2^+ , and SO^- are the neutral, protonated, and deprotonated surface sites, respectively, Ψ_o is the surface potential, F is the Faraday constant, R is the gas constant, and T is the temperature. The acidity constants are related to the pH_{PZC} , or pH of point of zero charge, which in the absence of other specifically binding anions and cations corresponds to the pH where the overall surface charge of the mineral is zero. The pH_{PZC} may vary significantly for different oxides ranging from approximately 2 for quartz to approximately 8.5 to 9.0 for some iron and aluminum oxides and hydroxides (Sposito, 1984; Stumm, 1992). All metal ions and anions sorb also at the o-plane, according to Equations (8) and (9).



resulting in the equilibrium constants given by Equations (10) and (11):

$$K_{\text{Me}} = \frac{(\equiv \text{SOMe}^+)(\text{H}^+)}{(\equiv \text{SOH})(\text{Me}^{2+})} \exp\left(\frac{F\Psi_o}{RT}\right) \quad (10)$$

$$K_{\text{L}} = \frac{(\equiv \text{SL})}{(\equiv \text{SOH})(\text{L}^-)(\text{H}^+)} \quad (11)$$

where K_{Me} and K_L are intrinsic binding constants for a metal cation and an anion, respectively. The CCM, therefore, cannot distinguish between qualitatively differently binding ions, namely between weakly and strongly binding ions. Differences in binding strength can only be accounted for by adjusting the binding constants; competition between different sorbing anions and cations and background electrolyte ions, however, cannot be represented. Background electrolyte ions do not reside in the o-plane but instead are assigned to a certain distance away from the surface, where the net charge is zero. The interface is modeled as a parallel plate capacitor with the two plates at charge σ_o and zero for the mineral and solution sides, respectively. The capacitance of this idealized capacitor, C_1 , is an additional model parameter. This representation of the mineral-water interface, i.e., a linear drop of the surface charge and potential to zero within a relatively short distance away from the surface is a pretty good approximation in constant high-ionic-strength solutions. The last model parameter is the surface site density, N_s , corresponding to the total number of active surface sites, typically reported as sites nm^{-2} . An overview of model parameter estimation methods will be given in the next section.

Diffuse Layer Model

The DLM is the simplest electrostatic SCM, which is why it has been used in a number of modeling studies. Just like in the CCM, all ions are assumed to sorb at the o-plane. The DLM, therefore, is also unable to distinguish qualitatively between strongly and weakly binding ions, and, therefore, unable to account for competition effects between weakly binding ions. The same acidity and surface complexation reactions presented above for the CCM are also valid for the DLM. Unlike the CCM, however, there is no inner-layer capacitance in the DLM; the Gouy-Chapman model of the diffuse double layer is assumed instead. All background electrolyte ions are assigned to the diffuse layer. The charge-potential relationship for the interface is given by Equation (12):

$$\sigma_d = 0.1174 \sqrt{I} \sinh(zF\Psi_d/2RT) \quad (12)$$

where σ_d and Ψ_d are the charge and potential of the diffuse layer (d-plane), respectively, I is the ionic strength of the medium, z is the charge of the ion, F is the Faraday constant, R is the ideal gas constant, and T is the temperature. The DLM, therefore, has only three adjustable parameters, namely, the two acidity constants and the surface site density (Dzombak and Morel, 1990). It should be made clear, however, that these parameters depend on the assumed structure of the mineral-water interface and that, therefore, the acidity constants and surface site density are not interchangeable between the different electrostatic SCMs. In addition, as opposed to the CCM, which is strictly valid only at constant high ionic strength conditions, the DLM is primarily valid under low-ionic-strength conditions.

Triple Layer Model

The TLM (Davis *et al.*, 1978; Davis and Leckie, 1978; Hayes and Leckie, 1987) is the most flexible SCM. The main difference between the TLM and the other SCMs is that the TLM includes an additional plane, the so-called β -plane. The three planes of the TLM are, therefore, the surface or o-plane, the β -plane, and the diffuse or d-plane, hence the

term triple layer model. The addition of the β -plane, placed away from the surface, allows sorption of weakly binding ions not necessarily at the mineral surface. Electrolyte ions are typically assigned to the β -plane and can therefore participate in competition reactions with other weakly binding radionuclides or other ions. The sorption of electrolyte ions at the β -plane can be represented by the reactions shown in Equations (13) and (14):



resulting in K_{Cat} and K_{An} that are defined by Equations (15) and (16):

$$K_{\text{Cat}} = \frac{(\equiv \text{SO}^- - \text{Cat}^+)(\text{H}^+)}{(\text{SOH})(\text{Cat}^+)} \exp\left(-\frac{F(\Psi_o - \Psi_\beta)}{RT}\right) \quad (15)$$

$$K_{\text{An}} = \frac{(\equiv \text{SOH}_2^+ - \text{An}^-)}{(\equiv \text{SOH})(\text{An}^-)(\text{H}^+)} \exp\left(\frac{F(\Psi_o - \Psi_\beta)}{RT}\right) \quad (16)$$

where K_{Cat} and K_{An} are the intrinsic binding constants for cations and anions, respectively. In addition to the electrolyte binding constants, the TLM requires two capacitances for the surface and β -plane, frequently referred to as inner- and outer-layer capacitance, C_1 and C_2 , respectively. Compared to the DLM, therefore, the TLM requires four additional parameters, the two electrolyte binding constants and the two capacitances. In summary, the TLM requires estimation of seven adjustable parameters, acidity and electrolyte binding constants, capacitances, and surface site density. As will be pointed out in more detail in subsequent sections, the large number of adjustable parameters is probably the major drawback of the TLM, but it also allows modeling of systems that cannot easily be modeled otherwise. Additional details about the model are given in the next section.

Nonelectrostatic Model

All SCMs discussed so far account for the effects of ion sorption on a charged surface by assuming a particular structure for the mineral-water interface. The nonelectrostatic model (NEM) completely ignores the effects of charge buildup at the mineral-water interface and relies solely on mass action expressions and the protonation-deprotonation reactions at the mineral surface to describe ion sorption. Consequently, there are no charge-potential relationships for the NEM. The NEM, therefore uses only three adjustable parameters: the two surface acidity constants and the site density.

The simplicity of the NEM makes this model a good alternative to the common equilibrium isotherm approach (K_d) used in flow and transport codes. The major advantage of the NEM over the K_d approach is that pH dependence of sorption reactions can be taken into account. Competition with other ions, as long as similar ions are considered, binding on the same type of surfaces, could presumably be accomplished by adjusting the binding constants for these ions and may lead to reasonable representation

of competition effects. The NEM, as well as other simple SCMs, like the CCM and DLM, however, cannot distinguish between ions binding by qualitatively different sorption mechanisms, i.e., formation of inner- and outer-sphere complexes or surface precipitation. These qualitative differences in binding mechanisms cannot be necessarily addressed by quantitative adjustments of binding constants. The NEM, therefore, may be entirely adequate to describe the transport of single radionuclides and other ions of concern in systems in which competition effects are not particularly significant (Davis *et al.*, 1998). It remains to be seen, however, how successful the NEM and other simple electrostatic models can be in incorporating competition effects from background electrolyte ions, especially when both weakly and strongly binding radionuclides are present.

TRIPLE LAYER MODEL DESCRIPTION AND PARAMETER ESTIMATION

In this section, a more detailed description of the TLM will be given, followed by a discussion of the individual model parameters and parameter estimation techniques. Finally, a discussion of methods used to determine radionuclide binding constants and the use of spectroscopic techniques to assist in determining surface complex stoichiometries will be given.

Model Description

As pointed out earlier, the TLM is the most complex of the frequently used electrostatic SCMs. It incorporates three planes, the surface or o-plane, the β -plane, and the diffuse or d-plane. Protonation and deprotonation of amphoteric surface sites occurs at the o-plane, giving rise to pH-dependent surface charge according to the reactions given by Equations (17) and (18):



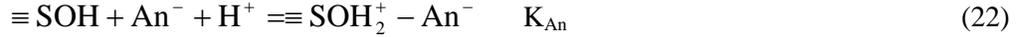
that result in the intrinsic equilibrium constants given by Equations (19) and (20):

$$K^+ = \frac{(\text{SOH}_2^+)}{(\text{SOH})(\text{H}^+)} \exp\left(\frac{F\Psi_o}{RT}\right) \quad (19)$$

$$K^- = \frac{(\text{SO}^-)(\text{H}^+)}{(\text{SOH})} \exp\left(-\frac{F\Psi_o}{RT}\right) \quad (20)$$

with acidity constants K^+ and K^- . The values of the acidity constants, in the absence of other strongly binding ions and assuming a symmetrical background electrolyte (an electrolyte with anions and cations having equivalent affinity for the mineral surface), determine the pH_{PZC} , i.e., the pH at which the mineral surface has no net charge.

Background electrolyte ions are assumed to maintain their primary hydration sheath upon sorption and cannot, therefore, bind directly at the o-plane; they are placed instead at the β -plane, forming ion-pair complexes represented by the surface complexes in Equations (21) and (22):



resulting in K_{Cat} and K_{An} that are defined in Equations (23) and (24):

$$K_{\text{Cat}} = \frac{(\equiv \text{SO}^- - \text{Cat}^+)(\text{H}^+)}{(\text{SOH})(\text{Cat}^+)} \exp\left(-\frac{F(\Psi_o - \Psi_\beta)}{RT}\right) \quad (23)$$

$$K_{\text{An}} = \frac{(\equiv \text{SOH}_2^+ - \text{An}^-)}{(\equiv \text{SOH})(\text{An}^-)(\text{H}^+)} \exp\left(\frac{F(\Psi_o - \Psi_\beta)}{RT}\right) \quad (24)$$

where K_{Cat} and K_{An} are the intrinsic binding constants for cations and anions, respectively. The structure of the charged interface in the TLM is considered analogous to a set of parallel plate capacitors with capacitances C_1 and C_2 for the inner- and outer-layers, respectively. Because of protonation, deprotonation, electrolyte binding, and radionuclide sorption reactions, the mineral surface acquires charge and corresponding potential. In addition, electroneutrality must be preserved, so that any charge buildup in the α - and β -planes must be neutralized by the charge in the diffuse layer according to Equation (25):

$$\sigma_o + \sigma_\beta + \sigma_d = 0 \quad (25)$$

where σ_o , σ_β , and σ_d are the charges in the α , β , and diffuse layers, respectively. The charges and corresponding potentials are connected by the following charge-potential relationships (Equations (26) to (28)):

$$\sigma_o = (\Psi_o - \Psi_\beta) / C_1 \quad (26)$$

$$\sigma_\beta = -(\Psi_\beta - \Psi_d) / C_2 \quad (27)$$

$$\sigma_d = 0.1174 \sqrt{I} \sinh(zF\Psi_d/2RT) \quad (28)$$

where Ψ_o , Ψ_β , and Ψ_d are the potentials in the α , β , and diffuse layers, respectively, and all other constants have the usual meaning. These equations are solved simultaneously and iteratively by including the charge balance with the mass-balance equations on element components that need to be satisfied. Iterations continue until the partition between the aqueous and sorbed phases results in a distribution of species that satisfies the charge-potential relationships and mass-balance equations.

