

CURRENT ADSORPTION MODELS AND OPEN ISSUES  
PERTAINING TO PERFORMANCE ASSESSMENT

by  
R. J. Serne

ABSTRACT

Recently several articles have been published that question the appropriateness of the distribution coefficient ( $R_d$ ) concept to quantify radionuclide migration. Several distinct issues are raised by various critics. In this paper I provide some perspective on issues surrounding the modeling of nuclide retardation. The first section defines adsorption terminology and discusses various adsorption processes. The next section describes five commonly used adsorption conceptual models, specifically emphasizing what attributes that effect adsorption are explicitly accommodated in each model. I also review efforts to incorporate each adsorption model into performance assessment transport computer codes. The five adsorption conceptual models are (1) the constant  $R_d$  model, (2) the parametric  $R_d$  model, (3) isotherm adsorption models, (4) mass action adsorption models, and (5) surface complexation with electrostatics models. The final section discusses the adequacy of the distribution ratio concept, the adequacy of transport calculations that rely on constant retardation factors and the status of incorporating sophisticated adsorption models into transport codes.

## 1.0 INTRODUCTION

Most safety analysis exercises that address deep geologic disposal of high-level nuclear wastes (spent unprocessed fuel and reprocessed solid wastes such as borosilicate glass or Synroc) conclude that the most likely transport vehicle for bringing radionuclides into the accessible environment is groundwater transport. The groundwater is likely to slowly dissolve metallic barriers/containers and eventually remove radionuclides from the solid waste forms via dissolution, complexation and colloid formation. Within the waste package and the very near-field host rock, radiation field and temperature gradients may vary enough or influence the groundwater chemistry enough that temperature- and redox-sensitive solubility reactions could control the amount of radionuclides leaving the repository. Another chemical process, alteration of primary minerals and precipitation of secondary minerals, is also likely in the high (but radially decreasing) temperature field around the waste packages. Once the groundwater exits the waste package and very near-field host rock, any radionuclides in solution or in suspension (colloids) will likely interact predominantly via (1) adsorption reactions on the surfaces of the host media, (2) matrix diffusion into micropores within the host grains, and (3) physical filtration of colloids. Adsorption reactions have been acknowledged as the most important contaminant retardation process in far-field transport analyses for all hazardous waste disposal options. Adsorption processes are known to increase the travel times for some radionuclides by  $10^3$  to  $10^6$  times relative to the groundwater. Such long travel times allow nuclides to decay to lower concentrations and less hazardous elements before reaching the accessible environment (i.e., the biosphere). Furthermore, some adsorption processes are effectively irreversible and permanently remove nuclides from groundwater, thus preventing their release to the biosphere.

To predict the effects of retardation on safety assessment predictions, adsorption processes must be described in quantitative terms. An empirical parameter, the distribution coefficient (often called  $R_d$  or  $K_d$ ), which is readily measured by laboratory experimentation, allows such a quantitative estimate of nuclide migration. Knowledge of the  $R_d$  and of media bulk density and porosity (for porous flow), or of media fracture surface area, aperture width and matrix diffusion attributes (for fracture flow) allows

one to calculate the retardation factor,  $R$  or  $R_r$ . The retardation factor is defined as  $R = V_w/V_n$ , where  $V_w$  is the velocity of water through a control volume and  $V_n$  is the velocity of the radionuclide. A detailed derivation and discussion of the retardation factor is given in Nuclear Energy Agency, NEA (1983a). To my knowledge, every existing computer code for safety assessment predictions of deep geologic disposal of nuclear waste relies on the retardation factor and thus on the distribution coefficient. In the last ten years several articles have been published that question the appropriateness of the distribution coefficient concept (e.g., Reardon 1981; Moody 1981; Coles et al. 1982; Muller et al. 1983; Carnahan et al. 1984 and Langmuir et al. 1984). These authors' concerns actually address several distinct issues, but the net result has been a general uneasiness and confusion within the nuclear waste management community about addressing adsorption in safety assessment calculations. Some of the distinct issues raised in these articles are (1) the adequacy of the distribution concept for describing adsorption, (2) the adequacy of constant  $R_d$  values used in many transport codes to predict radionuclide migration in the field, and (3) the discrepancy in  $R_d$  values obtained by different test methodologies.

In this report, I will attempt to lessen some of the confusion about adsorption and to provide some perspective on the first two issues. First I will define some adsorption terminology. Next I will briefly describe the various adsorption conceptual models, identifying the options available for describing adsorption. Finally I will elaborate the issues, identify the present status of issue resolution, and identify future efforts that should provide additional data to resolve these issues objectively.

## 2.0 DESCRIPTION OF ADSORPTION/DESORPTION

In the first part of this section, I define a number of terms that will help in understanding the description in the second part of how adsorption and desorption work.

### 2.1 Terminology

Nuclide retardation, encompasses all possible processes that hinder nuclide migration in solution, including ideal ion exchange, mineral precipitation, coprecipitation in amorphous coatings, chemisorption, selective adsorption, complexation onto solid adsorbents, redox or hydrolysis-mediated precipitation/sorption, and physical filtration of small particulates.

In this report, "adsorption" or "sorption" refers to surface processes in which radionuclides in solution become incorporated onto the solid phase surface. Adsorption and sorption are more general terms that include more processes than the term "ideal ion exchange," but where possible they exclude precipitation of identifiable mineral or amorphous compounds and physical filtration of small particulates.

To quantify adsorption, one typically measures the distribution of the adsorbate between the solid phase and the solution phase. Such a value or distribution coefficient is often called the  $R_d$ ,  $K_d$ , or  $D$ . Confusion arises because the term "distribution coefficient" has been used to refer to two special cases: (1) ideal binary ion exchange, where the element of interest is present in such trace concentrations that it does not appreciably affect the concentration of the macro constituent sorbed on the solid or the activity coefficient ratio of the mass action exchange (e.g., Meyer 1979; Routson et al. 1972), and (2) a Freundlich empirical isotherm, where sorption shows a linear trend with solution concentration (Travis 1978). Linear adsorption typically occurs only at trace adsorbate concentrations in solution and at trace loadings onto the solid adsorbent surfaces. In either case, adsorption refers to equilibrium conditions and, when used with mass transport theory, generally requires reversibility, meaning that desorption occurs at the same rate and leads to the same equilibrium ratio of adsorbate between solid and solution.

In this report, the distribution coefficient is called  $R_d$  and simply refers to the ratio of mass or activity of a particular radionuclide species present in the solid phase (rock or sediment) to the mass or activity of that same species present in solution (groundwater). This empirical ratio does not require

equilibrium conditions, quantitative reversibility, or ion exchange as the governing process (Serne et al. 1983). I would like to emphasize that the distribution coefficient parameter, this measurable ratio of an amount on the solid to the amount in solution, is the basis for all of the adsorption conceptual models I will discuss. That is, it is this ratio that is measured to provide input data into each of the conceptual models. I point this fact out to eliminate the confusion in some researchers' minds that the criticism of  $R_d$  theory means that some other parameter should be measured. What the critics are actually suggesting is that the dependency of the  $R_d$  parameter on other attributes of the rock and groundwater must also be quantified.

As discussed in the following paragraphs, distribution coefficients are a complex function of the chemical and physical parameters of the systems being studied. Their dependence on a large number of variables causes problems in most overall system performance codes, because at this time most codes can use only a single value for the distribution coefficient and cannot easily account for any change in the distribution coefficient caused by changes in the geochemical environment from the waste package to the biosphere. Some critics discredit the use of distribution coefficients because the values measured are specific to the laboratory system studied and do not necessarily represent radionuclide behavior in a repository. Despite these criticisms, existing safety assessments continue to rely on the distribution coefficient to model radionuclide adsorption.

To evaluate adsorption processes for base line geologic settings requires information on parameters similar to those for solubility evaluation. The master variables, temperature, pressure, pH, and system Eh, as well as the groundwater chemical composition and the solid adsorbent's mineralogic and petrologic attributes, surface area, and exchange capacity, all influence adsorption. Adsorption prediction relies upon a more detailed knowledge of the solid adsorbent than is required for solubility predictions, for which simple identification of the controlling solid phase often suffices. For predicting adsorption processes, knowing only that certain minerals are present is not adequate. One needs to know the quantity of each mineral, the surface area or sorption capacity and, ideally, the electrostatic characteristics of the surfaces of stable and slowly reacting mineral phases. The same level of characterization for the solute and solution is necessary for adsorption estimation as for solubility. That is, one should know the speciation and thermodynamic activities of solution components, not just total elemental concentrations.

Unfortunately, adsorption principles are not as well-developed and tested as solubility principles. Therefore, even with all this characterization, the accuracy of predictions of the distribution of a trace constituent between the solution and solid adsorbents cannot be determined.

## 2.2 Types of Adsorption

Several years ago, at a Nuclear Energy Agency (NEA) Workshop on sorption modelling and measurement (Nuclear Energy Agency 1983a), participants suggested a distinction between the types of sorption processes. There is no clear, practical way to distinguish among the processes in complex natural systems, because many systems exhibit intermediate or hybrid behavior. Nonetheless, idealized sorption processes were divided into four categories.

1. *Physical adsorption* is due to nonspecific, long range forces of attraction involving the entire electron shells of the radioelement in solution and of the adsorbing substrate (e.g., Van der Waal's forces). This process is rapid, reversible, largely independent of temperature and of the chemical composition of the sorbent and of the ionic strength and composition of the solution (as long as the solute of interest's solution concentration is well below saturation). The presence of complexing ligands and the pH of the solution have large influences on physical adsorption. An example of a process controlled by physical adsorption is the uptake of neutral metal hydrolysis complexes on surfaces that are also neutral following adsorption. This may be the principal mechanism for the

sorption of trivalent and tetravalent actinide complexes on metal oxide surfaces with nearly neutral pH.

