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USE OF THERMODYNAMIC SORPTION MODELS IN REACTIVE TRANSPORT MODELING: ADVANTAGES FOR U.S. NUCLEAR REGULATORY COMMISSION LICENSEESAND STAFF AND AREAS OF RESEARCH

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ABSTRACT

Staff of the U.S. Nuclear Regulatory Commission (NRC) use environmental models to evaluate the potential release of radionuclides into the accessible environment from sites containing nuclear materials. In most models used by the NRC, reactions between radionuclides and subsurface solids are modeled with a distribution coefficient, or K_d, that describes a constant proportion between the concentration of a radionuclide in the groundwater and the concentration of the radionuclide associated with the subsurface solids. Because the chemical reactions that cause the attachment of radionuclides to solids can be sensitive to water chemistry and subsurface mineralogy, generic literature ranges of K_d often span two or more orders of magnitude. Uncertainty in K_d values has been identified as a major source of uncertainty in dose analyses. Recently developments have been made in the application of Thermodynamic Sorption Models (TSMs) to natural sub
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INTRODUCTION

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Staff of the U.S. Nuclear Regulatory Commission (NRC) use environmental models to evaluate the potential release of radionuclides into the accessible environment from sites containing nuclear materials. In most models used by the NRC, reactions between radionuclides and subsurface solids are modeled with a distribution coefficient, or K_d, that describes a constant proportion between the concentration of a radionuclide in the groundwater and the concentration of the radionuclide associated with the subsurface solids. Because the chemical reactions that cause the attachment of radionuclides to solids can be sensitive to water chemistry and subsurface mineralogy, generic literature ranges of K_d often span two or more orders of magnitude. Uncertainty in K_d values has been identified as a major source of uncertainty in dose analyses. Recently developments have been made in the application of Thermodynamic Sorption Models (TSMs) to natural subsurface media. Because TSMs represent sorption by modeling the chemical reactions responsible for attachment of radionuclides to natural surfaces, they may provide a more realistic method of modeling reactive transport of radionuclides. In addition, they also may provide an economically efficient method for characterizing sorption variability at complex sites. The objective of this paper is to describe the opportunities that may be afforded to NRC staff and licensees by the recent advances in thermodynamic sorption modeling as well as projects that are being pursued or considered by the NRC to develop the use of TSMs.

INTRODUCTION

Environmental models are used by staff of the United States Nuclear Regulatory Commission (NRC) to assess potential releases of radionuclides into the accessible environment. Radionuclide transport in the subsurface is an area of interest because, at many sites, an evaluation must be made of the potential for humans to be exposed to radionuclides by consuming contaminated groundwater or by consuming plants or animal products that have been exposed to contaminated groundwater. Chemical reactions between contaminants and subsurface media can modify the transport of some species significantly as compared to the transport of non-reactive species that are subject only to advection and dispersion. Because the uncertainty in parameters used to quantify reactive transport can contribute significantly to uncertainties in the results of dose analyses [1, 2], the NRC participates in efforts to improve capabilities to model reactive transport of contaminants in the subsurface.

Many simplified environmental models represent the effects of all chemical reactions that affect contaminant transport with the approximation that the concentration of a contaminant in the aqueous phase is proportional to the concentration of the contaminant sorbed to the solid phase. The proportionality constant, called a partitioning coefficient, distribution coefficient, or simply a K_d, is given by:

$$K_d = \frac{q}{c}$$

where q represents the amount of contaminant adsorbed per mass of solid and c represents the aqueous concentration of the contaminant. K_d values typically are used to calculate retardation coefficients, which are used to estimate the effect of sorption on the net velocity of radionuclides. The retardation coefficient, or R_d, is determined by:

$$R_d = 1 + \frac{\rho \cdot K_d}{\theta}$$

where ρ represents the bulk density of the soil and θ represents its water content. The effect of sorption on the net velocity of a radionuclide is approximated as:

$$v_r = \frac{v_w}{R_d}$$

where v_r is the net velocity of the radionuclide and v_w is the net velocity of the groundwater.

