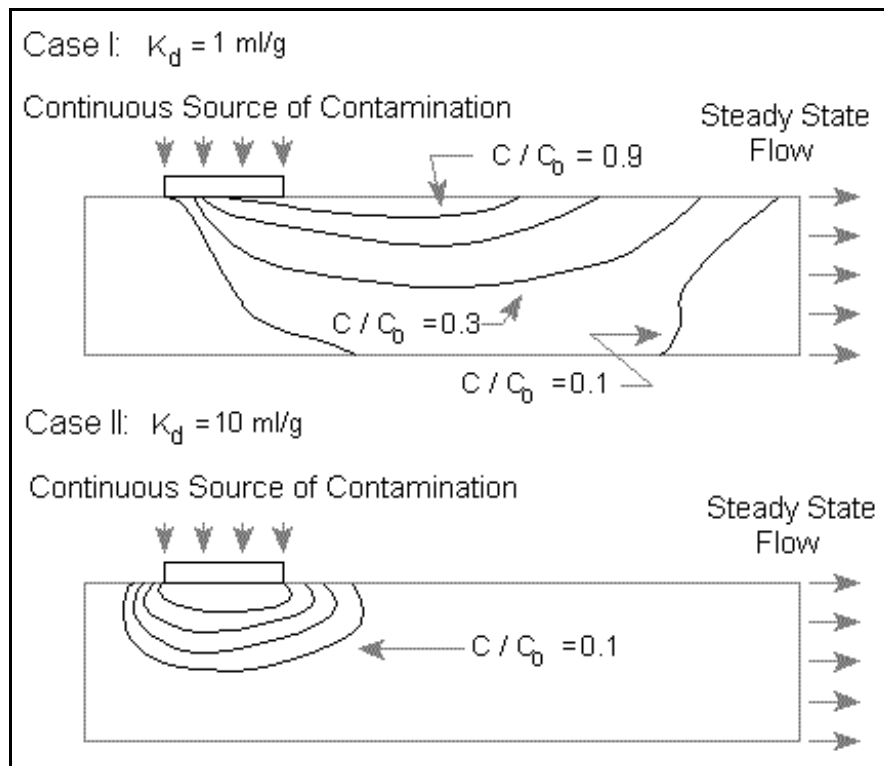


UNDERSTANDING VARIATION IN PARTITION COEFFICIENT, K_d , VALUES

Volume III:

Review of Geochemistry and Available K_d Values for Americium, Arsenic, Curium, Iodine, Neptunium, Radium, and Technetium



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Project Officer
Ronald G. Wilhelm
Office of Radiation and Indoor Air
U.S. Environmental Protection Agency
Washington, D.C. 20460

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FOREWORD

Understanding the long-term behavior of contaminants in the subsurface is becoming increasingly important as the nation addresses groundwater contamination. Groundwater contamination is a national concern as about 50 percent of the United States population receives its drinking water from groundwater. It is the goal of the Environmental Protection Agency (EPA) to prevent adverse effects to human health and the environment and to protect the environmental integrity of the nation's groundwater.

Once groundwater is contaminated, it is important to understand how the contaminant moves in the subsurface environment. Proper understanding of the contaminant fate and transport is necessary in order to characterize the risks associated with the contamination and to develop, when necessary, emergency or remedial action plans. The parameter known as the partition (or distribution) coefficient (K_d) is one of the most important parameters used in estimating the migration potential of contaminants present in aqueous solutions in contact with surface, subsurface and suspended solids.

This is the third volume in the series that describes: (1) the conceptualization, measurement, and use of the partition coefficient parameter; and (2) the geochemical aqueous solution and sorbent properties that are most important in controlling adsorption/retardation behavior of selected contaminants. Volumes I and II were published in 1999. Volume I of this document focuses on providing EPA and other environmental remediation professionals with a reasoned and documented discussion of the major issues related to the selection and measurement of the partition coefficient for a select group of contaminants. The selected contaminants investigated in Volume II of this document include: chromium, cadmium, cesium, lead, plutonium, radon, strontium, thorium, tritium (^3H), and uranium. The contaminants discussed in Volume III include: americium, arsenic, curium, iodine, neptunium, radium, and technetium. This three-volume report also addresses a void that has existed on this subject in both this Agency and in the user community.

It is important to note that soil scientists and geochemists knowledgeable of sorption processes in natural environments have long known that generic or default partition coefficient values found in the literature can result in significant errors when used to predict the impacts of contaminant migration or site-remediation options. Accordingly, one of the major recommendations of this report is that for site-specific calculations, partition coefficient values measured at site-specific conditions are absolutely essential.

For those cases when the partition coefficient parameter is not or cannot be measured, Volumes II and III of this document: (1) provide a "thumb-nail sketch" of the key geochemical processes affecting the sorption of the selected contaminants; (2) provide references to related key experimental and review articles for further reading; (3) identify the important aqueous- and solid-phase parameters controlling the sorption of these contaminants in the subsurface environment under oxidizing conditions; and (4) identify, when possible, minimum and maximum conservative partition coefficient values for each contaminant as a function of the key geochemical processes affecting their sorption.

In addition, this publication is produced as part of ORIA's long-term strategic plan to assist in the remediation of contaminated sites. It is published and made available to assist all environmental remediation professionals in the cleanup of groundwater sources all over the United States.

Elizabeth A. Cotsworth, Director
Office of Radiation and Indoor Air

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Kenneth M. Krupka
R. Jeffrey Serne

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U.S. Environmental Protection Agency
Office of Radiation and Indoor Air
Attention: Understanding Variation in Partition (K_d) Values
1200 Pennsylvania Avenue, N.W. (6608J)
Washington, D.C. 20460-2001

or

wilhelm.ron@epa.gov

ABSTRACT

This three-volume report describes the conceptualization, measurement, and use of the partition (or distribution) coefficient, K_d , parameter, and the geochemical aqueous solution and sorbent properties that are most important in controlling adsorption/retardation behavior of selected contaminants. The report is provided for technical staff from EPA and other organizations who are responsible for prioritizing site remediation and waste management decisions. Volumes I and II were published by the EPA in 1999.¹ Volume I focuses on the K_d concept and methods for measurement of K_d values. Particular attention is directed at providing an understanding of: (1) the use of K_d values in formulating retardation factor (R_f), (2) the difference between the original thermodynamic K_d parameter derived from ion-exchange literature and its “empiricized” use in contaminant transport codes, and (3) the explicit and implicit assumptions underlying the use of the K_d parameter in contaminant transport codes. A conceptual overview of chemical reaction models and their use in addressing technical defensibility issues associated with data from K_d studies is also presented. Volumes II and III provide “thumb-nail sketches” of the important aqueous speciation, coprecipitation/dissolution, and adsorption processes affecting the sorption of selected inorganic contaminants under oxidizing conditions. The K_d values listed in the literature for these contaminants are also summarized. The contaminants discussed in Volume II include chromium, cadmium, cesium, lead, plutonium, radon, strontium, thorium, tritium (^3H), and uranium. Volume III, which is an extension of Volume II, includes reviews of the sorption of americium, arsenic, curium, iodine, neptunium, radium, and technetium. However, due to the limited number of K_d adsorption studies for these contaminants and the large uncertainty, conservative minimum and maximums were not included. References to related key experimental and review articles are included for possible further reading.

¹ Both volumes (EPA, 1999b,1999c) can be downloaded and printed over the Internet at: <http://www.epa.gov/radiation/cleanup/partition.htm> This is found in the EPA Radiation, Information, Radiation Publications, Topical Publications, Protecting People and the Environment, Fate & Transport sections of the web site.

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1.0 Introduction

The objective of the report is to provide a reasoned and documented discussion on the technical issues associated with the measurement and selection of partition (or distribution) coefficient, K_d ,^{1,2} values and their use in formulating the retardation factor, R_f . The contaminant retardation factor (R_f) is the parameter commonly used in transport models to describe the chemical interaction between the contaminant and geological materials (*i.e.*, soil, sediments, rocks, and geological formations, henceforth simply referred to as soils³). It includes processes such as surface adsorption, absorption into the soil structure, precipitation, and physical filtration of colloids. Specifically, it describes the rate of contaminant transport relative to that of groundwater. This report is provided for technical staff from EPA and other organizations who are responsible for prioritizing site remediation and waste management decisions. The three-volume report describes the conceptualization, measurement, and use of the K_d parameter; and geochemical aqueous solution and sorbent properties that are most important in controlling the adsorption/retardation behavior of a selected set of contaminants.

This review is not meant to assess or judge the adequacy of the K_d approach used in modeling tools for estimating adsorption and transport of contaminants and radionuclides. Other approaches, such as surface complexation models, certainly provide more robust mechanistic approaches for predicting contaminant adsorption. However, as one reviewer noted, “ K_d ’s are the coin of the realm in this business.” For better or worse, the K_d model is an integral part of current methodologies for modeling contaminant and radionuclide transport and risk analysis.

The K_d concept, its use in fate and transport computer codes, and the methods for the measurement of K_d values are discussed in detail in Volume I and briefly introduced in Chapters 2 and 3 in Volumes II (EPA, 1999c) and III. Particular attention is directed at providing an understanding of: (1) the use of K_d values in formulating R_f , (2) the difference between the original thermodynamic K_d parameter derived from the ion-exchange literature and its “empiricized” use in contaminant transport codes, and (3) the explicit and implicit assumptions underlying the use of the K_d parameter in contaminant transport codes.

As typically used in fate and contaminant transport calculations, the K_d is defined as the ratio of the contaminant concentration associated with the solid to the contaminant concentration in the surrounding aqueous solution when the system is at equilibrium. Soil chemists and geochemists knowledgeable of sorption processes in natural environments have long known that generic or default K_d values can result in significant error when used to predict the impacts of contaminant migration or site-remediation options. To address some of this concern, modelers often incorporate a degree of

¹ Throughout this report, the term “partition coefficient” will be used to refer to the K_d “linear isotherm” sorption model. It should be noted, however, that the terms “partition coefficient” and “distribution coefficient” are used interchangeably in the literature for the K_d model.

² A list of acronyms, abbreviations, symbols, and notation is given in Appendix A. A list of definitions is given in Appendix B.

³ The terms “sediment” and “soil” have particular meanings depending on one’s technical discipline. For example, the term “sediment” is often reserved for transported and deposited particles derived from soil, rocks, or biological material. “Soil” is sometimes limited to referring to the top layer of the earth’s surface, suitable for plant life. In this report, the term “soil” was selected with concurrence of the EPA Project Officer as a general term to refer to all unconsolidated geologic materials.

conservatism into their calculations by selecting limiting or bounding conservative K_d values. For example, the most conservative K_d value from the perspective of off-site risks due to contaminant migration through subsurface natural soil and groundwater systems is to assume that the soil has little or no ability to slow (retard) contaminant movement (*i.e.*, a minimum bounding K_d value). Consequently, the contaminant would travel in the direction and at the rate of water. Such an assumption may in fact be appropriate for certain contaminants such as tritium, but may be too conservative for other contaminants, such as thorium or plutonium, which react strongly with soils and may migrate 10^2 to 10^6 times more slowly than the water.

On the other hand, when estimating the risks and costs associated with on-site remediation options, a maximum bounding K_d value provides an estimate of the maximum concentration of a contaminant or radionuclide sorbed to the soil. Conservatism for remediation calculations would tend to err on the side of underestimating the extent of contaminant desorption that would occur in the aquifer once pump-and-treat or soil flushing treatments commenced. Such an estimate would provide an upper limit to time, money, and work required to extract a contaminant from a soil. This would be accomplished by selecting a K_d from the upper range of literature values.

In some instances because of long groundwater flow paths, extremely arid site characteristics, or presence of impermeable soils, the final results of risk and transport calculations for some contaminants may be insensitive to the K_d value even when selected within the range of technically-defensible, limiting minimum and maximum K_d values. However, for most situations that are sensitive to the selected K_d value, site-specific K_d values are essential for obtaining defensible risk and transport predictions.

The K_d is usually a measured parameter that is obtained from laboratory experiments. The 5 general methods used to measure K_d values are reviewed in Volume I (EPA, 1999b). These methods include the batch laboratory method, the column laboratory method, field-batch method, field modeling method, and soil organic carbon/water partition coefficient (K_{oc}) method. Volume I (EPA, 1999b) identifies what ancillary information is needed regarding the adsorbent (soil), solution (contaminated ground-water or process waste water), contaminant (concentration, valence state, speciation distribution), and laboratory details (spike addition methodology, phase separation techniques, contact times). The advantages, disadvantages, and, perhaps more importantly, the underlying assumptions of each method are also presented.

A conceptual overview of geochemical modeling calculations and computer codes as they pertain to evaluating K_d values and modeling of adsorption processes is discussed in detail in Volume I (EPA, 1999b) and briefly described in Chapter 4 of Volumes II (EPA, 1999c) and III. The use of geochemical codes in evaluating aqueous speciation, solubility, and adsorption processes associated with contaminant fate studies is reviewed. This approach is compared to the traditional calculations that rely on the constant K_d construct. The use of geochemical modeling to address quality assurance and technical defensibility issues concerning available K_d data and the measurement of K_d values are also discussed. The geochemical modeling review includes a brief description of the EPA's MINTEQA2 geochemical code and a summary of the types of conceptual models it contains to quantify adsorption reactions. The status of radionuclide thermodynamic and contaminant adsorption model databases for the MINTEQA2 code is also reviewed.

The main focus of Volumes II (EPA, 1999c) and III is to: (1) provide a “thumb-nail sketch” of the key geochemical processes affecting the sorption of a selected set of contaminants; (2) provide references to related key experimental and review articles for further reading; (3) identify the important aqueous- and solid-phase parameters controlling the sorption of these contaminants in the subsurface environment; and (4) identify, when possible, minimum and maximum conservative K_d values for each contaminant (as a function key geochemical processes affecting their sorption). The contaminants chosen for the first phase of this project, Volume II (EPA, 1999c), included reviews on cadmium, cesium, chromium, lead, plutonium, radon, strontium, thorium, tritium (^3H), and uranium. This document (Volume III) represents the second phase of this project, and is an extension of Volume II. Volume III provides “thumb-nail sketches” of the key geochemical processes affecting the sorption of americium, arsenic(V) (as arsenate), curium, iodine [-I (as iodide) and +5 (iodate)], neptunium, radium, and technetium(VII) (as pertechnetate) to soils.

The selection of these contaminants by EPA and Pacific Northwest National Laboratory (PNNL) project staff was based on two criteria. First, the contaminant had to be of high priority to site remediation or risk assessment activities of EPA, DOE, and/or NRC. Second, because the available funding precluded a review of all contaminants that met the first criteria, a subset was selected to represent categories of contaminants based on their chemical behavior. The six nonexclusive categories are:

- Cations - americium, cadmium, cesium, curium, neptunium, plutonium, radium, strontium, thorium, and uranium.
- Anions - arsenic(V) (as arsenate), chromium(VI) (as chromate), iodine [-I (as iodide) and +5 (iodate)], technetium(VII) (as pertechnetate) and uranium(VI) complexes (*e.g.*, uranyl carbonate complexes).
- Radionuclides - americium, cesium, curium, iodine, neptunium, plutonium, radium, radon, strontium, technetium, thorium, tritium (^3H), and uranium.
- Conservatively transported contaminants - tritium (^3H) and radon.
- Nonconservatively transported contaminants - other than tritium (^3H) and radon.
- Redox sensitive elements - arsenic, chromium, iodine, neptunium, plutonium, technetium, and uranium.

The general geochemical behaviors discussed in this report can be used by analogy to estimate the geochemical interactions of similar elements for which data are not available. For example, contaminants present primarily in anionic form, such as Cr(VI), tend to adsorb to a limited extent to soils. Thus, one might generalize that other anions, such as nitrate, chloride, and U(VI)-anionic complexes, would also adsorb to a limited extent. Literature on the adsorption of these three solutes show no or very little adsorption.

The concentration of contaminants in groundwater is controlled primarily by the amount of contaminant present at the source; rate of release from the source; hydrologic factors such as dispersion, advection, and dilution; and a number of geochemical processes including aqueous geochemical processes, adsorption/desorption, precipitation, and diffusion. To accurately predict contaminant transport through the subsurface, it is essential that the important geochemical processes affecting contaminant transport be identified and, perhaps more importantly, accurately described in a mathematically and scientifically defensible manner. Dissolution/precipitation and adsorption/desorption are usually the most important processes affecting contaminant interaction with

soils. Dissolution/precipitation is more likely to be the key process where chemical nonequilibrium exists, such as at a point source, an area where high contaminant concentrations exist, or where steep pH or oxidation-reduction (redox) gradients exist. Adsorption/desorption will likely be the key process controlling contaminant migration in areas where chemical steady state exist, such as in areas far from the point source. Diffusion flux spreads solute via a concentration gradient (*i.e.*, Fick's law). Diffusion is a dominant transport mechanism when advection is insignificant, and is usually a negligible transport mechanism when water is being advected in response to various forces.

2.0 The K_d Model

The simplest and most common method of estimating contaminant retardation is based on the partition (or distribution) coefficient, K_d . The K_d parameter is a factor related to the partitioning of a contaminant between the solid and aqueous phases. It is an empirical unit of measurement that attempts to account for various chemical and physical retardation mechanisms that are influenced by a myriad of variables. The K_d metric is the most common measure used in transport codes to describe the extent to which contaminants are sorbed to soils. It is the simplest, yet least robust model available. A primary advantage of the K_d model is that it is easily inserted into hydrologic transport codes to quantify reduction in the rate of transport of the contaminant relative to groundwater, either by advection or diffusion. Technical issues, complexities, and shortcomings of the K_d approach to describing contaminant sorption to soils are summarized in detail in Chapter 2 of Volume I (EPA, 1999b). Particular attention is directed at issues relevant to the selection of K_d values from the literature for use in transport codes.

The partition coefficient, K_d , is defined as the ratio of the quantity of the adsorbate adsorbed per mass of solid to the amount of the adsorbate remaining in solution at equilibrium. For the reaction



the mass action expression for K_d is

$$K_d = \frac{\text{Mass of Adsorbate Sorbed}}{\text{Mass of Adsorbate in Solution}} = \frac{A_i}{C_i} \quad (2.2)$$

where A = free or unoccupied surface adsorption sites
 C_i = total dissolved adsorbate remaining in solution at equilibrium
 A_i = amount of adsorbate on the solid at equilibrium.

The K_d is typically given in units of ml/g. Describing the K_d in terms of this simple reaction assumes that A is in great excess with respect to C_i and that the activity of A_i is equal to 1.

Chemical retardation, R_f , is defined as,

$$R_f = \frac{v_p}{v_c}, \quad (2.3)$$

where v_p = velocity of the water through a control volume
 v_c = velocity of contaminant through a control volume.

The chemical retardation term does not equal unity when the solute interacts with the soil; almost always the retardation term is greater than 1 due to solute sorption to soils. In rare cases, the retardation factor is actually less than 1, and such circumstances are thought to be caused by anion exclusion (See Volume I, Section 2.7). Knowledge of the K_d and of media bulk density and porosity for porous flow, or of media fracture surface area, fracture opening width, and matrix diffusion attributes for fracture flow, allows calculation of the retardation factor. For porous flow with saturated

moisture conditions, the R_f is defined as

$$R_f = 1 + \frac{\rho_b}{n_e} K_d \quad (2.4)$$

where ρ_b = porous media bulk density (mass/length³)
 n_e = effective porosity of the media at saturation.

The K_d parameter is valid only for a particular adsorbent and applies only to those aqueous chemical conditions (*e.g.*, adsorbate concentration, solution/electrolyte matrix) in which it was measured. Site-specific K_d values should be used for site-specific contaminant and risk assessment calculations. Ideally, site-specific K_d values should be measured for the range of aqueous and geological conditions in the system to be modeled. However, literature-derived K_d values are commonly used for screening calculations. Suitable selection and use of literature-derived K_d values for screening calculations of contaminant transport is not a trivial matter. Among the assumptions implicit with the K_d construct is: (1) only trace amounts of contaminants exist in the aqueous and solid phases, (2) the relationship between the amount of contaminant in the solid and liquid phases is linear, (3) equilibrium conditions exist, (4) equally rapid adsorption and desorption kinetics exists, (5) it describes contaminant partitioning between one sorbate (contaminant) and one sorbent (soil), and (6) all adsorption sites are accessible and have equal adsorption binding energies. Many of these assumptions are not met for groundwater/soil environments. Thus, literature-derived K_d values should be used only to predict transport in systems similar to those used in the laboratory and field to measure the K_d . Variation in either the soil or aqueous chemistry of a system can result in extremely large differences in K_d values.

A more robust approach than using a single K_d to describe the partitioning of contaminants between the aqueous and solid phases is the parametric- K_d model. This model varies the K_d value according to the chemistry and mineralogy of the system at the node being modeled. The parametric- K_d value, unlike the constant- K_d value, is not limited to a single set of environmental conditions. Instead, it describes the sorption of a contaminant in the range of environmental conditions used to create the parametric- K_d equations. These types of statistical relationships are devoid of causality and therefore provide no information on the mechanism by which the radionuclide partitioned to the solid phase, whether it be by adsorption, absorption, or precipitation. Understanding these mechanisms is extremely important relative to estimating the mobility of a contaminant.

When the parametric- K_d model is used in the transport equation, the code must also keep track of the current value of the independent variables at each point in space and time to continually update the concentration of the independent variables affecting the K_d value. Thus, the code must track many more parameters and some numerical solving techniques (such as closed-form analytical solutions). It can no longer be used to perform the integration necessary to solve for the K_d value and/or retardation factor, R_f . Generally, computer codes that can accommodate the parametric- K_d model use a chemical subroutine to update the K_d value used to determine the R_f , when called for by the main transport code. The added complexity in solving the transport equation with the parametric- K_d sorption model and its empirical nature may be the reasons this approach has been used sparingly.