2. *Electrostatic adsorption* is due to short range coulombic forces of attraction between charged solute species and the adsorbing substrate. This process is rapid, largely reversible, somewhat dependent on temperature, and strongly dependent on the composition of the sorbent and on the ionic strength and composition of the solution. This type of adsorption is also called chemisorption, and it is thought to allow only one layer of adsorbed species on the solid. In contrast, physical adsorption may accumulate several layers of adsorbate on the surface. An example of a process controlled by electrostatic adsorption is ion exchange. The adsorption of  $\text{Cs}^+$  on clays is controlled by such a process.
3. *Specific adsorption* is either due to the sorbate ion inducing the formation of surface sites of opposite charge when adsorbed, or due to the sorbate ion, as a trace species, occupying some of the small number of sites of opposite charge that exist on a surface regardless of its net surface charge. This process may be either slow or rapid. Specific adsorption of cationic species can appear highly irreversible as long as the system pH is not lowered significantly. The process is temperature dependent and also highly dependent on the composition of the sorbent and on the concentrations of solutes. An example of specific adsorption is the nearly complete adsorption of  $\text{UO}_2(\text{OH})^+$  on a ferric oxyhydroxide surface at a pH below the point of zero charge of the oxyhydroxide, where the solid has a net positive surface charge.
4. *Chemical substitution* is the incorporation of minor elemental constituents into the structure of crystalline phases (solid solution). This process may be slow and only partly reversible. It is temperature dependent, highly solute selective, and highly dependent on the composition of the solid as well as on the concentrations of solute. Chemical substitution controls the uptake of ions on a solid containing counterions that can form a sparingly soluble compound on the surface. Although this is not truly a form of adsorption, it is difficult to distinguish from adsorption under experimental conditions. Nevertheless, it will not be discussed in detail in this report. It can be considered as a special case of precipitation. Americium interacting with the surface of phosphate minerals and iodine interacting with Cu(I) or Pb minerals are examples of this process.

The sensitivity of each true type of sorption to changes in the physicochemical environment is summarized in Table I. All three types of sorption are highly dependent on the chemical form of the sorbate in solution (i.e., on speciation). Many of the parameters listed in the table (e.g., Eh, pH, and concentrations of complexing species) influence adsorption by controlling speciation. The sorption behavior of a radioelement is therefore largely dependent on its chemical state, because this determines its availability for adsorption onto the geological substrate.

A potentially large number of species of a radioelement in solution may thus be involved in sorption. Each of these aqueous species exhibits individual sorption characteristics. For example, adsorption of  $\text{UO}_2(\text{OH})^+$  and  $(\text{UO}_2)_3(\text{OH})_5^{2+}$  is strong, whereas adsorption of uranyl carbonate complexes [ $\text{UO}_2(\text{CO}_3)_2^{2-}$  and  $\text{UO}_2(\text{CO}_3)_3^{4-}$ ] is very weak (Hsi et al. 1985). Similarly, the thorium hydroxide complexes can be strongly adsorbed, while thorium sulfate complexes are very weakly adsorbed (Riese 1982). Understanding the speciation of the solution is therefore one key to an understanding of adsorption.

Equally as important to this understanding are the properties and behavior of sorbing mineral phases. Some of the more important controls of sorbent behavior are the surface area and surface charge of the sorbent, the effects of species in solution on surface charge, and the properties of the layer of solution in immediate contact with the solid (the electrical double layer).

The surface charge of minerals results from two general types of effects: those caused by interior lattice charge and those caused by the specific adsorption of potential determining ions.

TABLE I. Dependence of Types of Adsorption on Environmental Physicochemical Parameters

	<u>Physical Adsorption</u>	<u>Electrostatic Adsorption</u>	<u>Specific Adsorption</u>
Hydrogen ion availability (pH)	variable <sup>(1)</sup>	appreciable	appreciable
Free electron availability (Eh)	variable <sup>(2)</sup>	large <sup>(5)</sup>	large <sup>(5)</sup>
Temperature	small	appreciable	appreciable
Speciation of sorbate	large	large	large
Concentration of sorbate	small <sup>(3)</sup>	large	large
Concentration of complexing or competing solutes	large	large	large
Ionic strength of solution	small	large	variable
Properties of the sorbent	small	large <sup>(6)</sup>	large
Time	small <sup>(4)</sup>	small	variable

- (1) Dependent on charge of species, effectively zero for uncharged species.  
 (2) Dependent on electroactivity of species.  
 (3) At concentrations well below saturation.  
 (4) Slow alteration of sorbed species (e.g., dehydration of hydroxides).  
 (5) If redox sensitive elements involved.  
 (6) e.g., ion exchange capacity.

Interior lattice charge effects are the major cause of surface charge in layered silicates such as the clays; in contrast, the adsorption of potential determining ions (chiefly H<sup>+</sup> and OH<sup>-</sup>) is the major cause of surface charge on hydrous oxides and hydroxides. Interior lattice charge controls the surface charge on basal surfaces of the clays and micas. Because this effect is unrelated to compositional variations in solution, the resultant surface charge effect is constant and independent of pH, and it is responsible for the simple ion exchange behavior of these minerals. The presence of corners and edges on clay and mica plates, where broken cation-oxygen bonds occur, gives these minerals a small component of total charge that is affected, as are the hydrous oxyhydroxides, by the adsorption of potential determining ions. However, in general, the surface charge and cation exchange capacity of clays and micas tend to be relatively constant and independent of pH in most waters (when pH ranges from 4 to 10); in contrast, the surface charge and total metal adsorption capacity of hydrous oxyhydroxides is strongly pH-dependent.

Physical, electrostatic, and specific adsorption, as defined above, represent ideal conceptualizations of the more general phenomena called adsorption. It is this complex behavior of a potentially large number of aqueous species interacting with a number of different surfaces having distinct or variable properties that must be modeled to quantitatively account for sorption of radionuclides in natural water/rock systems. Currently available conceptual models of adsorption will now be briefly reviewed to show how characterization data on the important solution and solid phase parameters are considered in the various models.

### 3.0. CONCEPTUAL MODELS FOR ADSORPTION

Various conceptual models are used to describe adsorption of trace contaminants such as radionuclides. These models are described in terms of their parameters, and are presented in order from the most simplistic to the most detailed.

#### 3.1 Constant $R_d$ Model

In this model, the distribution of the radionuclide of interest between the solid adsorbent and solution is assumed to be a constant value. There is no explicit accommodation of dependence on characteristics of the rock, sediments, groundwater, or radionuclide concentration. Typically, an  $R_d$  value for a given radionuclide is determined in the laboratory using actual rock or sediment from the study area and actual or simulated groundwater, to which a radionuclide tracer is added at some trace concentration. Then,

$$R_d = \frac{\text{amount of radionuclide adsorbed on solid per gm}}{\text{amount of radionuclide in solution per ml}} \quad (1)$$

Typically the term "trace" denotes that a low mass is added, but the mass or activity must be sufficient to facilitate good counting statistics. The experiments are often equilibrated by contacting the solid with several aliquots of the water before adding the radiotracer, to attempt to approach the condition expected in the field.

Most of the laboratory experiments performed to measure distribution coefficients for radionuclides do not systematically investigate the effect of important parameters and do not attempt to identify the processes causing the observed adsorption. Because it is an empirical measurement, the  $R_d$  value does not necessarily denote an equilibrium value or require some of the other assumptions inherent in the more rigorous use of the term " $K_d$ ". The term " $R_d$ " will be used as simply the observed distribution ratio of nuclide between the solid and solution. I reserve the term " $K_d$ " for true equilibrium reactions that show reversibility and further do not yield a distribution ratio that is dependent upon the tracer concentration in solution.

Furthermore, it is customary with the constant  $R_d$  model to measure the total concentration or radioactivity of the tracer and thus to treat the tracer as being one species. This assumption is not an inherent requirement, but it is generally applied for convenience. If one knows that the tracer distributes among several species and one can measure or predict the distribution, separate  $R_d$  values can be calculated for each species.

This conceptual model, which depends upon experimental determination of the distribution coefficient or  $R_d$  is quite simple, but it is also limited in that it does not address sensitivity to changing conditions. If the groundwater properties (e.g., pH, dissolved solids content) change, a new experiment must be performed.

The constant  $R_d$  model is mathematically very simple and readily incorporated into transport models and codes via the retardation-factor term. That is, for porous flow

$$R = 1 + \frac{\rho_b}{\phi_e} R_d \quad (2a)$$

or

$$R = 1 + \frac{1 - \phi_e}{\phi_e} \rho_p R_d \quad , \quad (2b)$$

where  $R$  = the retardation factor  $V_w/V_n$   
 $\rho_b$  = porous media bulk density (mass/length<sup>3</sup>)  
 $\phi_e$  = effective porosity of media  
 $R_d$  = distribution coefficient and  
 $\rho_p$  = particle density (mass/length<sup>3</sup>).

For one-dimensional advection-dispersion flow with chemical reaction the transport equation can be written as

$$\frac{\partial C_i}{\partial t} = \frac{D_x \frac{\partial^2 C_i}{\partial x^2} - V_x \frac{\partial C_i}{\partial x}}{R_i} \quad , \quad (3)$$

where  $C_i$  = concentration of a particular radioactive Species (i) in solution (mass/length<sup>3</sup>)  
 $D_x$  = dispersion coefficient of Species (i) (length<sup>2</sup>/time)  
 $V_x$  = Darcy velocity of groundwater (length/time) and  
 $R_i$  = retardation factor for Species (i).  
 (For simplicity, radioactive decay has been left out.)

For the constant  $R_d$  model, the retardation factor ( $R$ ) is a constant for each layer of geologic media (each layer is assumed to have a constant bulk density and effective porosity). Thus, this transport equation does not require knowledge of any other parameters such as pH, surface area, and it is easily solved to determine the solution concentration as a function of time and at any given point. It is the use of the constant  $R_d$  conceptualization in the retardation factor that has caused most of the criticism. Few natural groundwater pathways are spatially or geochemically homogeneous to the extent that the retardation factor for a species remains constant.