K_d values can be a significant source of uncertainty in dose assessments when modelers lack site-specific information about radionuclide sorption and instead use large generic K_d ranges from the literature [1, 2]. In addition, use of a single range of K_d values to represent sorption in all areas of a complex site neglects the potential for spatial correlations in sorption characteristics and can qualitatively misrepresent contaminant transport [3]. In addition to the limitations imposed by a lack of site specific data, there are limitations inherent to the use of the K_d model itself [4-6]. These limitations include an inability to represent the effects of strong binding sites and site saturation as well as a limited ability to represent the effects of competition for binding sites. Perhaps most importantly, use of an empirical K_d or generic range of K_d values limits a modeler's ability to relate variations in site mineralogy or chemical characteristics to predicted changes in sorption characteristics.

Recently research has been done to explore the possibility of using Thermodynamic Sorption Models (TSMs) in conjunction with contaminant transport models to predict the effects of sorption reactions on contaminant transport. TSMs are similar to other thermodynamic chemical speciation models and are referred to as sorption models because they include reactions between aqueous compounds and the surfaces they contact. In a TSM, adsorption is represented as an equilibrium chemical reaction between a dissolved compound and a reaction site on a surface. A molar balance is maintained on the total number of reactive surface sites, and reactions between the dissolved compounds and surface reaction sites are described with thermodynamic stability constants, or mass action constants. Most chemical reactions that affect radionuclide transport, such as ion exchange, surface complexation, precipitation/dissolution reactions, and aqueous reactions that affect radionuclide speciation, can be included in a TSM.

While much research has been done to investigate adsorption of radionuclides onto pure mineral phases, extension of such models to natural materials is difficult because 1) a natural mineral

assemblage can have a multitude of different binding sites corresponding to several site types on each of several minerals in the assemblage and 2) the interaction between electrical surface potentials on different component minerals is not well understood. TSMs used to predict adsorption on natural mineral assemblages may be described as using either a component additivity (CA) or generalized composite (GC) approach [7]. The term "component additivity" refers to a model in which each of the significant chemical reactions between aqueous chemical species and adsorption sites on each of the minerals that compose the natural particle are modeled. Inputs to a CA model include site-specific information about the relative abundance of minerals in the natural material and generic literature values of stability constants that describe aqueous species binding to pure phases of the minerals present in the natural material. The term "generalized composite" refers to a model in which site-specific adsorption data are used to develop site-specific stability constants that characterize radionuclide adsorption onto one or two generic sites that represent the average reaction between an aqueous compound and binding sites on the composite mineral. Because GC models are calibrated to site-specific adsorption data, they often are more successful in predicting sorption behavior than CA models [8].

TSMs offer solutions to some of the problems inherent to the use of a K_d, and also may offer a more cost efficient means of characterizing sorption behavior at complex sites. In addition, TSMs offer a sound method for relating variability in site mineralogy or chemical conditions to changes in sorption behavior, which can be useful in sensitivity and uncertainty analyses. The objectives of this paper are to describe the potential utility of TSMs to NRC licensees and staff and to describe NRC projects designed to develop the utility of TSMs.

Current Practice

Almost all performance assessment (PA) analyses submitted to the NRC represent reactive transport with a uniform K_d. The primary advantage of the K_d approach is that it is computationally simple to incorporate a retardation coefficient calculated with a K_d into the advection-dispersion equation. Two additional advantages of the linear K_d approach are that 1) standardized tests have been developed to measure K_d values and 2) ranges of K_d values relevant to various soil types and radionuclides are available in the literature. However, because adsorption often is sensitive to site-specific water chemistry and soil mineralogy, literature ranges of K_d values often are large. For example, when unconstrained by soil type, the range of K_d values for many radionuclides is four or five orders of magnitude [4]. Within a soil type, the range of K_d values for many radionuclides often spans two or three orders of magnitude [9].

NRC decommissioning guidance [10] indicates two acceptable methods to determine K_d values to be used in a site PA model. The simplest, and most common, approach is to select a conservative value from a compilation of K_d values (e.g., [9, 11]). For PA analyses in decommissioning plans, the more conservative of the 25th or 75th percentile of the appropriate K_d distribution used in the probabilistic version of RESRAD [12] is acceptable without further justification [10]. If soil characterization data are available, a range of K_d values based on literature values for the radionuclide and soil type can be used.