Mechanistic models explicitly accommodate for the dependency of K_d values on contaminant concentration, charge, competing ion concentration, variable surface charge on the soil, and solution species distribution. Incorporating mechanistic adsorption concepts into transport models is desirable because

the models become more robust and, perhaps more importantly from the standpoint of regulators and the public, scientifically defensible. However, truly mechanistic adsorption models are rarely, if ever, applied to complex natural soils. The primary reason for this is because natural mineral surfaces are very irregular and difficult to characterize. These surfaces consist of many different microcrystalline structures that exhibit quite different chemical properties when exposed to solutions. Thus, examination of the surface by virtually any experimental method yields only averaged characteristics of the surface and the interface.

Less attention will be directed to mechanistic models because they are not extensively incorporated into the majority of EPA, DOE, and NRC modeling methodologies. The complexity of installing these mechanistic adsorption models into existing transport codes is formidable. Additionally, these models also require a more extensive database collection effort than will likely be available to the majority of EPA, DOE, and NRC contaminant transport modelers. A brief description of the state of the science of mechanistic adsorption modeling is presented in Volume I (EPA, 1999b) primarily to provide a paradigm for sorption processes. Readers should note, that since the completion of Volumes I and II (EPA, 1999b, 1999c), Brown *et al.* (1999) published an extensive review of the interactions of metal oxide surfaces with aqueous solutions and microbial organisms. This review includes a detailed discussion of the theory and thermodynamic models for describing the adsorption of chemical species to oxide surfaces.

3.0 Methods, Issues, and Criteria for Measuring K_d Values

There are five general methods used to measure K_d values: the batch laboratory method, laboratory flow-through (or column) method, field-batch method, field modeling method, and K_{oc} method. The K_{oc} method is specific to adsorption of organics. These methods and the associated technical issues are described in detail in Chapter 3 of Volume I (EPA, 1999b). Each method has advantages and disadvantages, and perhaps more importantly, each method has its own set of assumptions for calculating K_d values from experimental data. Consequently, it is not only common, but expected that K_d values measured by different methods will produce different values.

3.1 Laboratory Batch Method

Batch tests are commonly used to measure K_d values. A batch test is conducted by spiking a solution with the element of interest, mixing the spiked solution with a solid for a specified period of time, separating the solution from the solid, and measuring the concentration of the spiked element remaining in solution. The concentration of contaminant associated with the solid is determined by the difference between initial and final contaminant concentration in solution. The primary advantage of the batch method is that such experiments can be completed quickly for a wide variety of elements and chemical environments. The primary disadvantage of the batch technique for measuring K_d is that it does not necessarily reproduce the chemical reaction conditions that take place in the real environment. For instance, in a soil column, water passes through at a finite rate and both reaction time and degree of mixing between water and soil can be much less than those occurring in a laboratory batch test. Consequently, K_d values from batch experiments can be high relative to the extent of sorption occurring in a real system, and thus result in an estimate of contaminant retardation that is too large. Another disadvantage of batch experiments is that they do not accurately simulate desorption of the radionuclides or contaminants from a contaminated soil or solid waste source. The K_d values are frequently used with the assumption that adsorption and desorption reactions are reversible. This assumption is contrary to most experimental observations that show that the desorption process is appreciably slower than the adsorption process, a phenomenon referred to as hysteresis. The rate of desorption may even go to zero, yet a significant mass of the contaminant remains sorbed on the soil. Thus, use of K_d values determined from batch adsorption tests in contaminant transport models is generally considered to provide estimates of contaminant remobilization (release) from soil that are too large (*i.e.*, estimates of contaminant retention that are too low).

Inherent in the K_d “linear isotherm” adsorption model is the assumption that adsorption of the contaminant of interest is independent of its concentration in the aqueous phase. Partitioning of a contaminant on soil can often be described using the K_d model, but typically only for low contaminant concentrations as would exist some distance away (far field) from the source of contamination. It is common knowledge that contaminant adsorption on soils can deviate from the linear relationship required by the K_d construct. This is possible for conditions as might exist in leachates or groundwater near waste sources where contaminant concentrations are large enough to affect the saturation of surface adsorption sites. In these latter situations, non-linear isotherm models [see Section 2.3.3 in Volume I (EPA, 1999b)] are used to describe the case where sorption relationships deviate from linearity.

3.2 Laboratory Flow-Through Method

Flow-through column experiments are intended to provide a more realistic simulation of dynamic field conditions and to quantify the movement of contaminants relative to groundwater flow. It is the second most common method of determining K_d values. The basic experiment is completed by passing a liquid spiked with the contaminant of interest through a soil column. The column experiment combines the chemical effects of sorption and the hydrologic effects of groundwater flow through a porous medium to provide an estimate of retarded movement of the contaminant of interest. The retardation factor (a ratio of the velocity of the contaminant to that of water) is measured directly from the experimental data. A K_d value can be calculated from the retardation factor. It is frequently useful to compare the back-calculated K_d value from these experiments with those derived directly from the batch experiments to evaluate the influence of limited interaction between solid and solution imposed by the flow-through system.

One potential advantage of the flow-through column studies is that the retardation factor can be inserted directly into the transport code. However, if the study site contains different hydrological conditions (*e.g.*, porosity and bulk density) than the column experiment, then a K_d value needs to be calculated from the retardation factor. Another advantage is that the column experiment provides a much closer approximation of the physical conditions and chemical processes occurring in the field site than a batch sorption experiment. Column experiments permit the investigation of the influence of limited spatial and temporal (nonequilibrium) contact between solute and solid have on contaminant retardation. Additionally, the influence of mobile colloid facilitated transport and partial saturation can be investigated. A third advantage is that both adsorption or desorption reactions can be studied. The predominance of one mechanism of adsorption or desorption over another cannot be predicted *a priori* and therefore generalizing the results from one set of laboratory experimental conditions to field conditions is never without some uncertainty. Ideally, flow-through column experiments would be used exclusively for determining K_d values, but equipment cost, time constraints, experimental complexity, and data reduction uncertainties discourage more extensive use. Another important issue for column studies is that a flow model (*e.g.*, piston flow or a mobile/immobile flow system) must be assumed to calculate a K_d value. A different result may be obtained depending on which flow model is chosen. The K_d values derived from column studies are also conditional on the flow rate; generally, the faster the flow rate, lower the calculated K_d .

3.3 Other Methods

Less commonly used methods include the K_{oc} method, *in-situ* batch method, and the field modeling method. The K_{oc} method is a very effective indirect method of calculating K_d values, however, it is only applicable to hydrophobic organic compounds. The K_{oc} method becomes increasingly inaccurate as the organic contaminant is increasingly hydrophilic, because hydrophilic organic compounds can also adsorb to mineral surfaces, in addition to partitioning to organic matter. The *in-situ* batch method requires that paired soil and groundwater samples be collected directly from the aquifer system being modeled and then measuring directly the amount of contaminant on the solid and liquid phases. The advantage of this approach is that the precise solution chemistry and solid phase mineralogy existing in the study site is used to measure the K_d value. However, this method is not used often because of the analytical problems associated with measuring the exchangeable fraction of contaminant on the solid phase. Finally, the field modeling method of calculating K_d values uses groundwater monitoring data

and source term data to calculate a K_d value. The accuracy of the field modeling method is highly dependent on the accuracy of the other input parameters used in the calculation. For instance, if the dispersion value or the hydraulic conductivity is incorrect, it is very unlikely that the true K_d value will be calculated. One key drawback to this technique is that it is very model dependent. Because the calculated K_d values are model dependent and highly site specific, the derived K_d values should not be used for contaminant transport calculations at other sites.

3.4 Issues

A number of issues exist concerning the measurement of K_d values and the selection of K_d values from the literature. These issues are discussed with supporting references in Volume I (EPA, 1999b), and are briefly summarized below. These issues include: using simple versus complex systems to measure K_d values, field variability, the “gravel issue,” the “colloid issue,” and contaminant solubility limits. Soils are a complex mixture containing solid, gaseous, and liquid phases. Each phase contains several different constituents. The use of simplified systems containing single mineral phases and aqueous phases with one or two dissolved species has provided valuable paradigms for understanding sorption processes in more complex, natural systems. However, the K_d values generated from these simple systems are generally of little value for importing directly into transport models. Values for transport models should be generated from geologic materials from or similar to the study site.

The “gravel issue” is the problem that transport modelers face when converting laboratory-derived K_d values based on experiments conducted with the <2-mm fraction into values that can be used in systems containing particles >2 mm in size (Kaplan *et al.*, 2000c). No standard methods exist to address this issue. There are many subsurface soils dominated by cobbles, gravel, or boulders. To base the K_d values on the <2-mm fraction, which may constitute only a low percent of the soil volume but is the most chemically reactive fraction, may grossly overestimate the actual K_d of the aquifer. Two general approaches have been proposed to address this issue. The first is to assume that all particles >2-mm have a $K_d = 0$ ml/g. Although this assumption is incorrect; *i.e.*, we know that cobbles, gravel, and boulders do in fact sorb contaminants, the extent to which sorption occurs on these larger particles may be small. The second approach is to normalize laboratory-derived K_d values by soil surface area. Theoretically, this latter approach is more satisfying because it permits some sorption to occur on the >2-mm fraction and the extent of the sorption is proportional to the surface area. The underlying assumptions in this approach are that the mineralogy is similar in the less than 2- and greater than 2-mm fractions and that the sorption processes occurring on the smaller particles are similar to those that occur on the larger particles.

Spatial variability provides additional complexity to understanding and modeling contaminant retention to subsurface soils. The extent to which contaminants partition to soils changes as field mineralogy and chemistry change. Thus, a single K_d value is almost never sufficient for an entire study site and should change as chemically important environmental conditions change. Three approaches used to vary K_d values in transport codes are the K_d look-up table approach, the parametric- K_d approach, and the mechanistic K_d approach. The extent to which these approaches are presently used and the ease of incorporating them into a flow model varies greatly. Parametric- K_d values typically have limited environmental ranges of application. Mechanistic K_d values are limited to uniform solid and aqueous systems with little application to **heterogeneous** soils existing in nature. The easiest and the most common variable- K_d model interfaced with transport codes is the look-up table. In K_d look-up tables, separate K_d values are assigned to a matrix of discrete categories defined by chemically important

ancillary parameters. No single set of ancillary parameters, such as pH and soil texture, is universally appropriate for defining categories in K_d look-up tables. Instead, the ancillary parameters must vary in accordance to the geochemistry of the contaminant. It is essential to understand fully the criteria and process used for selecting the values incorporated in such a table. Differences in the criteria and process used to select K_d values can result in appreciably different K_d values. Examples are presented in this volume.

Contaminant transport models generally treat the subsurface environment as a two-phase system in which contaminants are distributed between a mobile aqueous phase and an immobile solid phase (*e.g.*, soil). An increasing body of evidence indicates that under some subsurface conditions, components of the solid phase may exist as mobile colloids¹ that may be transported with the flowing water. Subsurface mobile colloids originate from (1) the dispersion of surface or subsurface soils, (2) decementation of secondary mineral phases, and (3) homogeneous precipitation of groundwater constituents. Association of contaminants with this additional mobile phase may enhance not only the amount of contaminant that is transported, but also the rate of contaminant transport. Most current approaches to predicting contaminant transport ignore this mechanism not because it is obscure or because the mathematical algorithms have not been developed, but because little information is available on the occurrence, the mineralogical properties, the physicochemical properties, or the conditions conducive to the generation of mobile colloids. There are two primary problems associated with studying colloid-facilitated transport of contaminants under natural conditions. First, it is difficult to collect colloids from the subsurface in a manner which minimizes or eliminates sampling artifacts. Second, it is difficult to unambiguously delineate between the contaminants in the mobile-aqueous and mobile-solid phases.

Some contaminants, such as americium, curium, and others, are very insoluble under certain groundwater conditions. Therefore, care must be taken not to exceed their solubilities when measuring their K_d values using laboratory batch and flow-through column techniques. Values of K_d determined under such conditions will overestimate the retardation due to the adsorption of the contaminant. Investigators must carefully analyze their results to insure that the K_d values were not measured at **oversaturated** conditions. If batch K_d measurements are completed for a range of initial contaminant concentrations for a fixed set of geochemical conditions (*e.g.*, pH), the final dissolved concentrations of the contaminant may eventually reach a constant value for those solution concentrations exceeding the solubility of the contaminant. The resulting sorption isotherm will be a vertical line at the solubility limit when plotting the final concentrations of sorbed contaminant (y-axis) as a function of final concentrations of dissolved contaminant (x-axis) [see “Isotherm Adsorption Models” in Section 2.3.3 in Volume I (EPA, 1999b)]. For K_d values measured using the flow-through column technique with constant step input [see Section 3.2.3 in Volume I (EPA, 1999b)], the ratio of the contaminant concentration in the effluent (C_{eff}) to that in the input at time 0 (zero) (C_0) for the effluent (or breakthrough) curve will never achieve a value of 1.0 when contaminant precipitation has occurred in the soil column. For flow-through measurements with a pulse input, the total mass of contaminant that is determined in the collected effluent after C_{eff} returns to zero will not equal the total mass injected into

¹ A colloid is any fine-grained material, sometimes limited to the particle-size range of <0.00024 mm (*i.e.*, smaller than clay size), that can be easily suspended (Bates and Jackson, 1980). In its original sense, the definition of a colloid included any fine-grained material that does not occur in crystalline form. The geochemistry of colloid systems is discussed in detail in sources such as Yariv and Cross (1979) and the references therein.

the column due to irreversible precipitation. Moreover, the shape of effluent break-through curve (C_{eff}/C_o) will not be very Gaussian in form and will have a protracted tail.

When planning K_d studies and analyzing the results, investigators can use chemical reaction computer models, like EPA's MINTEQA2 geochemical code, to estimate from thermodynamic principles solubility limits for a contaminant as a function of pH, redox, concentrations of complexing ligands, and temperature [see Section 5 in Volume I (EPA, 1999b)]. The results of these modeling calculations can be used to set limits for the maximum initial contaminant concentrations to be used in the K_d measurements and/or to alert investigators that solubility limits may have been exceeded during the course of study. An example of this type of application is described in Section 5.2.4.2 in Volume I (EPA, 1999b).

It is incumbent upon the transport modeler to understand the strengths and weaknesses of the different K_d methods, and perhaps more importantly, the underlying assumption of the methods in order to properly select K_d values from the literature. The K_d values reported in the literature for any given contaminant may vary by as much as six orders of magnitude. An understanding of the important geochemical processes and knowledge of the important ancillary parameters affecting the sorption chemistry of the contaminant of interest is necessary for selecting appropriate K_d value(s) for contaminant transport modeling.

4.0 Application of Chemical Reaction Models

Computerized chemical reaction models based on thermodynamic principles may be used to calculate processes such as aqueous complexation, oxidation/reduction, adsorption/desorption, and mineral precipitation/dissolution for contaminants in soil-water systems. The capabilities of a chemical reaction model depend on the models incorporated into its computer code and the availability of thermodynamic and/or adsorption data for aqueous and mineral constituents of interest. Chemical reaction models, their utility to understanding the solution chemistry of contaminants, and the MINTEQA2 model in particular are described in detail in Chapter 5 of Volume I (EPA, 1999b).

Chemical reaction models can be used to support evaluations of K_d values and related contaminant migration and risk assessment modeling predictions. Most models include options for calculating (1) the distribution of complexed and uncomplexed aqueous species for a specified water composition, (2) the dissolved concentration of an element based on the solubility of solids containing that element, and in some instances, (3) the mass of an element adsorbed by ion exchange or surface complexation onto a single, pure mineral phase. Results from aqueous complexation calculations indicate the ionic state and composition of the dominant aqueous species for a dissolved contaminant present in a soil-water system. This information may in turn be used to substantiate the conceptual model being used for calculating the adsorption of a particular contaminant. Solubility calculations provide a means of predicting technically defensible maximum concentration limits for contaminants as a function of key composition parameters (*e.g.*, pH) for any specific soil-water system. These values may provide more realistic bounding values for the maximum concentration attainable in a soil-water system when doing risk assessment calculations. Modeling computations can also be used to examine initial and final geochemical conditions associated with laboratory K_d measurements to determine if the measurements were affected by processes such as mineral precipitation, which might have compromised the derived K_d values.

Although K_d values cannot be *predicted* a priori with chemical reaction models, modeling results can provide aqueous speciation and solubility information that is exceedingly valuable in the evaluation of K_d values selected from the literature and/or measured in the laboratory. Moreover, some models include electrostatic adsorption submodels that may be used to estimate the changes in the composition of the aqueous phase due to adsorption onto a selected mineral phase such as hematite or amorphous iron oxyhydroxide. These results in turn can be used to back calculate a K_d value.

The MINTEQA2¹ computer code is an equilibrium chemical reaction model. It was developed with EPA funding by originally combining the mathematical structure of the MINEQL code with the thermodynamic database and geochemical attributes of the WATEQ3 code. The MINTEQA2 code includes submodels to calculate aqueous speciation/complexation, oxidation-reduction, gas-phase equilibria, solubility and saturation state (*i.e.*, saturation index), precipitation/dissolution of solid phases, and adsorption. The most current version of MINTEQA2 available from EPA is compiled to execute on a personal computer (PC) using the MS-DOS computer operating system. The MINTEQA2 software package includes PRODEFA2, a computer code used to create and modify input files for MINTEQA2.

¹ Since the publication of Volumes I and II, the EPA has released a new version, Version 4.0, of the MINTEQ software package (EPA, 1999a). The software package and documentation are available free on the EPA Internet site: <http://www.epa.gov/ceampubl/softwdos.htm>

The MINTEQA2 code contains an extensive thermodynamic database for modeling the speciation and solubility of contaminants and geologically significant constituents in low-temperature, soil-water systems. Of the contaminants selected for consideration in this project [americium, arsenic, cadmium, cesium, chromium, curium, iodine, lead, neptunium, plutonium, radon, radium, strontium, technetium, thorium, tritium (^3H), and uranium], the MINTEQA2 thermodynamic database contains speciation and solubility reactions for arsenic, including the valence states As(III) and As(V); chromium, including the valence states Cr(II), Cr(III), and Cr(VI); cadmium; iodide, lead; strontium; and uranium, including the valence states U(III), U(IV), U(V), and U(VI).

Individual users can supplement and/or update the MINTEQA2 database using thermodynamic constants listed in published sources. Particularly noteworthy are several extensive, critical reviews of thermodynamic data for radionuclides completed since 1992 by the Nuclear Energy Agency (NEA) Thermodynamic Database Project of the Organisation for Economic Co-operation and Development (OECD).¹ These reviews were conducted by international teams of experts, peer reviewed prior to publication, and commercially published in hard cover. These excellent sources include the reviews of thermodynamic data for americium (Silva *et al.*, 1995), neptunium (Lemire *et al.*, 2001), plutonium (Lemire *et al.*, 2001), technetium (Rard *et al.*, 1999) and uranium (Grenthe *et al.*, 1992).² The thermodynamic data in Grenthe *et al.* (1992) supersede the uranium thermodynamic database currently available with MINTEQA2.

The MINTEQA2 code includes seven adsorption model options. The non-electrostatic adsorption models include the activity K_d^{act} , activity Langmuir, activity Freundlich, and ion exchange models. The electrostatic adsorption models include the diffuse layer, constant capacitance, and triple layer models. The MINTEQA2 code does not include an integrated database of adsorption constants and reactions for any of the seven models. These data must be supplied by the user as part of the input file information.

Chemical reaction models, such as the MINTEQA2 code, cannot be used a priori to predict a partition coefficient, K_d , value. The MINTEQA2 code may be used to calculate the chemical changes that result in the aqueous phase from adsorption using the more data intensive, electrostatic adsorption models. The results of such calculations in turn can be used to back calculate a K_d value. However, the user must make assumptions concerning the composition and mass of the dominant sorptive substrate, and supply the adsorption parameters for surface-complexation constants for the contaminants of interest and the assumed sorptive phase. The EPA (EPA, 1992, 1996) has used the MINTEQA2 model and this approach to estimate K_d values for several metals under a variety of geochemical conditions and metal concentrations to support various waste disposal issues. The EPA in its "Soil Screening Guidance" determined MINTEQA2-estimated K_d values for barium, beryllium, cadmium, Cr(III),

¹ The Nuclear Energy Agency (NEA) is a specialized agency within the Organization for Economic Co-operation and Development (OECD), which is an intergovernmental organization of industrialized countries, based in Paris, France. Funding for the OECD/NEA Thermodynamic Database Project was provided from 17 organizations in 12 countries, including the U.S. Department of Energy (DOE). More information regarding the OECD/NEA Thermodynamic Database Project is available on the Internet at: <http://www.nea.fr/html/dbtdb/cgi-bin/tbdbocproc.cgi>

² The reviews of thermodynamic data by Rard *et al.* (1999) and Lemire *et al.* (2001) were published in hard cover and on companion compact disks (CDs).

Hg(II), nickel, silver, and zinc as a function of pH assuming adsorption on a fixed mass of iron oxide (EPA, 1996; RTI, 1994). The calculations assumed equilibrium conditions, and did not consider redox potential or metal competition for the adsorption sites. In addition to these constraints, EPA (1996) noted that this approach was limited by the potential sorbent surfaces that could be considered and availability of thermodynamic data. Their calculations were limited to metal adsorption on iron oxide, although sorption of these metals to other minerals, such as clays and carbonates, is well known.

Typically, the data required to derive the values of adsorption parameters that are needed as input for adsorption submodels in chemical reaction codes are more extensive than information reported in a typical laboratory batch K_d study. If the appropriate data are reported, it is likely that a user could hand calculate a composition-based K_d value from the data reported in the adsorption study without the need of a chemical reaction model.