With the constant  $R_d$  conceptual adsorption model, there is little incentive for a researcher to characterize or measure in detail the basic chemical and physical parameters of the rock and groundwater, because no dependency is explicitly accommodated. On the other hand, researchers will soon realize that the need to perform a new experiment to collect the  $R_d$  value for each different condition becomes burdensome and uneconomical. For this reason, and to satisfy their curiosity as to what mechanisms control adsorption, sorption experimenters often characterize their experimental systems by measuring selected parameters. Unfortunately, with no physicochemically-based

conceptual model, the experimenter has little guidance as to which parameters are more important and worthy of measurement.

### 3.2 Parametric $R_d$ Model

Parameters such as the amount and type of minerals (or more generally surface adsorption sites) present in the adsorbent, amount and types of ions in the groundwater (especially competing ions and complex-forming ligands), pH, Eh, temperature, and experimental procedures (e.g., solid/liquid separation techniques and contact times) can affect the observed distribution coefficient. Systematic, empirical studies have often been performed to investigate the effects of many of these variables on the adsorption of radionuclides on soils, sediments, or rocks. The most common approach is to vary one or more parameters systematically, to measure the resultant distribution coefficient, and then, using available statistical analyses schemes, to develop some predictor relationship.

Because the distribution coefficient is a function of so many variables, it is common to systematically vary several parameters simultaneously in one experimental study. Factorial design strategies are most often invoked to determine the systematics in varying the independent variables and the dependent variables (Yates 1958; Cochran et al. 1957; Davies 1954; Plackett et al. 1946; Box et al. 1960). (The dependent variables are typically the distribution coefficient.) Statistical methods commonly used to derive quantitative predictor equations include standard linear or nonlinear regression (e.g., Snedecor et al. 1967), stepwise regression (e.g., Hollander et al. 1973), and adaptive learning networks (e.g., Mucciardi et al. 1979, 1980).

All of these techniques have been used successfully to develop empirical relationships that describe the distribution coefficient in terms of other variables. Successful uses are reported by Routson et al. (1972, 1981), Delegard et al. (1983), Serne et al. (1973), and Mucciardi et al. (1979, 1980).

The empirical predictor equations commonly take the form of a nonlinear multinomial expression. For example an expression for strontium-90 adsorption might take the form

$$R_d(\text{Sr}) = a(\text{Ca}^{2+}) + b(\text{Na}^+) + c(\text{K}^+) + d(\text{Ca}^{2+})(\text{Na}^+) + e(\text{Ca}^{2+})(\text{K}^+) + f(\text{Na}^+)(\text{K}^+) + g(\text{Ca}^{2+})(\text{Na}^+)(\text{K}^+) + h \quad (4)$$

where  $a, b, \dots, h$  are regression coefficients and  $(\text{Ca}^{2+})$ ,  $(\text{Na}^+)$ , and  $(\text{K}^+)$  represent molar solution concentrations of competing macro cations. In this system, the independent variables were  $(\text{Ca}^{2+})$ ,  $(\text{Na}^+)$ , and  $(\text{K}^+)$ , and the dependent variable was the distribution coefficient for strontium. For this example, squared terms such as  $(\text{Ca}^{2+})^2$  or  $(\text{K}^+)^2$  were not found to increase the predictive equation's "goodness-of-fit" for the data significantly; therefore, these quadratic terms were ignored. For other empirical models, other powered, exponential or logarithmic terms may be useful. The International Sorption Information Retrieval System (ISIRS) is a computerized sorption data bank and sorting/retrieval/statistical manipulation software package designed especially for storing and generating the laboratory data parametric adsorption models (Hostetler et al. 1980; NEA 1983b,c).

Although the empirical relationships generated from these types of statistical analyses are more powerful than knowledge of individual distribution coefficients, they should not be used to predict  $R_d$  values for conditions beyond the range studied. Furthermore, the statistical relationships delineate only the apparent effects that the chosen independent variables have on the distribution coefficients; they do not identify conclusively the cause or process controlling adsorption. That is, the statistical analyses may suggest a very strong relationship between one variable, for instance pH and the distribution coefficient, when the actual adsorption process is controlled by hydrous iron oxide scavenging. Because the stability of iron oxide is a function of pH there could be a statistical relationship calculated that suggests the adsorption is solely caused by pH.



Empirical and purely statistical approaches are useful in assessing radionuclide adsorption tendencies, but they do not lead to a general understanding of the physicochemical processes controlling the interactions among rocks, groundwaters, and radionuclides. Therefore, more rigorous, mechanistic studies that rely on thermodynamic constructs have been and are currently being proposed to increase our knowledge of trace constituent adsorption processes. Systematic studies to determine the effects of competing ions and of pH (which is, after all, just another way of referring to competing H<sup>+</sup> ions) can be related to thermodynamic models.

The parametric R<sub>d</sub> conceptual model requires characterization of solid phase (rocks, sediments, etc.) and solution phase (groundwater and dissolved radionuclide content) parameters. The statistical model does not provide an a priori ranking of which parameters are most important to measure, but by using physicochemical knowledge of possible adsorption processes (see Table I for example) and experience, the more important parameters can be identified (Nuclear Energy Agency 1983a,b; Serne et al. 1983).

The parametric R<sub>d</sub> conceptual model can be used in the retardation factor term [see Equation (2)] and the transport equation [see Equation (3)]. When used in the transport equation, the code must also keep track of the current value of the independent variables [those like Ca<sup>2+</sup>, Na<sup>+</sup>, and K<sup>+</sup> see Equation (4)] at each point in space and at each time in order to continually update the value of R<sub>d</sub>. Thus, the code must track many more parameters, and some numerical solving techniques (such as closed form analytical solutions) can no longer be used to perform the integration necessary to solve for concentration. Generally, computer codes that can accommodate the parametric R<sub>d</sub> model use a chemical subroutine to update R<sub>d</sub> or R when called by the main transport code. Probably because of the added complexity in solving the transport equation with the parametric R<sub>d</sub> adsorption model and because of its empirical nature, this technique has not been used frequently for nuclear waste disposal safety assessment exercises.

### 3.3 Isotherm Adsorption Models

Many experimenters have performed adsorption studies in a systematic fashion to evaluate the effects of various parameters on the distribution coefficient. The results of a suite of experiments evaluating the effect of nuclide concentration on adsorption while other parameters are held constant are called an "adsorption isotherm." Three adsorption isotherm models used frequently are the Langmuir, Freundlich, and Dubinin-Radushkevich models.

The Langmuir model has been used to describe adsorption of gas molecules onto homogeneous solid surfaces (crystalline materials) that exhibit one type of adsorption site (Langmuir 1918). Many investigators have tacitly extended the Langmuir adsorption model to describe adsorption of solution studies onto solid adsorbates including heterogeneous solids. The Langmuir model for adsorption is

$$X = \frac{bX_m C}{1 + bC} \quad (5)$$

where X = amount of solute adsorbed per unit weight of solid

b = a constant related to the energy of adsorption

X<sub>m</sub> = maximum adsorption capacity of solid and

C = equilibrium solution concentration of the adsorbate.

Substituting 1/B for b, one obtains

$$X = \frac{X_m C}{B + C} \quad (6)$$

A plot of values of X (y-axis) versus values of C (x-axis) passes through the origin and is nearly linear at low values of C. As C increases, X should approach  $X_m$ . One can rearrange Equation (6) by taking its reciprocal and multiplying both sides by  $X \cdot X_m$ , to yield  $X = -B(X/C) + X_m$ . Then by plotting X on the y-axis and (X/C) on the x-axis, one can determine the value for  $-B$  from the slope of the best fit line and the value of  $X_m$  from the intercept. For radionuclide adsorption onto heterogeneous soils and sediments, the Langmuir model is typically a weak predictor of actual adsorption events, although Salter et al. (1981a) cite several instances where the Langmuir isotherm has successfully fit trace adsorption by natural substrates. Further, Salter et al. (1981b) discuss recent modifications of the Langmuir model to accommodate two distinct sites and competition of two adsorbates (the nuclide and the ion it replaces on the adsorbent) which should further extend this conceptual model's usefulness on natural substrates.

The Freundlich isotherm model (Freundlich 1926) is defined as:

$$X = KC^N \quad (7)$$

where X = amount of solute adsorbed per unit weight of solid

C = equilibrium solute solution concentration and

$K, N$  = constants.

The Freundlich model does not account for finite adsorption capacity at high concentrations of solute, but when considering trace constituent adsorption, ignoring such physical constraints is usually not critical. The Freundlich isotherm can be transformed to a linear equation by taking the logarithms of both sides of Equation (7):

$$\log X = \log K + N \log C \quad (8)$$

When  $\log X$  is plotted on the y-axis and  $\log C$  on the x-axis, the best-fit straight line has a slope of N, and  $\log K$  is its intercept. When  $N = 1$ , the Freundlich isotherm, represented by Equation (7) reduces to a linear relationship, and because  $X/C$  is the ratio of the amount of solute adsorbed to the equilibrium solution concentration (the definition of  $K_d$ ), the Freundlich K is equivalent to the value of the  $K_d$ .

Because adsorption isotherms at very low solute concentrations are often linear, either the Freundlich isotherm with N equalling 1 or the Langmuir isotherm with  $bC$  much greater than one fits the data. The value of N for the adsorption of many radionuclides is often significantly different from 1, such that nonlinear isotherms are observed. In such cases, the Freundlich model is a better predictor than the Langmuir model.

A third adsorption model that has been used recently in nuclide studies is the Dubinin-Radushkevich isotherm (Dubinin et al. 1947). This model is applicable for the adsorption of trace constituents. Should the adsorbent surface become saturated or the solute exceed its solubility product, the model is inappropriate. The Dubinin-Radushkevich model is more general than the

Langmuir model because it does not require either homogeneous adsorption sites or constant adsorption potential. Its mathematical form is

$$X = X_m e^{-K\varepsilon^2} \quad (9)$$

where  $X$  = observed amount of solute adsorbed per unit weight.

$X_m$  = sorption capacity of adsorbent per unit weight

$K$  = constant

$\varepsilon$  =  $RT \ln(1 + 1/C)$

$R$  = gas constant

$T$  = temperature (Kelvin scale) and

$C$  = solute equilibrium solution concentration (in M).