Activity corrections in the TLM (and the other SCMs) require special attention. Typically, a distinction is made between activity coefficients for aqueous and surface species. Activity corrections for aqueous species are usually incorporated using the Davies or the Debye-Huckel equation (Stumm and Morgan, 1996). For systems with ionic strength higher than the upper limit of applicability of the Davies expression (approximately 0.5 M), the Pitzer-Brewer equations can be used. Incorporation of activity corrections for surface species depends on the set of standard and reference states chosen. Different methods have been proposed (Hayes and Leckie, 1987; Hayes *et al.*, 1991), but

the important issue is that no matter how activity corrections are incorporated in the model, all other parameters must be consistent with the activity correction assumptions made. In other words, deriving different parameters with different activity correction assumptions would lead to erroneous results (Hayes and Katz, 1996). One implementation of the TLM can be found in Papelis *et al.* (1988), where a more complete description of the structure of the TLM is given.

Model Parameter Estimation

One of the most important aspects of any model is the estimation of appropriate input parameters and SCMs are no exception. Unfortunately, the literature is full of examples where models have been abused. The TLM, with seven adjustable parameters – excluding radionuclide-binding constants – is particularly vulnerable to abuse. Systematic and consistent estimation of model parameters is therefore of paramount importance. In this section, a brief overview of the different TLM adjustable parameters will be given and different estimation methodologies will be discussed.

Surface Site Density

The surface site density, usually reported as sites nm^{-2} , is one of the more elusive parameters in SCMs. When combining surface site density with the specific surface area of the mineral phase and the solid concentration used in the experiments, we can estimate the total concentration of sites in solution. Given that in SCMs surface sites are equivalent to complexing ligands in solution, the total concentration of surface sites would obviously influence the sorption characteristics of the system. Surface site density, therefore, is a crucial characteristic of the system.

In addition, one should keep in mind that the choice of surface site density, and therefore total site concentration, affects other parameters, such as surface acidity and electrolyte binding constants (Hayes *et al.*, 1991). Several methods have been proposed to estimate surface site density, including tritium exchange experiments, selection of a value based on crystallographic considerations, or selection of a rather arbitrary value that falls between a range of reasonable values. Tritium exchange experiments tend to overestimate the surface site concentration. When values obtained from such measurements are used to model radionuclide sorption it is usually found that a better fit is obtained by lowering the site density value.

Davis and Kent (1990) have proposed a value of 2.31 sites nm^{-2} , consistent with the value proposed by Dzombak and Morel (1990) for hydrous ferric oxide. Although, based on sensitivity analysis studies, this value is certainly within an accepted range of site densities, the implication of confidence to the second decimal place is preposterous. Estimating the site density based on crystallographic considerations appears to be a reasonable method. It should be kept in mind, however, that mineral surfaces might have several different types of surface hydroxyl sites having different reactivities (Sposito, 1984). Selecting one appropriate site density that would represent the entire assemblage may require knowledge about the relative proportions of different phases in a complex mineral assemblage. Such detailed knowledge is hardly ever available. Hayes and coworkers (Hayes *et al.*, 1991; Katz and Hayes, 1995a, b; Hayes and Katz, 1996) suggest optimizing the remaining parameters based on a systematic variation of the site density and selecting the value that results in the best fit. Sahai and Sverjensky (1997)

recommend using site density data based on tritium exchange experiments. It should be pointed out, however, that the selection of a given value may give adequate results under limited conditions, but fails to predict a broader range of experimental data. In summary, regardless of the method used to estimate the site density, the remaining model parameters must be determined using the selected site density value.

Surface Acidity Constants

Three different methods have been proposed for the estimation of surface acidity constants. All three methods require evaluation of potentiometric titration data. The first method involves graphical extrapolation techniques (James *et al.*, 1978; James and Parks, 1982). This method, however, has been criticized because the part of the titration curve that is used in the extrapolation is rather arbitrary and the particular method of polynomial fitting may result in different constants (Hayes *et al.*, 1991).

Sahai and Sverjensky (1997) proposed a method that involves experimental determination of the pH_{PZC} of the oxide followed by predicting a ΔpK value based on the method of Sverjensky and Sahai (1996). Finally, Hayes and coworkers (Hayes *et al.*, 1991; Katz and Hayes, 1995a, b), based on sensitivity analysis studies with three different oxides, propose the choice of a ΔpK of at least 3 for the TLM. Their results indicate that as long as the ΔpK is at least 3, the sensitivity of the model to this parameter diminishes. They add, however, that the optimum values for the acidity constants will ultimately be determined by fitting both potentiometric titration data and metal ion sorption data.

Electrolyte Binding Constants

The TLM is the only SCM that requires specification of electrolyte binding constants. As reported by Hayes *et al.* (1991), optimization routines such as FITEQL (Westall, 1982) cannot simultaneously optimize both acidity and electrolyte binding constants. Acidity binding constants must, therefore, be determined first before electrolyte binding constants can be estimated. Typically, an optimization routine, such as FITEQL, can be used. As pointed out earlier, the choice of both acidity constants and inner-layer capacitance affects the results. Typically, the acidity constants are estimated first, followed by estimation of the electrolyte binding constants as a function of the inner-layer capacitance.

Hayes *et al.* (1991) suggest that values of C_1 between 0.8 and 1.2 F m^{-2} would typically result in optimal electrolyte binding constants for essentially all oxides. As mentioned earlier, however, the ultimate test of goodness of fit must be based on fitting of sorption data in addition to the potentiometric titration data. The reason for this approach is that several sets of consistent input parameters may result in essentially identical good fitting of potentiometric titration data. Modeling of sorption data at different ionic strengths and under conditions as broad as possible can be used to differentiate between otherwise equally good fits.

A similar approach was used by Sahai and Sverjensky (1997) to arrive at internally consistent TLM parameters. After estimating the acidity constants as described above, they used fitting of charge data to estimate the electrolyte binding constants and C_1 . It is not clear, however, how the three parameters were optimized simultaneously, especially because they did not use an optimization routine to derive electrolyte binding constants

but rather the goodness of fit was determined by visual inspection. It appears that the value of C_1 was varied and the electrolyte binding constants were estimated until an apparent best fit was obtained.

Inner Layer Capacitance

Although, at least in theory, the inner layer capacitance could be estimated based on the properties of the mineral-water interface and the characteristics of the sorbed ion, the inner layer capacitance is essentially treated as a fitting parameter. As expected, variations in C_1 affect other parameters. In reality, therefore, C_1 is varied in a systematic way and the optimal set of model parameters is obtained.

Outer Layer Capacitance

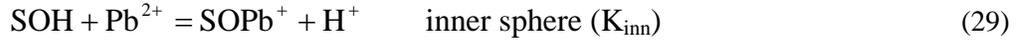
Although, strictly speaking, the outer layer capacitance, C_2 , is another adjustable parameter, in practice it is almost always treated as a constant and assigned the value of 0.2 F m^{-2} (Westall and Hohl, 1980; Hayes *et al.*, 1991). There are several reasons for this approach. First, there is experimental and theoretical evidence for this value, based on studies of the silver iodide-water interface. Although these results may not be directly transferable to oxide systems, additional studies have suggested similar, albeit slightly lower, values. Second, sensitivity analysis studies have shown that modeling results are rather insensitive to variations in the C_2 value. Finally, given the number of adjustable parameters in the TLM and the larger uncertainty associated with them, it seems reasonable to try to reduce the degrees of freedom in model calculations by treating C_2 as a constant.

Radionuclide Binding Constants

Binding Stoichiometry

The ultimate reason for using SCMs is to be able to improve our predictive capability with respect to radionuclide sorption and transport in aquifers. Although estimation of the TLM parameters provides valuable insight into the macroscopic description of the mineral-water interface, the desired outcome of the modeling effort is to develop a robust model that can be used to improve our estimates of migration potential of radionuclides. Optimization of the TLM parameters, therefore, is directly related to the stoichiometry of the proposed surface complexes.

The major advantage of the TLM over other SCMs, is that because of the added β -plane, the option exists to model ions as either strongly binding ions sorbed at the α -plane, or as weakly binding ions sorbed at the β -plane. This paradigm allows strongly binding ions to be modeled as inner-sphere complexes, i.e., as ions that form coordination complexes with atoms at the mineral surface after losing part of their hydration sheath. Weakly binding ions are presumed to form outer-sphere complexes at the β -plane while retaining their hydration sheath. One frequently used technique to determine whether inner- or outer-sphere complexes are being formed involves experiments at different ionic strengths. The sorption of weakly sorbing ions can be reduced substantially or even suppressed entirely by an increase in ionic strength. Sorption of strongly binding ions, on the other hand, is essentially not affected by changes in ionic strength (Hayes and Leckie, 1987; Hayes *et al.*, 1988). Formation of inner- and outer-sphere complexes can be represented by the reactions shown in Equations (29) and (30):



resulting in the equilibrium expressions given by Equations (31) and (32):

$$K_{\text{inn}} = \frac{(\text{SOPb}^+)(\text{H}^+)}{(\text{SOH})(\text{Pb}^{2+})} \exp\left(\frac{F\Psi_o}{RT}\right) \quad (31)$$

$$K_{\text{out}} = \frac{(\text{SO}^- - \text{Sr}^{2+})(\text{H}^+)}{(\text{SOH})(\text{Sr}^{2+})} \exp\left(-\frac{F(\Psi_o - \Psi_\beta)}{RT}\right) \quad (32)$$

It is obvious from the above reactions that the stoichiometry is entirely different in the two cases, resulting in a completely different structure of the mineral-water interface and therefore entirely different scenarios when competing ions are present in solution. It is the ability of the TLM to best model these competition effects, under a variety of geochemical conditions, that justifies the additional effort required in parameter estimation compared to other SCMs. In addition, fitting of sorption data under different surface coverages provides an additional constraint in parameter estimation (Katz and Hayes, 1995a, b).

Use of Spectroscopic Evidence in Binding Stoichiometry Determination

The reactions outlined above represent the formation of mononuclear complexes. Unfortunately, macroscopic experiments alone cannot be used to determine a sorption mechanism or to distinguish between formation of mononuclear complexes, polynuclear complexes, or surface precipitates (Sposito, 1986). In the absence of molecular level information about the structure of surface complexes, any postulated reaction is little more than a curve-fitting exercise. Use of spectroscopic techniques, however, has allowed the determination of the molecular structure of sorbed complexes, thereby providing an independent method to determine reaction stoichiometries.

The two most useful techniques in that respect are, primarily, x-ray absorption spectroscopy (XAS) and, secondary, x-ray photoelectron spectroscopy (XPS). XAS can be used to determine the average coordination environment of sorbed ions, including the average number of neighbors, and the average distance and identity of the neighboring atoms (Brown, 1990). Based on this type of information we can distinguish, for example, between inner- and outer-sphere complex formation (Hayes *et al.*, 1987). This type of information has direct applications in choosing a realistic model stoichiometry.

An additional consideration when formulating sorption complex stoichiometries is the potential transition to a different stoichiometry as surface coverage increases. Several divalent metal cations form mononuclear complexes at low surface coverage; at increasingly higher surface coverages, however, first polynuclear complexes are formed, followed by formation of surface precipitates (O'Day *et al.*, 1994a, b; Bargar *et al.*, 1998). This trend, however, is not universal, not even for all divalent metal ions. XAS studies, for example, have been unable to show formation of cadmium polynuclear complexes and precipitates, even at high surface coverages and on different oxides (Spadini *et al.*, 1994; Papelis *et al.*, 1995).