5.0 Contaminant Geochemistry and K_d Values

The important geochemical factors affecting the sorption¹ of americium (Am), arsenic (As), curium (Cm), iodine (I), neptunium (Np), radium (Ra), and technetium (Tc) are discussed in this chapter. The objectives of this chapter are to: (1) provide a “thumb-nail sketch” of the key geochemical processes affecting sorption of these contaminants, (2) provide references to key experimental and review articles for further reading, (3) identify the important aqueous- and solid-phase parameters controlling contaminant sorption in the subsurface environment, and (4) discuss the availability of sorption data and K_d values for each contaminant. Unlike the contaminants reviewed in Volume II (EPA, 1999c), the availability of K_d values and/or our understanding of the adsorptive behavior as a function of key geochemical factors is more restricted for each contaminant reviewed in Volume III. These limitations precluded selection of minimum and maximum conservative K_d values as a function of key geochemical factors as was done for the contaminants in Volume II.

5.1 General

Important chemical speciation, (co)precipitation/dissolution, and adsorption/desorption processes for each contaminant are discussed. Emphasis of these discussions is directed at describing the general geochemistry that occurs in oxic environments containing low concentrations of organic carbon located far from a point source (*i.e.*, in the far field). These environmental conditions comprise a large portion of the contaminated sites of concern to the EPA, DOE, and/or NRC. We found it necessary to focus on the far-field, as opposed to near-field, geochemical processes for two main reasons. First, the near field frequently contains very high concentrations of salts, acids, bases, and/or contaminants which often require unusual chemical or geochemical considerations that are quite different from those in the far field. Secondly, the differences in chemistry among various near-field environments varies greatly, further compromising the value of a generalized discussion. Some qualitative discussion of the effect of high salt conditions and anoxic conditions are presented for contaminants whose sorption behavior is profoundly affected by these conditions.

The distribution of aqueous species for each contaminant was calculated for an oxidizing environment containing the water composition listed in Table 5.1 and the chemical equilibria code MINTEQA2 (Version 3.10, Allison *et al.*, 1991). The water composition in Table 5.1 is based on a “mean composition of river water of the world” estimated by Hem (1985). We use this chemical composition simply as a proxy for the composition of a shallow groundwater. Obviously, there are significant differences between surface waters and groundwater, and considerable variability in the concentrations of various constituents in surface and groundwater. For example, the concentrations of dissolved gases and complexing ligands, such as carbonate, may be less in a groundwater as a result of infiltration of surface water through the soil column. Additionally, the redox potential of groundwater, especially deep groundwater, will likely be more reducing than surface water. As explained later in this chapter, the adsorption and solubility of certain contaminants and radionuclides may be significantly different under reducing groundwater conditions compared to oxidizing conditions. However, as explained in

¹ When a contaminant is associated with a solid phase, it is commonly not known if the contaminant is adsorbed onto the surface of the solid, absorbed into the structure of the solid, precipitated as a three-dimensional molecular coating on the surface of the solid, or absorbed into organic matter. “Sorption” will be used in this report as a generic term devoid of mechanism to describe the partitioning of aqueous phase constituents to a solid phase. Sorption is frequently quantified by the partition (or distribution) coefficient, K_d .

the Foreword, it was necessary to limit the scope of this review to oxidizing conditions. Use of the water composition in Table 5.1 does not invalidate the aqueous speciation calculations discussed later in this chapter relative to the behavior of the selected contaminants in oxidizing and transitional groundwater systems. The calculations demonstrate what complexes might exist for a given contaminant in any oxidizing water as a function of pH and the specified concentrations of each inorganic ligand. If the concentration of a complexing ligand, such as phosphate, is less for a site-specific groundwater compared to that used for our calculations, then aqueous complexes containing that contaminant and ligand may be less important for that water. Importantly, the water composition in Table 5.1 has a low ionic strength and contains no natural (*e.g.*, humic or fulvic acids¹) or anthropogenic (*e.g.*, EDTA) organic ligands.

Throughout this chapter, particular attention will be directed at identifying the important aqueous- and solid-phase parameters controlling retardation² of contaminants by sorption in soil. This information was used to guide the review and discussion of published K_d values according to the important chemical, physical, and mineralogical characteristics or variables. Perhaps more importantly, we chose parameters that are readily available. For instance, particle size and pH data are often available, whereas such parameters as abundance of iron oxide or surface area are not as frequently available.

¹ “Humic and fulvic acids are breakdown products of cellulose from vascular plants. Humic acids are defined as the alkaline-soluble portion of the organic material (humus) which precipitates from solution at low pH and are generally of high molecular weight. Fulvic acids are the alkaline-soluble portion which remains in solution at low pH and is of lower molecular weight” (Gascoyne, 1982).

² Retarded or attenuated (*i.e.*, nonconservative) transport means that the contaminant moves slower than water through geologic material. Nonretarded or nonattenuated (*i.e.*, conservative) transport means that the contaminant moves at the same rate as water.

Table 5.1. Estimated mean composition of river water of the world from Hem (1985).

| Dissolved Constituent | Total Concentration ¹ | |
|--|----------------------------------|-------------------------|
| | mg/l | mol/l |
| Silica, as H ₄ SiO ₄ | 20.8 | 2.16 x 10 ⁻⁴ |
| Ca | 15 | 3.7 x 10 ⁻⁴ |
| Mg | 4.1 | 1.7 x 10 ⁻⁴ |
| Na | 6.3 | 2.7 x 10 ⁻⁴ |
| K | 2.3 | 5.9 x 10 ⁻⁵ |
| Inorganic Carbon, as CO ₃ | 57 | 9.5 x 10 ⁻⁴ |
| SO ₄ | 11 | 1.1 x 10 ⁻⁴ |
| Cl | 7.8 | 2.2 x 10 ⁻⁴ |
| F | 1 | 5 x 10 ⁻⁵ |
| NO ₃ | 1 | 2 x 10 ⁻⁵ |
| PO ₄ | 0.0767 | 8.08 x 10 ⁻⁷ |

¹ Most values from this table were taken from Hem (1985: Table 3, column 3). Mean concentrations of total dissolved fluoride and phosphate are not listed in Hem (1985, Table 3). The concentration of dissolved fluoride was taken from Hem (1985, p. 120) who states that the concentration of total dissolved fluoride is generally less than 1.0 mg/l for most natural waters. Hem (1985, p. 128) lists 25 µg/l for average concentration of total dissolved phosphorous in river water estimated by Meybeck (1982). This concentration of total phosphorus was converted to total phosphate (PO₄) listed above.

5.2 Americium Geochemistry and K_d Values

5.2.1 Overview: Important Aqueous- and Solid-Phase Parameters Controlling Retardation

Americium is a transuranic (actinide) element, and can exist in the +3 oxidation state in natural waters. Over the pH range of most natural waters, dissolved americium III (Am(III)) is present primarily as the uncomplexed cation Am³⁺ in moderately to highly acidic conditions, and aqueous americium carbonate complexes in near neutral to alkaline pH conditions. Americium readily sorbs to soil, mineral, and crushed rock materials, and exhibits high K_d values. Americium is therefore considered to be immobile in soil environments. However, the tendency of americium to strongly adsorb to soil particles indicates that there is potential for colloid-facilitated transport of americium. Concentrations of dissolved americium may be controlled by precipitation of hydroxide or carbonate solids in some systems.

Therefore, some sorption measurements resulting in very high K_d values may reflect americium precipitation reactions.

5.2.2 General Geochemistry

Americium [Am, atomic number (Z) = 95] has 19 isotopes (Tuli, 2000). The atomic masses of these isotopes range from 231 to 249. Most americium isotopes have short half lives of minutes or less, and only three americium isotopes have half lives longer than a few days. The americium isotopes present in radioactive wastes include the radionuclides Am-241 ($t_{1/2} = 432.2$ years) and Am-243 ($t_{1/2} = 7,370$ years) (Onishi *et al.*, 1981). Americium found in the environment occurs primarily from decay of Pu-241 ($t_{1/2} = 14.29$ years) in nuclear fallout and waste steams from nuclear fuel reprocessing plants.

Americium can exist in the +3, +4, +5, and +6 valence states. The +3 state is the most stable valence state and the one most important in environmental systems. The higher oxidation states are strong oxidizing agents, and stable only in systems containing no oxidizable compounds (Ames and Rai, 1978). The environmental behavior of americium has been reviewed by Silva and Nitsche (1995), Coughtrey *et al.* (1984), Onishi *et al.* (1981), and Ames and Rai (1978).

5.2.3 Aqueous Speciation

Silva *et al.* (1995) have published an extensive, detailed review of the chemical thermodynamics of americium aqueous species and solids. Moulin *et al.* (1988, 1992) review the aqueous speciation of Am(III) in natural waters and in the presence of humic substances in natural waters, respectively. Studies indicate that Am(III) may form strong complexes with humic substances. Possible inorganic aqueous species of Am(III) include those listed in Table 5.2.

Table 5.2. Americium(III) aqueous species.

| Aqueous Species |
|---|
| Am^{3+} , AmOH^{2+} , $\text{Am}(\text{OH})_2^+$, $\text{Am}(\text{OH})_3^\circ$ (aq) |
| AmCO_3^+ , $\text{Am}(\text{CO}_3)_2^-$, $\text{Am}(\text{CO}_3)_3^{3-}$ |
| $\text{AmH}_2\text{PO}_4^{2+}$, $\text{Am}(\text{H}_2\text{PO}_4)_2^+$, $\text{Am}(\text{H}_2\text{PO}_4)_3^\circ$ (aq), $\text{Am}(\text{H}_2\text{PO}_4)_4^-$, AmSO_4^+ , $\text{Am}(\text{SO}_4)_2^-$ |
| AmCl^{2+} , AmCl_2^+ , AmF^{2+} , AmF_2^+ , AmF_3° (aq), AmNO_3^{2+} , $\text{Am}(\text{NO}_3)_2^+$ |

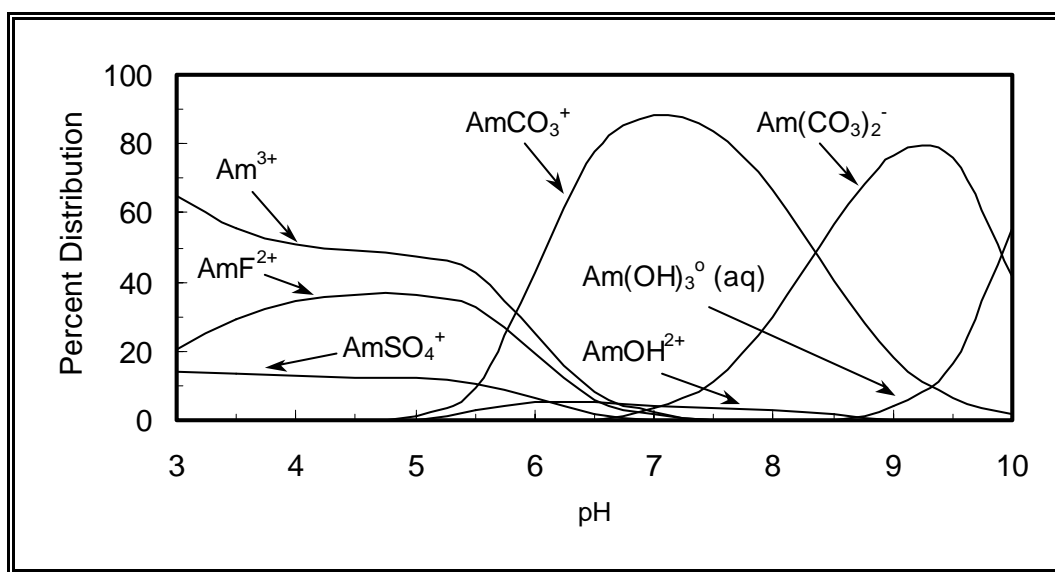
The distribution of aqueous species for Am(III) (see Figure 5.1) as a function of pH was calculated for an oxidizing environment containing the water composition listed in Table 5.1. The speciation calculations indicate that the uncomplexed ion Am^{3+} is the dominant aqueous species for moderately to highly acidic conditions. At near neutral to alkaline pH conditions, Am(III) carbonate complexes will dominate the aqueous speciation of Am(III). Aqueous complexes, such as $\text{Am}(\text{CO}_3)_3^{3-}$, will be increasingly important with increasing concentrations of dissolved carbonate at these pH conditions.

At highly alkaline pH values, Am(III) hydroxyl complexes, such as $\text{Am}(\text{OH})_3^{\circ}(\text{aq})$, may become more important than the Am(III) carbonate species.

5.2.4 Dissolution/Precipitation/Coprecipitation

Concentrations of dissolved Am(III) in soil environments may be controlled by the precipitation of solids such as $\text{Am}(\text{OH})_3$ and AmOHCO_3 , and $\text{Am}_2(\text{CO}_3)_3$, especially at near neutral and alkaline pH conditions (Felmy *et al.*, 1990; Vitorge, 1992; Silva, 1984; and others). With increasing pH and dissolved carbonate concentrations, AmOHCO_3 will be the likely solubility control for dissolved americium. Vitorge (1992) used thermodynamic calculations to predict the stability domains of these americium solids as a function of pH and dissolved carbonate.

Figure 5.1. Calculated aqueous speciation for Am(III) as a function of pH. [Americium(III) aqueous speciation was calculated based on a total dissolved concentration of americium of 1×10^{-12} mol/l (2.43×10^{-7} mg/l), and the water composition in Table 5.1.]



5.2.5 Adsorption/Desorption

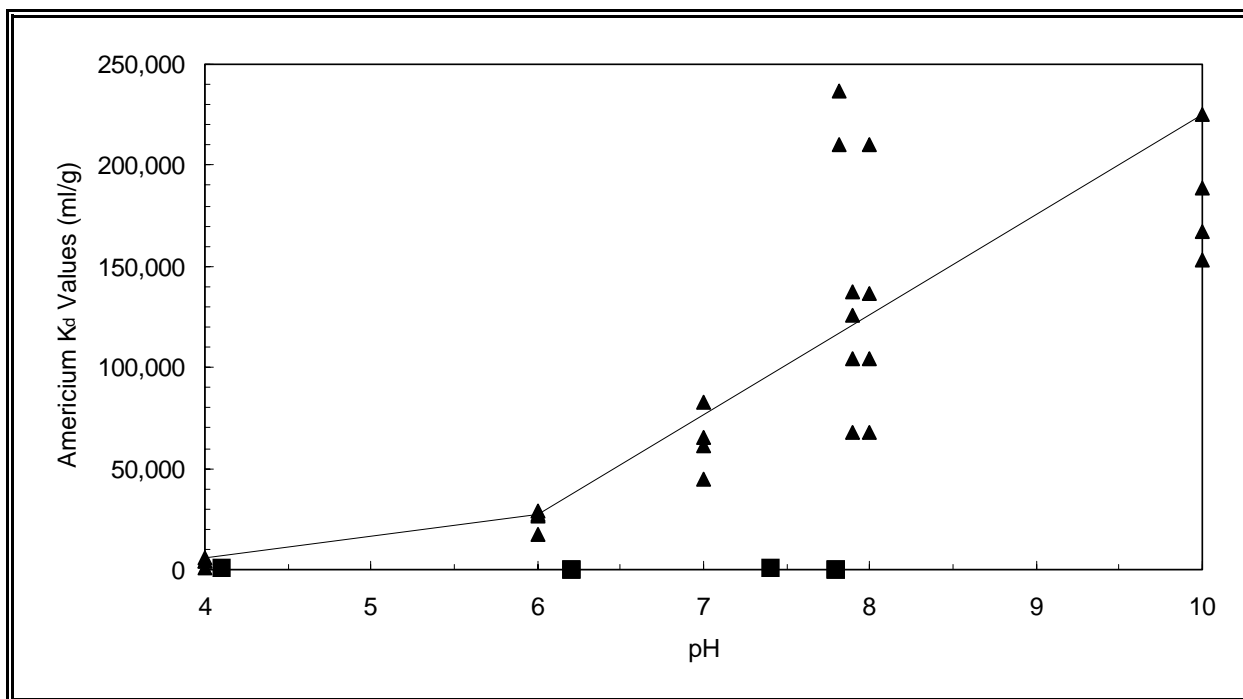
5.2.5.1 *Guidance for Screening Calculations of Adsorption*

Most sorption studies indicate that Am(III) readily sorbs to minerals, crushed rock, and soil materials, and is therefore considered one of the most immobile actinide elements in the environment. Americium adsorption studies published prior to 1984 have been reviewed by Coughtrey *et al.* (1984), Onishi *et al.* (1981), and Ames and Rai (1978). Some of these early studies and more recent studies of Am(III) adsorption are summarized in the sections below. Americium(III) exhibits large K_d values often in the range of 1,000 to $>100,000$ ml/g. However, the concentrations of dissolved americium may be controlled in some geochemical systems by precipitation of hydroxide or carbonate solids. The

reader should therefore be cautious because some sorption measurements resulting in very high K_d values may have been affected by americium precipitation reactions.

A limited number of K_d studies was identified during this review for the adsorption of Am(III) on soil as a function of key geochemical parameters such as pH. The limited availability of such values precluded development of K_d look-up tables of conservative minimum and maximum K_d values for Am(III). Of the studies reviewed below, only Routson *et al.* (1975, 1977) and Sanchez *et al.* (1982) report K_d values and corresponding pH values for Am(III) adsorption on soil (Figure 5.2). For the pH range from 4 to 10, it is suggested that a K_d of 4 ml/g be used as a minimum K_d value for screening calculations of americium transport in soils. This value was reported for pH 7.8 by Routson *et al.* (1975, 1977) and is the lowest K_d value that they gave for experiments conducted with very to moderately dilute calcium and sodium electrolyte solutions. The other K_d values reported by Routson *et al.* (1975, 1977) for these solution concentrations ranged from 6 ml/g at pH 6.2 to 1,200 ml/g at pH 4.1 and 7.4.

Figure 5.2. K_d values (ml/g) for Am(III) adsorption on soil reported by Routson *et al.* (1975, 1977) (solid squares) and Sanchez *et al.* (1982) (solid triangles).



The solid line segments in Figure 5.2 connect the maximum K_d values reported at pH values of 4, 6, and 10 by Sanchez *et al.* (1982). The K_d values corresponding to integer pH values between 4 to 10 are, respectively, 5,600, 16,500, 27,300, 76,700, 126,000, 176,000, and 225,000 ml/g based on straight line extrapolations between these 3 K_d values from Sanchez *et al.* (1982). The reader may want to consider these values as conservative maximum K_d values for Am(III) adsorption on soil.

A large uncertainty however is associated with these roughly estimated, conservative minimum and

maximum K_d values due the limited number of K_d adsorption studies for Am(III) on soil. Accordingly, one of the major recommendations of this report is that for site-specific calculations, partition coefficient values measured at site-specific conditions are absolutely essential.

Based on studies of Am(III) on single mineral phases and crushed rock, the adsorption of Am(III) is strongly pH dependent, and increases with increasing pH with peak adsorption occurring between pH values of 5 and 6 (see studies discussed below). This observed pH dependence is expected, because the dominant aqueous species of americium in the pH range of natural waters are primarily Am^{3+} and cationic carbonate complexes at acidic and basic pH values, respectively (see Figure 5.1).

Americium(III) is more mobile at low to moderate pH values where the net surface charge on minerals becomes more positive and in high ionic strength solutions. Adsorption of Am(III) might decrease in the pH range from approximately 8.5 to 10 due to the dominance of the anionic complex $\text{Am}(\text{CO}_3)_2^-$ (Figure 5.1).

5.2.5.2 *General Adsorption Studies*

Sheppard *et al.* (1979) used batch equilibration experiments to study the sorption of americium and curium to colloidal-size soil particles that are potentially diffusible in soil/water systems. The experiments were conducted with distilled water and 14 soils from Muscatine, Illinois; Hanford, Washington; Barnwell, South Carolina; Idaho Falls, Idaho; and Paradise and Placerville, California. Centrifugation measurements indicated that much of the Am-241 was retained by the colloidal-size soil particles. The sorption of Am-241 on the soil particles was not complete after 4 to 6 months, and percentage of radionuclide retained by the colloidal-size fraction decreased with time. Sheppard *et al.* (1979) found it difficult to correlate the sorption results with chemical and physical properties of the soils. They attributed this to the lack of precise distribution ratios, competition with cation exchange reactions, and complexation with humic and fulvic acid materials. The results also indicated that the sorption behavior of Am-241 and curium (Cm-244) under these experimental conditions was identical. Sheppard *et al.* (1979) suggested that colloids of clay and humic acids are potentially important processes for the transport of actinides in soil/water systems.

Other studies have shown the potential importance of colloid-facilitated transport of americium in soil systems. Laboratory studies by Penrose *et al.* (1990) predicted that the movement of americium and plutonium would be limited to less than a few meters through a shallow aquifer within the site of the Los Alamos National Laboratory (LANL) which is in a semiarid region. However, both actinides were detected in monitoring wells as far as 3,390 m down gradient from the point source. Almost all of the americium and plutonium in the groundwater at the 3,390 m well were associated with colloids 0.025 to 0.45 μm in diameter. Similarly, the results of laboratory measurements using site-specific soils and a two-phase solute transport code indicated that americium, curium, plutonium, and uranium would migrate less than 10 m in the F-Area of the Savannah River Site (Kaplan *et al.*, 1994). The contaminants however were found associated with groundwater colloids 1,200 m away from the point source. Colloid-facilitated migration of contaminants is reviewed in Section 2.7 in Volume I (EPA, 1999b). The reader is cautioned that importance of colloid-facilitated migration, especially in aquifer systems that do not involve fracture flow of groundwater, is still the subject of debate.