If a licensee determines that a K_d value based on generic data is too conservative and that it is worthwhile to obtain the data necessary to support the choice of a more realistic value, K_d values

can be measured with groundwater and subsurface soil samples taken from the site. The NRC's consolidated decommissioning guidance [10] and low level waste (LLW) PA methodology [13] suggest several standard methods for the measurement of site-specific K_d values (i.e., ASTM methods D4319, D4646, and D4874). If the experiments are conducted with a range of experimental conditions expected at the site (e.g., partial pressures of CO_2 (PCO_2) and pH), a range of K_d values can be based on the range of chemical conditions expected at the site. This technique can be used to limit the range of K_d values to the uncertainty due to site heterogeneity and lack of knowledge about future chemical conditions of the site, rather than the entire range due to lack of knowledge about the interaction between the radionuclide and host material.

If a licensee determines that it is worthwhile to represent the spatial variability of K_d values, the results of adsorption experiments conducted with a range of chemical conditions may be used to determine empirical relationships between K_d values and important chemical parameters. The empirical relationships can then be used in a "parametric K_d model" [4], in which different K_d values are computed for different areas of the site based on site-specific chemical information. However, because of the effort required to derive the empirical relationships between K_d and the relevant chemical parameters, as well as the computational capabilities required to evaluate K_d in each cell of a transport model, this technique rarely is used [4].

The subject of complex geochemical models is not discussed in detail in current guidance for PA analyses of sites undergoing decommissioning or LLW sites. The NRC's decommissioning guidance [10] states that licensees may use geochemical speciation models (e.g., MINTEQA2 [14] or EQ3/6 [15]) to quantify geochemical mechanisms that affect transport, but does not describe the use of such geochemical codes to determine an appropriate range of K_d values. Similarly, the NRC's methodology for PA analyses for LLW sites indicates that complex geochemical models may be used by the staff to support the use of specific parameter ranges, but does not discuss specific uses of complex geochemical models [13].

More complex groundwater transport modeling is possible at Uranium Mill Tailings Remedial Action (UMTRA) sites as compared to most sites undergoing decommissioning because UMTRA sites typically have a relatively large number of monitoring wells and historical information about plume migration. One can estimate K_d values for reactive contaminants by using the K_d values as fitting parameters to match historical concentration data for each reactive component with the predictions of a transport model that has been calibrated to site-specific hydrologic data. The NRC standard review plan for the review of reclamation plans for mill tailings sites [16] encourages the use of reactive transport codes that are coupled to chemical speciation codes (e.g., PHREEQC [17]). Although other approaches are more common, coupled reactive transport models have been used to support applications for Alternate Concentration Limits (ACLs) for UMTRA sites. For example, although a K_d approach was used for the primary transport prediction made in support of ACLs at the Rio Algom Mining Corporation's Lisbon, Utah, site, the coupled reactive transport code PHREEQC was used to evaluate the potential remediation strategy of injecting hydrogen sulfide into the aquifer to cause the reduction and precipitation of uranium [18]. More extensive use of a coupled geochemical reactive transport model was made to support the Umetco application for ACLs for the Gas Hills, Wyoming, site, in which PHREEQC was the primary geochemical model used to predict a reduction in contaminant concentrations between the point of compliance and point of exposure [19].

Utility and Implementation of Thermodynamic Sorption Models

Utility

The deficiencies of the common approach to modeling reactive transport can be grouped into those that result from a lack of site-specific information and those that result from inherent limitations in representing complex chemical behavior with a single parameter. TSMs currently do not provide a substitute for site-specific sorption information. However, TSMs may provide a method to characterize sorption behavior at a complex site more economically. In addition, thermodynamic sorption modeling is a tool that can be used to test the significance of different processes or potential changes in site characteristics to radionuclide transport.