The Dubinin-Radushkevich equation can be transformed to

$$\ln X = \ln X_m - K\varepsilon^2 \quad (10)$$

A plot of  $\ln X$  (y-axis) versus  $\varepsilon^2$  (x-axis) allows the estimation of  $\ln X_m$  as the intercept and  $-K$  as the slope of the resultant straight line. Ames et al. (1982) successfully used this model to describe adsorption of uranium and cesium onto basalt and its weathering products.

All three isotherm models can be compared against data from experiments that systematically vary the mass of trace constituent or radionuclide while holding all other parameters as constant as possible. It is important to consider the total mass of the element present including all stable and other radioactive isotopes, when evaluating isotherms. It is incorrect to calculate isotherms based on only one isotope if the system includes several (both stable and radioactive) for a particular element. For convenience, isotherm experiments tend to consider only the total concentration or radioactivity content and thus lump all species for a given isotope.

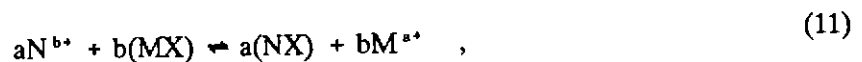
It can be argued that all three models, but especially the Langmuir and Dubinin-Radushkevich models, are based on physicochemical processes or mechanisms. If the experiments are performed and characterized rigorously to assure equilibrium conditions and constancy of variables aside from the trace constituent concentration, then the resultant constants undoubtedly have some relationship to adsorption capacities and to site adsorption energies, provided only one species predominates in solution for each radionuclide. On the other hand, any suite of experiments that can be plotted as amount adsorbed versus amount in solution at the time of measurement can also be analyzed using these models to see whether predictive equations can be determined. The latter empirical approach is a step up in sophistication over the constant  $R_d$  model's distribution coefficient determinations.

It must be stressed that isotherm models as expressed by Equations (5), (7), and (9) explicitly consider dependency of the distribution coefficient on only the solution concentration of the radionuclide of interest. Isotherm models do not consider dependence on other solid and solution parameters that can influence adsorption, (like those listed in Table I).

The incorporation of isotherm adsorption models into transport codes is relatively easy. Each of the aforementioned isotherm equations can be rearranged to calculate a distribution coefficient,  $R_d$ , that is a function of  $C$ , the solution concentration of the radionuclide, and one or two constants. As the transport model solves for  $C$ , substitution of an equation that depends only upon  $C$  (and derivable constants) for the  $R_d$  in the retardation factor [see Equations (2) and (3)] should be straightforward. For simple cases, analytical closed-form solutions are possible, or numerous numerical approximation schemes can be used. Thus, with little additional work or increases in computer storage requirements, most transport codes can be formulated to predict radionuclide migration with an isotherm adsorption model. I restate that this approach accounts for the dependency of  $R_d$  on only one parameter, the concentration of the radionuclide.

### 3.4 Mass Action Adsorption Models

Ion-exchange processes (e.g., electrostatic adsorption) use mass action laws and equilibrium constant constructs to derive rigorous predictive equations for trace constituent adsorption. Ideal binary ion exchange is a simple case often used to illustrate this model. For radionuclide ideal binary ion exchange, one assumes that the nuclide of interest is present in such trace concentrations that it does not appreciably affect either the concentration of the major constituent adsorbed on the solid or the activity coefficient ratio of the binary mass action equation components. The thermodynamically rigorous mass action equilibrium expression for a binary cation-exchange reaction, such as strontium or cesium adsorbing onto a calcium saturated clay, is



where  $a$  = valence of macro ion (e.g., calcium)

$N$  = trace component

$b$  = valence of trace ion (e.g., radionuclide)

$M$  = macro component in binary system and

$X$  = solid adsorbent.

The equilibrium constant,  $K$ , can be expressed as

$$K = \frac{[NX]^a [M^{a+}]^b}{[MX]^b [N^{b+}]^a} \quad , \quad (12)$$

where the brackets,  $[ ]$ , indicate thermodynamic activities. If one assumes that the exchange capacity,  $C$ , of the solid adsorbent is constant (equivalents per unit weight) and that  $N$  is present at low (trace) concentration, then, the concentration of the trace constituent adsorbed,  $(NX)$  is much smaller than  $C$ , and the concentration of macro ions adsorbed on exchange sites,  $(MX)$  is approximately equal to  $C/a$  [i.e.,  $(MX) \sim C/a$ ] in terms of moles per unit of weight, because  $C = (NX)b + (MX)a$ . Then, by using the standard definition of the distribution coefficient,  $K_d = (NX)/(N^{b+})$ , where  $(N^{b+})$  is the solution concentration of the trace constituent at equilibrium with the solid, and by substituting the relationship

that activity is equal to the concentration times an activity coefficient, i.e.,  $[A] = \gamma_A(A)$ , one can rewrite Equation (12) as

$$K = \frac{(K_d)^a (M^{+a})^b}{(C/a)^b} \cdot \Gamma \quad (13)$$

where  $\Gamma$  is the ratio of the activity coefficients:

$$\Gamma = \frac{\gamma^a\{NX\} \gamma^b\{M^{+a}\}}{\gamma^b\{MX\} \gamma^a\{N^{+b}\}} \quad (14)$$

For ideal ion exchange of a trace constituent where the exchange capacity,  $C$  is constant, the ratio of activity coefficients for the adsorbed ions,  $\gamma\{NX\}/\gamma\{MX\}$  is constant. Further, for low ionic strength solutions the ratio  $\gamma\{M^{+a}\}/\gamma\{N^{+b}\}$  is also a constant, and thus  $\Gamma$  becomes a constant. Using these conditions/assumptions and a logarithmic transform of Equation (13), the dependence of  $K_d$  (the trace constituent distribution coefficient) on the macro ion concentration,  $M$ , reduces to  $-b/a$ , the ratio of tracer ion charge to the macro ion charge.

A plot of  $\log K_d$  (y-axis) versus  $\log (M^{+a})$  (x-axis) should yield a straight line with a slope equal to  $-b/a$ . Kraus et al. (1955, 1958), Rafferty et al. (1981), and Shiao et al. (1981a,b) discuss the use of this ion-exchange approach to model both cation and anion exchange of trace constituents onto hydrous oxides and clays. Theoretical and experimental efforts to model mixtures of solid adsorbents, e.g., clays plus oxides, are discussed by Triolo et al. (1980) and by Palmer et al. (1981). The underlying principle used in dealing with mixtures is the assumption of additivity of the individual adsorption capacities of each solid adsorbent, based on the weight fraction of each solid present.

Routson et al. (1972) and Langmuir et al. (1984) present a slight variation of this ideal ion-exchange approach that also uses the mass action equations and the equilibrium constant concept. In their derivations, the mass action expression for binary ion-exchange reactions, Equation (11), is expressed as an empirical equilibrium constant

$$K^* = \frac{[M^{+a}]^b}{[N^{+b}]^a} \left( \frac{NX}{MX} \right)^P \quad (15)$$

where the activity ratio of the ions  $N$  and  $M$  adsorbed to the solid is replaced by its concentration ratio or mole fraction of total sites raised to some empirical constant,  $P$ . The true equilibrium constant is replaced by a pseudo-equilibrium constant,  $K^*$ .

For analysis of experimental data, the logarithmic transform of Equation (15), along with the substitution of the solution concentration times an activity coefficient,  $\gamma$ , for the activity is used. The activity coefficients of ions can be estimated from Davies' extension of the Debye-Huckel theory (Butler 1964), and the concentrations of ions in solution are determined by standard chemical analysis techniques. Alternately, a thermodynamic chemical code, such as EQ3 (Wolery 1979), WATEQ3 (Ball et al. 1981), MINEQL (Westall et al. 1976), MINTEQA2 (Felmy et al. 1984) or PHREEQE (Parkhurst et al. 1980), can be used to calculate activities for  $M$  and  $N$  in solution. By plotting  $\log$

$[M^{+a}]^b/[N^{+b}]^a$  on the y-axis and  $\log (NX)/(MX)$  on the x-axis, and then calculating the best-fit line, the slope (an estimate of the empirical constant P) and the intercept (an estimate of  $\log K^*$ ) can be calculated.

Detailed discussions on the derivation and limitations of this empirical approach for both trace constituent adsorption and competition between two macro components are presented in Garrels et al. (1965). Briefly, the approach relies on the same assumptions described for the ideal ion-exchange approach, that the number of bonding sites of the solid ( $-X$ ) are constant and have essentially the same binding energy, and that the ions being adsorbed do not cause appreciable changes in the surface structure of the adsorbent. Walton (1949) and Serne et al. (1973) describe experiments in which Equation (15) was used to develop predictive models for exchange of one macro cation for another onto aluminosilicates and natural soils. The approach allows investigators to evaluate the dependence of the adsorption of one cation on the concentration of a second cation.

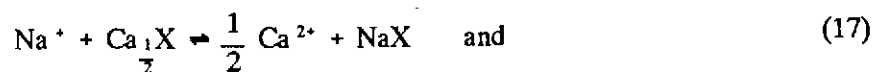
By developing computer algorithms based on Equation (15), with laboratory-derived values for  $K^*$  and P, for sets of binary exchange reactions, Routson et al. (1972) were able to model the simultaneous adsorption/exchange of  $Na^+$ ,  $Ca^{+2}$ ,  $Mg^{+2}$ , and  $K^+$  in a synthetic waste water onto several sandy soils. The binary reaction sets (Na-Ca), (Mg-Ca), and (Na-K), were solved numerically on a computer by iterating through each equation until the change in predicted solution concentration for each species at the beginning and end of one complete pass was less than a specified value, such as 0.1%.