EVALUATION OF AVAILABLE DATA

Data Organization

In this section, all available data are presented and are organized in terms of either radionuclides, or in terms of the mineral or rock used in the sorption experiments. All data are organized in terms of transuranic elements, other radionuclides, or any other metal cation or anion. Sorption data are organized and presented as a function of the rock or mineral surface used in the experiments. All data are summarized in Tables and are discussed in the text.

Radionuclides and Surrogates

All sorption data are discussed in this section as a function of the sorbate ion. These sorbates are uranium (U) or the transuranic elements neptunium (Np), plutonium (Pu), americium (Am), and curium (Cm). In addition, data are summarized for any available REEs, most notably europium (Eu). Finally, sorption data for other cations are presented. These cations are either radionuclides commonly generated during nuclear testing, in general, and at the NTS, in particular, such as strontium (Sr), cesium (Cs), and cobalt (Co), or other metal cations, such as cadmium (Cd) or lead (Pb). Sorption modeling of such cations is still important because these metals are often present in nuclear test sites and both Cd and Pb are considered significant health hazards, even in their non-radioactive form. The only anion sorption discussed is the anion of technetium (Tc), pertechnetate.

All sorption data are summarized in Tables 1 through 9. For each ion and each study, the following information is included, if available: the types of minerals or rock sorbents, including rock mineralogy, if known and reported; the type of electrolyte or synthetic groundwater used; the ion concentration; the solid-solution ratio; and the maximum sorption density. Comments that provide additional information are also included. These comments are provided as a summary and reference only and are not meant to replace the more detailed discussion in the body of the report. Finally, the source of the data is included. Not all the data that are included in the tables are discussed in the text. The discussion here focuses on the modeling aspects of the work and the approach used in the modeling.

Americium

A number of studies of americium sorption on several different minerals have been reported in the literature (Shanbhag and Morse, 1982; Allard *et al.*, 1989; Triay *et al.*, 1989; Stammose and Dolo, 1990; Kitamura *et al.*, 1999). Minerals included alumina, zeolitized tuffs, granite, clays, calcite, and iron oxides. Several of these studies involved only determination of a linear distribution coefficient at a single pH value (Shanbhag and Morse, 1982; Triay *et al.*, 1989, 1991), while others report equilibrium sorption distribution coefficients as a function of pH (Allard *et al.*, 1982, 1989; Righetto *et al.*, 1988; Stammose and Dolo, 1990; Moulin *et al.*, 1992; Kitamura *et al.*, 1999). Fewer studies, however, attempted modeling Am sorption on these mineral surfaces (Stammose and Dolo, 1990; Moulin *et al.*, 1992; Kitamura *et al.*, 1999).

Table 1. Summary of sorption data for Americium.

Sorbent Minerals	Electrolyte	Ion Conc	Solid - Solution Ratio	Maximum Sorption Density	Comments	Source
Al ₂ O ₃ , SiO ₂ , montmorillonite	Synthetic GW, NaClO ₄	??	0.01	NR	K _d pH dependence	(Allard <i>et al.</i> , 1982)
clinoptilolite, montmorillonite, calcite, hematite, goethite, hollandite, romanechite	NTS J-13 Well Water	10 ⁻⁶ M	0.05	NR	K _d for several minerals	(Triay <i>et al.</i> , 1991)
calcite	NaCl, NaCl- MgCl ₂ , seawater	10 ⁻⁷ to 10 ⁻¹² M	0.05 to 0.0001	NR	K _d , kinetics	(Shanbhag and Morse, 1982)
alumina	NaClO ₄	10 ⁻⁸ M	0.01	NR	Humic Acid, variable pH, ionic strength	(Allard <i>et al.</i> , 1989)
alumina colloids	NaClO ₄	10 ^{-9.3} M	10 to 200 ppm	NR	Humic Acid, colloids, variable pH	(Righetto <i>et al.</i> , 1988)
natural clay- kaolinite/smectite	NaClO ₄	10 ⁻⁸ M	0.005	NR	K _d , variable pH, ionic strength, SCM model attempt	(Stammose and Dolo, 1990)
granite, Japan	NaClO ₄	10 ⁻¹⁰ M	0.025	NR	K _d , BET, variable pH, ionic strength, DLM parameters	(Kitamura <i>et al.</i> , 1999)
α-alumina, silica	NaClO ₄	10 ⁻⁸ M	0.01	NR	K _d , BET, CEC, variable pH, ionic strength, SCM estimates of binding constant, K _s	(Moulin <i>et al.</i> , 1992)
clinoptilolite, feldspar	NTS J-13 groundwater	10 ⁻⁷ to 10 ⁻¹¹ M	0.01	NR	K _d estimates only	(Triay <i>et al.</i> , 1989)

Table 2. Summary of sorption data for Cesium.

Sorbent Minerals	Electrolyte	Ion Conc	Solid - Solution Ratio	Maximum Sorption Density	Comments	Source
montmorillonite, kaolinite, quartz, corundum, gibbsite	NaClO ₄	0.1 to 0.01 M	0.01	NR	variable pH, T	(Westrich <i>et al.</i> , 1995)
corundum	NaCl	unknown	unknown	NR	K _d , variable pH	(Shiao <i>et al.</i> , 1981)
magnetite	NaNO ₃	10 ^{-4.7} to 10 ^{-4.1} M	0.0002	NR	BET, acid-base titration, variable pH	(Catalette <i>et al.</i> , 1998)

Table 3. Summary of sorption data for Europium.

Sorbent Minerals	Electrolyte	Ion Conc	Solid - Solution Ratio	Maximum Sorption Density	Comments	Source
hematite	NaClO ₄	unknown	0.044	NR	BET, acid-base titration, SCM parameter determination, CC model	(Rabung <i>et al.</i> , 1998)
corundum, quartz	NaClO ₄	10 ^{-8.15} M	0.005	NR	Fulvic acid, K _d , variable pH, ionic strength,	(Norden <i>et al.</i> , 1994)
goethite, magnetite	NaClO ₄	10 ⁻⁵ M	0.000017	NR	Zeta potential, BET, variable pH, carbonate addition dependence, TLM complexation constant determination	(Fujita and Tsukamoto, 1997)
illite	NaClO ₄	10 ⁻⁸ M	0.001	NR	BET, CEC, DLM parameter determination	(Wang <i>et al.</i> , 1998)
corundum	NaCl	unknown	unknown	NR	K _d , variable pH	(Shiao <i>et al.</i> , 1981)
magnetite	NaNO ₃	10 ^{-3.7} M	0.0002	NR	BET, acid-base titration, variable pH	(Catalette <i>et al.</i> , 1998)
bentonite, kaolinite, montmorillonite, quartz	NaClO ₄	10 ⁻⁹ M	0.02 to 0.002	NR	humic acid, zeta potential, BET, CEC, variable pH, fixed ionic strength	(Fairhurst <i>et al.</i> , 1995)
colloidal HFO, quartz	NaClO ₄	10 ⁻⁸ M	0.00005 to 0.0005	NR	Fulvic acid, potentiometric titration, K _d	(Ledin <i>et al.</i> , 1994)

Table 4. Summary of sorption data for Neptunium.

Sorbent Minerals	Electrolyte	Ion Conc	Solid - Solution Ratio	Maximum Sorption Density	Comments	Source
Al ₂ O ₃ , SiO ₂ , montmorillonite	Synthetic GW, NaClO ₄	??	0.01	NR	K _d pH dependence	(Allard <i>et al.</i> , 1982)
clinoptilolite, montmorillonite, calcite, hematite, goethite, hollandite, romanechite	NTS J-13 Well Water	10 ⁻⁶ M	0.05	NR	K _d for several minerals	(Triay <i>et al.</i> , 1991)
alumina colloids	NaClO ₄	10 ⁻¹⁴ M	200 ppm	NR	humic acid, colloids, variable pH	(Righetto <i>et al.</i> , 1988)
hematite, magnetite, goethite, biotite, alumina, lepidocrocite, boehmite	NaNO ₃	10 ⁻⁶ to 10 ⁻⁵ M	1.0	NR	K _d , sorption hysteresis, kinetics, variable pH	(Nakayama and Sakamoto, 1991)
quartz, clinoptilolite, montmorillonite, α- Al ₂ O ₃	NaNO ₃	10 ⁻⁷ to 10 ⁻⁶ M	0.004 to 0.08	NR	BET, K _d , variable pH	(Bertetti <i>et al.</i> , 1998)
montmorillonite	NaNO ₃	10 ⁻⁶ M	0.004	NR	BET, K _d , variable pH, DLM inversion to adsorption data, FITEQL	(Turner <i>et al.</i> , 1998)
am HFO	NaNO ₃	10 ⁻¹⁰ to 10 ⁻¹² M	0.0014	NR	acid-base titration, TLM inversion	(Girvin <i>et al.</i> , 1991)
YM Tuffs, minerals: calcite, hematite, mont., bentonite clinoptilolite, quartz, albite	J-13 and UE-25 p #1 groundwater	10 ⁻⁵ to 10 ⁻⁷ M	0.05	NR	BET, K _d , kinetics	(Triay <i>et al.</i> , 1996a)
quartz, clinoptilolite, montmorillonite	NaNO ₃	10 ⁻⁶ to 10 ⁻⁷ M	0.004 to 0.08	NR	BET, K _d , kinetics, reversibility, variable pH	(Bertetti <i>et al.</i> , 1995)
YM Tuffs, minerals: hematite, clinoptilite, quartz, albite	J-13 groundwater	10 ⁻⁵ to 10 ⁻⁷ M	0.05	NR	BET, K _d , variable pH	(Triay <i>et al.</i> , 1996b)
montmorillonite	NaNO ₃	10 ⁻⁶ M	0.004	NR	BET, K _d , variable pH, DLM inversion, FITEQL	(Turner <i>et al.</i> , 1998)
YM Tuffs, minerals: quartz, clinoptilolite, montmorillonite, hematite	J-13 and UE-25 p#1 groundwater	10 ⁻⁶ M	0.05	NR	K _d , column experiments, breakthrough curve inversion	(Triay <i>et al.</i> , 1993)
kaolinite, montmorillonite	Sackingen groundwater	10 ⁻⁶ to 10 ⁻⁹ M	0.01	NR	K _d , K _f	(Aksoyoglu <i>et al.</i> , 1991)

Table 5. Summary of sorption data for Plutonium.