Uncertainty in K_d values can dominate the uncertainty in doses predicted by PA analyses because of the enormous range of many generic K_d distributions [1, 2]. In cases in which site-specific adsorption measurements are either physically or economically infeasible, an uncalibrated CA approach may offer a basis for predicting adsorption characteristics or limiting the range of literature K_d values. However, the ability of uncalibrated CA TSMs to reduce uncertainty in sorption predictions is at a formative stage. A comparison of GC and CA approaches recently indicated that, in some cases, uncalibrated CA models over or underestimated measured K_d values by more than an order of magnitude [8]. CA models are susceptible to error because they are not calibrated with the results of adsorption tests conducted with site-specific samples.

While both calibrated GC [3, 20, 21] and uncalibrated CA [22] models have been shown to predict contaminant adsorption successfully in specific cases, in general, the predictions of calibrated GC models agree with measured K_d values better than the predictions of CA models [8]. Because TSMs provide a theoretical basis for predicting the relationship between chemical conditions and K_d values, it may require fewer adsorption experiments to calibrate a GC model than it would to characterize a complex site with a series of K_d measurements or to develop empirical relationships between chemical parameters and measured Kd values, as in the parametric K_d model described by the EPA [4]. The relative cost of using conservative literature values of K_d, a series of K_d measurements, a calibrated GC model, or a CA model in conjunction with conservative assumptions will depend on the complexity of the site.

The cost savings associated with not characterizing a site and treating K_d as uniform in all areas of a site must be compared to the potential cost savings of implementing less conservative criteria developed from a more realistic representation of reactive transport at the site. At a site where subsurface chemical conditions are uniform and are not expected to change with time or vary substantially in space, a single K_d value may be sufficient to represent reactive transport at the site. However, if substantial variability exists, it may be economically advantageous to characterize the site sufficiently to support a more realistic model. For example, the results of experiments with two-dimensional groundwater transport models indicate that spatial heterogeneity in K_d values can decrease the predicted peak dose as compared to the dose predicted by models that represent reactive transport with a uniform K_d value by more realistically representing the effects of dispersion [23].

There are two main advantages of using TSMs to select K_d values as compared to simply performing multiple site-specific measurements of K_d values for a site. The first is that, once a GC TSM has been calibrated with several site-specific measurements, the calibrated TSM provides a scientifically sound basis for estimating K_d values in new sample locations based only on chemical characteristics of water samples rather than the results of new adsorption experiments. Thus, fewer adsorption experiments may be required to calibrate a GC model to characterize adsorption at a complex site than to make enough K_d measurements to characterize the site. The second advantage is that once the dependence of K_d on subsurface chemical characteristic is understood, it is easier to quantify the uncertainty due to potential changes or uncertainty in chemical conditions. For example, after a GC model has been calibrated, it could be used to predict the effect of a change in pH or PCO_2 on contaminant sorption. This strategy recently has been implemented by contractors for the Department of Energy who developed a TSM to describe uranium sorption at the Hanford, WA site to provide insights into which chemical and mineralogical characteristics most influence uranium transport at the site [24].

In addition to being used in sensitivity analyses or to establish appropriate ranges of K_d values, TSMs may be coupled directly to transport codes. If a TSM is coupled to a transport model, the extent of contaminant partitioning between the aqueous and solid phases is recalculated for each time step in each cell of the transport model based on the chemical conditions in the cell during the time step. Direct coupling of a TSM to a transport code can be used to represent sorption that is sensitive to temporally varying chemical conditions, in which case a model that uses a constant K_d may not be able to represent contaminant transport accurately. For example, results of recent NRC-funded research at the Naturita, Colorado, UMTRA site indicate that a transport code coupled to a TSM predicted higher onsite well-water concentrations than a model that used a constant K_d [3]. When the same values of biosphere parameters (e.g., water ingestion rate, dose conversion factors) were used in a PA model of each case, the predicted peak dose based on the results of a coupled geochemical transport model was 24% greater than the predicted peak dose based on a model that used a nominally conservative K_d value of 0 mL/g, and 43% greater than the predicted peak dose based on a model that used a nominally more realistic K_d value of 2.7 mL/g [3, Table 11.1]. The coupled geochemical transport model predicted a higher peak concentration because it predicted chemical conditions that varied in time as well as in space, while the model that used a constant K_d could not predict the drop in K_d that caused the higher peak uranium groundwater concentration. The implication of this result is that a model based on a constant K_d value may yield non-conservative results in some cases if chemical conditions vary with time as well as space.