With a similar iteration technique, Robbins et al. (1980a,b) use a pseudothermodynamic mass action equation variation of Equation (15) to model the transport of alkali metals, specifically  $K^+$  and  $Na^+$ , and alkaline earths, specifically  $Mg^{2+}$  and  $Ca^{2+}$ , through soils and clays. Robbins et al. use the mass action equation

$$K = \frac{[M^{+a}]^b X_{1N}}{[N^{+b}]^a X_{1M}} \quad (16)$$

where  $X_{1N}$  and  $X_{1M}$  are the equivalents of each cation adsorbed on the solid adsorbent, given in units of meq per 100 g.

The pseudoequilibrium constant,  $K^*$ , is frequently called the "selectivity coefficient" in soils literature. For example, sodium exchange onto a calcium saturated soil is



$$K^* = \frac{[Ca^{2+}]^{1/2} X_{Na}}{[Na^+] X_{1Ca}} \quad (18)$$

This approach like the true thermodynamic mass action conceptual models for Equations (11) through (14) assumes that (1) only free cation species are adsorbed; (2) the adsorbent cation exchange capacity is constant and independent of pH and solution composition or total ionic strength; (3) the solutes are a true solution (i.e., the species' activities are not affected by the presence of the solids); and (4) the exchange is reversible and there is no hysteresis between adsorption and desorption. Most derivations also consider only one type of adsorption site with a fixed adsorption energy.

Brouwer et al. (1983) give a detailed discussion of a mass action adsorption model with several types of adsorption sites having different energies or selectivities for adsorption of ions. Brouwer et al. also treat several simplifying cases, such as allowing one type of site to be more selective than another. These cases show that the adsorption of cesium and rubidium onto illite clay originally saturated with calcium, strontium, barium, sodium, or potassium is best described by assuming that there are three types of sites. Likely, most natural adsorption substrates are best modeled as a mixture of sites with differing adsorption energies.

Langmuir (1981) reviews the use of the pseudothermodynamic mass action conceptual model for both exchange of macro constituents and adsorption of trace constituents. Because Equation (15) includes an exponent,  $P$ , on the ratio of the adsorbed phases, Langmuir has called this conceptual model the Power Exchange Model. From reviewing numerous adsorption publications Langmuir found that when two competing cations, especially alkali and alkaline earths, are present at near equal molar concentrations that  $P=1$ . But when one of the competing ions is present at very low concentrations relative to the other,  $P$  does not equal one. Most heavy-metal elements in nature are present at concentrations much less than alkali and alkaline earths and the best fit power exchange equation typically requires  $P$  to be greater than 1. A  $P$ -value greater than one means that the trace constituent is preferably adsorbed as its concentration decreases. In other words the  $R_d$  value gets larger as the solution concentration of the trace constituents decreases. (This trend is often observed in radionuclide adsorption studies and corroborates Langmuir's findings.) Further Langmuir found that a complete description of trace metal adsorption over a wide range in solution concentrations of the trace metal requires that several regions be designated where distinct  $K^*$  and  $P$  values are determined. Conceptually one might suggest that each distinct region describes a separate adsorption process or separate type of adsorption site but as the Power Exchange Model is strictly empirical there is no fundamental basis for such a suggestion. At any rate, Langmuir cites numerous studies in which this empirical mass action conceptual model readily describes the adsorption of cationic species onto clays, hydrous oxides, zeolites and soils, provided the user segments the data versus concentration in solution or studies systems with only small ranges (e.g., two orders of magnitude) of solution concentrations for the trace constituent.

Further, Langmuir shows that the Power Exchange Model [Equation (15)] where the  $NX$  and  $MX$  solid terms are expressed as mole fraction reduces to the Freundlich adsorption model when the minor component mole fraction,  $NX$  is less than 0.05. As derived in Equation (7) the Freundlich equation exponent  $N$  would be less than one for most trace radionuclides as it is similar to the reciprocal of  $P$  in Equation (15) which Langmuir finds is typically greater than one for trace metal adsorption.

A potential limitation for the study of trace constituent adsorption using this pseudoequilibrium-constant approach is the difficulty of obtaining accurate values of the ratio  $(NX)/(MX)$  when the ratio is either less than 0.05 or more than 0.95. In the case of trace constituent adsorption, it is quite common for this ratio to be less than 0.1. The use of radiotracers often helps make measurements more precise but there will always be a level below which accurate results are impossible. Many real-world cases may fall in this region.

The mass action approach requires the investigator to track the activities of the free cations or free anions in solution and the amounts adsorbed on the solid phase (in terms of either mole fractions, equivalents per gram or moles per gram). This need to keep track of the distribution of elements other than the contaminant of interest increases significantly the storage requirements for transport codes. Probably of greater concern is the fact that numerical solution algorithms to solve equations like Equations (12), (13), (15), (16), and (18) often have convergence problems due to their highly nonlinear nature. This is particularly a problem for the binary exchange reaction, when one exchanging ion is present in much smaller quantities than the other.

Probably for these reasons, few transport codes exist that accommodate the mass action conceptual adsorption model. Furthermore, the behavior of many trace contaminants appear to be only

poorly modeled by the mass action approach without segmenting the system and using distinct  $K^*$  and  $P$  values in each segment. Classical soil problems, such as salt transport by irrigation of saline soils, have provided the impetus to build mass action adsorption transport codes (e.g., Robbins et al. 1980a,b; and Dutt et al. 1963 and 1972). However, so far few of these codes have found any usage in the nuclear waste management community for predicting radionuclide transport.

### 3.5 Surface Complexation Models

For many radionuclides and trace constituents, the literature states or implies that specific adsorption (i.e., adsorption occurring onto surfaces having the same net surface charge as the sorbing ion) is a major contributor to the adsorption at low solution concentrations (see for example Rai et al. 1984). Hydrous oxides of Fe, Mn, and Al, and amorphous aluminosilicates occurring either as discrete grains or surface coatings are assumed to be the prime adsorbents responsible for specific adsorption. These solid phases have variable surface charges and exhibit amphoteric behavior. The solids have a net positive charge at pH values below their point of zero charge (PZC) and a net negative charge at pH values above the PZC. James et al. (1972) and Langmuir et al. (1984) explain why specific adsorption occurs. Briefly, the free energy of adsorption is the sum of three terms, a coulombic term, a solution term, and a chemical reaction term. Mathematically the free energy of adsorption is

$$\Delta G_{ads}^{\circ} = \Delta G_{coul}^{\circ} + \Delta G_{solv}^{\circ} + \Delta G_{chem}^{\circ}$$

For adsorption to occur,  $\Delta G_{ads}^{\circ}$  must be negative. The free energy of solvation,  $\Delta G_{solv}^{\circ}$ , represents the energy needed to dehydrate a species to bring it close enough to the adsorbent surface to attach. This quantity is always positive but is smaller for low valence state species, that is,  $\Delta G_{solv}^{\circ} = f(\text{valence})^2$ . The coulombic term,  $\Delta G_{coul}^{\circ}$  is positive for like-charged entities (that is, if the adsorbent site is of the same charge as the adsorbing species, then  $\Delta G_{coul}^{\circ}$  is positive). Thus for specific adsorption,  $\Delta G_{coul}^{\circ}$  and  $\Delta G_{solv}^{\circ}$  are both positive; in order for  $\Delta G_{ads}^{\circ}$  to be negative,  $\Delta G_{chem}^{\circ}$  must be both negative and numerically larger than the sum of  $\Delta G_{coul}^{\circ}$  and  $\Delta G_{solv}^{\circ}$ . The  $\Delta G_{chem}^{\circ}$  represents the free energy of chemical bonding between the adsorbent and the adsorbate, and obviously it must be negative in charge and relatively large for species that specifically adsorb.

Surface complexation adsorption models treat the adsorbent surface as a plane of hydroxyl groups, X-OH, where X represents structural Al, Fe, Mn, Si, or other atoms. The adsorption sites, -OH, or hydroxyl groups are thought of as ligands that are acid-base sensitive and form complexes with solutes in solution. The model assumes that (1) adsorption occurs on the sites with neither chemical nor electrostatic interactions between adsorbed species (i.e., no neighbor interactions); (2) all of the adsorption sites have equal binding energies (i.e., each site is identical); (3) no matter how many sites are full, each remaining site has the same probability of adsorbing the next solute ion (i.e., the binding energy does not depend upon sorption density); and (4) the maximum adsorption capacity allows only a single layer coverage of each site. All four of these assumptions are also invoked for the Langmuir isotherm and ideal ion-exchange approaches described earlier.

In the surface complexation model, adsorption reactions are considered analogous to soluble complexation reactions in solution, with one fundamental difference. The adsorption reaction includes an electrostatic energy term to account for the interaction of the charged adsorbing ion and the surface charge on the solid. The conceptual model is shown schematically in Figure 1. For the surface complexation model, dubbed the "triple-layer model," originally suggested by James et al. (1972, 1975), and applied by Davis et al. (1978a,b, 1980) and Leckie et al. (1980), the space around the solid surface (usually represented as a semi-infinite planar surface) is arbitrarily broken into three layers or zones, separated by the 0 plane, the b plane, and the d plane, as shown in Figure 1. The 0 plane represents the interface between the solid surface and solution. Generally, only hydrogen and hydroxyl



ions are allowed to enter the 0 layer to interact with the solid. Just beyond the 0 layer is the b layer, which extends out farther from the surface and ends at the boundary of the diffuse zone, the d plane. Solution ions, such as the macro cations and anions ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , etc.), and the trace constituents [ $\text{Sr}^{2+}$ ,  $\text{PuO}_2^+$ ,  $\text{Am}(\text{OH})^{2+}$ ], that are adsorbing onto the solid surface are allowed in the b layer. The third layer is the diffuse zone, where ions are not influenced strongly by electrostatic forces emanating from the solid surface. The ions in this region are considered to be counterions that neutralize any residual charge caused by the surface and specifically adsorbed ions in the b layer. The d layer blends into the bulk solution farther from the surface.