Sorbent Minerals	Electrolyte	Ion Conc	Solid - Solution Ratio	Maximum Sorption Density	Comments	Source
Al ₂ O ₃ , SiO ₂ , montmorillonite	Synthetic GW, NaClO ₄	??	0.01	NR	K _d pH dependence	(Allard <i>et al.</i> , 1982)
clinoptilolite, montmorillonite, calcite, hematite, goethite, hollandite, romanechite	NTS J-13 Well Water	10 ⁻⁶ M	0.05	NR	K _d for several minerals	(Triay <i>et al.</i> , 1991)
YM Tuffs, minerals: hematite, clinoptilite, quartz, albite	J-13, groundwater	10 ⁻⁵ to 10 ⁻⁷ M	0.05	NR	BET, K _d , variable pH	(Triay <i>et al.</i> , 1996b)
goethite, aragonite, calcite, δ-MnO ₂	NaCl, seawater	10 ⁻⁷ to 10 ⁻¹² M	0.001 to 100 m ² /L	NR	kinetics, fixed pH, ionic strength	(Keeney-Kennicutt and Morse, 1985)
goethite	NaNO ₃	10 ⁻¹⁰ to 10 ⁻¹¹ M	28.5 m ² /L	NR	variable pH, ionic strength, carbonate alkalinity, DOC	(Sanchez <i>et al.</i> , 1985)

Table 6. Summary of sorption data for Strontium.

Sorbent Minerals	Electrolyte	Ion Conc	Solid - Solution Ratio	Maximum Sorption Density	Comments	Source
corundum, quartz	NaClO ₄	10 ^{-9.40} M	0.005	NR	Fulvic acid, K _d , variable pH, ionic strength	(Norden <i>et al.</i> , 1994)
corundum	NaCl	unknown	unknown	NR	K _d , variable pH	(Shiao <i>et al.</i> , 1981)
calcite	HClO ₄ , Ca(ClO ₄) ₂ , NaClO ₄ , NaHCO ₃ , NaOH	Ba, Sr, Cd, Mn, Zn, Co, Ni: 10 ⁻⁴ to 10 ⁻⁸ M	0.025	NR	kinetics, variable pH, CEC determination, SCM modeling with FITEQL	(Zachara <i>et al.</i> , 1991)
sandstone	'brine'	undetermined	N/A	N/A	High-pressure flow experiment in sandstone core, estimated K _d and retardation factor from transport data	(Weed <i>et al.</i> , 1980)

Table 7. Summary of sorption data for Uranium.

Sorbent Minerals	Electrolyte	Ion Conc	Solid - Solution Ratio	Maximum Sorption Density	Comments	Source
Al ₂ O ₃ , SiO ₂ , montmorillonite	Synthetic GW, NaClO ₄	??	0.01	NR	K _d pH dependence	(Allard <i>et al.</i> , 1982)
YM Tuffs, minerals: hematite, clinoptilite, quartz, albite	J-13 groundwater	10 ⁻⁴ to 10 ⁻⁷ M	0.05	NR	BET, K _d , variable pH	(Triay <i>et al.</i> , 1996b)
goethite, am-HFO, hematite	NaNO ₃	10 ⁻⁶ M	unknown	NR	BET, PZC, variable pH, competing adsorption Ca, Mg, TLM modeling	(Hsi and Langmuir, 1985)
montmorillonite	NaNO ₃	10 ⁻⁶ to 10 ⁻⁷ M	0.0032 and larger	NR	BET, K _d , variable pH, M/V, DLM modeling, FITEQL	(Pabalan and Turner, 1997)
synthetic ferrihydrite	NaNO ₃	10 ⁻⁶ M	variable	NR	Synthetic mineral, EXAFS, variable pH, DLM modeling	(Waite <i>et al.</i> , 1994)
synthetic hematite	NaCl	10 ⁻⁶ M	0.001	NR	waste package corrosion product, column experiments, DLM	(Viani and Torretto, 1998)
YM Zeolite, clinoptilolite	unknown	10 ⁻⁶ M	0.001	NR	kinetics, variable pH	(Pabalan <i>et al.</i> , 1993)
phyllite minerals: quartz, chlorite, muscovite, feldspar	NaClO ₄	10 ⁻⁴ to 10 ⁻⁷ M	0.0125	NR	acid-base titration data, BET, DLM modeling, FITEQL	(Arnold <i>et al.</i> , 2001)
quartz, clinoptilolite, montmorillonite, α-alumina	NaNO ₃	10 ⁻⁶ to 10 ⁻⁸ M	variable	NR	BET, K _d , variable pH, ionic strength, DLM, FITEQL	(Pabalan <i>et al.</i> , 1998)
synthetic hematite	NaCl	10 ⁻⁶ M	0.001	NR	BET, variable T, pH, column experiments, DLM modeling, REACT	(Viani and Torretto, 1998)
natural clay (smectite)	NaClO ₄ , Ca(ClO ₄) ₂	10 ⁻⁶ M	unknown	NR	acid-base titration, BET, TLM, FITEQL	(Turner <i>et al.</i> , 1996)
corrensite (chlorite, smectite)	NaClO ₄	10 ⁻⁷ M	0.0001	NR	BET, potentiometric titrations, zeta potential, Ca, Mg competitive adsorption, variable pH, TLM parameter estimation	(Park <i>et al.</i> , 1995)
quartz, clinoptilolite	NaNO ₃	10 ⁻⁷ M	0.0001 to 0.02	NR	BET, K _d , variable M/V, pH, DLM modeling, parameter estimation	(Prikryl <i>et al.</i> , 2001)
montmorillonite, gibbsite, silica	NaClO ₄	10 ⁻⁸ M	0.00001 to 0.0057	NR	variable pH, ionic strength, TLM, parameter estimation, FITEQL	(McKinley <i>et al.</i> , 1995)

Table 7. Summary of sorption data for Uranium (continued).

Sorbent Minerals	Electrolyte	Ion Conc	Solid - Solution Ratio	Maximum Sorption Density	Comments	Source
Ag. soil, mineral: goethite	groundwater and ag. drainage water	2 mg/L	0.04	NR	BET, various electrolytes, DLM parameter estimation, FITEQL	(Duff and Amrhein, 1996)
montmorillonite	unknown	1 to 40 mg/L	0.0003	NR	??	(Tsunashima <i>et al.</i> , 1981)
phylite-minerals: muscovite, quartz, chlorite, albite	NaClO ₄	10 ⁻⁶ M	0.0125	NR	BET, variable pH, DLM	(Arnold <i>et al.</i> , 1998)
quartz	??	10 ⁻⁶ M	0.01	NR	BET, variable pH, carbonate addition, sorption ratios	(Lieser <i>et al.</i> , 1992)

Table 8. Summary of sorption data for miscellaneous radionuclides.

Sorbent Minerals	Electrolyte	Ion Conc	Solid - Solution Ratio	Maximum Sorption Density	Comments	Source
Al ₂ O ₃ , SiO ₂ , montmorillonite	Synthetic GW, NaClO ₄	Pa, Th	0.01	NR	K _d , pH dependence	(Allard <i>et al.</i> , 1982)
alumina colloids	NaClO ₄	Th, 10 ⁻¹¹ M	10 ppm	NR	humic acid, colloids, variable pH	(Righetto <i>et al.</i> , 1988)
bentonite, smectite	NaCl	Ra, 10 ⁻⁸ M	0.02 to 0.002	NR	K _d , diffusion experiments	(Tachi <i>et al.</i> , 2001)
hematite	NaClO ₄	Th, 10 ⁻¹⁵ M	various	NR	variable pH, ionic strength, TLM, FITEQL	(Quigley <i>et al.</i> , 1995)
NTS alluvium, bentonite	NTS RNM-2S groundwater	¹⁴⁴ Ce, ¹⁵² Eu, ¹³³ Ba, ⁸⁵ Sr, ⁹⁵ Zr- ⁹⁵ Nb, ¹³⁷ Cs, ⁶⁰ Co, ¹²⁴ Sb: unknown concentrations	unknown	NR	range of K _d values	(Wolfsberg, 1978)
corundum	NaCl	Co, Cd unknown conc.	unknown	NR	K _d , variable pH	(Shiao <i>et al.</i> , 1981)
magnetite	NaNO ₃	Ba, 10 ^{-4.3} M	0.0002	NR	BET, acid-base titration, variable pH	(Catalette <i>et al.</i> , 1998)

Table 9. Summary of sorption data for nonradiogenic rare earth elements.

Sorbent Minerals	Electrolyte	Ion Conc	Solid - Solution Ratio	Maximum Sorption Density	Comments	Source
Al ₂ O ₃ , SiO ₂ , montmorillonite	Synthetic GW, NaClO ₄	Th, Pd, Conc?	0.01	NR	K _d pH dependence	(Allard <i>et al.</i> , 1982)
montmorillonite, kaolinite, quartz, corundum, gibbsite	NaClO ₄	Cd, 10 ^{-4.15} M	0.01	NR	variable pH, T	(Westrich <i>et al.</i> , 1995)
granite	NaNO ₃	Sr, Pb, Cs, selenite, potassium chromate: 10 ^{-3.77} to 10 ^{-1.77} M	0.01	NR	whole rock analysis, variable ionic strength, pH, K _d , K _f	(Papelis, 2001)
calcite	HClO ₄ , Ca(ClO ₄) ₂ , NaClO ₄ , NaHCO ₃ , NaOH	Ba, Sr, Cd, Mn, Zn, Co, Ni: 10 ⁻⁴ to 10 ⁻⁸ M	0.025	NR	kinetics, variable pH, CEC determination, SCM modeling with FITEQL	(Zachara <i>et al.</i> , 1991)

Stammose and Dolo (1990) attempted to model the sorption of Am on a clay sample composed of kaolinite and montmorillonite. A nonelectrostatic model was used to model the equilibrium distribution coefficient. Speciation was incorporated by including the species AmOH²⁺ and AmCO₃⁺ in the computations. Because the model ignores all electrostatic interactions of charged species with the charged surface, no additional parameters are needed other than an overall apparent surface complexation constant. No electrolyte binding is included in the model and therefore no competition between Am and background electrolyte ions can be incorporated. The model, therefore, cannot be used to classify Am sorption in terms of strength of binding.

Kitamura *et al.* (1999) reported modeling of Am sorption on granite. They used essentially a triple layer electrostatic model and the species Am³⁺ and Am(OH)₂⁺ to represent Am sorption. The values of the model input parameters, however, were chosen somewhat arbitrarily and do not appear to be consistent. For example, the value for the selected surface site density is not adequately justified. In addition, the inner layer capacitance, C₁, acidity and electrolyte binding constants, K_{a2}^{int} and K_{Na}^{int}, and the Am binding constant, K_{Am}^{int}, were all determined simultaneously, based on optimization of the sorption data, without consideration for the acid-base properties of the granite rock; in other words, they were all treated as fitting parameters. As a result, the value of K_{Na}^{int} was different depending on whether Am³⁺ or Am(OH)₂⁺ was considered as the sorbing species, a physically rather unlikely situation. The values obtained for the Am binding constants, therefore, are questionable and not necessarily consistent.

Moulin *et al.* (1992) reported Am sorption on corundum (α-Al₂O₃) and amorphous silica. They conducted experiments as a function of pH and ionic strength. They also reported an apparent Am binding constant obtained from the linearization of a mass action expression for the sorption of Am on the oxide surfaces. The linearization was performed according to the Kurbatov approach. These results, therefore, are not

comparable to values obtained from other modeling approaches, including surface complexation models. In addition, the authors compare sorption of Am on these minerals to sorption of other cations, including alkaline earths, transition metals, and uranium species. It is not at all clear that the same model and approach were used by these investigators to obtain these apparent binding constants, thereby rendering the reported comparisons of rather limited use.