Additional research is needed to determine when the predictions of a transport code coupled to a TSM are likely to be significantly different than the predictions of a constant K_d model. Temporally varying chemical conditions may have a significant influence on contaminant transport at sites where the natural subsurface characteristics have been altered significantly, such as UMTRA or in-situ leach sites, or sites at which the magnitude and extreme chemical characteristics of the contaminant plume itself may impact groundwater conditions. At Naturita, the changing chemical conditions were attributable to a moving plume of alkalinity that was introduced by disposal of tailings from carbonate leaching [3]. Although coupled reactive transport codes currently are not combined with PA models because of the computational resources required to run a coupled transport code many times to support a probabilistic PA

assessment, NRC licensees and reviewers could use reactive transport codes independently of probabilistic PA models to determine if a K_d approach is likely to yield non-conservative results.

While using TSMs can reduce the range of K_d values that needs to be included in a performance assessment, the limitations inherent in using a constant and uniform K_d are not addressed if a uniform K_d model ultimately is used to represent reactive transport in a PA analysis. For example, spatially varying adsorption must be modeled with a two-dimensional reactive transport code or by breaking the transport path into units characterized by their geologic properties and determining appropriate K_d values for each unit. Similarly, the effects of non-linear sorption characteristics are accounted for if a TSM is coupled directly to a transport code, but are not accounted for if a TSM simply is used to select a more appropriate range of K_d values.

Implementation

Although TSMs coupled to reactive transport models recently have been used to support ACL applications for UMTRA sites, direct coupling of TSMs with transport models in probabilistic PA analyses is not yet believed to be computationally feasible [25, 26]. Recent reports by the NEA emphasize the use of TSMs to determine better ranges of K_d values to be used in PA models [8, 27].

There are different approaches available to use K_d values selected with TSMs in PA analyses. The simpler approach is to run a TSM with input parameters representing the range of geochemical conditions expected at the site and to use the results to establish a range of K_d values for each radionuclide to be used in the PA analysis (e.g., as in [28]). One complication of this approach is that the K_d values for different elements must be correlated to limit selection of non-realistic combinations of distribution coefficients. For example, if the distribution coefficients were not correlated, in a single realization a high sorption coefficient, corresponding to a neutral pH and low PCO_2, may be selected for one radioelement while a very low distribution coefficient, representative of a low pH or high PCO_2, is selected for another element. Although correlating distribution coefficients limits sampling of such non-physical realizations, a simple correlation cannot always represent accurately the potentially complex relationship between the adsorption coefficient of one radionuclide and another, especially if the adsorption characteristics of the two radionuclides do not have the same dependence on pH or complexing ligands such as carbonate, phosphate, or sulfate.

One may refine this method by using TSMs to generate a response surface for each element that summarizes the effect of the most important parameters on the predicted adsorption of the element. For example, Turner et al. [25] used a TSM to generate response surfaces for K_d values for several radioelements based on pH and PCO_2. For each realization, pH and PCO_2 values were chosen randomly, and the appropriate values of K_d for each radioelement were selected from the response surfaces. The advantage of this approach is that it relates the K_d values to chemical conditions, facilitating an understanding of the sensitivity of model results to chemical conditions, and automatically includes only physically reasonable combinations of K_d values for various radionuclides. One limitation of this approach is that it can be difficult to represent the impacts of several parameters at once. For example, in the demonstration of the technique by

Turner et al. [25], the effects of competition from major cations (e.g., Ca^{2+} and Mg^{2+}) were not included in the response surfaces.

A unique aspect of the technique demonstrated by Turner et al. [25] is that the response surfaces generated from the TSMs were generated in terms of a partitioning coefficient normalized to specific surface area, or K_a'. This procedure facilitates the use of site-specific information about soil specific surface area to generate a partitioning coefficient, or K_d value. If two- or three-dimensional hydrologic modeling is performed off-line to predict flow paths and if mineralogical information is available for different areas of the site, K_a' values can be paired with values of the specific surface area of minerals in individual flow paths to generate K_d values that reflect the effects of mineralogical heterogeneity on contaminant sorption.