The electrostatic interactions modify the thermodynamic activities of ions as they move from the bulk solution into the various adsorption zones. The ion activity of a species near the surface,  $[\text{Ion}_s]$ , is related to its activity in the bulk solution,  $[\text{Ion}_b]$ , by the following relationship

$$[\text{Ion}_s] = [\text{Ion}_b] e^{(-ZF\psi/RT)} \quad (19)$$

where  $Z$  = charge of ion (e.g.,  $\text{Sr}^{2+} = +2$ ,  $\text{SO}_4^{2-} = -2$ )

$F$  = Faraday constant

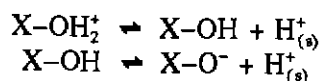
$\psi$  = electrostatic potential for the designated zone

$R$  = gas constant and

$T$  = temperature (Kelvin scale).

Figure 1 shows the shape of the potential curve as an ion approaches the surface. The figure also defines two capacitance terms and three surface charges. Adsorption reactions onto oxide surfaces have been successfully described using the relationships between surface charges, capacitances, and potentials (see James et al. 1972) and equations like Equation (19) for each species adsorbed onto the solid.

Adsorption dependence on acid-base reactions is explicitly accommodated by the following two reactions:



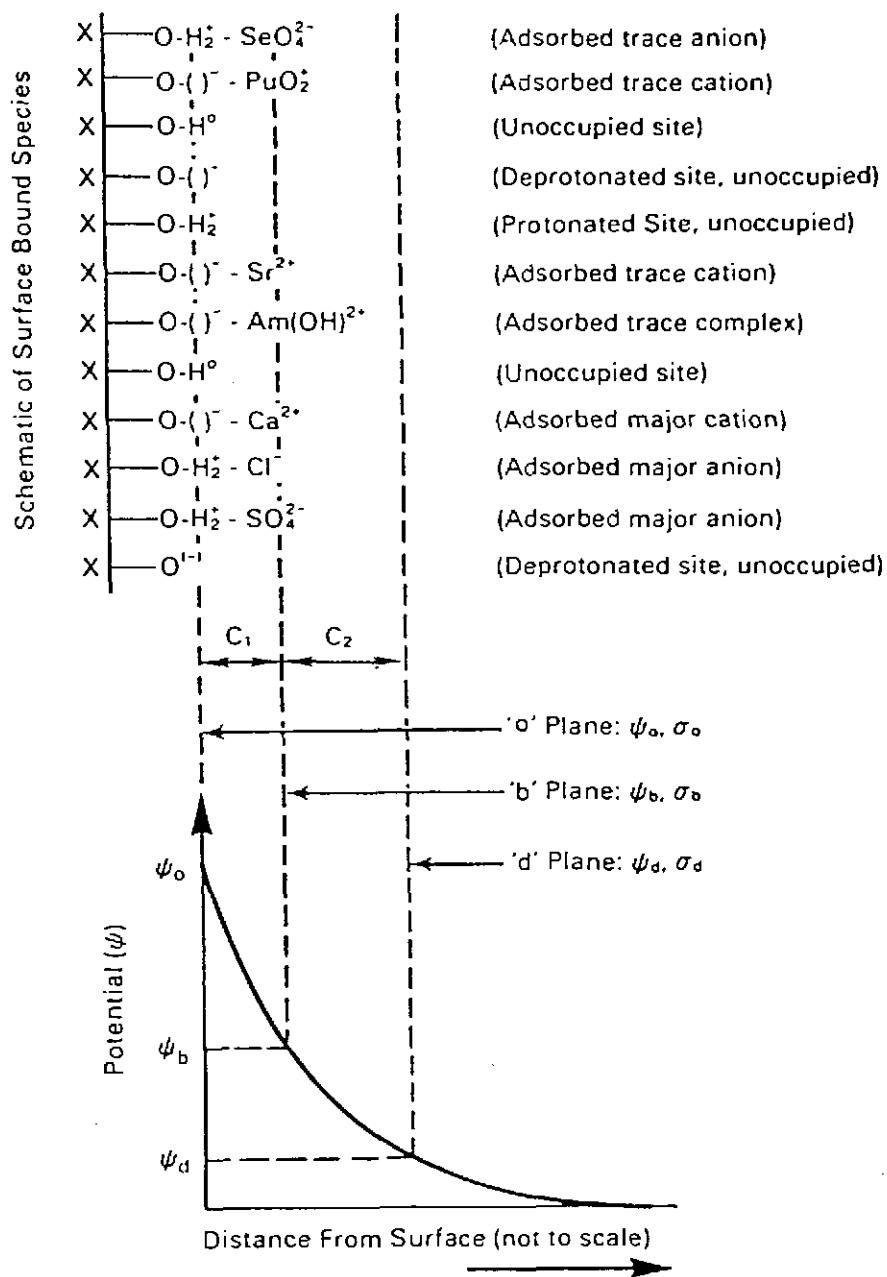
as

$$K_{a_1}^{\text{int}} = \frac{[\text{X-OH}] [\text{H}^+]_s}{[\text{X-OH}_2^+]} = \frac{[\text{X-OH}] [\text{H}^+]_s e^{(-F\psi_s/RT)}}{[\text{X-OH}_2^+]} \quad (20)$$

and

$$K_{a_2}^{\text{int}} = \frac{[\text{X-O}^-] [\text{H}^+]_s}{[\text{X-OH}]} = \frac{[\text{X-O}^-] [\text{H}^+]_s e^{(-F\psi_s/RT)}}{[\text{X-OH}]} \quad (21)$$

where the equilibrium constants,  $K_{a_1}^{\text{int}}$  and  $K_{a_2}^{\text{int}}$  are similar to association constants for soluble complex



Electroneutrality requires  $\sigma_o + \sigma_b + \sigma_d = 0$

Where  $\sigma_i$  = Surface charge at designated plane

Charge-potential relationships

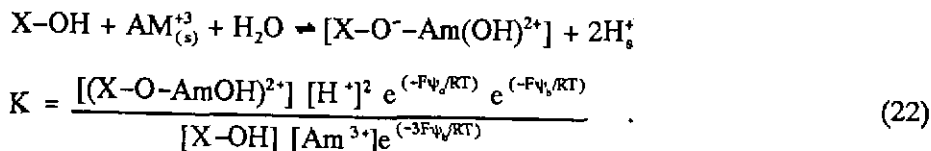
$$\psi_o - \psi_b = \sigma_o / C_1$$

$$\psi_b - \psi_d = -\sigma_d / C_2$$

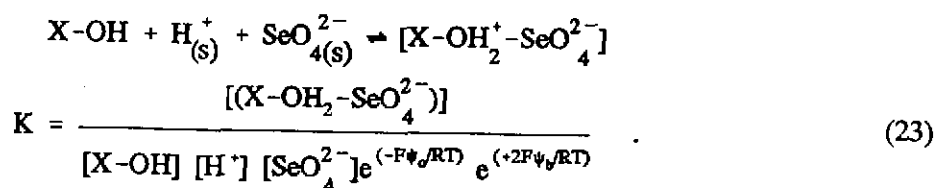
Figure 1. Schematic Representation of Triple Layer Adsorption Model.

formation and can be determined in the laboratory by systematic acid-base titrations (see Davis et al. 1978a). The other variables in these equations are those defined for Equation (19).

Examples of cation and anion adsorption reactions for trace contaminants, such as radionuclides, are shown in Equations (22) and (23). Recall that these ions and the macro cations and anions are bound in the b layer not the 0 layer; therefore the electrostatic terms differ from those in Equations (20) and (21). The first reactions show the adsorption of the first hydrolysis species for americium:



The second reaction shows the adsorption of the selenate anion:



The triple-layer conceptual model explicitly accommodates variable surface charge, pH effects, ionic strength effects, speciation (that is, it allows for simultaneous adsorption of free cations or anions, and of hydrolyzed and complexed species), macro cation/anion competition [reactions similar to Equations (22) and (23) for major constituents are included]. When incorporated into a thermodynamic code, this model can explicitly address oxidation/reduction effects on ion speciation and on the stability of solid adsorbents such as iron oxides. Serne et al. (1984) and Peterson et al. (1986) have combined triple-layer adsorption algorithms with the MINTEQA thermodynamic code (Felmy et al. 1984) to describe uranium mill tailings waste leachate interactions with sediments. Their exercise modeled both solubility and adsorption (onto hydrous iron oxide) processes under variable pH, Eh, and solution ionic strength (Peterson et al. 1986).

A second surface complexation conceptual model is called the "constant-capacitance model" (Schindler et al. 1976; Schindler 1981; and Hohl et al. 1976). In general, it is conceptually similar to the triple-layer model just discussed, but it considers only two planes for adsorption and assumes that all species adsorb in the inner zone, outside of which lies the diffuse layer of counter ions that melds into the bulk solution. Morel et al. (1981) and Westall et al. (1980) discuss the finer details of similarities and differences between these popular surface complexation models, but in general both models can be used to explain observed adsorption onto hydrous oxide surfaces.

The use of the surface complexation model requires detailed characterization of the adsorbent's adsorption capacity (i.e., number of sites or site density and surface area), of its dependency on pH (determined by acid-base titrations), of its dependency on major cations/anions, and of the electrical properties of the surface (electrokinetic potential, specific conductivity, etc.), as well as detailed studies of the adsorption of trace constituents. Currently the model has been used successfully to predict adsorption of hydrolyzable trace metals (Zn, Cd, Cu, and others) and oxyanions, ( $CrO_4^{2-}$ ,  $SeO_4^{2-}$ , and others) onto oxide/hydroxide surfaces of Fe, Ti, Al, and Si. Several recent conferences have discussed the use of this approach to describe the adsorption of uranium onto hydrous iron oxides, of

thorium and radium onto quartz and kaolinite and of lead onto manganese oxide (Catts et al. 1983; Hsi et al. 1980, 1983; Langmuir et al. 1982; Riese et al. 1981, 1983). The approach has also been used to model cesium adsorption onto montmorillonite (Silva et al. 1981), neptunium (V) adsorption onto hydrous iron oxide and alluvial sediments (Fruchter et al. 1985) and uranium VI species adsorption onto goethite, amorphous ferric oxyhydroxide, hematite (Hsi et al. 1985) and the clay corrensite (Siegel et al. 1990).