Means *et al.* (1978) studied the mineralogy of the adsorbents for americium in soil near a disposal trench at the nuclear waste burial grounds at the Oak Ridge National Laboratory in Oak Ridge, Tennessee.

Their analyses indicated that americium concentrations were highly correlated to the concentrations of manganese oxides, even though the concentrations of iron oxyhydroxides and organic carbon were significantly greater than those of manganese oxides. Means *et al.* (1978) expected americium to be adsorbed by iron oxyhydroxides, but their correlation coefficients for americium sorption versus total iron oxyhydroxides and organic carbon matter were low.

5.2.5.3 *K_d Studies for Americium on Soil Materials*

Carroll *et al.* (1999) investigated the sorption of radionuclides in waters and sediments from the Arctic Sea. Field and laboratory K_d batch measurements were made for the sorption of americium using freshly collected sediment and water samples from stations in the Novaya Zemlya Trough and on the continental shelf of the Ob/Yenisey Rivers. The K_d values measured for americium ranged from 7×10^3 to 1.1×10^6 ml/g.

Nakayama and Nelson (1988) measured the pH dependency of K_d values for the sorption of ^{243}Am and CM-244 onto sediment. They found that changes in pH had a significant effect on the adsorption of these 2 radionuclides. However, the relative adsorption behaviors of these two radionuclides to each other were not significantly different as a function of pH.

Table 5.3. Measured K_d values (ml/g) for americium as a function of pH for Hudson River estuary environment [Sanchez *et al.* (1982)].

| pH | Station Location at Hudson River Estuary for Sediment Samples | | | |
|------|---|--------------------|---------------------|--------------------|
| | MP 0.1 | MP 18.6 | MP 43.3 | MP 59.8 |
| 4.0 | 0.43×10^4 | 0.11×10^4 | 0.43×10^4 | 0.56×10^4 |
| 6.0 | 2.91×10^4 | 1.77×10^4 | 2.67×10^4 | 2.73×10^4 |
| 7.0 | 8.24×10^4 | 4.5×10^4 | 6.12×10^4 | 6.5×10^4 |
| 8.0 | 13.7×10^4 | 21.0×10^4 | 10.43×10^4 | 6.8×10^4 |
| 10.0 | 18.9×10^4 | 22.5×10^4 | 16.7×10^4 | 15.3×10^4 |

Burton *et al.* (1986) studied the sorption of americium on intertidal sediment from the Ravenglass Estuary in seawater from the North Sea. The K_d values were of the magnitude 10^3 - 10^4 ml/g. Results from desorption experiments conducted with seawater diluted with river water indicated that the K_d values were essentially constant at salinities from 34 to 2-5‰, and decreased by 2 orders of magnitude at salinities less than 2-5‰. Burton *et al.* (1986) attributed this decrease in K_d in part to a decrease in pH.

Sanchez *et al.* (1982) used the batch method to measure K_d values for americium for a variety of freshwater, estuarine, and marine environments. The adsorption K_d values ranged from 6.76×10^4 to 2.27×10^6 ml/g for all environments studied. Experiments conducted as a function of pH (Table 5.3.)

indicated that the K_d values increased with increasing pH. The americium K_d values increased by a factor of 5 over the pH range 4 to 6, and continued to increase at high pH values. Sanchez *et al.* (1982) found no apparent effect of salinity on the americium K_d values.

Table 5.4. Measured americium K_d values (ml/l) and soil properties for soils studied by Nishita *et al.* (1981).

| Soil Type | pH ¹ | OM ² Fraction (%) | CEC ³ (meq/100 g) | Free Fe Oxides (%) | Mn ⁴ Fraction (%) | Extract pH | K_d (ml/g) |
|---------------------------|-----------------|------------------------------|------------------------------|--------------------|------------------------------|--------------|------------------|
| Silt Clay Loam Sharpsburg | 5.9 | 2.8 | 20 | 1.29 | 0.06 | 5.41 6.56 | 29,800 17,280 |
| Sandy Loam Malbis | 5.3 | 2.4 | 15 | 1.65 | 0.05 | 4.39 5.71 | 9,635 8,063 |
| Sandy Loam Lyman | 5.0 | 5.7 | 15 | 1.52 | 0.04 | 4.58 6.17 | 1,549 182 |
| Silty Clay Holtsville | 7.8 | 0.6 | 30 | 1.20 | 0.04 | 7.12 8.04 | 35,630 47,230 |
| Loam Aiken | 6.0 | 8.4 | 15 | 5.29 | 0.10 | 5.71 6.72 | 21,870 10,660 |
| Silt Loam Yolo | 6.7 | 2.5 | 25 | 2.41 | 0.08 | 6.12 6.98 | 23,870 20,210 |
| Muck Egbert | 7.2 | 40.8 | 60 | 1.57 | 0.10 | 7.14 7.54 | 7,266 5,529 |

¹ Saturated paste. ⁴ In 4 M HNO₃ extract.
² Organic matter.
³ Cation Exchange Capacity

Nishita *et al.* (1981) studied the extractability of Am-241 from several types of soils as a function of pH. The extractability of americium was considered to parallel the solubilization of aluminum, iron, and/or manganese hydroxous oxides, which are important adsorbents for dissolved contaminants in soil systems (Nishita *et al.*, 1981). The americium K_d values and soil characteristics determined for these soils by Nishita *et al.* (1981) are listed in Table 5.4. At pH values more acidic than those studied, Nishita *et al.* (1981) suggested that americium would be present in ionic form and highly mobile. At higher pH values, americium formed hydroxyl complexes that were readily sorbed by the soils.

Routson *et al.* (1975, 1977) used batch equilibration experiments to measure K_d values for Am-241 on 2 soils as a function of the concentrations of dissolved calcium and sodium. The soil samples were selected to represent a range of weathering intensities. For arid conditions in the western United States, a sandy (coarse-textured), low-exchange capacity soil was selected from a low rainfall area in eastern Washington. For humid conditions in southeastern United States, a moderate-exchange capacity soil

was selected from South Carolina. Properties of the soils used for these measurements are listed in Table 5.5.

Table 5.5. Properties of soils used in K_d measurements by Routson *et al.* (1975, 1977).

| Soil | CaCO ₃ (mg/g) | Silt (%) | Clay (%) | CEC (meq/100 g) | pH |
|----------------|-----------------------------|-------------|-------------|--------------------|-----|
| Washington | 0.8 | 10.1 | 0.5 | 4.9 | 7.0 |
| South Carolina | <0.2 | 3.6 | 37.2 | 2.5 | 5.1 |

The K_d values were measured in 0.002, 0.02, 0.05, 0.10, and 0.20 M Ca(NO₃)₂ solutions, and 0.015, 0.030, 0.30, 0.75, and 3.0 M NaNO₃ solutions. The pH values for selected samples of the Am-241 solutions in the calcium and sodium systems were 6.9 and 4.1 for the Washington soil, and 7.1 and 6.1 for the South Carolina soil. The K_d values decreased with increasing concentrations of dissolved calcium and sodium. For the solution concentrations used in these experiments, the K_d values for Am-241 on the South Carolina soil ranged from 67 to 1.0 ml/g as a function of dissolved calcium, and 280 to 1.6 ml/g as a function of dissolved sodium. For the Washington soil, the K_d values were >1,200 ml/g, and were independent of the concentrations of dissolved calcium and sodium. Their calculated K_d values ranged from 1,200 to 8,700 ml/g. The sorption of Am-241 on the Washington soil was greater than that expected by investigators.

5.2.5.4 *Published Compilations Containing K_d Values for Americium*

Because the references in this section are often cited or used for comparison in other publications, the following summaries are provided for completeness. It is recommended that the reader review the original reference and the references cited therein to understand the procedures and sources of the K_d values used for each compilation. The compilations do not typically consider important factors that contribute to variability in sorption, such as pH. Moreover, in cases where very large K_d values are listed, there is a risk that the original K_d measurement may have included precipitated components.

Baes and Sharp (1983) present a simple model developed for order-of-magnitude estimates for leaching constants for solutes in agricultural soils. As part of this model development, they reviewed and determined generic default values for input parameters, such as K_d . A literature review was completed to evaluate appropriate distributions for K_d values for various solutes, including americium. Because Baes and Sharp (1983) are cited frequently as a source of K_d values in other published K_d reviews (*e.g.*, Looney *et al.*, 1987, Sheppard and Thibault, 1990), the americium K_d values listed by Baes and Sharp are reported here for completeness. Based on the distribution that Baes and Sharp determined for the K_d values for cesium and strontium, they assumed a lognormal distribution for the K_d values for all other elements in their compilation. Baes and Sharp listed an estimated default K_d of 810 ml/g for americium based on 46 K_d values that ranged from 1.0 to 47,230 ml/g for agricultural soils and clays

over the pH range 4.5 to 9.0. Their compiled K_d values represent a diversity of soils, pure clays (other K_d values for pure minerals were excluded), extracting solutions, measurement techniques, and experimental error.

Looney *et al.* (1987) tabulated estimates for geochemical parameters needed for environmental assessments of waste sites at DOE's Savannah River Plant in South Carolina. Looney *et al.* list K_d values for several metal and radionuclide contaminants based on values that they found in one to five published sources. For americium, Looney *et al.* list a "recommended" K_d of 100 ml/g, and a range from 1 to 100,000 ml/g. Looney *et al.* note that their recommended values are specific to the Savannah River Plant site, and they must be carefully reviewed and evaluated prior to use in assessments at other sites.

Table 5.6. Americium K_d values (ml/g) listed by Thibault *et al.* (1990, Tables 4 to 8).

| Soil Type | K_d Values (ml/g) | | |
|-----------|---------------------|------------------------|-----------------|
| | Geometric Mean | Number of Observations | Range |
| Sand | 1,900 | 29 | 8.2 - 300,000 |
| Silt | 9,600 | 20 | 400 - 48,309 |
| Clay | 8,400 | 11 | 25 - 400,000 |
| Organic | 112,000 | 5 | 6,398 - 450,000 |

Thibault *et al.* (1990) (also see Sheppard and Thibault, 1990) present a compilation of soil K_d values prepared to support radionuclide migration assessments for a Canadian geologic repository for spent nuclear fuel in Precambrian Shield plutonic rock. Thibault *et al.* collected K_d values from other compilations, journal articles, and government laboratory reports for important elements, such as americium, that would be present in the nuclear fuel waste inventory. The americium K_d values listed in Thibault *et al.* (1990) are included in Table 5.6. Thibault *et al.* (1990) describe the statistical methods used for analysis of the compiled K_d values. The range for the K_d values used to calculate the "geometric mean" cover several orders of magnitude. Readers are cautioned against using "geometric mean" values or any other form of averaged K_d values as "default" K_d values, as such values are usually calculated from data compiled from different investigators for different soil systems. These mean or average values do not represent any particular environmental system and geochemical conditions. As discussed in Volume I (EPA, 1999b), the variation observed in the literature for K_d values for a contaminant is due to differences in sorption mechanisms, geochemical conditions, soil materials, and methods used for the measurements.

McKinley and Scholtis (1993) compare radionuclide K_d sorption databases used by different international organizations for performance assessments of repositories for radioactive wastes. The americium K_d values listed in McKinley and Scholtis (1993, Tables 1, 2, and 4) are listed in Table 5.7.

The reader should refer to sources cited in McKinley and Scholtis (1993) for details regarding their source, derivation, and measurement. Radionuclide K_d values listed for cementitious environments in McKinley and Scholtis (1993, Table 3) are not included in Table 5.7. The organizations listed in the tables include: AECL (Atomic Energy of Canada Limited); GSF (Gesellschaft für Strahlen- und Umweltforschung m.b.H., Germany); IAEA (International Atomic Energy Agency, Austria); KBS (Swedish Nuclear Safety Board); NAGRA [Nationale Genossenschaft für die Lagerung radioaktiver Abfälle (Swiss National Cooperation for Storage of Radioactive Waste), Switzerland]; NIREX (United Kingdom Nirex Ltd.); NRC (U.S. Nuclear Regulatory Commission); NRPB (National Radiological Protection Board, United Kingdom); PAGIS [Performance Assessment of Geological Isolation Systems, Commission of the European Communities (CEC), Belgium; as well as PAGIS SAFIR (Safety Assessment and Feasibility Interim Report)]; PSE (Projekt Sicherheitsstudien Entsorgung, Germany); RIVM [Rijksinstituut voor Volksgezondheid en Milieuhygiene (National Institute of Public Health and Environment Protection), Netherlands]; SKI [Statens Kärnkraftinspektion (Swedish Nuclear Power Inspectorate)]; TVO [Teollisuuden Voima Oy (Industrial Power Company), Finland]; and UK DoE (United Kingdom Department of the Environment).

Table 5.7. Americium K_d values (ml/g) listed by McKinley and Scholtis (1993, Tables 1, 2, and 4) from sorption databases used by different international organizations for performance assessments of repositories for radioactive wastes.

| Organization | Argillaceous (Clay) | | Crystalline Rock | | Soil/Surface Sediment | |
|--------------|----------------------|------------------|----------------------------|--------------|-----------------------|--------------|
| | Sorbing Material | K_d (ml/g) | Sorbing Material | K_d (ml/g) | Sorbing Material | K_d (ml/g) |
| AECL | Bentonite-Sand | 300 | Granite | 1,000 | | |
| GSF | Sediment | 2,000,000 | | | | |
| IAEA | Pelagic Clay | 2,000,000 | | | | |
| KBS-3 | Bentonite | 29,400 | Granite | 5,000 | | |
| NAGRA | Bentonite | 5,000 | Granite | 5,000 | Soil/Sediment | 5,000 |
| | Clay | 70 | | | | |
| NIREX | Clay Mudstone | 5,000 | | | | |
| NRC | Clay, Soil Shale | 10,000 | Granite | 300 | | |
| | | | Basalt | 50 | | |
| | | | Tuff | 100 | | |
| NRPB | Clay | 80 | | | Soil/Sediment | 3,000 |
| PAGIS | Bentonite | 2,000 | | | Soil/Sediment | 8,800 |
| PAGIS SAFIR | Clay | 600 | | | | |
| PSE | Sediment | 10,000 | | | | |
| RIVM | Sandy Clay | 1,000 | | | | |
| SKI | Bentonite | 7,000 | Granite | 5,000 | | |
| TVO | Bentonite | 2,900 | Crystalline Rock, Reducing | 3,000 | Soil/Sediment | |
| | Lake Sediment | 1,000 100,000 | Crystalline Rock | 400 | Soil/Sediment | 100,000 |
| UK DoE | Coastal Marine Water | 1,000,000 | | | Soil/Sediment | 800 |

5.2.5.5 *K_d Studies of Americium on Pure Mineral, Oxide, and Crushed Rock Materials*

Numerous adsorption studies have been conducted of americium on pure minerals, oxide phases, and other geologic-related materials. The K_d values listed in these studies are not necessarily relevant to the mobility and sorption of americium in soils. However, they are listed in Appendix C for completeness. The references cited in Appendix C are listed in the main reference list in Chapter 6. The potential value of the references that they cite and the sorption processes that they discuss is left to the reader. The studies of americium sorption on crushed rock were conducted typically as part of national research programs to investigate the feasibility of geological disposal of high-level radioactive waste (HLW).

5.3 Arsenic Geochemistry and K_d Values

5.3.1 Overview: Important Aqueous- and Solid-Phase Parameters Controlling Retardation

Arsenic is a known carcinogen, and occurs in natural systems in the +5 (arsenate) and +3 (arsenite) valence states. Arsenic(III) (As(III)) is more mobile (adsorbs less) and is many times more toxic than As(V). The pH and redox conditions are the two most important geochemical factors affecting the mobility of arsenic in the environment. Sorption studies indicate that the concentrations of dissolved As(V) and As(III) are controlled by adsorption on iron and aluminum oxides and clays. The adsorption of As(V) is high and independent of pH at acidic pH values, and decreases with increasing pH in the range of 7 to 9. Arsenic(V) adsorption will be decreased in soils with high phosphate concentrations because of anion competition. Iron-reducing bacteria may cause arsenic mobilization from soils as a consequence of reductive dissolution of iron oxyhydroxide adsorbents. Sulfate-reducing bacteria, in addition, may promote arsenic reduction by producing hydrogen sulfide.

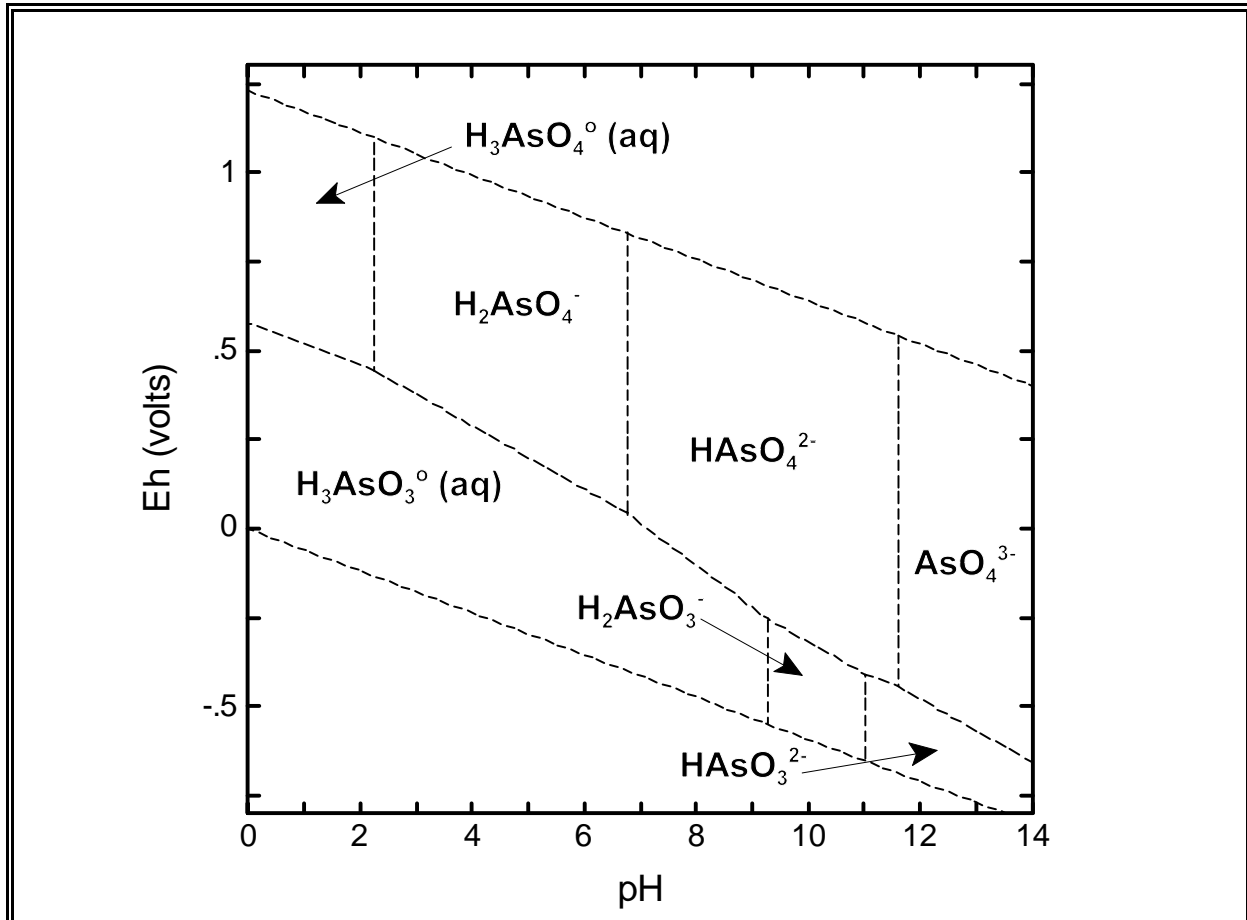
5.3.2 General Geochemistry

Arsenic [As, atomic number (Z) = 33] is a known carcinogen. Arsenic contamination of groundwater may result from a variety of sources, such as weathering of rocks, mining activities, discharges of industrial waste, and application of arsenical herbicides and pesticides. Arsenic exhibits a complex geochemical behavior. It can occur in the valence states -3, 0, +3, and +5 in natural systems. Arsenic(V) (arsenate) and As(III) (arsenite) are the main valence states of arsenic in natural waters under oxidizing and reducing conditions, respectively. Elemental (metal) arsenic [As(0)] occurs rarely, and As(-III) exists only at extremely low redox potential (*i.e.*, Eh values). Arsenic(III) is more mobile (adsorbs less) and many times more toxic than As(V). Although As(V) should be the dominant valence state in oxidizing waters based on thermodynamic considerations, the results of some studies indicate that As(III) concentrations exceed those of As(V) in some surface waters (Korte and Fernando, 1991). Arsenic(III) may be more prevalent than generally believed in such environments due to oxidation/reduction disequilibrium and biotic processes.

It should be noted that only three published studies containing K_d values for arsenic sorption on soil were identified during the course of this review. This is an important finding given the increasing concern over arsenic contamination in the environment and associated risks to plants, animal, and human health. We suspect that the limited availability of K_d values for arsenic may be related to the K_d approach being used prior to the 1990's primarily in risk and site performance assessments

associated with radionuclides and their disposal and potential migration in the subsurface environment.