Cesium

Because of the abundance of Cs in nuclear test sites, sorption studies have been conducted using a number of different minerals (Wolfsberg, 1978; Rundberg, 1987; Westrich *et al.*, 1995; Papelis, 2001). None of these studies, however, included any kind of surface complexation modeling. Wolfsberg (1978) determined batch equilibrium sorption-desorption distribution coefficients for a number of radionuclides, including Cs, on alluvium from the NTS. The alluvium consisted of mineral and tuff fragments in an iron-oxide-rich, fine-grained matrix. Major mineral components included quartz, feldspars, calcite, and glass shards; minor constituents included amphibole, biotite, orthopyroxene, and clinopyroxene.

Rundberg (1987) reported the uptake kinetics of Cs, Sr, and Ba, as well as uptake of the actinides Am and Pu by Yucca Mountain tuff wafers and elution through crushed-tuff columns. The results were consistent with diffusion-limited sorption, especially for the cations Cs, Sr, and Ba. The kinetics of the actinides, however, were more complicated. The sorption of Cs, as well as Pb, chromate, and selenite on granite from the Shoal Test Area, Nevada, was studied by Papelis (2001). Linear and Freundlich equilibrium partitioning coefficients were reported as a function of pH and background electrolyte concentration. Sorption of Cs was almost pH-independent, suggesting sorption primarily on cation exchange, permanent charge sites.

Westrich *et al.* (1995) studied the sorption behavior of Cs and Cd onto oxide and clays, including quartz, corundum, gibbsite, kaolinite, and montmorillonite. The study included a combination of macroscopic sorption experiments and spectroscopic and microscopic techniques, including x-ray photoelectron spectroscopy (XPS), nuclear magnetic resonance (NMR), and atomic force microscopy (AFM). They concluded that Cs binds primarily on the edge and basal sites of kaolinite and on the interlayer (permanent charge) sites of montmorillonite. Sorption on corundum, kaolinite, and montmorillonite was much stronger than on gibbsite.

Europium and Other Lanthanides

Europium has been used in several sorption studies as an analog to trivalent actinides (Am^{III} , Pu^{III}) (Shiao *et al.*, 1981; Ledin *et al.*, 1994; Norden *et al.*, 1994; Fairhurst *et al.*, 1995; Fujita and Tsukamoto, 1997; Catalette *et al.*, 1998; Rabung *et al.*, 1998; Wang *et al.*, 1998). Many mineral surfaces have been used for these experiments, including oxides (quartz, corundum, goethite, hematite, magnetite, hydrous ferric oxide) and clay minerals (kaolinite, montmorillonite, illite). In some studies, an attempt was made to model Eu sorption using surface complexation models (Fujita and Tsukamoto, 1997; Catalette *et al.*, 1998; Rabung *et al.*, 1998; Wang *et al.*, 1998), while in others, some type of equilibrium distribution coefficients were used to describe sorption or ion

exchange reactions (Shiao *et al.*, 1981; Ledin *et al.*, 1994; Norden *et al.*, 1994; Fairhurst *et al.*, 1995).

The adsorption of Cs, Sr, Eu, Co, and Cd by chromatographic and precipitated alumina was reported by Shiao *et al.* (1981). They determined a distribution coefficient as a function of pH and ionic strength and interpreted the results in terms of an ion exchange reaction. Very small effects of ionic strength were observed, consistent with specific sorption as opposed to an ion exchange process. The strong pH dependence of sorption was also consistent with cation sorption on an amphoteric oxide surface, as expected for cation sorption on alumina.

Additional sorption studies focused on the interaction of Eu with mineral surfaces in the presence of humic and fulvic acids (Ledin *et al.*, 1994; Norden *et al.*, 1994; Fairhurst *et al.*, 1995). Sorption of Eu and Sr on alumina and quartz in the presence of fulvic acid as a function of pH and ionic strength was studied by Norden *et al.* (1994). They derived equilibrium distribution coefficients as a function of Eu speciation, pH, and fulvic acid concentration. The sorption of Eu on iron oxides and quartz as a function of pH and in the presence of fulvic acid was reported by Ledin *et al.* (1994). No attempt was made to model the sorption, but the reported results, in the absence of fulvic acid, are consistent with cation binding on an amphoteric surface hydroxyl site, as expected for the minerals used in the study. Sorption of Eu on bentonite, kaolinite, montmorillonite, and quartz in the presence of humic acid as a function of pH was reported by Fairhurst *et al.* (1995). Although no modeling of the data was attempted, the Eu sorption behavior suggests it is consistent with Eu sorption as a ternary complex with humic acid on these surfaces.

The sorption of Eu and Ba on magnetite was studied by Catalette *et al.* (1998). The reported surface area of magnetite, $18.3 \text{ m}^2/\text{g}$, is very high for a natural sample with the particle size given ($180 \text{ }\mu\text{m}$) and can possibly be explained by the presence of clay impurities, although the authors attributed the high surface area to the presence of very high surface area silica ($400 \text{ m}^2/\text{g}$). The solid point-of-zero charge (PZC) was determined by potentiometric titrations at two different ionic strengths and the acidity constants were determined by fitting potentiometric titration data, presumably using a DLM. The authors used a DLM and two surface species, SOEu^{3+} and $\text{SOEu}(\text{OH})_2$, to model Eu sorption as a function of pH.

The effect of carbonate ions on Eu sorption on goethite and magnetite as a function of pH was studied by Fujita and Tsukamoto (1997). They found that sorption of Eu was enhanced by carbonate for both oxides. Sorption of Eu was pH dependent for both oxides and ionic-strength independent, therefore implying specific Eu sorption on these iron oxide minerals. Sorption results on goethite were modeled using the TLM, but not enough data are given to allow evaluation of the parameter estimation approach.

Sorption of Eu on a natural hematite was modeled using several models (Rabung *et al.*, 1998). The constant capacitance surface complexation model was used to model Eu sorption at high ionic strengths. The PZC of the hematite was determined by potentiometric titrations at different ionic strengths and was determined to be approximately 6. This value is very low for an iron oxide and can only be explained by the presence of impurities. All parameters of the constant capacitance model, acidity constants, capacitance, and total concentration of the surface hydroxyl groups, were

obtained by fitting the potentiometric titration data with the optimization code FITEQL. Modeling of the sorption data over several orders of magnitude was also attempted using the Langmuir isotherm. The data could not be modeled using a single Langmuir isotherm; at least two isotherms were required. Finally, the data were modeled using a non electrostatic surface complexation model, based on the assumption that the electrostatic component of these reactions was negligible. The surface complex SOEu^{2+} was postulated and was assigned two different binding constants representing strong and weak binding sites, respectively. The weak binding site was necessary to fit the data at high surface coverages.

Sorption of Eu on illite was modeled by Wang *et al.* (1998). Acidity constants for the illite sample were estimated based on modeling of potentiometric titration data using the DLM. It is not entirely clear whether electrostatic interactions were ignored during the modeling process. In addition, proton exchange with interlayer sites was apparently not accounted for. Sorption of Eu was accomplished by a multi-site model assuming sorption at both interlayer cation exchange sites and edge surface hydroxyl sites. It was determined that the selectivity coefficient for the Eu-Na exchange was not constant but a function of background electrolyte concentration.

The partitioning of lanthanides, or REEs, between calcite and seawater solutions was investigated by Zhong and Mucci (1995). Specifically, the authors studied the partitioning of lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm), europium (Eu), dysprosium (Dy), holmium (Ho), gadolinium (Gd), terbium (Tb), erbium (Er), and ytterbium (Yb) in calcite overgrowths from seawater under steady-state conditions and 70 nM metal concentration. They found that the partition coefficients decrease systematically with atomic number, from $10^{3.6}$ for La to $10^{1.9}$ for Yb, the heaviest REE used in the study, and are correlated to the solubility of the corresponding carbonate minerals. The experiments were conducted in artificial seawater solutions under predetermined calcite supersaturation attained by adding an appropriate amount of sodium carbonate and sodium bicarbonate. The corresponding pH, however, was not reported.

Neptunium

There have been several studies of neptunium sorption onto a variety of mineral surfaces (Allard *et al.*, 1982; Righetto *et al.*, 1988; Aksoyoglu *et al.*, 1991; Girvin *et al.*, 1991; Nakayama and Sakamoto, 1991; Triay *et al.*, 1991, 1993, 1996a, b; Bertetti *et al.*, 1995, 1998; Turner *et al.*, 1998). Most of these studies attempt to describe neptunium sorption through a mass distribution approach with little to no success. Several of these studies examine the pH-dependent behavior of neptunium sorption (Nakayama and Sakamoto, 1991; Bertetti *et al.*, 1995, 1998). Only two studies attempt to model neptunium sorption with surface complexation models.

A diffuse double-layer model is applied to sorption data for montmorillonite in Turner *et al.* (1998). The model is a two-site approach, using gibbsite and quartz surface acidity and complexation constants. The constants used in this model were assumed from a variety of sources, and the selection of these values and their applicability to the montmorillonite sample are not adequately justified. As a first attempt, this approach is reasonable; however, applicability to other transport problems is compromised.

A triple layer model developed for neptunium adsorption onto amorphous iron hydroxide was considerably more successful than the previously described approach (Girvin *et al.*, 1991). The parameters needed to conduct a triple layer surface complexation modeling effort are determined without reliance on previous studies. In particular, estimates of surface site density and surface acidity constants are made from sorption and titration data collected by the authors.

Plutonium

Plutonium has been the subject of several sorption studies on several minerals (Allard *et al.*, 1982; Keeney-Kennicutt and Morse, 1985; Sanchez *et al.*, 1985; Triay *et al.*, 1991, 1996b). Sanchez *et al.* (1985) examined the sorption behavior of Pu(IV) and Pu(V) on goethite in a variety of ionic strength, pH, and alkalinity conditions that were representative of natural estuarine environments. They conclude that the redox chemistry of plutonium is a primary process affecting the sorption behavior and subsequent fate in natural environments. Keeney-Kennicutt and Morse (1985) studied the sorption behavior of plutonium on calcite, aragonite, goethite, and δ -MnO₂. They conducted experiments in deionized-distilled water and seawater, and observed that the sorption capacity of calcite, aragonite, and goethite was not inhibited by the increase in ionic strength of seawater. However, the sorption capacity of δ -MnO₂ was significantly reduced in seawater. They further observe that the sorption behavior of plutonium is significantly different than that of neptunium under similar conditions.

Triay *et al.* (1991, 1996b) reported studies of plutonium sorption onto minerals present in Yucca Mountain rocks, including: clinoptilolite, quartz, albite, hematite, cristobalite, feldspar, calcite, and clays. However, neither of these studies applies surface complexation modeling approaches to describe the sorption data. Furthermore, the mineral properties needed for a surface complexation model were not determined.

Strontium

Several studies have examined the sorption of strontium onto various minerals (Weed *et al.*, 1980; Shiao *et al.*, 1981; Zachara *et al.*, 1991; Norden *et al.*, 1994). Weed *et al.* (1980) used strontium as a tracer in a high-pressure transport experiment in a sandstone core. This experiment resulted in breakthrough data that could not be explained with unretarded transport, and a K_d for strontium was determined from an inversion of column breakthrough data. Shiao *et al.* (1981) and Norden *et al.* (1994) examined strontium sorption onto corundum (α -Al₂O₃) but did not attempt to develop a surface complexation model. An electrostatic model developed for strontium sorption onto calcite is given by Zachara *et al.* (1991). This study also includes sorption and electrostatic binding constant estimates for Ba, Cd, Co, Ni, Mn, and Zn. However, the simple complexation model presented is overly simplistic and it is not clear why a more complete complexation modeling approach was not undertaken.