Leckie et al. (1980) discuss the extension of the triple-layer model to accommodate multiple and distinct types of sites. They suggest that highly accurate modeling of trace constituent adsorption onto hydrous oxides requires accommodations of variable binding energies on sites as a function of the amount of the species adsorbed. This adaptation would significantly increase the complexity of using the surface complexation conceptual model.

Surface complexation modeling requires detailed characterization of the solid adsorbent. Before surface complexation conceptual models can gain wide acceptance in the nuclear waste management community, their application to natural rocks and sediments must be addressed. However, to date, only simple and pure oxide solids, corrensite and kaolinite clays have been successfully characterized to obtain the necessary input values. Thus, solid substrates currently modeled are pure single-phase minerals or amorphous oxides/hydroxides. In principle, the conceptual model should work for natural adsorbents that are mixtures of pure minerals, sometimes mixed with amorphous coatings. One current approach is to treat the natural system as a linear combination of pure phases. That is, the natural solid is broken down into its primary components, and the individual properties of the primary components are weighted by the percentage of the whole mass that each component represents. The weighted values of such properties as surface area, site density, and so on, are then added to determine a value for the natural composite. Such a "weighted building block" approach has been explored by Honeyman (1984) and Altmann (1984). More work on various types of natural solids will be required to evaluate the applicability of the linear summation of primary components. The other approach is to measure the "average" properties of the bulk media such as "average" site density or "average" intrinsic acidity constants.

Use of the surface complexation model also requires access to an ion-speciation code such as PHREEQE, MINTEQ, or EQ3. If the thermodynamic data for a particular radionuclide is suspect or missing in the ion-speciation code, the activity of adsorbing species cannot be determined. In addition, systematic batch adsorption experiments that include complete solution analyses must be performed to determine the necessary adsorption constants corresponding to the K terms in Equations (22) and (23).

The need for detailed solids characterization appears to be another problematical aspect to be overcome before most experimenters involved in radionuclide adsorption studies will become interested in surface complexation concepts because they generally are not experienced in solids characterization. With the increasing use of ion-speciation codes and with the elucidation of the applicability of either the building block or "bulk average" approaches, then facile techniques to properly perform the detailed solids characterization will become the key to acceptance. Work is needed to evaluate the usefulness of current techniques to characterize pure mineral surfaces on natural solids. As a corollary, it is necessary to discover whether natural systems can be dissected into their individual pure minerals and amorphous coating components without significantly altering their adsorption properties.

Conceptually, the surface complexation model is the most elegant and comprehensive adsorption theory available. Its explicit accommodation, based on theoretical principles, of solid characteristics (site density, electrostatics), and of the effects of pH and solution characteristics (ionic strength effects, speciation effects, redox effects, etc.) is a persuasive reason to endorse further study. The mathematical expressions are compatible with and readily included in thermodynamic geochemical computer codes (e.g., MINTEQ, MINEQL) referenced earlier so that the processes speciation, complexation, solubility, redox, and sorption-desorption can be treated simultaneously as happens in the natural system.

At present only a few attempts have been made to incorporate surface complexation adsorption models into transport codes. The same requirements discussed for the mass action conceptual model apply. That is, the transport model must track other species and elements besides the radionuclide of interest and the solution algorithms must be very robust to accommodate the highly nonlinear nature of the adsorption equations. The surface complexation conceptual model further exacerbates the convergence problem in that it requires that the charge electroneutrality and charge-potential constraints identified in Figure 1 be satisfied as well as the various mass action equations (with electrostatic terms) such as Equations (20) through (24). Murali et al. (1981) discuss some convergence problems when modeling the adsorption of phosphate onto goethite. Murali et al. further imply that the simulation of transport is not easily performed using models that include electrostatic constraints.

Recent attempts at coupling a surface complexation adsorption model with transport codes have relied upon simplifications such as setting the electrostatic terms as constants (e.g., Jennings et al. 1982 and Miller et al. 1983) or relying on the constant capacitance model and a fixed system pH (e.g., Cederberg et al. 1985). Further, these types of transport codes inevitably are illustrated on one-dimensional transport problems although the authors usually remark that there are no conceptual problems to converting to multidimensions. There may in fact, currently, be practical problems such as computer storage limitations and excessive run times.

#### 4.0 DISCUSSION OF ISSUES

In this section, I will briefly discuss the issues that were listed in the introduction. I will draw on the material presented on terminology and conceptual models as well as opinions that I have formed during experiences as a member of teams that have performed numerous nuclear waste disposal safety assessments. My experience is not exhaustive and thus my opinions should be subject to scrutiny. Therefore, I solicit comments from other workers on the incorporation of adsorption, or more generally, retardation processes into transport codes used in safety assessment analysis for the disposal of hazardous wastes in geologic media.

##### 4.1 Adequacy of the Distribution Ratio Concept

Each of the conceptual adsorption models, from the simple constant  $R_d$  model to the comprehensive surface complexation model, rely upon the experimental determination of distribution ratios for the amount of radionuclide bound to the solid to the amount of radionuclide remaining in solution. That is, the basic measurement performed to quantify adsorption for each conceptual model is the distribution ratio,  $R_d$ . What differs among the conceptual models is the degree of system characterization, and thus system variability that can be explicitly accommodated. As discussed in Sections 2 and 3, adsorption of a particular radionuclide is determined or controlled by many characteristics or attributes of the system under study. Therefore, any generalized adsorption model must be capable of accommodating the dependency of the distribution ratio on the system parameters (i.e., rock, sediment, groundwater and radionuclide attributes). For the experimentalist, the use of the more sophisticated adsorption models requires more time spent measuring other attributes of the solution, the rock or sediment, and the radionuclide in their experimental system. It is obvious that care should be taken in any adsorption experiment to facilitate solution and solid separation prior to measurement of the distribution ratio. Because the more elegant conceptual models require more characterization, the experimentalist usually becomes more aware of the conditions occurring in the experiments, and by controlling some variables, improves the reproducibility and the accuracy of the resulting distribution ratio. The experimentally determined distribution ratio will remain the backbone of conceptual adsorption models, but the ratio will also remain sensitive to the many other parameters discussed. Until the variation of such parameters as pH, complexing ligands, Eh, solid surface area, and mineral composition, in experimental systems is known, wide ranges of distribution ratios for

radionuclides should not be construed as evidence that the  $R_d$  approach is flawed. What such variation means is that, in a variable geochemical environment, a more systematic study is required to quantify the variability of  $R_d$  with system parameters. Furthermore, once the variability is quantified, it should be incorporated into transport codes, either explicitly or implicitly.

#### 4.2 Adequacy of the Constant $R_d$ or Constant Retardation Factor in Transport Codes

A large percentage of overall safety assessment exercises to estimate the effects of nuclear waste disposal on the environment rely upon the constant  $R_d$  distribution and thus constant retardation factor,  $R$ , [see Equation (2)] to describe nuclide migration potential. As discussed throughout this paper radionuclide adsorption is influenced by many attributes of the system and can vary significantly in differing environments. Therefore a constant  $R_d$  value should be expected only in cases where all the attributes of the rock, sediments, groundwater, colloids and dissolved radionuclides remain fixed.

There are two instances when the use of a constant  $R_d$  retardation approach is technically defensible. The first instance is when the groundwater, rock and sediments along the hydrologic flow path are in fact homogeneous (constant in composition). For some disposal sites it may be possible to segment the flow path into a discrete number of zones where geochemical conditions are considered relatively constant in each zone. Each zone would then be assigned a unique  $R_d$  value for each radionuclide based on empirical studies on materials that have the same attributes as those for the materials in the zones.

The second instance when the use of a constant  $R_d$  approach is defensible is for bounding calculations. Many of the published overall safety assessment exercises are considered as bounding, scoping, preliminary or worst case analyses. For such exercises it is defensible to select a constant  $R_d$  value that is representative of the values found on materials from the geologic setting. Typically an  $R_d$  value that represents a minimum value observed in experiments is chosen for worst case or conservative analyses. Often for deep geologic disposal the path length of concern and flow rate are so long and so slow, respectively, that a small  $R_d$  value is adequate to prevent enough activity to reach the biosphere to be considered hazardous. For example, if the travel time for water is sufficiently long that a radionuclide with a half-life of  $10^4$  years would decay to miniscule levels if the distribution ratio was 10 ml/g, then it is of little concern if experiments on the radionuclide yield  $R_d$  values that consistently vary over the range 100 - 10 000. This situation often occurs and needs to be put in perspective. The experimenter may be quite concerned that he can not explain why the  $R_d$  for a specific radionuclide varies between 100 and 10 000 ml/g in seemingly identical experiments. Yet if he can show on numerous repetitions of the experiment that the value is always above 10 ml/g it is of little concern to the overall safety assessment calculation. There is little need for concern as long as the  $R_d$  value is greater than 10 the travel time is so large that the radionuclide decays to innocuous levels.

#### 4.3 Unexplained Variability in $R_d$

Much of the debate on variability of  $R_d$  values is of no consequence to the bounding safety assessment calculations for the reason just presented. Variability in  $R_d$  values for a given radionuclide usually occurs for sparingly soluble and redox-sensitive actinides and group VII A and VIII A fission products (e.g.,  $^{99}\text{Tc}$ ,  $^{106}\text{Ru}$ ). I suggest that much of the observed variability reflects the fact that solubility controlled retardation reactions (precipitation) are controlling the fate of these radionuclides. For systems where solubility processes are controlling, the observed distribution ratio is extremely sensitive to the initial mass or radioactivity of the nuclide present. That is, the equilibrium concentration of the radionuclide in solution is fixed and the amount of radionuclide that appears to adsorb is very sensitive to the initial mass present. Further, for precipitation reactions there is no limit or maximum capacity to the amount of radionuclide that can be "adsorbed" on the solid phase. Thus, the distribution ratio,

$$R_d = \frac{\text{amount on the solid phase}}{\text{amount in solution}}$$

can become very large and appear quite variable because the numerator can be very large and the denominator very small. A small change in the measured solution concentration (denominator) makes a very large change in the calculated  $R_d$  value when the denominator is small. For sparingly soluble radionuclides a precise measurement of the solution concentration is difficult to obtain thus the resultant  $R_d$  can be quite variable.