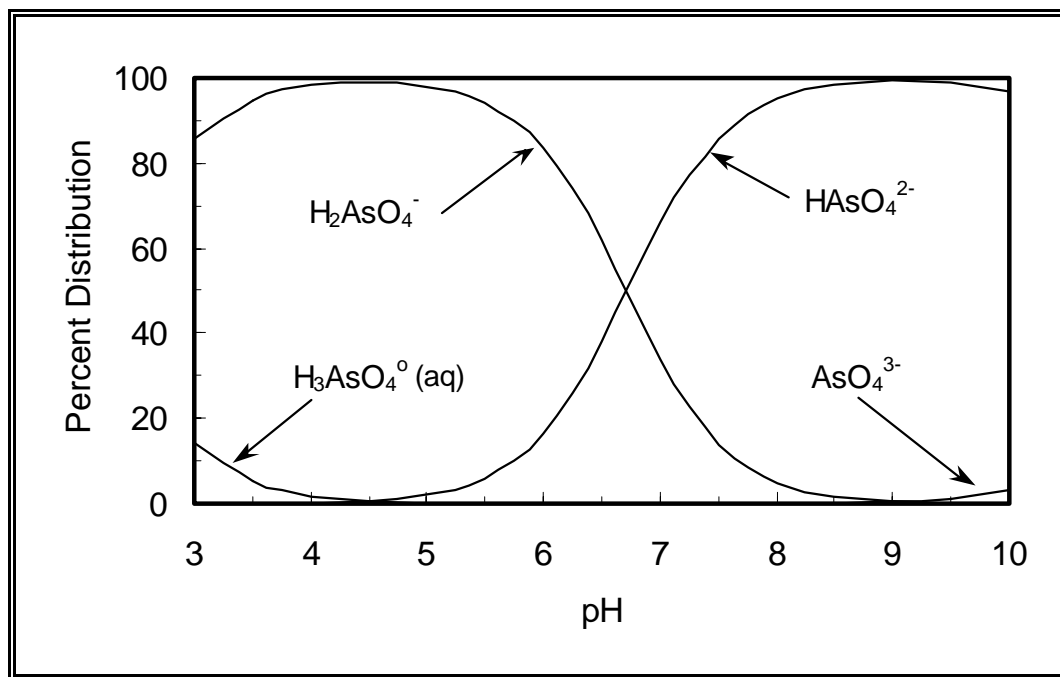
Figure 5.3. Eh-pH stability diagram for the dominant arsenic aqueous species at 25°C. [Diagram based on a total concentration of 10^{-6} mol/l dissolved arsenic.]



Arsenic contamination of drinking water is a major concern recognized in areas of the United States, and internationally in many countries. Arsenic contamination of groundwater in Bangladesh has been highly publicized, and has generally been attributed to a geologic origin. The following models (WHO, 1999) have been proposed for how groundwater contamination occurs:

- Pyrite oxidative dissolution - Pumping of air or water containing dissolved oxygen into the subsurface results in the dissolution of arsenic-containing pyrite, and mobilization of arsenic.
- Oxyhydroxide reductive dissolution - Iron oxyhydroxide particles containing sorbed arsenic are exposed to a reducing geochemical environment that results in the dissolution of the iron oxyhydroxides and mobilization of the sorbed arsenic.

Figure 5.4. Calculated aqueous speciation for As(V) as a function of pH. [Arsenic(V) aqueous speciation was calculated based on a total concentration of dissolved arsenic of 6.7×10^{-7} mol/l (50 ppm) and the water composition in Table 5.1.]



The mechanisms responsible for arsenic mobility in groundwater in Bangladesh and West Bengal have discussed by many, including Nickson *et al.* (2001).

Various aspects of the behavior of arsenic in natural systems are reviewed by Sadiq (1997), Korte and Fernando (1991), Cullen and Reimer (1989), Creclius *et al.* (1986), Rai *et al.* (1984), Woolson (1983), Braman (1983). Biotic processes are potentially of considerable significance to the environmental chemistry of arsenic (see Section 5.3.3.1). The review by Cullen and Reimer (1989) is particularly noteworthy because of its magnitude (51 pages), level of detail, and extensive reference list (458 references cited). Reviews of arsenic geochemistry and behavior in fossil fuel combustion residues (Rai *et al.*, 1987) and geothermal systems (Ballantyne and Moore, 1988) have also be published. Korte and Fernando (1991) review in detail the behavior of As(III) in groundwater.

Remediation of arsenic-contaminated environments has also been studied. Recently published studies, for example, include arsenic immobilization in contaminated soil by the addition of ferrous sulfate and water, followed by the addition of $Ca(OH)_2$, Portland cement, and water (Voigt and Brantley, 1996), and formation of solid calcium arsenate (Both and Brown, 1999); and *in situ* removal of dissolved arsenate and arsenite in contaminated groundwater by introduction of metallic iron fillings (zero valent iron) (Su and Puls, 2001; Lackovic *et al.*, 2000).

5.3.3 Aqueous Speciation

Sadiq and Lindsay (1981) reviewed the thermodynamic data for arsenic aqueous and solids species. They concluded that the majority of thermodynamic constants for arsenic were not reliable. We have not identified any compilation of arsenic thermodynamic constants more current than Sadiq and Lindsay (1981).

The aqueous speciation of dissolved arsenic has been reviewed in detail by Sadiq (1997) and Cullen and Reimer (1989). The stable forms of dissolved arsenic in natural waters are primarily a series of aqueous As(V) (arsenate, AsO_4^{3-}) and As(III) (arsenite, AsO_3^{3-}) oxyanion species under oxidizing and reducing conditions, respectively. Figure 5.3 is an Eh-pH diagram that shows the dominant aqueous species of arsenic as a function of pH and Eh (redox potential) at 25°C with respect to the thermodynamic stability of water.

The known aqueous species of As(V) include AsO_4^{3-} , HAsO_4^{2-} , H_2AsO_4^- , and H_3AsO_4^0 (aq) (Wagman *et al.*, 1982; Sadiq, 1997). The distribution of these As(V) aqueous species (Figure 5.4) as a function of pH was calculated for an oxidizing environment containing the water composition listed in Table 5.1. The calculations indicate that the oxyanions H_2AsO_4^- and HAsO_4^{2-} dominate the aqueous speciation of As(V) at pH values less than and greater than approximately pH 7, respectively. Because As(V) will be present primarily as anions in oxidizing waters, As(V) is expected to adsorb to geologic materials under acidic conditions and not to adsorb to any significant extent at neutral and alkaline pH conditions. Similarly, the dominant As(III) aqueous species are H_3AsO_3^0 (aq) and H_2AsO_3^- at pH values less than and greater than approximately pH 9, respectively.

Arsenic is not expected to form aqueous complexes with other inorganic complexing ligands, such as dissolved sulfate, because dissolved arsenic is present in anionic form. However, the results of Kim *et al.* (2000) indicate that carbonation reactions with arsenic sulfide minerals may be an important process in leaching arsenic into groundwater under anaerobic conditions. Kim *et al.* (2000) investigated the role of bicarbonate in leaching arsenic from a sandstone into groundwater. They determined that the release of arsenic from arsenic sulfides in the sandstone was strongly related to the bicarbonate concentrations in the leachate. Kim *et al.* (2000) proposed that the released As(III) was converted to As(III) carbonate complexes with the presumed compositions $\text{As}(\text{CO}_3)_2^-$, $\text{As}(\text{CO}_3)(\text{OH})_2^-$, and/or AsCO_3^+ . Kim *et al.* (2000) expected that once formed, the As(III) carbonate complexes would be stable under anaerobic groundwater conditions at acidic to neutral pH. No published stability constants are known to exist for such aqueous complexes.

Organoarsenic species, such as methyl arsonic acid ($\text{CH}_3\text{AsO}(\text{OH})_2$) and dimethyl arsenic acid [$(\text{CH}_3)_2\text{AsOOH}$], can be formed by biologically-mediated methylation in the environment, and have been detected in soils and aquatic systems. Because their formation requires the involvement of anaerobic bacteria, the literature refers to the origin of these organoarsenic compounds as biomethylation. Methylated arsenic species typically comprise only a small fraction of the available arsenic (Sanders, 1980). Thermodynamic data are not available for such compounds, and no stability diagrams have been published regarding their range of stability (Cullen and Reimer, 1989). The chemistry, formation, and behavior of these organoarsenic compounds are reviewed by Cullen and Reimer (1989) and Sadiq (1997).

5.3.4 Dissolution/Precipitation/Coprecipitation

Although it can be argued, concentrations of dissolved As(V) in natural waters and soils are not likely controlled by formation of arsenic solids unless elevated concentrations of arsenic exist, such as in mining waste waters, industrial waste streams, or fossil fuel combustion residues. The formation of arsenic solids that would limit the solubility of arsenic in waste waters, natural waters, and soils has been the subject of considerable study and conjecture. For example, see Lumsdon *et al.* (2001), Davis (2000), Tempel *et al.* (2000), Rochette *et al.* (1998); Sadiq (1997), Fruchter *et al.* (1990), and Crecelius *et al.* (1986). Searches of mineralogy databases available on the Internet indicate that there are more than 490 known minerals that contain arsenic as a primary component. These minerals include arsenic sulfides, arsenates, and arsenides, and are present in unique geologic settings such as ore deposits and geothermal settings. Many attempts at identifying possible solubility controls for dissolved As(V) and As(III) have relied on geochemical solubility calculations. Because thermodynamic constants and kinetic data exist for a very limited number of arsenic solids (Sadiq, 1997), and even these data are not well established, arsenic thermodynamic-based solubility calculations are problematic at best.

Several investigators have suggested $Ba_3(AsO_4)_2$ as a solubility-limiting solid for As(V). However, Crecelius *et al.* (1986) noted that there is no physical evidence for the existence of such a solid in geologic systems and thus its thermodynamic properties are in error or kinetic constraints inhibit its precipitation.

Under reducing conditions in the presence of dissolved sulfide, arsenic sulfide solids, such as orpiment may control the solubility of dissolved As(III). Moreover, pyrite (FeS_2) has been found to contain a significant mass of coprecipitated (*i.e.*, absorbed) arsenic in its crystal structure [*e.g.*, see Schreiber *et al.* (2000)], and to be a source and/or solubility control for dissolved As(III).

5.3.5 Adsorption/Desorption

5.3.5.1 Guidance for Screening Calculations of Adsorption

Only three published studies containing K_d values for arsenic sorption on soil were identified during the course of our review. These studies are discussed in the sections below. The studies by Cornett *et al.* (1992) and Mok and Wai (1990) involve sampling environments affected by ore milling operations and list extremely high K_d values (>1000 's ml/g) for arsenic sorption on sediment. These high K_d values are surprising given the large mobility expected for As(V) and As(III) based on the results of other published sorption studies at all but the very acidic pH values. The results from Cornett *et al.* (1992) and Mok and Wai (1990) are therefore suspect and were not considered further in this review.

The limited availability of K_d values for arsenic on soil (*i.e.*, 1 study) precluded calculation of K_d look-up tables for arsenic as a function of important geochemical parameters such as pH. Because dissolved As(V) will exist primarily as anionic aqueous species in the pH range of 4 to 10, a K_d value of 0 ml/g is suggested as a conservative minimum value for site screening calculations of the maximum extent of off-site migration of As(V) in soil. However, one of the major recommendations of this report, as noted previously, is that for site-specific calculations, partition coefficient values measured at site-specific conditions are absolutely essential.

Given the limited availability of As(V) K_d values for soil, readers may want to consider using geochemical models [see Section 5 in Volume I (EPA, 1999b)] to estimate the mass of adsorbed As(V). This approach was recently taken by Lumsdon *et al.* (2001). Characterization studies indicated that hydrous ferric oxide (HFO) was an important mineral in the soils at the site being studied. Assuming that HFO was the dominant adsorbent for As(V) in these soils, Lumsdon *et al.* (2001) used the generalized two-layer surface complexation model (GTLM) and As(III)-HFO surface complexation parameters listed in Dzombak and Morel (1990) to estimate the mass of adsorbed As(V). Based on the HFO content of the soils, K_d values could then be estimated from the modeling results.

The results of sorption studies of arsenic on single mineral phases indicate that the concentrations of dissolved As(V) and As(III) are controlled by adsorption on iron and aluminum oxides and clays. Adsorption of arsenic exhibits a marked pH dependency. While adsorption of As(V) is high and independent of pH at acidic pH values, adsorption decreases with increasing pH in the range of 7 to 9.

At a given pH, the adsorption of As(V) is typically greater than As(III). Arsenic(V) and dissolved phosphate compete for adsorption sites, and the adsorption of arsenic will be reduced in soils with high phosphate concentrations. Microbial-mediated reactions may affect arsenic mobilization in soils. Studies have shown that iron-reducing bacteria may cause arsenic mobilization from soils as a consequence of reductive dissolution of iron oxyhydroxide adsorbents. Microbial-mediated reactions can cause the precipitation and dissolution of minerals, and thus affect the mobility of contaminants in aqueous environments. The interactions between microbes and minerals are reviewed in detail elsewhere, such as Banfield and Nealson (1997). Additionally, sulfate-reducing bacteria may promote arsenic reduction by producing hydrogen sulfide.

5.3.5.2 *General Adsorption Studies*

Sorption studies conducted with soils indicate that arsenic sorption on soil is a function of the iron oxyhydroxide and clay contents (Manning and Goldberg, 1997b; Wauchope and McDowell, 1984; Livesey and Huang, 1981; Wauchope, 1975, Jacobs *et al.*, 1970; and others). Manning and Goldberg (1997) measured the adsorption of As(V) and As(III) on three arid-zone soils from California as a function of varying arsenic concentrations, pH, and ionic strength. The greatest extent of As(V) and As(III) adsorption was measured for the soil having the highest citrate-dithionite extractable iron and percent clay content. Manning and Goldberg (1997) noted that the arsenic adsorption behavior for this soil was similar to the arsenic adsorption behavior that they measured for goethite. The sorption measurements also indicated that As(V) adsorbed more strongly than As(III) under most conditions. Wauchope and McDowell (1984) measured the sorption of As(V) on 14 lake sediments collected in the Delta Mississippi River flood plain. Wauchope and McDowell (1984) found that the extent of arsenic adsorption was related to the hydrous oxide and clay contents of the sediments. Based on their results, Wauchope and McDowell (1984) proposed that the clay content of sediment was the best predictor for arsenic adsorption in soils and dilute water-sediment mixtures. Wauchope (1975) used batch reaction experiments to study the sorption of As(V) on 16 soils from the Mississippi River alluvial flood plain. Wauchope (1975) determined that the sorption of As(V) was strongly correlated with the iron oxide and clay contents of the soils. Based on measurements of 24 soils representing a range of chemical and physical properties from throughout Wisconsin, Jacobs *et al.* (1970) showed that the mass of sorbed arsenic increased with an increase of the free Fe_2O_3 content of soil.

Carrillo and Drever (1998) conducted a series of sorption experiments for As(V) and As(III) on soils taken from an aquifer in the San Antonio-El Triunfo mining area in Baja California peninsula, Mexico. The aquifer material consisted of quartz, feldspar, calcite, chlorite, illite, and magnetite/hematite. The experiments were conducted using background electrolyte solutions of 0.1 and 0.01 M NaNO₃ solutions, and pH ranges of 4 to 13 and 6 to 12 as adjusted with HCl and NaOH solutions. The observed percent of sorbed total arsenic, As(V), and As(III) versus pH agreed with that expected for the adsorption of arsenic on iron oxyhydroxides. Sorption of arsenic on the aquifer material was high at acidic pH values, and low at alkaline pH values. Arsenic sorption decreased quickly in the pH range 6 to 9.

Sorption studies have also been conducted to determine the effect on arsenic sorption by the presence of other anions, such as dissolve phosphate, sulfate, nitrate, and chloride (Reynolds *et al.*, 1999; Livesey and Huang, 1981). The results of these studies indicate that dissolved phosphate competes with arsenic for adsorption sites, and thus suppressing arsenic adsorption and enhancing the mobility of arsenic. Livesey and Huang (1981) found that dissolved sulfate, nitrate, and chloride present at concentrations present in saline soils had little effect on arsenic adsorption. As noted previously, As(III) is more mobile and toxic than As(V), and thus redox conditions affect the relative sorption behavior of As(V) and As(III). Biotic processes affecting the reduction of As(V) to As(III) have recently been the subject of considerable study. Recently published studies confirm that microbial processes can affect the mobilization of arsenic in environmental systems by a variety of direct and indirect oxidation/reduction processes (*e.g.*, Ahman *et al.*, 1997; Cummings *et al.*, 1999; Jones *et al.*, 2000; Langner and Inskeep, 2000; Zobrist *et al.*, 2000). Ahman *et al.* (1997) studied the mobilization of solid-phase arsenic in sediment microcosms from the Aberjona Watershed. Sediment suspensions were incubated with iron arsenate, which was used as an analogue for sedimentary arsenic, to investigate the potential for arsenic mobilization by microbial reactions in these sediment samples. The results indicated that arsenic could be mobilized by microbial-mediated reductive dissolution of the iron arsenate solids. Arsenic(V) released from the dissolution of the iron arsenate was also reduced to As(III) under these reducing conditions.

Ahman *et al.* (1997) also determined that the microbial dissolution/reduction processes could be prevented by sterilization of the sediment suspensions, which helped to confirm that the processes were microbially mediated.

Cummings *et al.* (1999) studied arsenic mobilization by dissimilatory iron-reducing bacteria (DIRB). Using the dissimilatory iron-reducing bacterium *Shewanella alga* strain BrY, their experiments showed that arsenic could be mobilized from crystalline ferric arsenate (the mineral scorodite, FeAsO₄·2H₂O) and from As(V) sorbed to sediments from Lake Coeur d'Alene, Idaho. Arsenic mobilization was the result of dissimilatory (*i.e.*, respiratory) reduction of Fe(III), to Fe(II). Analyses of iron and arsenic in the solid phases and aqueous solutions indicated that arsenic and iron were present as As(V) and Fe(II) in both the solid and aqueous phases. Cummings *et al.* (1999) concluded that even in the absence of reduction to As(III), As(V) could be mobilized from sediments by biotic reactions of dissimilatory iron-reducing bacteria.

Jones *et al.* (2000) investigated the mechanisms controlling the rates of microbial-mediated reduction of dissolved and adsorbed arsenic. The experiments were conducted with microorganisms obtained from fine loamy agricultural soil that contained naturally elevated concentrations of arsenic. The results of microbial-mediated mobilization experiments conducted in the presence of the iron oxides

goethite or ferrihydrite indicated that the extent of arsenic solubilization depended on the arsenic surface coverage and on the surface area or crystallinity of the iron oxide phase. During microbial-mediated reduction, the rate of arsenic desorption from ferrihydrite was determined to be two orders magnitude greater than that from goethite at similar concentrations of dissolved arsenic. Jones *et al.* (2000) proposed that this difference in solubilization rates was due to differences in the rates of reductive dissolution of the iron oxide phases.

Langner and Inskeep (2000) studied the effect of microbial reduction of dissolved As(V) on the desorption of As(V) sorbed to ferrihydrite in the absence of reductive dissolution of the Fe(III)-oxide solid phase. The reduction of As(V) was investigated using a glucose-fermenting *Clostridium sp.* strain CN8 enriched from an arsenic contaminated soil. Despite rapid reduction of dissolved As(V) to As(III), the sorbed arsenic remained primarily as As(V), and desorption of As(V) was too slow to cause a significant increase in dissolved concentrations of arsenic over the 24-day experiment. Based on their results, Langner and Inskeep (2000) proposed that the reduction of dissolved As(V) plays a minor role in the remobilization of As(V) sorbed to iron oxyhydroxide phases, and arsenic release from contaminated soils may proceed faster via microbial-mediated reductive dissolution of the iron oxyhydroxides adsorbents.

Zobrist *et al.* (2000) studied the ability of the bacterium *Sulfurospirillum barnesii* strain SES-3 to reduce As(V) adsorbed on ferrihydrite and aluminum hydroxide. Their results indicated that cell suspension of *S. barnesii* were able to reduce As(V) to As(III) when As(V) is present in solution or when adsorbed on ferrihydrite or aluminum hydroxide. The results from the experiments conducted with aluminum hydroxide show that reduction of adsorbed As(V) does not require microbial-mediated reductive dissolution of ferrihydrite because the aluminum hydroxide does not undergo reductive dissolution.

5.3.5.3 *K_d Studies for Arsenic on Soil Materials*

Only three published studies containing K_d values for arsenic sorption on soil were identified during the course of our review. Only one of the identified published studies listing K_d values for arsenic sorption on soil is reviewed below. In agreement with the other studies of arsenic on single mineral phases and soils (see above), the results of Mariner *et al.* (1996) indicate a limited extent of arsenic adsorption at alkaline pH values. The other two K_d studies (Cornett *et al.*, 1992; Mok and Wai, 1990) were for environments affected by ore milling operations, and list extremely high K_d values (>1000's ml/g) for arsenic sorption on sediment. These high K_d values are surprising given the mobility expected for As(V) and As(III) based on the results of other published sorption studies at all but the very acidic pH values. Review of the studies by Cornett *et al.* (1992) and Mok and Wai (1990) indicate that the reported sorption values were desorption K_d studies, which are typically greater than adsorption K_d values, and were possibly affected by the presence of arsenic in particulate form (*i.e.*, arsenic minerals) in the sediment as opposed to being adsorbed to iron oxyhydroxide mineral coatings or clays.

Mariner *et al.* (1996) investigated the effects of high pH on arsenic mobility in a shallow sandy aquifer at the Commencement Bay Superfund Site in Tacoma, Washington. The groundwater plume contaminated with arsenic derived from a chemical plant is characterized by high pH and high silica concentrations. Values of K_d (Table 5.8) calculated from arsenic analyses of core sediment and pore water samples (*i.e.*, *in situ* K_d values) at this site decrease by at least an order of magnitude as the pH increased from 8.5 to 11.