Uranium

There have been a number of studies that have examined uranium sorption onto a wide range of rock and mineral species (Tsunashima *et al.*, 1981; Hsi and Langmuir, 1985; Lieser *et al.*, 1992; Pabalan *et al.*, 1993, 1998; Waite *et al.*, 1994; McKinley *et al.*, 1995; Park *et al.*, 1995; Duff and Amrhein, 1996; Turner *et al.*, 1996; Pabalan and

Turner, 1997; Arnold *et al.*, 1998, 2001; Viani and Torretto, 1998; Prikryl *et al.*, 2001). Three of these studies describe the sorption of uranium onto minerals with a sorption isotherm approach with limited success (Tsunashima *et al.*, 1981; Lieser *et al.*, 1992; Pabalan *et al.*, 1993). The remaining studies all use a surface complexation modeling approach to describe uranium sorption.

A study of uranyl sorption onto a smectite clay is presented by Turner *et al.* (1996). This study attempted to measure the PZC of the study material. However, the model fit to the titration data is poor, and the authors conjecture that dissolution of sorption binding sites occurred during the analysis. However, no apparent effort was made to correct for this problem. As a result, the acidity constants derived from these data, coupled with the use of mineral-specific parameter values from other studies, may be directly responsible for the poor fit of the TLM to the experimental sorption data.

McKinley *et al.* (1995) present the results of a study of sorption of uranium onto montmorillonite. While this study did not attempt to perform a titration analysis of the study mineral to obtain acidity constants, the authors did use consistent values for acidity constants and electrolyte binding constants for silica and gibbsite from other sources. The authors conducted titration and sorption experiments on a pure gibbsite and silica to obtain data necessary for model calibration. The TLM fits to the gibbsite and silica titration and sorption data are very good. The authors conducted a model sensitivity analysis to determine a best-fit of the triple layer model to gibbsite-uranyl sorption data within a reasonable range of model parameters. The gibbsite and silica surface complexation models were joined to form a composite model of the montmorillonite material. Model-fitting parameters were not adjusted; rather, relative amounts of gibbsite and silica were selected based on collected CEC data for the study mineral. In spite of this, the TLM does a reasonable job fitting the uranyl sorption onto the montmorillonite material across a range of ionic strength and pH.

A study by Hsi and Langmuir (1985) represents a complete, consistent study of uranium sorption onto iron oxyhydroxide minerals. The authors conducted a thorough campaign to determine the mineral-specific properties of a synthetic goethite (α -FeOOH), synthetic amorphous ferric oxyhydroxide, synthetic hematite (α -Fe₂O₃), and a natural specular hematite (α -Fe₂O₃). Reasonable TLM parameters were determined from the acid titration, tritium adsorption, and BET analyses. Furthermore, a reasonable approach was used to determine the remaining model parameters, and the resulting model is a reasonable approximation of the uranium sorption data for these minerals. The authors point out that the model does not work well below about 1 ppb U, and hypothesize that this is due to an inefficient mineral-water separation technique used in the sorption experiments. This issue may be the cause of other problematic SCM fits to low-concentration radionuclide sorption data. Hsi and Langmuir (1985) extended this work further by incorporating a set of carbonate complexing reactions to simulate the observed decrease in uranyl sorption loading in the presence of the carbonate ion. This model addition provides a reasonable fit to the observed uranyl-carbonate competitive sorption data.

An effort to develop a TLM representation of uranyl sorption on a naturally occurring corrensite was presented by Park *et al.* (1995). This effort provides high-quality determinations of specific surface area (BET), acid-base titration (PZC), zeta potential,

and cation exchange capacity (CEC). The authors apply the TLM to uranyl sorption data for corrensite, however, it is not clear what the interlayer capacitance model parameters are for these simulations. A reference is made to a range of capacitances seen in the literature, but no specific values are given for the uranyl-corrensite surface complexation simulations.

There are multiple studies of uranium sorption onto a variety of minerals that employ the DLM to describe sorption behavior (Duff and Amrhein, 1996; Pabalan and Turner, 1997; Arnold *et al.*, 1998, 2001; Pabalan *et al.*, 1998; Viani and Torretto, 1998; Prikryl *et al.*, 2001). An early work by Waite *et al.* (1994) examined the sorption behavior of uranyl on ferrihydrite. This paper seeks to extend the results of Hsi and Langmuir (1985) by identifying the nature of the inner-sphere coordination complex. The result is that uranyl forms a bidentate complex as confirmed by Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy and hypothesis testing with an SCM. This work suggests that the surface complexes for uranium are simpler than previously thought in that carbonate-uranium complexes do not necessarily exist at the mineral surface though they may be present in the aqueous phase.

Duff and Amrhein (1996) attempted to model uranium sorption onto a naturally occurring soil by constructing a diffuse double layer complexation model with complexation parameters from a variety of studies using goethite. In particular, the authors hypothesized the existence of several uranyl aqueous complexes and attempted to include these complexes and their binding constants into the model. The model may not be realistic given the wide range of parameter sources, which may or may not be consistent, and the lack of evidence for some of the aqueous complexes included in the model.

Pabalan and Turner (1997) studied the sorption of uranium onto montmorillonite. The study focused on the surface complexation of uranyl onto hydroxylated edge sites similarly to previous studies of clay minerals. As such, the study constructed a DLM by combining generic aluminol and silanol edge sites together with two uranyl surface complexation reactions per site. While the surface acidity constants are from the same source for both the generic aluminol and silanol edge sites (Turner and Sassman, 1996), the site concentrations for these generic analog sites are calculated based on a presumed fraction of total surface area. Because the value of the acidity constant is dependent upon site concentration, or site density, the assumed values for site concentration used in this study may not be consistent with the rest of the surface complexation model. Therefore, though the model appears to represent the uranyl sorption data presented in the paper, the model may not be internally consistent and may not be used to make sorption predictions outside the experimental bounds of this study.

Arnold *et al.* (1998) studied the sorption of uranium on phyllite, a mineral associated with uranium-bearing ore. The experimental results indicate that phyllite exhibits a larger sorption capacity for uranium than expected from the major mineral constituents in phyllite. The authors conclude that a ferrihydrite mineral species precipitated during the course of the sorption experiments, resulting in the larger apparent sorption capacity. Model parameters from literature values were used to assemble a DLM, and the result is a rough approximation of the observed sorption behavior. While this study does not provide new model parameter information, it does point out the

difficulty associated with conducting experiments in such a way as to provide meaningful data. This study was later extended by Arnold *et al.* (2001) by incorporating a series of complexation reactions between uranyl and ferrihydrite. The resulting DLM provides improved fit to the sorption data for uranium on phyllite.

Viani and Torretto (1998) conducted a study of uranium sorption onto synthetic hematite. The purpose of this research was to determine the transport behavior of uranium from failed waste packages. The hematite sorbate did not constitute a rock mineral, but rather a corrosion product of the steel in the waste package. The study results are interesting, but do not provide any new information beyond that reported by Hsi and Langmuir (1985).

The extensive study by Pabalan *et al.* (1998) explores the sorption behavior of uranium on silicate minerals. In particular, quartz, clinoptilolite, montmorillonite, and α -alumina minerals were used as sorbate minerals in the study. The results indicate that the sorption capacities of these minerals are similar to each other, consistent with earlier findings reported in this report for these minerals. An attempt was made in the study to model the observed sorption behavior with a diffuse double layer model. However, the specific surface properties of the minerals used in the study were assumed from literature values. Surface acidity constants were obtained from a different source than that of the sorption site density. Because surface acidity constants are dependent upon the sorption site density, it is not known if the assumed parameter values are consistent with each other. Therefore, the modeling results are not necessarily applicable. However, the sorption data may be useful for further modeling efforts, which are applied in a more consistent framework.

A recent study by Prikryl *et al.* (2001) examined the sorption behavior of uranium on silicate mixtures with the objective of demonstrating that surface complexation models can be 'assembled' from pure-phase mineral data to simulate sorption on a rock consisting of a mineral assemblage. Though this technique is used extensively to model the surface complexation of a variety of aqueous species, including radionuclides, onto clay minerals, the authors did not seem to view this earlier work as applicable to silicate minerals. Furthermore, the model results are not particularly impressive, perhaps due to a poor selection of SCM parameters. In addition, though the batch sorption experiments were conducted at a variety of $p\text{CO}_2$ conditions, the authors ignored the possibility of uranyl-carbonate aqueous complexes in their SCM, an oversight that could also contribute to the poor model performance demonstrated in the paper.

Other Actinides and Radionuclides

Sorption and desorption kinetics of thorium (Th) on hematite was reported by Quigley *et al.* (1995). The sorption of Th was examined as a function of pH and ionic strength. Based on ionic strength sorption experiments, the investigators proposed that Th forms inner-sphere complexes on hematite. Sorption of Th was modeled with the TLM using a single sorption reaction. The reaction appeared to be irreversible within the time frame of the experiments (four days). A relatively large intrinsic constant value was required to compete with strong hydroxy- and carbonate complexes at higher pH values. The TLM modeling parameters were derived from a combination of adopting literature values and potentiometric data. Acidity constants were determined from an estimated

PZC of 8.75 and by assuming a ΔpK_a of 4.0. Electrolyte binding constants were determined by fitting potentiometric titration data. The values of site density and inner-layer capacitance were assumed to be $2.31 \text{ sites nm}^{-2}$ and 0.8 F m^{-2} , respectively.

Equilibrium sorption, desorption, and diffusion of radium (Ra) in bentonite and purified smectite were investigated as a function of pH and ionic strength by Tachi *et al.* (2001). Sorption was a function of both pH and ionic strength. The investigators attributed Ra sorption to both cation exchange reactions in the smectite interlayer and sorption on amphoteric edge sites. The increasing sorption on amphoteric sites with increasing pH was attributed to calcite precipitation-dissolution reactions and the corresponding Ca concentration changes. Sorption experiments were modeled by combining an ion exchange model and the generalized two-layer model of Dzombak and Morel (1990). The specific model parameters were listed as obtained from a previous publication and were not justified in the text.

Finally, the sorption of metal cations and anions on calcite was reviewed by Zachara *et al.* (1993). They presented a generalized sorption model for calcite based on metal exchange with Ca ions on the calcite surface. The authors propose that the exchange is not limited to electrostatic attraction but is stabilized through formation of coordination complexes. Similarly, anion sorption is assumed to be promoted by surface exchange of anions in solution with the carbonate ions on the calcite surface. The number of cation-specific exchange sites was estimated by isotopic dilution using isotopic exchange data with ^{45}Ca on calcite over a range of pH values. Similarly, the concentration of anion-specific exchange sites was estimated by isotopic exchange of ^{14}C -tagged bicarbonate.