There is one circumstance when unexplained variability in  $R_d$  values and the use of the low representative  $R_d$  value may not lead to conservative transport calculations. Unexplained variability in the  $R_d$  value for seemingly identical experiments should be considered as a danger signal especially at  $R_d$  values in the range 0 to 50 ml/g or below values where precipitation reactions can be ruled out. Most  $R_d$  determinations rely upon batch equilibration methods and measure only the total amount of radionuclide distributed between the solid and solution. In cases where two or more distinct species are present [e.g.,  $\text{TcO}_4^-$  and  $\text{TcO}_2$ ,  $\text{Ru}^{3+}$  and  $\text{RuO}_4^-$ ,  $\text{PuO}_2^+$  and  $\text{Pu}(\text{OH})_4^0$ ,  $\text{UO}_2^{2+}$  and  $\text{UO}_2(\text{CO}_3)_3^{4-}$  or,  $\text{Co}^{2+}$  and  $\text{Co-EDTA}^{-1}$ ] for a given radionuclide an  $R_d$  value based on the total distribution can be misleading. The above examples of pairs of species that might coexist in groundwaters would likely exhibit very distinct adsorption tendencies as the overall charge and size of the species differ significantly. For example, assume that a radionuclide tracer solution with two species that do not rapidly interchange, A and B, present as a 50%-50% mixture, is used in a batch adsorption experiment where 1 gram of rock is contacting 20 milliliters of solution. Also assume that the individual species exhibit  $R_d$  values of 1 and 100 ml/g respectively. The observed  $R_d$  for the mixture would be 15.7 ml/g. Yet when the solution is percolated through a column of the rock as a pulse followed by flushing with groundwater, I would expect to see a peak representing Species A break through the column at a pore volume equivalent to a  $R_d = 1$  and another peak representing Species B at a pore volume equivalent to a  $R_d = 100$ . A computer prediction based on the measured  $R_d$  value would break through at a pore volume equivalent to  $R_d = 15.7$ . Depending upon the column bulk density and porosity [see Equation (2)], the velocity of the water, and radionuclide half-life, the activity versus time emanating from the actual column likely would exceed that predicted and certainly would show some release much earlier than the predictions. Therefore, when experimenters suspect that two species with significantly different  $R_d$  values are present in a groundwater, they should not rely solely on a one-batch equilibration experiment in which only total radioactivity remaining in solution and that adsorbed on the solid are measured.

To identify multiple species with significantly different  $R_d$  values, the experimentalist should perform an additional experiment. Two choices are (1) to perform a second batch equilibration on a "clean" sample of rock using the effluent solution from the first test or (2) perform an independent flow-through column test with the radiotraced groundwater or waste package leachate.

The former test, the repeat batch equilibration, is likely the simplest and least time consuming. If most of the highly adsorbing species (e.g., Species B in our example), adsorbed in the first test, then the observed  $R_d$  in the second test should be much less than the 15.7 ml/g calculated in the first test because the activity that remained in the solution is mainly Species A. Species A would adsorb slightly resulting in an observed  $R_d$  value close to 1 ml/g. On the other hand, as discussed in Section 3, trace element adsorption often shows more favored adsorption as the mass of the trace element decreases, thus even if the system under study included only one species with a  $R_d$  value of 15.7, the second equilibration might yield an  $R_d$  value greater than 15.7 ml/g. Thus the differences in the two systems, single species versus two species, should be large enough to allow identification even in experiments that exhibit variability in  $R_d$ .

The flow-through column test approach is likely more expensive, time consuming and difficult. On the other hand a flow-through experiment simulates the coupled chemical reaction and hydrologic transport process. In a flow-through experiment the occurrence of other potentially adverse processes can be explored. For instance if more rapid than expected breakthrough is observed, kinetic considerations, colloid transport, dispersion or some other mechanism might need to be considered. Alternately, the flow-through test can also identify beneficial processes, such as irreversible retardation, matrix diffusion, or physical filtration, from cases when the mass eluted and time of elution are much lower and longer than expected.

Column experiments are difficult to perform and interpret. I suggest that experimentalists consider the guidance offered in publications such as Serne et al. (1983), Relyea (1982) and Failor et al. (1982). Proper design of the experiment is very important in allowing realistic interpretations to be made from the data. As no standard experimental protocol has been adopted it is critical to consider the view points expressed by experienced practitioners.

#### 4.4 Status of Incorporation of Sophisticated Adsorption Models into Transport Codes

The following is a brief summary of my opinion on this subject and some recommendations for future activities to aid in closure of adsorption issues.

Conceptual adsorption models based on theoretical constructs such as mass action and surface complexation consider explicitly many of the attributes that control adsorption but still usually require that adsorption sites be considered homogeneous and of constant energy. Extensions to multiple sites with variable binding energies complicate already complex mathematical equations and would require even more detailed system characterization. Natural adsorbents, rocks, sediments and amorphous coatings are not easily modeled or characterized. Detailed adsorption models have been incorporated into geochemical reaction codes (but not coupled transport codes) and appear to simulate observed distributions of trace solutes in selected "beaker" experiments in which one simple adsorbent is considered.

I feel that the weakest links in the application of conceptual adsorption models in geochemical reaction codes to address nuclear waste disposal are the lack of the adsorption constants,  $K$  in Equations (12), (13), (22) and (23), for important radionuclides and the need to extend the models such that they can accurately describe adsorption onto heterogeneous natural adsorbents (e.g. rocks and sediments). Two methods have been proposed to characterize natural solids. The first approach splits the solid into its pure components, calculates adsorption onto the individual components and finally sums the components' contributions weighted by their mass fraction or surface area fraction in the original substrate. The second approach determines an "average" value for all the necessary adsorption parameters for the bulk adsorbent. Experimenters should explore both approaches to delineate whether acceptable models can be developed for natural solids germane to nuclear waste disposal.

It appears to me that the linking of detailed chemical reaction codes with hydrologic codes in order to simulate radionuclide transport is not practical at the present time for most safety assessment exercises. The linking necessitates large computer storage, excessive run times and robust numerical solution algorithms. Secondly the necessary input data such as the adsorption constants,  $K$ , are not readily available for important radionuclides on adsorption substrates of interest.

As most current performance assessment exercises are being performed as bounding or sensitivity studies I suggest that less detailed chemical reaction models can be effectively used. Near term activities should follow two thrusts, computer sensitivity studies and experimental sensitivity studies.

Computer activities should concentrate on sensitivity analysis of the overall system performance. A reasonable range for all parameters such as Darcy velocity, container degradation rate, waste form release rate, and path length to the biosphere should be chosen. Then, using some sensitivity analysis scheme, values for these parameters should be combined in transport analyses to determine what range



of retardation factors are necessary to assure that radionuclides do not reach the biosphere at concentrations that exceed standards.

A companion laboratory activity is to perform adsorption experiments on important radionuclides using a reasonable range of groundwater compositions, radionuclide contents and adsorbent types. This seemingly simple task of gathering data to delineate the probable range of  $R_d$  values for each important radionuclide that might be expected at each disposal site would greatly clarify the issue on how important it is to abandon the simple constant  $R_d$  model. The experimenters should strive to perform experiments that are not biased by precipitation processes that often occur as artifacts of adsorption experiment methodology. For instance, realistic tracer concentrations must be used instead of choosing concentrations that facilitate easy counting. Further, if the system is well characterized several of the conceptual models discussed in Section 3 can be used to describe or interpret the data. The observed range in the experimental adsorption data can then be compared with the range generated by the computer sensitivity exercise. If the observed experimental  $R_d$  values lie within or are larger than the range of values necessary to assure no hazards in the computer sensitivity then the element will likely not need further study provided future circumstances do not require changes in the ranges of key variables used in the sensitivity studies. If the observed experimental  $R_d$  values are lower than the values required to assure no hazard, based on the computer sensitivity studies, then a potential problem exists that requires resolution.

To lessen the criticisms of recent performance assessment efforts that use the constant  $R_d$  approach for radionuclide migration estimates, I recommend that some discussion be presented in each report. The modelers should explain the intent of their exercise and attempt to assess the impact of using the constant  $R_d$  assumption on the results. Where data are available, safety assessment modelers should explore the incorporation of one of the other adsorption conceptual models into their transport codes. If data are not available, the modeler could still attempt to incorporate some of the other adsorption models into their codes and test them with hypothetical data. Once it is clear that the codes are functional, the modelers could request that the experimenters who supply  $R_d$  data start reporting data in a form compatible with the chosen adsorption model.

Finally, I suggest that separation of solubility-precipitation processes from adsorption processes in both the conceptual models and transport codes may clarify migration estimates. I feel this separation may also remove much of the variability in adsorption  $R_d$  values. It may require that much of the experimental  $R_d$  data available be rejected because of the confounding and biasing effects of precipitation. From a practical standpoint it might be appropriate to rely entirely upon a solubility constraint for such sparingly soluble elements as the reduced valence states of the actinides. That is, after solubility constraints are invoked the solution concentrations may be lower than detection limits such that adsorption experimentation is not feasible. If the solubility constraint allows a solution concentration much lower than permissible levels there will be no health consequence or need to rely upon adsorption in safety assessments. It is likely that adsorption would still occur but measurement would not be possible nor necessary for performance assessment needs.

The above suggestions address performance assessment needs from the "overall systems" perspective. There will always be the need and should always be support for detailed mechanistic studies. Detailed mechanistic studies that elucidate controlling physicochemical processes are necessary to enhance the credibility of long-term performance assessment predictions or estimates. The two needs, improved systems performance assessment and improved understanding of processes, require different viewpoints and likely require distinct approaches. Both activities require support and the two disciplines should strive to communicate their findings and share their respective endeavors with the objective of someday working on a common goal—a sophisticated, linked, chemical reaction/hydrologic mass transport conceptual model and code.

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