Table 5.8. Measured arsenic K_d values (ml/g) based on analyses of an arsenic-contaminated aquifer at a Superfund Site (Mariner *et al.*, 1996).

| Core | Depth (m) | Pore Water pH | K_d (ml/g) | Core | Depth (m) | Pore Water pH | K_d (ml/g) |
|------|-----------|---------------|--------------|------|-----------|---------------|--------------|
| S | 6.2 | 8.48 | 0.92 | T | 6.4 | 9.94 | 6.46 |
| S | 6.4 | 8.39 | 1.44 | T | 6.5 | 10.1 | 3.91 |
| S | 6.5 | 8.42 | 1.76 | T | 6.7 | 9.89 | 1.97 |
| S | 6.7 | 8.37 | 2.14 | T | 7.0 | 10.0 | 0.44 |
| S | 6.8 | 8.30 | 2.63 | T | 7.2 | 10.4 | 0.42 |
| S | 7.0 | 8.41 | 1.57 | T | 7.3 | 10.6 | 0.21 |
| S | 7.1 | 8.39 | 1.80 | T | 7.5 | 10.8 | 0.14 |
| S | 7.3 | 9.73 | 0.31 | T | 7.7 | 10.8 | 0.69 |
| S | 7.9 | 10.4 | 0.19 | T | 7.8 | 11.0 | 0.19 |
| S | 8.0 | 10.5 | 0.12 | T | 8.0 | 10.8 | 0.28 |

5.3.5.4 *Published Compilations Containing K_d Values for Arsenic*

Because the references in this section are often cited or used for comparison in other publications, the following summaries are provided for completeness. It is recommended that the reader review the original reference and the references cited therein to understand the procedures and sources of the K_d values used for each compilation. The compilations do not distinguish between oxidation states for those contaminants that are redox sensitive or consider other important factors that contribute to variability in sorption, such as pH. Moreover, in cases where very large K_d values are listed, there is a risk that the original K_d measurement may have included precipitated components.

Baes and Sharp (1983) present a simple model developed for order-of-magnitude estimates for leaching constants for solutes in agricultural soils. As part of this model development, they reviewed and determined generic default values for input parameters, such as K_d . A literature review was completed to evaluate appropriate distributions for K_d values for various solutes, including arsenic. Because Baes and Sharp (1983) are cited frequently as a source of K_d values in other published K_d reviews (e.g., Looney *et al.*, 1987), the arsenic K_d values listed by Baes and Sharp are reported here for completeness. Based on the distribution that Baes and Sharp determined for the K_d values for cesium and strontium, they assumed a lognormal distribution for the K_d values for all other elements in their compilation. Baes and Sharp listed an estimated default K_d of 6.7 ml/g for As(V) based on 37 arsenic K_d values from 1.9 to 18 ml/g for agricultural soils and clays in the pH range 4.5 to 9.0. Their compiled K_d values represent a diversity of soils, pure clays (other K_d values for pure minerals were excluded), extracting solutions, measurement techniques, and experimental error.

Looney et al. (1987) tabulated estimates for geochemical parameters needed for environmental assessments of waste sites at DOE's Savannah River Plant in South Carolina. Looney et al. list K_d values for several metal and radionuclide contaminants based on values that they found in 1-5 published sources. For arsenic, Looney et al. list a "recommended" K_d of 3.2 ml/g, and a range of 1 to 10 ml/g. Looney et al. note that their recommended values are specific to the Savannah River Plant site, and must be carefully reviewed and evaluated prior to use in assessments at other sites.

5.3.5.5 K_d Studies of Arsenic on Pure Mineral, Oxide, and Crushed Rock Materials

Numerous adsorption studies have been conducted of arsenic on pure minerals and oxide phases. The K_d values listed in these studies are not necessarily relevant to the mobility and sorption of arsenic in soils. However, they are listed in Appendix D for completeness. The references cited in Appendix D are listed in the main reference list in Chapter 6. The potential value of the references that they cite and the sorption processes that they discuss is left to the reader.

A significant number of arsenic adsorption studies (Appendix D) have been conducted on iron oxyhydroxides and clay minerals. The results of these studies demonstrate that adsorption/desorption and coprecipitation reactions on these minerals can control the concentrations of dissolved arsenic. The focus of most of these studies, especially those with iron oxyhydroxides such as ferrihydrite, was primarily on understanding the mechanisms for As(V) and As(III) adsorption. The adsorption of both As(V) and As(III) on iron oxyhydroxides and clay minerals varies with pH. As expected for the adsorptive behavior of anions, arsenic is strongly sorbed under acid conditions where the net surface charge of most minerals is positive. The extent of As(V) adsorption then decreases with increasing pH in the range of 7 to 9. At alkaline pH conditions, As(V) is expected to be highly mobile because of the negative net surface charge on most minerals. The laboratory studies also indicate that As(V) adsorbs more strongly than As(III) to iron and manganese oxides. Dissolved As (V) and phosphate compete for adsorption sites, and the sorption of arsenic will be reduced in soils with high phosphate concentrations. Concentrations of other anions, such as dissolved chloride, nitrate, and sulfate, appear to have little effect on arsenic adsorption.

No sorption studies of arsenic on crushed rock materials were identified during our review. This was expected, because studies of contaminant (radionuclide) sorption on crushed rock materials were/are motivated by performance and risk assessment studies conducted in support of national programs for the geologic disposal of nuclear waste and long-lived arsenic radioisotopes are not found in nuclear waste.

5.4 Curium Geochemistry and K_d Values

5.4.1 Overview: Important Aqueous- and Solid-Phase Parameters Controlling Retardation

Curium is a transuranic (actinide) element, and can exist in the +3 oxidation state in natural waters. Curium(IV) is not stable in solutions because of self-radiation reactions (Onishi *et al.*, 1981). A very limited number of laboratory and field studies of the aqueous speciation, solubility, and sorption behavior of Cm(III) exist. However, Cm(III) geochemistry is expected and widely accepted to be very similar to that of Am(III) and trivalent lanthanide elements, such as europium (III), Eu(III). Compared to other actinides, Cm(III) and Am(III) are considered to be immobile in soil environments, and both exhibit high K_d values. However, the tendency of curium, like americium, to strongly adsorb to soil particles indicates that there is potential for colloid-facilitated transport of curium. The concentrations of dissolved curium may be controlled by hydroxide or carbonate solids in some systems. Therefore, some sorption measurements resulting in very high K_d values may reflect curium precipitation reactions.

5.4.2 General Geochemistry

Curium [Cm, atomic number (Z) = 96] has 21 isotopes (Tuli, 2000). The atomic masses of these isotopes range from 232 to 252. Most curium isotopes have relatively short half lives of minutes or less. Although both ^{242}Cm ($t_{1/2} = 162.8$ days) and CM-244 ($t_{1/2} = 18.1$ years) are released to the environment from nuclear facilities, CM-244 is probably more significant due to its longer half life (Coughtrey *et al.*, 1984).

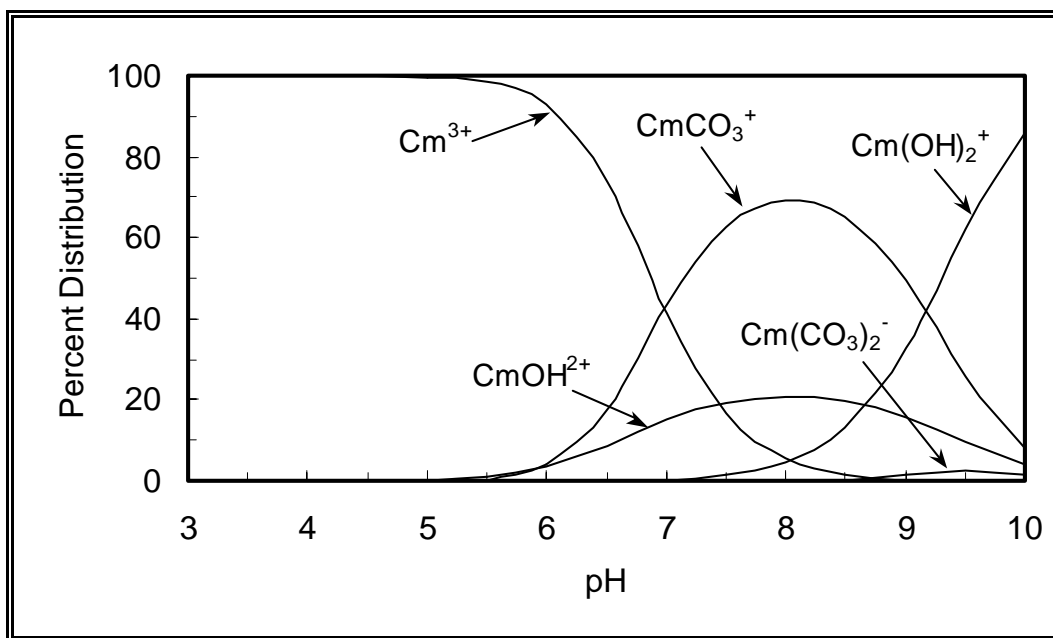
Balsley *et al.* (1997) Curium can exist in the +3 and +4 valence states, but the +3 state is the dominant valence state in natural waters. Curium(IV) is not stable in solutions because of self-radiation reactions (Onishi *et al.*, 1981). Because the electronic structures of the Cm(III), Am(III), and trivalent lanthanides [rare earth elements (REE)] are similar, the environmental behavior (*i.e.*, aqueous speciation, solubility, and sorption) of Cm(III) is expected to be very similar to those of Am(III) (see Section 5.2) and trivalent lanthanide elements, such as Eu(III). This analogy is well established; for example, see Choppin (1989). The environmental behavior of curium has been reviewed by Silva and Nitsche (1995), Coughtrey *et al.* (1984), Onishi *et al.* (1981), and Ames and Rai (1978).

5.4.3 Aqueous Speciation

Curium(III) should form complexes with inorganic ligands present in natural waters. However, the thermodynamic data for curium aqueous species are limited and not well established. We did not identify any published reviews of thermodynamic properties of curium aqueous species and solids. With respect to the hydrolysis of curium, Baes and Mesmer (1976) suggest that a good analogy is the hydrolysis of the lanthanide elements. Curium aqueous and solid compounds are not listed in the technically recognized compilation of thermodynamic data by Wagman *et al.* (1982) from the National Bureau of Standards [NBS, currently NIST (National Institute of Standards and Technology)]. Wimmer *et al.* (1992) determined the equilibrium constants for several Cm(III) hydrolytic and carbonate aqueous complexes by time-resolved laser-induced fluorescence spectroscopy. Figure 5.5 shows the aqueous speciation for Cm(III) based on the constants listed by Wimmer *et al.* (1992).

By analogy, the aqueous speciation of dissolved curium is likely to be similar to those of Am(III) and trivalent lanthanide elements, such as Eu(III). As shown in Section 5.2, the aqueous speciation of Am(III) is dominated by the uncomplexed ion Am^{3+} at acidic to near neutral pH conditions, Am(III) carbonate complexes at neutral to high pH conditions, and Am(III) hydroxyl complexes at very high pH conditions.

Figure 5.5. Calculated aqueous speciation for Cm(III) as a function of pH. [Curium(III) aqueous speciation was calculated based on a total dissolved concentration of curium of 1×10^{-12} mol/l (2.43×10^{-7} mg/l), and the water composition in Table 5.1]



Recent aqueous speciation studies of Cm(III) include, for example, those on aqueous complexation by dissolved carbonate (Fanghänel *et al.*, 1998); sulfate (Paviet *et al.*, 1996); fluoride (Aas *et al.*, 1999); chloride (Könnecke *et al.*, 1997); and humic substances (Hummel *et al.*, 1999; Panak *et al.*, 1996; Shin *et al.*, 1995; Kim *et al.*, 1993).

5.4.4 Dissolution/Precipitation/Coprecipitation

No studies pertaining to solubility controls for dissolved curium in natural environments were identified during the course of this review. Given the widely accepted idea that the environmental behavior of curium is analogous to Am(III), and trivalent lanthanides, such as Eu(III), solubility controls for curium may be similar to those for Am(III). As discussed in Section 5.2, concentrations of dissolved Am(III) in soil environments may be controlled by the precipitation of solids such as Am(OH)_3 and AmOHCO_3 .

5.4.5 Adsorption/Desorption

5.4.5.1 Guidance for Screening Calculations of Adsorption

Relative to the other contaminants reviewed in Volume II (EPA, 1999c) and this volume, there are very few experimental and field studies of the sorption behavior and mobility of curium in environmental systems. The results of curium adsorption studies published prior to 1981 have been reviewed by Ames and Rai (1978) and Onishi *et al.* (1981). More current studies are reviewed in the sections below. All of the available sorption studies indicate that Cm(III) readily sorbs to minerals, crushed rock, and soil materials, and is therefore considered one of the most immobile actinide elements in the environment.

The limited number of K_d adsorption studies for Cm(III) in soils prevents calculation of K_d look-up tables. However, the sorption behavior of Cm(III) is very similar to that of Am(III) (see Section 5.2) and trivalent lanthanide elements, such as Eu(III). Guidance given above for K_d values for Am(III) in Section 5.2 can be used for screening calculations of Cm(III) migration in soils. Given the absence of definitive maximum and minimum K_d values for Cm(III) as a function of the key geochemical parameters, such as pH, EPA suggests that K_d values measured for Cm(III) at site-specific conditions are thus essential for site-specific contaminant transport calculations and conceptual models. One of the major recommendations of this report is that for site-specific calculations, partition coefficient values measured at site-specific conditions are absolutely essential.

The geochemical behavior of Eu(III) has been determined to be similar to the trivalent actinides, such as Cm(III). Therefore, the following generalities made by Clark *et al.* (1998) regarding the adsorption of Eu(III) should also apply to Cm(III) and Am(III):

- European (III) adsorption increases with increasing pH.
- European (III) adsorption is sensitive to the ionic strength at low concentrations of total Eu(III) and to calcium at higher concentrations of total europium.
- Ion exchange is an important sorption mechanisms for Eu(III), especially at pH values less than 4.5.
- Mobility of Eu(III) in the environment increases at low to moderate pH values and in high ionic strength solutions.

Available curium sorption studies indicate that sorption of curium is strongly pH dependent and increases with increasing pH with peak adsorption occurring between pH values of 5 and 6. The observed pH dependence is expected, because the dominant aqueous species of curium in the pH range of natural waters are primarily cations such as Cm^{3+} and Cm(III) carbonate complexes at acidic and basic pH values, respectively.

Compared to other actinides, Cm(III) is considered to be immobile in soil environments, and exhibits high K_d values. Because the concentrations of dissolved curium may be controlled by hydroxide or carbonate solids in some systems, some sorption measurements resulting in very high K_d values may have been affected by curium precipitation reactions.

Because Cm(III) strongly adsorbs to soil particles, there is potential for colloid-facilitated transport of curium. Laboratory measurements by Kaplan *et al.* (1994) using site-specific soils and a 2-phase

solute transport code indicated that americium, curium, plutonium, and uranium would migrate less than 10 meters (m) in the F-Area of the Savannah River Site. The contaminants however were found associated with colloidal-size particles in groundwater 1,200 m away from the point source. Colloid-facilitated migration of contaminants is reviewed in Section 2.7 in Volume I (EPA, 1999b). The reader is cautioned that the importance of colloid-facilitated migration, especially in aquifer systems that do not involve fracture flow of groundwater, is still the subject of debate.

5.4.5.2 General Adsorption Studies

Sheppard *et al.* (1979) used batch equilibration experiments to study the sorption of curium to colloidal-size soil particles that are potentially diffusible in soil/water systems. The experiments were conducted with distilled water and 14 soils from Muscatine, Illinois; Hanford, Washington; Barnwell, South Carolina; Idaho Falls, Idaho; and Paradise and Placerville, California. Centrifugation measurements indicated that much of the Cm-244 was retained by the colloidal-size soil particles. Sheppard *et al.* (1979) found it difficult to correlate the sorption results with chemical and physical properties of the soils. They attributed this to the lack of precise distribution ratios, competition with cation exchange reactions, and complexation with humic and fulvic acid materials. The results also indicated that the sorption behavior of Am-241 and Cm-244 under these experimental conditions was identical. Sheppard *et al.* (1979) suggest that colloids of clay and humic acids are potentially important processes for the transport of actinides in soil/water systems.

Means *et al.* (1978) studied the mineralogy of the adsorbents for Cm-244 in soil near a disposal trench at nuclear waste burial grounds at the Oak Ridge National Laboratory in Oak Ridge, Tennessee. Their analyses indicated that curium concentrations were highly correlated to the concentrations of manganese oxides, even though the concentrations of iron oxyhydroxides and organic carbon were significantly greater than those of manganese oxides.

5.4.5.3 K_d Studies for Curium on Soil Materials

Nakayama and Nelson (1988) measured the pH dependency of K_d values for Am-243 and Cm-244 sorption onto sediment. Changes in pH were found to have a significant effect on the adsorption of these two radionuclides. However, variation of pH did not cause a significant difference in the adsorption behaviors of these two radionuclides relative to each other. Sibly and Wurtz (1986) measured the K_d values for Cm-244 on freshwater and estuary sediments. They found that K_d values previously reported for americium were equivalent to their measured values for curium. Adsorption of curium was pH dependent and increased from pH 4 to pH 7. The measured adsorption remained high in low organic, carbonate-buffered systems. It should be noted that the measured adsorption of several lanthanide trivalent cations on amorphous $\text{Fe}(\text{OH})_3$, hematite, and magnetite were also determined to be strongly dependent on pH (Music and Ristic, 1988).

Nishita *et al.* (1981) studied the extractability of Cm-244 from several types of soils as a function of pH. The extractability of curium was considered to parallel the solubilization of aluminum, iron, and/or manganese hydrous oxides, which are important adsorbents for dissolved contaminants in soil systems (Nishita *et al.*, 1981). The curium K_d values and soil characteristics determined for these soils by Nishita *et al.* (1981) are listed in Table 5.9. Under highly acidic conditions, Nishita *et al.* (1981) concluded that curium was present in ionic form and was mobile. At higher pH values, curium formed hydroxyl complexes that were readily sorbed by the soils.

Table 5.9. Measured curium K_d values (ml/l) and soil properties for soils studied by Nishita *et al.* (1981).

| Soil Type | pH ¹ | OM ² Fraction (%) | CEC ³ (meq/100 g) | Free Fe Oxides (%) | Mn ⁴ Fraction (%) | Extract pH | K_d (ml/g) |
|---------------------------|-----------------|------------------------------|------------------------------|--------------------|------------------------------|--------------|------------------|
| Silt Clay Loam Sharpsburg | 5.9 | 2.8 | 20 | 1.29 | 0.06 | 5.41 6.56 | 23,350 13,860 |
| Sandy Loam Malbis | 5.3 | 2.4 | 15 | 1.65 | 0.05 | 4.39 5.71 | 8,523 6,809 |
| Sandy Loam Lyman | 5.0 | 5.7 | 15 | 1.52 | 0.04 | 4.58 6.17 | 1,374 186 |
| Silty Clay Holtsville | 7.8 | 0.6 | 30 | 1.20 | 0.04 | 7.12 8.04 | 36,260 51,900 |
| Loam Aiken | 6.0 | 8.4 | 15 | 5.29 | 0.10 | 5.71 6.72 | 30,920 15,020 |
| Silt Loam Yolo | 6.7 | 2.5 | 25 | 2.41 | 0.08 | 6.12 6.98 | 21,780 17,090 |
| Muck Egbert | 7.2 | 40.8 | 60 | 1.57 | 0.10 | 7.14 7.54 | 6,772 5,056 |

¹ Saturated paste. ² Organic matter. ³ Cation exchange capacity. ⁴ In 4 M HNO₃ extract.

5.4.5.4 *Published Compilations Containing K_d Values for Curium*

Because the references in this section are often cited or used for comparison in other publications, the following summaries are provided for completeness. It is recommended that the reader review the original reference and the references cited therein to understand the procedures and sources of the K_d values used for each compilation. The compilations do not typically consider important factors that contribute to variability in sorption, such as pH. Moreover, in cases where very large K_d values are listed, there is a risk that the original K_d measurement may have included precipitated components.

Baes and Sharp (1983) present a simple model developed for order-of-magnitude estimates for leaching constants for solutes in agricultural soils. As part of this model development, they reviewed and determined generic default values for input parameters, such as K_d . A literature review was completed to evaluate appropriate distributions for K_d values for various solutes, including curium. Because Baes and Sharp (1983) are cited frequently as a source of K_d values in other published K_d reviews (*e.g.*, Looney *et al.*, 1987, Sheppard and Thibault, 1990), the curium K_d values listed by Baes and Sharp are reported here for completeness. Based on the distribution that Baes and Sharp

determined for the K_d values for cesium and strontium, they assumed a lognormal distribution for the K_d values for all other elements in their compilation. Baes and Sharp listed an estimated default K_d of 3,300 ml/g for curium based on 31 K_d values that ranged from 93.3 to 51,900 ml/g for agricultural soils and clays over the pH range 4.5 to 9.0. Their compiled K_d values represent a diversity of soils, pure clays (other K_d values for pure minerals were excluded), extracting solutions, measurement techniques, and experimental error.

Looney *et al.* (1987) tabulated the estimates for geochemical parameters needed for environmental assessments of waste sites at DOE's Savannah River Plant in South Carolina. Looney *et al.* list K_d values for several metal and radionuclide contaminants based on values that they found in 1-5 published sources. For curium, Looney *et al.* list a "recommended" K_d of 3,160 ($10^{3.5}$) ml/g, and a range of 100 to 1,000,000 ml/g. Looney *et al.* note that their recommended values are specific to the Savannah River Plant site, and they must be carefully reviewed and evaluated prior to use in assessments at other sites.