Minerals

Data pertaining to the sorbents used in these studies are discussed in this section. The emphasis is focused on parameters used to model the sorption data using SCMs. The major objective of this section is to provide a critical evaluation of the source of the model parameters used. As pointed out earlier, in general, parameters are obtained either from independent direct measurements, a combination of measurements and fitting of an appropriate model, or obtained directly from the literature. The problem with using data obtained from the literature is that the resulting set may not be internally consistent. Some of these inconsistencies are pointed out during the discussion of the results.

Sorption experiments and modeling have been performed with a number of different minerals and the summary of the characterization for these minerals is shown in Table 10. Different types of data are reported in the different types of work, depending on whether the author(s) attempted to model the sorption data or not. In cases where no sorption data modeling was attempted, typically only parameters such as the surface area were reported and these values are included in Table 10. Whenever an attempt was made to use a surface complexation model to model the data, additional parameters are included. The type of parameters is dependent on the model used. Typical parameters include the surface site density, N_s , the specific surface area, typically determined by the BET method, acidity constants, electrolyte binding constants, if required by the model, and the capacitance(s) of the double layer of the adsorbent, if an electrostatic surface complexation model was used. All these parameters are included in Table 10 along with the model used and any pertinent comments.

A number of different rocks and minerals have been used in sorption and sorption modeling experiments, as reported here. The specific rocks and minerals were chosen either because they were considered as controlling the sorption of the ions of interest, or because they comprised the aquifer material of the study area. Common minerals include oxides, mostly of iron, manganese, silicon, and aluminum, clay minerals, most commonly kaolinite and montmorillonite, feldspars and zeolites, and finally carbonate minerals.

Certain mineral properties are determined with direct measurement techniques. The specific surface area is commonly determined with a gas-adsorption technique, commonly called a BET measurement. Estimates of charge density, N_s , are often made from BET measurements. Acid-base titration methods are used to determine the PZC of a mineral surface. This measurement is also commonly referred to as zeta potential. From the PZC measurement, and an assumption of the ΔpK_a of the adsorbing acid-base pair, estimates of the surface-acidity constants can be made through optimization of inverse modeling of the acid-base titration data. The remaining TLM constants needed to estimate ion-sorption behavior at the water-mineral interface are determined through inversion and optimization of experimentally derived sorption data. These additional parameters include the electrolyte binding constants, the ion-surface complexation constants and the double layer capacitances. In most cases, a value for the outer layer capacitance, C_2 , of 0.2 F m^{-2} is assumed based on TLM model sensitivity analyses for a range of mineral species (Hayes *et al.*, 1991). The results of this study indicate that the model accuracy of the TLM is insensitive to the value of C_2 . The following reviews are of studies that examined radionuclide adsorption onto minerals *and* attempted a surface complexation modeling exercise. While a large body of work is published regarding radionuclide sorption onto minerals, as presented in Table 10, the subset of papers that attempt a surface complexation modeling exercise are comparatively few and are presented in Table 10 together with the relevant mineral-specific surface complexation modeling parameters.

Table 10. Mineral parameters.

Mineral, Metal, Model	N_s	BET/[CEC]	$C_{1,2}$	$\log K_{H^+}$	$\log K_{OH^-}$	$\log K_{\text{electrolyte}}$	Source
illite, Eu, DLM	$10^{-4.27}$ eq/g total edge site density	16.4 m ² /g [71 $\mu\text{eq/g}$]	N/A	5.05	-7.56	N/A	(Wang <i>et al.</i> , 1998)
goethite, Eu, TLM	2.3 sites/nm ²	36 m ² /g	not reported	7.90 (Geen <i>et al.</i> , 1994)	-9.90 (Geen <i>et al.</i> , 1994)	8.89 (Geen <i>et al.</i> , 1994)	(Fujita and Tsukamoto, 1997)
magnetite, Eu, TLM	2.3 sites/nm ²	4.8 m ² /g	not reported	7.90 (Geen <i>et al.</i> , 1994)	-9.90 (Geen <i>et al.</i> , 1994)	8.89 (Geen <i>et al.</i> , 1994)	(Fujita and Tsukamoto, 1997)
hematite, Eu, CC	$10^{-5.158}$ moles sites/g	4 m ² /g	N/A	not useable in TLM	not useable in TLM	not useable in TLM	(Rabung <i>et al.</i> , 1998)
montmorillonite, Np, DLM	2.3 sites/nm ²	97 m ² /g	N/A	assemblage of quartz, gibbsite	assemblage of quartz, gibbsite	N/A	(Turner <i>et al.</i> , 1998)
gibbsite, Np, DLM	unknown	unknown	N/A	8.33 (Turner and Sassman, 1996)	-9.73 (Turner and Sassman, 1996)	N/A	(Turner <i>et al.</i> , 1998)
quartz, Np, DLM	unknown	unknown	N/A	-7.20 (Turner and Sassman, 1996)	unknown	N/A	(Turner <i>et al.</i> , 1998)
am-HFO, Np, TLM	$10^{-2.007}$ moles sites/g Fe	not measured	1.25, 0.20 F/m ²	-5.4	-10.4	Na = -8.6 NO ₃ = 7.5	(Girvin <i>et al.</i> , 1991)
goethite, U, DLM	2.3 sites/nm ²	58.5 m ² /g	N/A	7.91	-10.02	20.78, 12.71	(Duff and Amrhein, 1996)
montmorillonite, U, TLM	$10^{-4.45}$ mol/g, estimated	31 m ² /g [0.95 mmol/g]	1.2, 0.20 F/m ² fixed, no ref.	assemblage of quartz, gibbsite	assemblage of quartz, gibbsite	assemblage of quartz, gibbsite	(McKinley <i>et al.</i> , 1995)
quartz, U, TLM	$10^{-5.19}$ mol/g, (White and Zelazny, 1988)	180 m ² /g	1.2, 0.20 F/m ² fixed, no ref.	-0.95 (Zachara and Smith, 1994)	-6.95 (Zachara and Smith, 1994)	-6.6 (Zachara and Smith, 1994)	(McKinley <i>et al.</i> , 1995)
gibbsite, U, TLM	$10^{-5.27}$ mol/g, (White and Zelazny, 1988)	3.4 m ² /g	1.2, 0.20 F/m ² fixed, no ref.	12.3	-13.6	-10.37	(McKinley <i>et al.</i> , 1995)
corrensite, U, TLM	$10^{-5.585}$ moles sites/nm ²	44.6 m ² /g [10 ^{-4.839} moles sites/nm ²]	not determined	3.7	7.3	6.5	(Park <i>et al.</i> , 1995)

Table 10. Mineral parameters (continued).

Mineral, Metal, Model	N_s	BET/[CEC]	C_1, C_2	$\log K_{H^+}$	$\log K_{OH^-}$	$\log K_{\text{electrolyte}}$	Source
quartz, U, DLM	2.3 sites/nm ²	0.31 m ² /g	N/A	-7.06 (Sverjensky and Sahai, 1996)	-1.24 (Sverjensky and Sahai, 1996)	N/A	(Prikryl <i>et al.</i> , 2001)
smectite, U, TLM	10 ^{-3.37} mol/g, estimated	99 m ² /g [10 ^{-0.34} mol/kg]	1.05, 0.20 F/m ²	composite of quartz, gibbsite	composite of quartz, gibbsite	10.0	(Turner <i>et al.</i> , 1996)
quartz, U, TLM	4.5 sites/nm ² , estimated	183 m ² /g	1.30, 0.20: fixed	not reported	-6.95 (Zachara and Smith, 1994)	-6.6 (Zachara and Smith, 1994)	(Turner <i>et al.</i> , 1996)
gibbsite, U, TLM	4.0 sites/nm ² , estimated	11 m ² /g	0.80, 0.20: fixed	7.6 (McKinley <i>et al.</i> , 1995)	-10.6 (McKinley <i>et al.</i> , 1995)	-7.3 (McKinley <i>et al.</i> , 1995)	(Turner <i>et al.</i> , 1996)
hematite, U, DLM	2.31 sites/nm ² (Turner, 1995)	1.5 m ² /g	N/A	7.35 (Turner, 1995)	-9.17 (Turner, 1995)	-7.7 (Turner, 1995)	(Viani and Torretto, 1998)
quartz, U, DLM	2.3 sites/nm ² (Davis and Kent, 1990)	0.3 m ² /g	N/A	not available	-7.20 (Turner and Sassman, 1996)	N/A	(Pabalan <i>et al.</i> , 1998; Pabalan and Turner, 1997)
gibbsite, U, DLM	2.3 sites/nm ² (Davis and Kent, 1990)	not determined	N/A	8.33 (Turner and Sassman, 1996)	-9.73 (Turner and Sassman, 1996)	N/A	(Pabalan <i>et al.</i> , 1998; Pabalan and Turner, 1997)
montmorillonite, U, DLM	2.3 sites/nm ² (Davis and Kent, 1990)	97 m ² /g	N/A	assemblage of quartz, gibbsite	assemblage of quartz, gibbsite	N/A	(Pabalan <i>et al.</i> , 1998; Pabalan and Turner, 1997)
ferrihydrite, U, DLM	0.875 mol sites/mol Fe (Dzombak and Morel, 1990)	600 m ² /g (Dzombak and Morel, 1990)	N/A	6.51 (Dzombak and Morel, 1990)	-9.13 (Dzombak and Morel, 1990)	N/A	(Waite <i>et al.</i> , 1994)
quartz, U, DLM	4.81 sites/nm ²	0.2 m ² /g	N/A	-5.62	not presented	N/A	(Arnold <i>et al.</i> , 2001)
chlorite, U, DLM	4.81 sites/nm ²	1.8 m ² /g	N/A	10.3	not presented	N/A	(Arnold <i>et al.</i> , 2001)

Table 10. Mineral parameters (continued).

Mineral, Metal, Model	N_s	BET/[CEC]	$C_{1,C2}$	$\log K_{H^+}$	$\log K_{OH^-}$	$\log K_{\text{electrolyte}}$	Source
muscovite, U, DLM	4.81 sites/nm ²	1.4 m ² /g	N/A	-7.81	6.06	N/A	(Arnold <i>et al.</i> , 2001)
albite, U, DLM	4.81 sites/nm ²	0.2 m ² /g	N/A	-7.87	not presented	N/A	(Arnold <i>et al.</i> , 2001)
amorphous ferric oxyhydroxide, U, TLM	20 sites/nm ²	306 m ² /g	130/20 $\mu\text{F}/\text{cm}^2$	4.8	11.1	Na = 9.3 NO ₃ = 7.0	(Hsi and Langmuir, 1985)
synthetic hematite, (α -Fe ₂ O ₃), U, TLM	19 sites/nm ²	3.1 m ² /g	90/20 $\mu\text{F}/\text{cm}^2$	6.7	10.3	Na = 9.5 NO ₃ = 7.5	(Hsi and Langmuir, 1985)
goethite (α - FeOOH), U, TLM	18 sites/nm ²	45 m ² /g	140/20 $\mu\text{F}/\text{cm}^2$	4.5	12.0	Na = 10.1 NO ₃ = 7.0	(Hsi and Langmuir, 1985)
natural specular hematite (α -Fe ₂ O ₃), U, TLM	15 sites/nm ²	1.8 m ² /g	90/120 $\mu\text{F}/\text{cm}^2$	6.7	10.3	Na = 9.5 NO ₃ = 7.5	(Hsi and Langmuir, 1985)

Oxides

Goethite

Several studies examined the adsorption of radionuclide ions onto the iron oxide mineral goethite (Hsi and Langmuir, 1985; Duff and Amrhein, 1996; Fujita and Tsukamoto, 1997). Two of these (Duff and Amrhein, 1996; Fujita and Tsukamoto, 1997) assume an N_s value of 2.31 sites nm^{-2} based on previous studies. While this assumption in and of itself is adequate, neither of these studies performed acid-base titrations and assume acidity constants from other sources, which may not be consistent with the value of N_s used, rendering the modeling results from these studies of limited applicability. The modeling results in Hsi and Langmuir (1985) are applicable, as the acidity constants were determined from surface potential data.