Areas of Research and Development

Beneficial application of TSMs to reactive transport modeling could be enhanced by developments in several areas. Specifically, NRC licensees and staff could benefit from 1) updated guidance regarding the use of TSMs 2) integration of TSMs with software used in PA analyses 3) demonstrations of the use of TSMs to predict the mobility of a variety of radionuclides at sites with a variety of chemical and mineralogical characteristics and estimates of the costs associated with TSM development 4) use of TSMs to evaluate the significance of spatial heterogeneity, non-linear adsorption, changing chemical conditions, and other aspects of contaminant transport at complex sites and 5) further development of the scientific basis for TSMs. Projects in each of these areas that are being supported by the NRC or that are under consideration for NRC involvement are described in this section.

Development of Updated Guidance

Evidence suggests that modelers of complex sites are beginning to understand the potential benefits of using TSMs in conjunction with transport models. For example, TSMs recently have been used in ACL applications to the NRC [18, 19] and by contractors for the Department of Energy [24]. Because the NRC anticipates the submittal of other applications that use TSMs, NRC staff will be working with staff of Sandia National Laboratories (Sandia) to develop practical guidance on the use of TSMs in groundwater transport modeling.

The scope of the guidance being developed in conjunction with Sandia currently is being determined. NRC staff and licensees would benefit from a review of topics important to ensuring that a TSM leads to a realistically conservative model of radionuclide transport in the subsurface. For example, the NRC recently participated in the development of an NEA report [8] that presents a thorough comparison of the success of different approaches to model reactive transport. One major conclusion of the report is that the choice of modeling approach has a significant effect on the model predictions, but the choice typically is subjective and poorly justified. Reasons for using specific approaches, such as different ways to model ion exchange or different mathematical representations of the electrical characteristics of mineral surfaces, would be useful for NRC licensees and reviewers.

In addition, specific guidance regarding important features of a self-consistent TSM would be useful. For example, it is common practice in PA modeling to use parameter values from different sources. However, stability constants developed in a model with a certain site density or model of surface potential cannot be transferred to models that use a different site density or model of surface potential (see, e.g., [29, 30]). This type of guidance would assist new users in the correct use of TSMs.

Because of the potential appeal of a CA modeling approach to licensees wishing to minimize sampling costs, guidance regarding important features of a conservative approach to a CA model would be useful. Similarly, licensees and reviewers must understand the implications of the selection of an unrealistic surface species in a CA model, and need to have a basis for reviewing the plausibility of licensee's modeled surface species. Selection of appropriate surface complexes is an area that will require ongoing experimental research in addition to guidance development.

Software Development

The NRC supports several projects to improve reactive transport modeling in dose assessments. Because using a constant K_d approach is a reasonable way to model radionuclide transport at many sites, the NRC is supporting the development of RESRAD-Offsite [31], which will use a K_d approach to model radionuclide transport to offsite locations. At sites at which there is substantial spatial heterogeneity in mineralogical and chemical characteristics, it may be beneficial to represent dispersion more realistically than can be done with the uniform K_d approach implemented in RESRAD-Offsite. For this reason, the NRC is supporting linkage of the Framework for Risk Analysis in Multi-Media Environmental Systems (FRAMES) [33] used for PA analyses with the Army Corp of Engineers' Groundwater Modeling System (GMS) [32], which is capable of representing spatial heterogeneity in radionuclide partitioning and hydrological characteristics. In addition, NRC staff are evaluating the use of FRAMES, RESRAD-Offsite, and GoldSim [34] to predict radionuclide transport at complex sites.

The NRC also is funding two projects to develop capabilities to use TSMs. The first is the development of the program RATEQ [35] which couples a TSM with a transport model to predict contaminant concentrations as a function of space and time. The results of the model can then be input into a dose assessment tool to produce dose predictions, as was done in an assessment of the Naturita, Colorado UMTRA site [3]. The most immediate advancement of the implementation of TSMs with PA models may be made if TSMs can be included directly in performance assessment models used by NRC staff and licensees. To this end, NRC staff are cooperating with staff from Sandia to develop a TSM module for use with FRAMES. The scope of the project and capabilities of the proposed module currently are under development.