Thibault *et al.* (1990) (also see Sheppard and Thibault, 1990) present a compilation of soil K_d values prepared to support radionuclide migration assessments for a Canadian geologic repository for spent nuclear fuel in Precambrian Shield plutonic rock. Thibault *et al.* collected K_d values from other compilations, journal articles, and government laboratory reports for important elements, such as curium, that would be present in the nuclear fuel waste inventory. The curium K_d values listed in Thibault *et al.* (1990) are included in Table 5.10. Thibault *et al.* (1990) describe the statistical methods used for analysis of the compiled K_d values. The range for the K_d values used to calculate the "geometric mean" cover several orders of magnitude. Readers are cautioned against using "geometric mean" values or any other form of averaged K_d values as "default" K_d values, as such values are usually calculated from data compiled from different investigators for different soil systems. These mean or average values do not represent any particular environmental system and geochemical conditions. As discussed in Volume I (EPA, 1999b), the variation observed in the literature for K_d values for a contaminant is due to differences in sorption mechanisms, geochemical conditions, soil materials, and methods used for the measurements.

Table 5.10. Curium K_d values (ml/g) listed in Thibault *et al.* (1990, Tables 4 to 8).

| Soil Type | K_d Values (ml/g) | | |
|-----------|---------------------|------------------------|----------------|
| | Geometric Mean | Number of Observations | Range |
| Sand | 4,000 | 2 | 780 - 22,970 |
| Silt | 18,000 | 4 | 7,666 - 44,260 |
| Clay | 6,000 | 1 | |
| Organic | 6,000 | 1 | |

5.4.5.5 *K_d Studies of Curium on Pure Mineral, Oxide, and Crushed Rock Materials*

Few adsorption studies have been conducted of curium on pure minerals, oxide phases, and other geologic-related materials. The K_d values listed in these studies are not necessarily relevant to the mobility and sorption of curium in soils. However, they are listed in Appendix E for completeness. The references cited in Appendix E are listed in the main reference list in Chapter 6. The potential value of the references that they cite and the sorption processes that they discuss is left to the reader. The studies of curium sorption on crushed rock were conducted typically as part of national research programs to investigate the feasibility of geological disposal of high-level radioactive waste (HLW).

5.5 Iodine Geochemistry and K_d Values

5.5.1 Overview: Important Aqueous- and Solid-Phase Parameters Controlling Retardation

Although the environmental chemistry of iodine is normally assumed to be simple and well known, recent studies suggest that the fate and mobility of iodine in environmental systems may be more complex than expected. This complexity is caused by the multiple redox states of iodine that may exist under oxidizing conditions. The -1, +5, and molecular I_2 oxidation states are those most relevant for iodine in environmental systems. In most aqueous environments, iodine is present as the iodide ion, I^- . In marine and highly oxidizing environments such as surface waters and some oxygenated shallow ground waters, iodine may be present in the +5 oxidation state as the iodate ion, IO_3^- . Under oxidizing, acidic conditions, molecular I_2^0 (aq) may form from the reduction of IO_3^- or oxidation of I^- . Some sorption studies suggest (Section 5.5.5) that these iodine oxidation/reduction reactions may affect the observed sorption behavior of iodine in soils and the reactions may be affected by the organic content and/or microbial processes in soils and sediments. Although iodine is a primary component of several naturally occurring minerals, the formation of such minerals represent unique geological conditions and is not likely to occur in soils due to the low concentrations of iodine typically present in the environment.

Sorption of iodine species appears to be controlled in part by soil organic matter and in part by iron and aluminum oxides, with adsorption of iodine becoming increasingly important under more acid conditions. Although the extent of sorption is typically low, especially in systems containing little or no organic matter, I^- and IO_3^- are sorbed to a measurable extent by soils and some oxide and sulfide minerals at near neutral and alkaline pH conditions. The adsorption behavior of IO_3^- also appears to be appreciably different from that of I^- , in that IO_3^- sorbs much more strongly than I^- to soil and mineral surfaces. Mechanisms causing this sorption behavior of iodine at near neutral and alkaline pH conditions are not completely understood. Some have proposed that this observed adsorption behavior in soils may be a result of the oxidation of I^- and/or reduction of IO_3^- to the more reactive molecular I_2^0 (aq) and/or its hydrolysis products.

5.5.2 General Geochemistry

Iodine [I, atomic number (Z) = 53] is a halide element, like fluorine, chlorine, and bromine. Iodine is known to occur in the -1, +1, +3, +5, and +7 oxidation states. There are 37 reported isotopes of iodine (Tuli, 2000). Only 1 isotope, ^{127}I is stable. Isotopes ^{131}I and ^{129}I are generated during the operation of nuclear power plants, reprocessing of nuclear fuels, and testing of nuclear weapons.

Due to its long half life ($t_{1/2} = 1.57 \times 10^7$ y), ^{129}I is the only iodine isotope of major environmental concern. Fission products ^{131}I ($t_{1/2} = 8.02$ days) and ^{125}I ($t_{1/2} = 59.4$ days) are often short term disposal hazards. Most of the remaining iodine isotopes have half lives of a few hours to fractions of a second. The environmental behavior of iodine has been reviewed by others, such as Lieser and Steinkopff (1989), Whitehead (1984), Coughtrey *et al.* (1983), and Ames and Rai (1978).

5.5.3 Aqueous Speciation

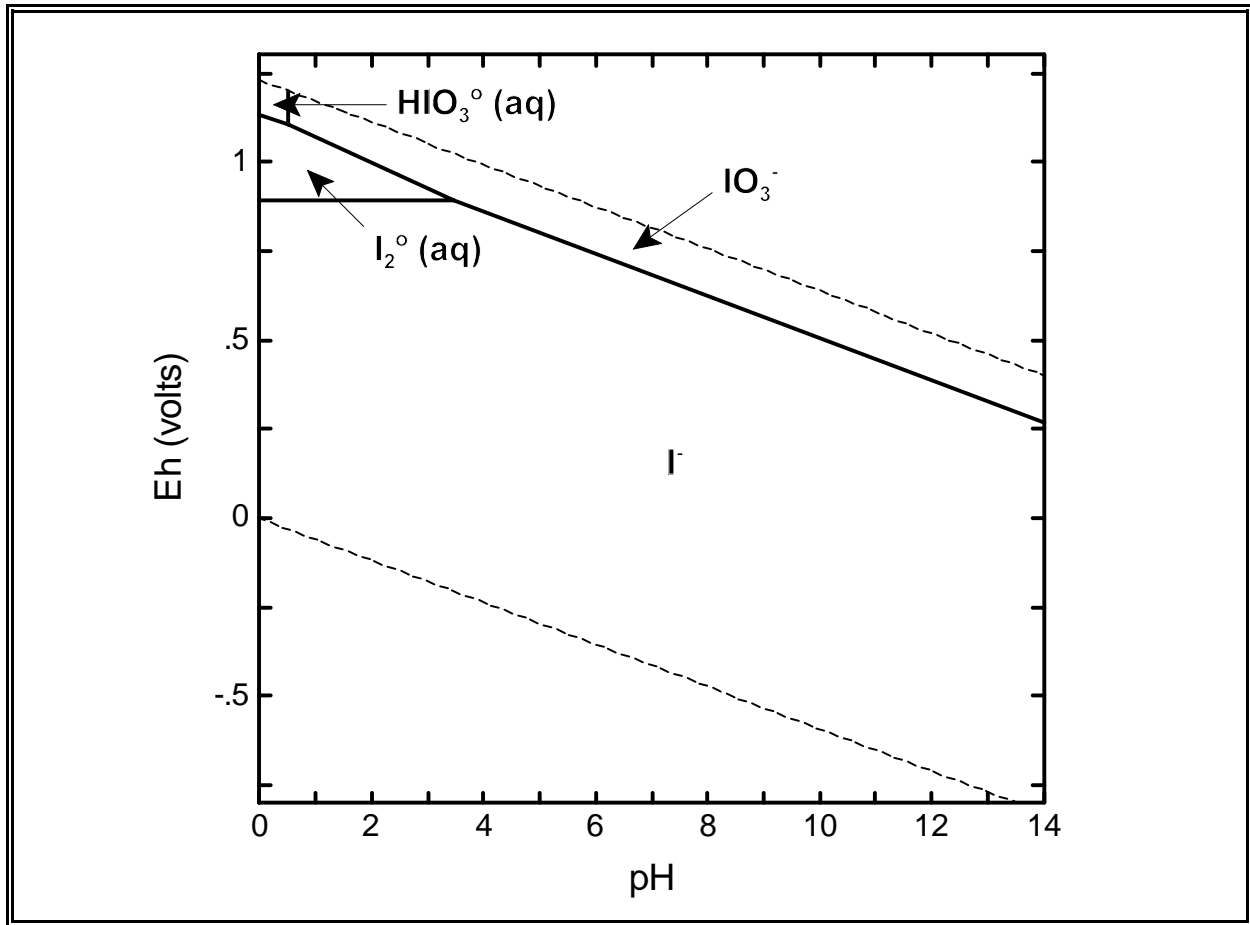
Iodine is known to occur in several oxidations. Of these, the -1, +5, and molecular I_2 oxidation states are those most relevant to environmental systems. Figure 5.6 is an Eh-pH diagram that shows the dominant aqueous species of iodine as a function of pH and Eh (redox potential) at 25°C with respect to the thermodynamic stability of water.

In most aqueous environments, iodine is present in the -1 valence state as the iodide ion, I^- . The stability range of I^- extends almost over the entire pH and Eh range for the thermodynamic stability of water. In marine and highly oxidizing environments such as surface waters and some oxygenated shallow ground waters, iodine may be present in the +5 oxidation state as the iodate ion, IO_3^- (Figure 5.6). Under oxidizing, acidic conditions, the Eh-pH diagram indicates that molecular I_2 (aq) may form from the reduction of IO_3^- or oxidation of I^- . Some iodine sorption studies suggest (Section 5.5.5) that these iodine oxidation/reduction reactions may affect the observed sorption behavior of iodine in soils and the reactions may be affected by the organic contents and/or microbial processes in soils and sediments. For example, studies, such as Skogerboe and Wilson (1981), indicate that fulvic acid derived from soil is capable of reducing molecular I_2 (aq) and IO_3^- to I^- under conditions generally characteristic of natural waters.

The volatilization of iodine from soil to the atmosphere may occur as a result of both chemical and microbiological processes (Whitehead, 1984). The chemical processes generally result in molecular iodine or hydrogen iodide, and the microbiological processes yield organic compounds, such as methyl iodide. Methyl iodide is not strongly retained by soil components and is only slightly soluble in water (Whitehead, 1984).

Vovk (1988) completed a review of the literature regarding the influence of radiolysis on the migration of iodine in the geosphere, including published studies of iodine liberation from uranium ore into groundwater and iodine in formation waters (*i.e.*, brines in oilfields and gasfields) from deep strata. A variety of other iodine species are known to form radiolytically, such as HOI° (aq) and OI^\cdot . Although these species are unstable, they may be important in some chemical reactions that affect iodine in the environment. Radiolytic reactions lead to conversion of non-volatile and relatively unreactive species, such as I^- and IO_3^- , into volatile forms, such as molecular I_2 , which are fairly reactive and react rapidly with organic compounds to form organic iodide species (Vovk, 1988).

Figure 5.6. Eh-pH stability diagram for dominant iodine aqueous species at 25°C. [Diagram based on a total concentration of 10^{-6} mol/l dissolved iodine.]



5.5.4 Dissolution/Precipitation/Coprecipitation

Iodine can be found as a primary component in some rare, naturally occurring minerals that are associated with evaporite¹ and brine deposits (Johnson, 1994; Doner and Lynn, 1977). The iodine is commonly present in substitution for other halogen elements, such as chloride and bromide. Iodate is typically associated with sulfate- or nitrate-type minerals. For example, the northern Chilean nitrate deposits contain iodine minerals, such as bruggenite $[\text{Ca}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}]$, lautarite $[\text{Ca}(\text{IO}_3)_2]$, and dietzeite $[\text{Ca}_2\text{H}_2\text{O}(\text{IO}_3)_2(\text{CrO}_4)]$ (Johnson, 1994). Such minerals are expected to be highly soluble in geochemical systems. Therefore, the formation of iodine-containing minerals is not likely to be important in most soil systems due to the low concentrations of iodine typically present in the environment.

¹ An evaporite is a sedimentary rock composed principally of minerals precipitated from a saline solution as a result of extensive or total evaporation of the solution.

5.5.5 Adsorption/Desorption

5.5.5.1 Guidance for Screening Calculations of Adsorption

Sorption of iodine species appears to be due in part to soil organic matter and in part to iron and aluminum oxides, with adsorption of iodine becoming increasingly important under acidic conditions. Because iodine is present as either the anions I^- or IO_3^- in most soils, conventional wisdom suggests that their adsorption on soils and most individual mineral phases should be negligible at near neutral and alkaline pH conditions, and increase as pH values become more acidic. Sorption studies of iodine published prior to 1976 are reviewed by Onishi *et al.* (1981) and Ames and Rai (1978). More recent studies are reviewed in the sections below. The majority of these studies pertain to the adsorption of iodide.

Numerous studies have been conducted in which K_d values for iodide adsorption on soil have been reported along with associated pH values and/or soil organic carbon contents. These include the K_d measurements by Kaplan *et al.* (1996, 1998a, 1998b, 2000a, 2000b), Fukui *et al.* (1996), Bird and Schwartz (1996), Sheppard *et al.* (1995), Serne *et al.* (1993), Muramatsu *et al.* (1990), Sheppard and Thibault (1988), and Gee and Campbell (1980) (see reviews below). However, these data are too scattered or limited in scope to determine K_d look-up tables of conservative minimum and maximum K_d values for iodide as a function of key geochemical parameters such as pH and organic carbon content of soil. One of the key recommendations of this report is that for site-specific calculations, partition coefficient values measured at site-specific conditions are absolutely essential.

Based on the studies by Kaplan and coworkers, it is suggested that K_d values of 0.6 and 0 ml/g be considered, respectively, as conservative minimum K_d values for the pH ranges from 4 to <6 and ≥ 6 to 10 for screening calculations of iodide migration in soils. These values represent primarily low adsorptive, quartz-feldspar-rich soils with low contents of organic carbon matter. The available K_d data are too unevenly distributed and limited as a function of pH to estimate a conservative maximum K_d values for iodide. Values of K_d for iodide have been reported in the range from 1 to 10 ml/g for the pH range from 4 to 10. Most of the reported K_d values are however typically less than 3 ml/g.

Studies suggest that the adsorption of iodide increases with increasing soil organic matter. Unfortunately, the majority (>90%) of the reported K_d values for iodide adsorption on soil are limited to mineral soils with organic matter contents of less than 0.2 wt%. Development of a look-up table for iodide K_d values as a function of organic matter contents is precluded by this limited range of data.

Sorption studies (see studies reviewed in sections below and references cited therein) indicate that the adsorption of iodine anions does increase with decreasing pH. However, although the extent of sorption is typically low, especially in systems containing little or no organic matter, I^- and IO_3^- are sorbed to a measurable extent by soils and some oxide and sulfide minerals at near neutral and alkaline pH conditions. The adsorption behavior of IO_3^- also appears to be appreciably different than that of I^- , in that IO_3^- sorbs much more strongly than I^- to soil and mineral surfaces.

Mechanisms causing this sorption behavior of iodine at near neutral and alkaline pH conditions are not completely understood. Some have proposed that this observed adsorption behavior in soils

may be a result of the oxidation of I^- and/or reduction of IO_3^- to the more reactive molecular I_2 (aq) and/or its hydrolysis products (Yu *et al.*, 1996; Behrens, 1982; Whitehead, 1974). Such a reaction process would help explain why some adsorption measurements do not reach steady-state conditions even after many weeks or months of contact time. Some investigators believe that this iodine oxidation/reduction process may be affected by the organic matter and/or microbial processes in the soils. Some researchers have found positive correlations between the sorption of iodine and organic matter in soils, and some studies indicate that the iodine sorption is decreased when soils are treated with fungicide, bactericide, irradiation or heat. Others have proposed that iodine sorption was primarily caused by physical processes associated with the surfaces and entrapment in the micropores and structural cavities in the organic matter.

5.5.5.2 General Adsorption Studies

Kaplan *et al.* (2000b) investigated the sorption of $^{125}I^-$ on calcite, chlorite, goethite, montmorillonite, quartz, vermiculite, and illite. These minerals were components of the sediments used for iodine sorption studies by Kaplan *et al.* (1996). Kaplan *et al.* (2000b) measured little or no sorption of I^- on calcite, chlorite, goethite, montmorillonite, quartz, and vermiculite. However, a significant amount of I^- sorption ($K_d = 15.14 \pm 2.84$ ml/g) was measured for the illite sample, and was also determined to be strongly dependent on pH. The K_d values for I^- on illite decreased from 46 to 22 ml/g over the pH range 3.6 to 9.4, respectively. Kaplan *et al.* (2000a) were able to desorb a significant fraction of the I^- by treating the $^{125}I^-$ sorbed illite samples with dissolved fluoride (43 percent desorbed), dissolved chloride (45 percent desorbed), dissolved bromide (52 percent desorbed), and dissolved stable I^- (83 percent desorbed). Based on these results, Kaplan *et al.* (2000a) proposed that I^- was sorbed to the illite by reversible physical adsorption to pH-dependent edge sites.

Rädlinger and Heumann (2000) studied the conversion of inorganic I^- into humic substance/iodine species in aquatic systems, and whether microorganisms affected such reactions. For natural samples, I^- was exclusively fixed by humic substance fractions where natural humic substance/iodine species have also been observed in the original samples. Their results indicated that the transformation was strongly affected by microbiological activity of the sample and occurred by a complicated transfer mechanism by the formation of different intermediate humic substance/iodine species.

Yu *et al.* (1996) completed a series of experiments to compare the reaction of I^- with a series of volcanic-ash soils to those for noncrystalline materials that constitute much of the inorganic fraction of these soils. The measured uptake of I^- by volcanic soils was different than the I^- on the noncrystalline phases that make up much of the clay-size fraction of some of these soils. Sorption of I^- onto imogolite and ferrihydrite was rapid (<30 min), but was not particularly great. Iodide sorption on imogolite was 3-to-4 times greater than that on ferrihydrite on a mass basis. In contrast, rates of I^- retention by volcanic-ash soils were slow and did not attain a steady-state after 300 h. Yu *et al.* (1996) determined that this reaction was and its extent could be attenuated, but not be suppressed, by sterilization. The I^- sorbed by the soils could only be completely desorbed by boiling the soils in 2 molar (M) sodium hydroxide solution. The results indicated that the amount of I^- sorbed by soils was inversely correlated with pH. However, no relationship with organic matter concentrations, surface area, or imogolite and ferrihydrite concentrations was found. Yu *et al.* (1996) determined that the reaction of I^- with volcanic-ash soils was consistent with a rapid initial uptake by soil mineral surfaces, followed by a slower reaction of soil organic matter with oxidized forms of I^- .

They proposed that the sorption of I⁻ to soils is primarily controlled by the slow oxidation of I⁻ to I₂^o (aq) and that I₂^o (aq) or its hydrolysis product HOI^o (aq) then reacts with soil organic matter.

Sheppard and Hawkins (1995) studied bog water and peat from an iodine-rich bog to investigate the role of microorganisms in the retention and accumulation of iodine in a temperate wetland. Their results indicated that sorption of iodine on fresh peat was slightly slower and more limited under anoxic conditions. Autoclaving the peat and the addition of sucrose to the peat both decreased iodine sorption. In addition, the reinoculation of the treated peat with a fresh microbial population was not effective in increasing iodine sorption. This suggested that microbes may only play a minor and indirect role in iodine sorption through the decomposition of organic matter.

Sheppard and Thibault (1992) investigated the behavior of iodine in organic and mineral soils. Their results showed that microbes played an indirect role in sorption of iodine on soils, and their effect was very short term. Desorption experiments indicate that the released iodine was generally anionic, with some neutral or positively charged species also present. They found no firm evidence that retention of iodine in soils was due to any specific chemical reaction. Sheppard and Thibault (1992) proposed that iodine sorption was primarily through physical processes associated with the surface and entrapment in the micropores and structural cavities of the organic matter.

Bors *et al.* (1991) conducted batch adsorption experiments of ¹²⁵I on two types of soils, chernozem¹ and podzol.² Generally higher K_d values were observed for the chernozem soil, which is characterized by a higher amount of organic matter and soil biomass. Incubation of soil samples under varied conditions suggested that soil microflora participated in iodine immobilization. Bors *et al.* (1988) used batch experiments to study the relationship of iodine sorption to soil organic C-contents of different horizons of a podzolic soil profile. The measurements indicated that the sorption of iodine tended to increase with increasing organic C-content of different soil horizons. Analyses of the organic substances suggested that a considerable part of the radioiodine was fixed in humic and fulvic acids.

Koch *et al.* (1989) investigated the role of microbial processes in the mobility of ¹²⁹I for 12 samples of nine organic soils, which varied widely in degree of humification and parent vegetation. The soils samples were collected mainly on the Precambrian Shield of Ontario, Canada. Their experiments were conducted using glucose, thymol, gamma irradiation (⁶⁰Co) to stimulate or suppress microbial activity in the soils. The presence of glucose generally increased I⁻ removal from solution, whereas thymol depressed removal. Gamma irradiation of the soils decreased I⁻ removal from solution in all samples. The iodine content of soils was directly related to both biologically- and nonbiologically-mediated processes of I⁻ removal from solution. Koch *et al.* (1989) concluded that microorganisms play an important role in the processes of I⁻ removal from solution in organic soils.

¹ Chernozem and podzol are great soil groups of the 1938 USDA classification system. It is a group of zonal soils whose surface horizon is dark and highly organic, below which is a lighter-colored horizon and accumulation of lime. The soil group is developed under conditions of temperate to cool subhumid climate (USDA, 1938).