Magnetite

Two papers present efforts to model radionuclide sorption onto magnetite. In addition to goethite, Fujita and Tsukamoto (1997) also studied magnetite, and like the goethite results, the SCM presented is of limited applicability. Like the goethite results, the model results presented for magnetite in Hsi and Langmuir (1985) are consistent.

Hematite

Three studies present data for both natural hematite and synthetic hematite. The model parameters presented in Hsi and Langmuir (1985) are consistent and applicable. However, the results presented by Rabung *et al.* (1998) are not useable without significant analysis. The paper presents surface acidity data, which is consistent with a constant capacitance model. Since the constant capacitance model is valid only for constant ionic strength, the surface acidity constants are also ionic strength dependent. To determine the ionic strength independent surface acidity constants from these data would require a TLM model optimization effort. An additional study examining the sorption of uranium on synthetic hematite is given by Viani and Torretto (1998). However, this study measured only BET. The model parameters used in the DLM were obtained from other sources.

Amorphous Iron Hydroxide/Ferrihydrite

Three studies examined the sorption behavior of radionuclides onto amorphous iron hydroxide (am-HFO) and ferrihydrite minerals (Hsi and Langmuir, 1985; Girvin *et al.*, 1991; Waite *et al.*, 1994). Like the results presented in Hsi and Langmuir (1985) for goethite, hematite and magnetite, the modeling effort for am-HFO is consistent and applicable to radionuclide adsorption. Neptunium sorption onto am-HFO is presented in Girvin *et al.* (1991). This study conducted acid-base titrations and developed a consistent set of TLM model parameters by fixing surface site density, N_s . While it is not clear how N_s is determined, as no measurement of surface area is performed, the TLM model parameters associated with this N_s are consistent. A single study examining the sorption behavior of uranium onto ferrihydrite is presented in Waite *et al.* (1994). This study does not present any new mineral property information relevant to a modeling effort, but does present internally consistent model results based on model parameters from a single source (Dzombak and Hayes, 1992).

Silicates

Montmorillonite

There are few studies that model radionuclide sorption onto montmorillonite (McKinley *et al.*, 1995; Pabalan and Turner, 1997; Pabalan *et al.*, 1998; Turner *et al.*, 1998). Because montmorillonite is not a pure phase mineral, but is a type of clay, McKinley *et al.* (1995) assembled a TLM model from gibbsite and quartz data using these mineral species as analogs to edge-site binding behavior. Thus, the mineral-specific model parameters reported in Table 10 reflect these mineral analogs and no data are reported directly for montmorillonite for this reference. While the use of mineral analogs is acceptable, and is in fact necessary, the study fails to recognize the importance of maintaining parameter consistency in the modeling phase of the project. The inner-layer capacitances are arbitrarily fixed, while the sorption site density value for montmorillonite is fixed through an interpretation of the relative contributions of quartz and gibbsite to the overall sorption density. The remaining acidity and electrolyte binding constants are determined through an inversion fitting process. While the modeling results shown are reasonable approximations of the sorption data for uranium, the process used did not produce model parameters that are entirely consistent.

Efforts to model the sorption of neptunium onto montmorillonite with the DLM are also not applicable (Pabalan and Turner, 1997; Pabalan *et al.*, 1998; Turner *et al.*, 1998). Like the previous montmorillonite modeling efforts, these studies model montmorillonite as a compilation of quartz and gibbsite. The authors chose a generic sorption site density together with acidity constants from separate studies to use with a diffuse double-layer model. It is unknown if the acidity constants are consistent with the chosen sorption site density, and invalidates the applicability of these efforts to general transport problems.

Silica

There are a number of studies that have been conducted on silica or quartz as reported in Table 10 (McKinley *et al.*, 1995; Pabalan and Turner, 1997; Pabalan *et al.*, 1998; Turner *et al.*, 1998; Arnold *et al.*, 2001; Prikryl *et al.*, 2001). Three of these studies have been reviewed as part of the montmorillonite section of this report and the problems reported are applicable to silica as well (McKinley *et al.*, 1995; Pabalan and Turner, 1997; Pabalan *et al.*, 1998; Turner *et al.*, 1998). A study examining the efficacy of applying the DLM to phyllite used the minerals quartz, chlorite, muscovite and albite as an assembled conglomerate (Arnold *et al.*, 2001). The surface site densities for these minerals were determined by adsorption experiments; however, the acidity constants were taken from other studies that may or may not have been determined with similar material or assumptions.

Corrensite

An effort to develop a triple-layer model for uranium sorption onto corrensite may be applicable to uranium transport modeling efforts (Park *et al.*, 1995). The specific surface area and PZC of a naturally occurring mineral sample is presented by the authors (Table 10). These data are used to develop the surface acidity constants through a double extrapolation technique. The double extrapolation technique is not as robust as the numerical inversion approach assuming a ΔpK_a , but the resulting surface acidity constants may be acceptable. The data presented in the paper could be reexamined, and TLM parameters determined by numerical inversion.

Illite

An effort to develop a surface complexation model for Eu onto an illite clay was presented by Wang *et al.* (1998). The specific surface area, and PZC of the mineral sample, is presented in Table 10. The authors used the acid-base titration data together with FITEQL to produce an optimized set of surface acidity coefficients. The resulting DLM is a reasonable representation of the adsorption data for Eu on the natural illite. The surface titration data together with the adsorption data could be used to develop the electrolyte binding constant and surface complexation coefficients for the TLM representation of Eu adsorption.

Smectite

In a similar technique that researchers have applied to modeling surface complexation of montmorillonite, Turner *et al.* (1996) have modeled the sorption of U to a smectite clay. A composite of quartz and gibbsite is used to simulate the multiple edge-site behavior of smectite. The surface areas of quartz and gibbsite were measured, and uranium sorption data for quartz and gibbsite were used to assemble a TLM of smectite. Potentiometric titrations were presented for both quartz and gibbsite.

CONCLUSIONS AND RECOMMENDATIONS

In this project, we attempted to review literature pertaining to radionuclide and other surrogate cation sorption on minerals that are likely to control migration of radionuclides in aquifers. The emphasis of the work was on surface complexation modeling of the interactions of radionuclides with aquifer materials. The evaluation process included an investigation of the availability of sorption data as well as a critical evaluation of methods of parameter estimation. The process described above led to identification of common model misrepresentations and data gaps. The major conclusions from this work and relevant recommendations are summarized below.

Several SCMs have been described in the literature and several have been used to model radionuclide sorption on a variety of minerals, with mixed success. Most of these studies have focused on modeling one or more sets of data, unfortunately, sometimes without understanding the intricate details of the models, thereby treating several of the model parameters merely as adjustable parameters. These models are fairly useless with respect to creating robustness and predictive capability.

Part of the problem arises from the nature of the models. As the models become more complex and more versatile, the number of adjustable parameters increases, thereby rendering the task of parameter estimation more challenging. The TLM, the more complex of the SCMs considered, has at least six adjustable parameters. Although not all of them are equally important, parameter estimation for the TLM can still be a major task. A few good attempts to streamline parameter estimation for these models have been reported in the literature and they were summarized in the main text. Unfortunately, they are not always followed and several authors “pick and choose” parameters and methodology. At least methods exist to determine parameters appropriate for the model chosen and can be followed by researchers willing to arrive at judiciously selected parameters.

Simpler models than the TLM have been used to model radionuclide sorption, often with considerable success. The fact that these models have fewer adjustable parameters, however, does not necessarily guarantee correct use. In addition, the applicability of these models is

generally more restricted compared to the more general TLM. In fact, it is a recommended procedure for all models, regardless of complexity and sophistication, to attempt to apply the model to as broad a data set as possible. This broad data set may include data at different radionuclide and solid concentrations, a range of pH values, different ionic strengths, and different types of background electrolyte ions. These highly variable data sets can provide guidance on the suitability of the model and the selected model parameters.

Clearly, simpler models are preferred compared to more complex ones when the use can be justified. For example, the nonelectrostatic SCM (NEM), with three adjustable parameters, would be preferred compared to the more complex TLM, provided that the NEM could adequately describe the system considered. This decision can only be made after evaluation of the performance of the model when attempting to model competitive reactions with different ions of varying affinities for the mineral surface considered.

Several more specific conclusions and recommendations will be discussed next. It appears that although sorption data are available for some important radionuclides, little effort has been devoted to modeling interactions of these radionuclides with mineral surfaces. Important examples of such paucity of modeling data include Cs and Pu.

A common problem when modeling radionuclide sorption on natural samples is the identification of the types of sites responsible for the observed behavior. The problem is evident in minerals that have more than one type of sorption sites. For example, montmorillonite, a smectite clay mineral, has two different types of sites: internal cation exchange (permanent charge) sites and external, amphoteric surface hydroxyl edge sites. The relative importance of these two types of sites is a function of background electrolyte concentration and type, as well as pH. The sorption on the two types of sites must be modeled differently. If, therefore, the assumption is made that either site is always predominant, regardless of conditions, substantial errors may result. This mistake was found in a few studies of radionuclide sorption on montmorillonite. Unfortunately, the macroscopic experiments alone cannot provide a definitive answer to this question. Additional spectroscopic evidence, however, can help elucidate the relative importance of the different sites under varying conditions and greatly improve the predictive capability of the models.

With respect to data available for surface complexation modeling of radionuclides on different minerals, it appears that a few minerals have been used extensively and several sets of data are available. This group includes minerals that either are thought to be strong radionuclide sorbents, or are very common. Such common minerals include iron oxides, such as goethite, hematite, and hydrous ferric oxide, aluminum oxide (alumina), silicon oxide (silica), and titanium oxide (oxide). Notably absent are feldspar minerals. The surface characteristic data of feldspars are sparse and the few data sets that exist are sometimes contradictory. Although the argument can be made that feldspars are not strong radionuclide sorbents and that their surface chemistry is similar to the surface chemistry of quartz, the literature data cast some doubt on the similarity of these two groups of minerals. In addition, the simple fact of great feldspar abundance in rocks justifies additional studies to clarify the surface chemistry of this important group of minerals. These studies should include potentiometric titrations and estimation of surface acidity and electrolyte binding constants.

One of the major issues facing modelers of radionuclide migration in natural systems is the deconvolution of the relative importance of different minerals and mineral coatings on the

observed sorption behavior of a complex natural mineral assemblage. The only way to improve our knowledge of such complex systems and therefore our sorption models is by a combination of careful characterization studies of these mineral assemblages and simultaneous macroscopic sorption studies and spectroscopic studies.

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