Demonstration of Applications of Thermodynamic Sorption Models

TSMs may offer a way for licensees to characterize complex sites efficiently, thereby avoiding the costs associated with making many K_d measurements to characterize a site or the costs of complying with stricter standards that can result from analyses based on conservative assumptions. For example, a GC approach may offer a way to reduce the number of adsorption measurements necessary to characterize reactive transport at a complex site by providing a

scientifically sound basis to interpolate between adsorption data points based on groundwater chemistry and soil characteristics. However, it is difficult to assess the potential cost savings associated with using a GC approach without more information about the costs of developing the model. For this reason, the NRC is considering support for an investigation of the cost of calibrating a GC model, which was proposed as a research need at the April 2004 meeting of the Working Group on Subsurface Reactive Solute Transport of the Federal Interagency Steering Committee on Multimedia Environmental Models [36].

The use of a GC approach coupled with a transport code to predict the transport of uranium at a uranium mill site has been demonstrated [3]. In addition, use of a GC approach coupled with a transport code to predict the transport of zinc in a sandy aquifer has been shown [21]. NRC staff are working with staff from the U.S. Geological Survey to provide examples of the use of TSMs with transport codes to model the transport of other radionuclides at sites with a variety of chemical conditions. Lessons learned from these examples will inform staff and licensees about the conditions under which a TSM used with a transport code is likely to be successful in predicting radionuclide transport.

Evaluation of the Significance of Spatial Heterogeneity, Non-Linear Sorption, Changing Chemical Conditions, and Other Aspects of Contaminant Transport at Complex Sites

Decisions regarding the level of detail in which a process should be modeled typically are made based on parametric sensitivity analyses and professional judgment. Because TSMs can provide a scientific basis to relate measurable chemical conditions such as pH and carbonate concentration to K_d values, they can facilitate improvements in parametric sensitivity analyses if ranges of relevant chemical parameters can be determined. In addition, TSMs could be used in the evaluation of the significance of spatial variability in chemical conditions to determine whether a uniform K_d is likely to capture the essential characteristics of reactive transport at a complex site. TSMs may be able to facilitate modeling of spatial heterogeneity because it may take fewer adsorption measurements to calibrate a TSM than it would to characterize a complex site or to develop empirical relationships between chemical parameters and K_d values, as in the parametric K_d model approach described by the EPA [4].

In addition, TSMs may be used in evaluations of the significance of phenomenon that cannot be evaluated with a K_d model. An example of this type of work is Chapter 11 of NUREG/CR-6820 [3], in which the results of modeling uranium sorption at a complex site with a calibrated GC model were compared to the results of modeling sorption with a K_d approach. In this exercise, selection of an acceptably conservative K_d value did not ultimately yield a conservative result because of temporally varying chemical conditions. Results of this study also indicated that uranium K_d values may have been reduced in some areas because of locally high concentrations of uranium, indicating that the effects of non-linear sorption may be important in some cases. Modeling experiments similar to this one would improve the professional judgment of PA modelers, who must make decisions regarding the level of complexity necessary to capture the essence of various geochemical characteristics and processes.

Advancement of the Scientific Basis of Thermodynamic Sorption Models

Several improvements in the understanding of sorption could contribute to successful uses of TSMs. Three areas for improvement are: 1) development of self-consistent surface complexation databases, 2) additional identifications of likely surface species of radionuclides under environmentally relevant conditions, and 3) increased understanding of how information relevant to pure mineral phases can be used to represent adsorption onto complex mineral assemblages.

The most widely known self-consistent database of surface stability constants is the database developed by Dzombak and Morel [30] to describe sorption onto ferrihydrite based on a generalized two-layer model of surface electrical properties. While the database includes data for many cationic and anionic species, few radionuclides are represented. Self-consistent TSM parameters for Am(III), Np(V), Pu(IV), Pu(V), Th(IV), U(VI), and C sorption onto various iron and aluminum oxides and clays calculated based on the diffuse layer, constant capacitance, and triple layer models have been provided by Turner [38]. More recently Wang and others have used a diffuse layer model to determined surface stability constants for Am(III), Pu(IV), Pu(V), Np(V), I^-, IO_3^-, SeO_3^{2-}, and TcO_4^- on various minerals [39, 40]. In addition, surface stability constants that describe adsorption of several cations, including Co^{2+}, Ni^{2+}, and Sr^{2+}, onto several manganese oxide phases, recently have been determined using a diffuse-layer model [41]. Because surface stability constants for different elements can be used in the same model only if they were developed using the same site densities and the same model of the effects of surface charge, future efforts to determine self-consistent databases of surface stability constants of species of interest to the NRC could benefit from a coordinated effort of database development. A system to assist users in selecting self-consistent sets of surface stability constants and site densities recently has been developed at the Institute of Radiochemistry, Dresden, Germany [42]. Use of this system may be evaluated by the NRC during the development of guidance for the use of TSMs.

Another area for improvement is an increased understanding of relevant surface species based on spectroscopic experiments and molecular modeling. The use of the correct surface species is especially important to the successful use of a CA model, but also could improve the implementation of GC models because correct surface species stoichiometry is more likely to lead to robust relationships with constituents in the aqueous phase. For example, if a ternary complex with Ca^{2+} is the dominant sorbing species but sorption is modeled with a species that does not include Ca^{2+}, changes in the concentration of Ca^{2+} in the aqueous phase could result in departures from modeled behavior. Spectroscopic evidence of surface species under environmentally relevant conditions is necessary because the choice of the correct surface species is not a trivial extension of the choice of more well-established aqueous speciation (see, e.g., [43]), and few experiments have been performed to determine binding constants in the presence of environmentally relevant concentrations of naturally occurring electrolytes. Thus projects that guide the choice of surface complexes formed between radionuclides present at complex decommissioning and waste sites and common subsurface minerals will allow both GC and CA analyses to be used more accurately by licensees and reviewed more effectively by NRC staff.

Currently, even when adsorption data for relevant pure mineral phases are available, CA models often produce poor prediction of adsorption onto natural minerals [8]. One reason for poor predictions of models based on the CA approach may be insufficient or inaccurate

characterization of the phases responsible for sorption of radionuclides. For example, bulk soil characterization may not differentiate between minerals on the interior of soil particles and surface coatings that can dominate contaminant adsorption. However, even if improvements in soil characterization are made, the accuracy of predictions based on a CA approach may be limited by our current understanding of the effects different minerals in close proximity may have on each other's ability to adsorb chemical species. Fundamentally, the CA approach depends on the "additivity" of contaminant sorption to different component minerals. Because minerals in individual soil particles influence the electrical characteristics of the entire surface, simple additivity may not always yield accurate predictions of radionuclide sorption. Advances in the understanding of how component minerals influence the electrical characteristics of complex particles would improve predictions of radionuclide adsorption onto natural soil media based on adsorption data from experiments with pure mineral phases.

CONCLUSIONS

Thermodynamic sorption modeling is a tool that can be used to gain insight into the factors controlling radionuclide sorption and transport and to predict the effect of variability or temporal changes in site mineralogical or chemical characteristics on radionuclide transport. In addition, TSMs may be able to provide a means to characterize radionuclide sorption at complex sites more economically, facilitating more realistic modeling of heterogeneity in chemical conditions. Because of these potential benefits, the NRC is participating in projects to develop the use of TSMs in radionuclide transport modeling. Work is underway to develop practical guidance regarding the use of TSMs in conjunction with groundwater transport models and to develop software that integrates TSMs with code used to perform PA analyses. Future work may include efforts to quantify the costs of implementing a GC model and a comparison of the utility of an uncalibrated CA approach implemented with conservative assumptions as compared to the common approach of using generic K_d values to represent sorption. Advancements in the fundamental understanding of sorption of compounds onto natural particles are expected to improve both GC and CA approaches.

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