² Podzol is a group of zonal soils having an organic mat and a very thin organic-mineral layer overlying gray, leached A2 horizon and a dark brown, illuvial B horizon enriched in iron oxide, alumina, and organic matter. It develops under coniferous or mixed forests or under heath, in a cool to temperate moist climate (USDA, 1938).

Behrens (1982) found that iodine in both surface and soil water was to a large extent chemically converted to an inert form by microbial processes. He presented evidence of involvement of microorganisms in that autoclaving of the soils greatly reduced iodine sorption by the soil. Behrens (1982) suggested that the reactions involve extracellular, enzymatic oxidation of I^- to molecular I_2^0 (aq) which then reacts with organic matter.

Beneš *et al.* (1976) studied the interaction between humus and iodine in lake water using centrifugation, ultrafiltration, and filtration through ion exchange membranes. Iodine was retained to a considerable degree by the ultrafilter. This observation suggested that iodine was present not only as simple halide ion, which should not be retained by the filter or simple adsorption reactions. Beneš *et al.* (1976) suggested that some kind of reaction between the halides and humus might be responsible for the observed uptake of iodine.

Whitehead (1973,1974,1978) conducted several studies on iodine adsorption on geologic materials and organic matter. Whitehead (1973) determined the iodine contents of soils from sites in the United Kingdom. His results showed that soil organic matter and iron and aluminum oxides were largely responsible for the retention of iodine in soils. The total concentrations of iodine in these soils were positively correlated with aluminum oxide extracted by Tamm's reagent, with ferric oxide extracted by citrate-dithionite, and with soil organic matter. Whitehead (1974) studied the uptake of I^- , elemental iodine, and IO_3^- , when added to sandy loam and to mixtures of the soil with organic matter (composted grass roots), chalk, ferric oxide, and aluminum oxide (sesquioxides). The behavior of elemental iodine was similar to I^- in response to the various soil treatments. Iodate, however, differed considerably from the other two forms of iodine. With soil alone and with the soil/chalk mixture, the decrease in the concentrations of dissolved IO_3^- with time was relatively slow, although after 160 days its solubility was similar to that of I^- and elemental iodine. The incorporation of composted grass roots cause a rapid reduction in IO_3^- solubility, suggesting that the organic matter accelerated the reduction of IO_3^- to elemental iodine or I^- . The results obtained when the soil was treated with composted grass roots suggest that, in the presence of readily decomposable organic matter, IO_3^- may be quickly reduced to elemental iodine or I^- . Whitehead (1978) measured the iodine content in successive 10-cm horizons of 18 soil profiles from England and Wales. The iodine content was correlated with the contents of "free" aluminum and iron oxides (oxalate-soluble) and organic matter. In all 154 samples, the iodine content was closely correlated with oxalate-soluble aluminum, but not with oxalate-soluble iron or organic matter. In the 5 most acidic soils with pH values less than 4.8, however, the iodine content was more closely correlated with iron than with aluminum.

5.5.5.3 *K_d Studies of Iodine on Soil Materials*

Kaplan and coworkers have conducted a series of laboratory studies on the adsorption of I^- on soils and mineral phases. Kaplan *et al.* (2000a) measured K_d values for I^- as a function of pH on two sediments from the Savannah River Site at Aiken, South Carolina. The K_d values ranged from 3.96 to 0.05 ml/g depending on sediment type and especially pH. The K_d values were consistently greater for a wetland versus an upland sediment. Kaplan *et al.* (2000a) attributed this result to the greater organic matter content of the wetland sediment. Their measurements also indicated that the K_d values increased with decreasing pH as would be expected for dissolved anionic contaminants. For the wetland sediment, the K_d values ranged from 3.96 to 1.17 ml/g. For the upland sediment, the K_d values ranged from 0.90 to 0.05 ml/g.

Kaplan *et al.* [2000b; also see Kaplan *et al.* (1996)] used the batch technique to measure the K_d values for iodine, as I⁻, on three sediment samples from the Hanford Site in southeastern Washington. The measurements were conducted with a groundwater sample (pH 8.46) taken from a well located in an uncontaminated area of the Hanford Site. The sediment samples included a Touchet bed sand (sample TBS-1), a silty loam (sample Trench AE-3), and a very coarse sand (sample Trench-94). The average measured K_d values at 330 days were 9.83, 6.83, and 4.72 ml/g for the very coarse sand, Touchet bed sand, and the silty loam sediment samples, respectively. Kaplan *et al.* (2000b) also noted that the K_d values increased as a function of time. For example, the K_d values measured for the very coarse sand increased from 0.19 to 9.83 over 330 days of contact time.

Kaplan *et al.* (1998a) used the batch equilibration technique to measure the K_d values for I⁻ under oxic conditions on 20 sediment samples taken from a borehole in the Hanford formation at the Hanford Site in southeastern Washington. Each sediment sample was equilibrated with uncontaminated groundwater from the Hanford Site, which was subsequently spiked with ¹²⁵I prior to the K_d measurements. The groundwater solution has a low ionic strength and a pH of 8.4 [see Table 1 in Kaplan *et al.* (1998a)]. The mean K_d values of three replicates measured for I⁻ on each Hanford sediment sample are listed in Table 5.11, and range from -0.03 to 0.23 ml/g. The measurements indicated essentially no sorption of I⁻ on Hanford sediments under these conditions.

Kaplan *et al.* (1998b) studied the effects of high pH on the sorption of iodine under oxic conditions on sediments from the Hanford Site in Washington. Batch sorption experiments were completed using the <2-mm size fraction of sediment collected from Trench AE-3 in the 200 Area of the Hanford Site. The sediment was characterized as a silty loam with a cation exchange capacity (CEC) of 6.4 meq/100 g. The carbonate content of the sediment consisted of primarily of calcite. Based on analyses reported by Kaplan *et al.* (1996) for a sediment from a nearby location, the sediment was expected to contain approximately 0.2-0.5 wt. percent amorphous Fe₂O₃ (Kaplan *et al.*, 1998b). The <2-mm size fraction contained 41 percent sand, 50 percent silt, and 9 percent clay. The clay fraction of sediment contained primarily smectite (57 percent), illite (19 percent), and vermiculite (14 percent). The groundwater selected for the sorption studies was an uncontaminated groundwater from the Hanford Site with a low ionic strength and pH of 8.4 [see Table 2 in Kaplan *et al.* (1998b)]. Based on the experimental conditions and geochemical modeling calculations, the dissolved iodine was assumed to present as dissolved I⁻. The mean K_d values of three replicates measured for iodine in the high pH experiments are listed in Table 5.11.

Yoshida *et al.* (1998) used the batch equilibration method and ¹²⁵I to measure the K_d values for I⁻ and IO₃⁻ on 68 soils. The soils were collected from upland fields, paddies, forests and open areas throughout Japan. The soils were characterized with respect to soil pH, cation exchange capacity (CEC), anion exchange capacity (AEC), active aluminum (extractable by oxalic acid and ammonium oxalate), and total organic carbon (TOC). Two sets of experiments were conducted. One set of experiments consisted of equilibrating wet (fresh) samples of each soil with deionized water. In the second set of experiments, samples of each soil were autoclaved prior to equilibration with deionized water. Table 5.12 lists the median K_d values for the 9 soil types. The measured K_d values range widely for the wet soils from 1.1 to 10,200 ml/g for I⁻, and from 2.1 to 8,210 ml/g for IO₃⁻. These values were almost 2 orders of magnitude higher than K_d values previously reported for air-dried Japanese soils. The K_d values for the sandy soil samples were low. Yoshida *et al.* (1998) found relatively good correlations between K_d for wet soils and TOC and total nitrogen, indicating the contribution of organic materials on the sorption of iodine. The K_d values decreased substantially after autoclaving (Table 5.12). The effects of autoclaving on the sorption of I⁻ were greater than

those measured for IO₃ sorption. Yoshida *et al.* (1998) estimated that 86 percent of I⁻ sorption and 50 percent of IO₃ sorption were attributable to microbial activities and/or soil fractions that were affected by autoclaving.

Table 5.11. K_d values (ml/g) for the adsorption of iodine to sediments from the Hanford Site in southeastern Washington state (Kaplan *et al.*, 1998a,1998b).(milliequivalent -meq)

| pH | K _d (ml/g) | CEC (meq/100 g) | Solution | Soil Identification | Reference |
|------|--------------------------|--------------------|-------------|-------------------------------|---------------------------------|
| 8.54 | 0.00 ±0.01 | 5.07 | Groundwater | Hanford sediment B8500-07A | Kaplan <i>et al.</i> (1998a) |
| 8.80 | -0.01 ±0.02 | 4.73 | Groundwater | Hanford sediment B8500-10A | Kaplan <i>et al.</i> (1998a) |
| 8.77 | 0.00 ±0.03 | 4.60 | Groundwater | Hanford sediment B8500-12A | Kaplan <i>et al.</i> (1998a) |
| 8.73 | -0.03 ±0.02 | 4.62 | Groundwater | Hanford sediment B8500-14A | Kaplan <i>et al.</i> (1998a) |
| 8.75 | -0.03 ±0.03 | 4.11 | Groundwater | Hanford sediment B8500-15A | Kaplan <i>et al.</i> (1998a) |
| 8.77 | 0.06 ±0.17 | 2.32 | Groundwater | Hanford sediment B8500-16A | Kaplan <i>et al.</i> (1998a) |
| 8.52 | 0.00 ±0.02 | 4.98 | Groundwater | Hanford sediment B8500-17A | Kaplan <i>et al.</i> (1998a) |
| 8.50 | -0.01 ±0.01 | 4.72 | Groundwater | Hanford sediment B8500-19A | Kaplan <i>et al.</i> (1998a) |
| 8.52 | -0.01 ±0.02 | 4.67 | Groundwater | Hanford sediment B8500-20A | Kaplan <i>et al.</i> (1998a) |
| 8.56 | -0.01 ±0.01 | 4.56 | Groundwater | Hanford sediment B8500-21A | Kaplan <i>et al.</i> (1998a) |
| 8.94 | 0.12 ±0.04 | 7.33 | Groundwater | Hanford sediment B8500-22A | Kaplan <i>et al.</i> (1998a) |
| 8.82 | 0.13 ±0.06 | 8.41 | Groundwater | Hanford sediment B8500-23A | Kaplan <i>et al.</i> (1998a) |
| 8.81 | 0.02 ±0.03 | 9.03 | Groundwater | Hanford sediment B8500-24A | Kaplan <i>et al.</i> (1998a) |
| 8.89 | 0.09 ±0.05 | 6.63 | Groundwater | Hanford sediment B8500-25A | Kaplan <i>et al.</i> (1998a) |

Continuation of Table 5.11

| pH | K _d (ml/g) | CEC (meq/100 g) | Solution | Soil Identification | Reference |
|------|--------------------------|--------------------|----------------------|---------------------------------|---------------------------------|
| 8.88 | 0.06 ±0.05 | 8.36 | Groundwater | Hanford sediment B8500-27A | Kaplan <i>et al.</i> (1998a) |
| 8.84 | 0.23 ±0.06 | 7.77 | Groundwater | Hanford sediment B8500-29A | Kaplan <i>et al.</i> (1998a) |
| 8.56 | 0.04 ±0.07 | 10.98 | Groundwater | Hanford sediment B8500-31A | Kaplan <i>et al.</i> (1998a) |
| 8.93 | -0.01 ±0.01 | 8.39 | Groundwater | Hanford sediment B8500-32A | Kaplan <i>et al.</i> (1998a) |
| 8.92 | 0.08 ±0.08 | 6.21 | Groundwater | Hanford sediment B8500-34A | Kaplan <i>et al.</i> (1998a) |
| 8.89 | 0.01 ±0.02 | 6.65 | Groundwater | Hanford sediment B8500-35A | Kaplan <i>et al.</i> (1998a) |
| 8.1 | 0.22 ±0.01 | 6.4 | Groundwater and NaOH | Hanford Trench AE-3 Sediment | Kaplan <i>et al.</i> (1998b) |
| 9.9 | 0.01 ±0.01 | 6.4 | Groundwater and NaOH | Hanford Trench AE-3 Sediment | Kaplan <i>et al.</i> (1998b) |
| 10.2 | -0.02 ±0.02 | 6.4 | Groundwater and NaOH | Hanford Trench AE-3 Sediment | Kaplan <i>et al.</i> (1998b) |
| 11.0 | -0.04 ±0.02 | 6.4 | Groundwater and NaOH | Hanford Trench AE-3 Sediment | Kaplan <i>et al.</i> (1998b) |
| 11.9 | 0.01 ±0.01 | 6.4 | Groundwater and NaOH | Hanford Trench AE-3 Sediment | Kaplan <i>et al.</i> (1998b) |

Bird and Schwartz (1996) studied effect of sediment-to-water ratios, oxic and anoxic conditions, alkalinity, microbial activity, and time on the partitioning of iodine, as ¹²⁵I, on representative lake sediments from the Canadian Shield. The K_d values were determined using the shaking, batch equilibration technique with sediment-to-solution ratios of 1, 10, and 50 percent for organic sediment, peaty sediment, clayey silt/sand sediment, and sand sediment. Bird and Schwartz (1996) found that the alkalinity of water, which ranged from <1.0 to 250 mg/l as CaCO₃, had only a minor effect on K_d with values changing less than a factor of two. Treating organic soil with a fungicide, bactericide, irradiation or heat decreased K_d values by a factor of 1.1, 2.3, 7.5, and 22, respectively. These results suggested that microbial processes were important on the sorption of ¹²⁵I to sediment, although chemical and/or physical changes, as results of radiation or heat treatment, may also be important. Under anoxic conditions, K_d values were low (generally less than 1 ml/g. Over a 48-day period, K_d values increased from about 690 ml/g on day 6 to 3,840 ml/g on day 48 under oxic conditions, and from about 0.5 to 16 ml/g under anoxic conditions. Most of the iodine adsorbed to sediment under oxic conditions was released back into the water under anoxic conditions. Geometric mean K_d values for iodine measured in untreated river water under oxic conditions, after shaking for 48 hours, are listed in the Table 5.13. Lower K_d values were observed for clayey

silt/sand sediment and sand sediment than for the high organic sediment and peaty sediment. The measured K_d values tended to decrease with increasing sediment-to-water ratio, except for the sand sediment. Under anoxic conditions, the K_d for iodine is much lower (approximately 1 ml/g). The K_d values for sand sediment were low under both oxic and anoxic conditions.

Table 5.12. Median K_d values (ml/g) for I^- and IO_3^- measured in deionized water (Yoshida *et al.*, 1998). [Median total organic carbon (TOC) and median K_d values listed for volcanogenous regosol and peat soils are mean and single-sample values, respectively. Characterization information for soil types are listed in Table 2 in (Yoshida *et al.*, 1998).]

| Soil Type | n | Median TOC (g/kg) | Median K_d for Iodide (I^-) (ml/g) | | Median K_d for Iodate (IO_3^-) (ml/g) | |
|--|----|-------------------|--|--------------------------|---|--------------------------|
| | | | Wet Soil | Soil That Was Autoclaved | Wet Soil | Soil That Was Autoclaved |
| Andosols | 20 | 63.4 | 1,610 | 4.3 | 1,480 | 19.5 |
| Gray Lowland Soils (Dystric Fluvisols) | 14 | 15.7 | 413 | 2.0 | 412 | 7.2 |
| Red and Yellow Soils (Orthic Acrisols) | 10 | 10.8 | 209 | 1.6 | 217 | 19.7 |
| Gley Soils (Dystric Gleysols) | 5 | 21.0 | 1,540 | 2.2 | 1,190 | 9.0 |
| Brown Forrest Soils (Humic Cambisols) | 3 | 54.0 | 1,290 | 4.8 | 1,120 | 48.9 |
| Sand-Dune Regosols (Arensols) | 3 | 0.6 | 8.5 | 0.7 | 7.9 | 3.0 |
| Volcanogenous Regosols (Vitric Andosols) | 2 | 9.9 | 3,180 | 17.1 | 1,040 | 383 |
| Peat Soils (Dystric Histosols) | 1 | 213 | 5,590 | 11.4 | 5,650 | 13.4 |
| Others | 10 | 16.1 | 230 | 1.3 | 133 | 10.7 |

Table 5.13. Geometric mean K_d values (ml/g) for iodine measured in untreated river water under oxic conditions (Bird and Schwartz, 1996)

| Sediment Type | Sediment-to-Water Ratio (Percent) | | |
|------------------|-----------------------------------|-----|-----|
| | 1 | 10 | 50 |
| High Organic | 247 | 109 | 21 |
| Peaty | 104 | 68 | 14 |
| Clayey Silt/Sand | 32 | 15 | 2.9 |
| Sand | 0.1 | 0.5 | 0.2 |

Fukui *et al.* (1996) used batch equilibration experiments to study the sorption of I^- and IO_3^- on a sandy loam soil dried at 100°C and mixtures of that soil with various types of organic matter. The experiments were conducted with three pH 6.5 groundwater solutions, a pH 8.6, 0.5×10^{-3} mol/l $CaCO_3$ solution, and a pH 7.1 pond water. The groundwater solutions had essentially the same composition except that one (GW1) was used as sampled, the second (GW2) was the same groundwater solution after having N_2 bubbled through for continuously for one month, and the third (GW3) was the same groundwater solution after having been allowed to stand in air for one month without N_2 bubbling through it. Fukui *et al.* (1996) proposed multiple sorption mechanisms for I^- , and a simple anion exchange process for IO_3^- . To study the effect of pH on the sorption of I^- and IO_3^- , batch experiments were conducted with a ^{125}I -spiked $CaCO_3$ solution; the initial pH of the solution was adjusted over the range of 3.2 to 10.6 using 1 mol/l HCl or NaOH solutions. After the seven-day equilibration period, the pH ranged from 6.1 to 7.1 due to the buffer capacity of the soil. In the initial pH range of 3.2 to 10.6, the uptake of both iodine species decreased with pH, especially in the weakly acidic region. Fukui *et al.* (1996) indicated that for the experiments at the initial pH 3.2, approximately 60 percent of the I^- species were converted to molecular I_2 and approximately 30 percent of the IO_3^- species to I^- . The K_d values for both iodine species on insoluble humic substances were one order of magnitude larger than those for soil. The average K_d values for I^- after 14 days of contact time in the five solutions were 3.0, 1.9, 1.4, 3.3, and 6.4 ml/g, respectively, for the GW1, GW2, GW3, the $CaCO_3$ solution, and the pond water. The average K_d values for IO_3^- for the same solutions were 11, 8.3, 10, 12, and 10 ml/g, respectively.

Serne *et al.* (1993) used the batch adsorption technique to measure the K_d values for I^- on three characterized sediments from the Hanford Site in southeastern Washington. The sediment samples included two loamy sands (samples TBS-1 and Trench-8) and one sand (sample CGS-1). The measurements were conducted using an uncontaminated groundwater (pH 8.14) sample from the Hanford site. After 35 days of contact time, the pH values for the CGS-1, TBS-1, and Trench-8 sediment suspensions were 7.9-8.4., 8.0-8.4, and 8.22, respectively. The K_d values measured for I^- were 1.2 ml/g for CGS-1 sediment at 35 days, 2.6 ml/g for TBS-1 sediment at 35 days, and 1.5 ml/g for Trench-8 sediment at 44 days.

Muramatsu *et al.* (1990) used the batch equilibration method to study the effects of heating and gamma-irradiation of soil relative to the sorption of I^- and IO_3^- on soil and selected soil components in deionized water. The K_d values were measured for I^- and IO_3^- on soils identified as a field soil (andosol),¹ rice paddy soil, and sandy soil, and on bentonite, kaolinite, quartz sand, Fe_2O_3 , Al_2O_3 , and humic acid. The organic carbon contents of the dry soils were 4.4, 2.4, and 1.4 percent for the field, rice paddy, and sandy soils, respectively. The soil pH values were 5.4, 5.7, and 5.5, for the field, rice paddy, and sandy soils, respectively. The sorption measurements were completed on the untreated samples of each soil type as well as samples of each soil that were dried at several temperatures (in air at ambient conditions and at 100, 150, 200, and 300°C) and that were gamma-irradiated. Desorption experiments were also conducted at 25 and 95°C using the field soil and several leachates, such as deionized water, NaOH, K_2SO_4 , HCl, and others. The K_d values measured for the untreated soils are listed in Table 5.14. The reader is referred to Table III in Muramatsu *et al.* (1990) for the K_d values for the soils with different drying treatments. They noted that the measured K_d values probably represented a mixture of the sorption of I^- and IO_3^- , because part of the initial concentration of IO_3^- probably reduced to I^- during the course of the measurements. Sorption of I^- and IO_3^- on the untreated field soil was considerably greater than their sorption on the sandy soil. These results indicated that the sorbed iodine was associated with the organic matter in the soil samples (Muramatsu *et al.*, 1990). The K_d values decreased with increasing temperature of the soil drying treatments. Iodine did not sorb significantly on quartz sand, bentonite, kaolinite, or Al_2O_3 under these conditions. Significant sorption was measured for both I^- and IO_3^- on Fe_2O_3 and humic acid reagent used in these experiments.

Sheppard and Thibault (1988) studied the vertical migration of iodine in two types of mires typical of the Precambrian Shield in Canada. Sheppard and Thibault (1988) derived *in situ* K_d values from analyses of the dried peat and pore water. The K_d values determined for iodine ranged from 0.2 to 64 ml/g. The investigators proposed that the mobility of iodine was related to the aeration status and botanical origin of the peat.

Gee and Campbell (1980) used batch equilibration methods to measure K_d values for ^{125}I on a sandy sediment from the Hanford Site in southeastern Washington. The iodine sorption experiments were conducted with six synthetic groundwater solutions as well as with low and high nitrate salt solutions. The ^{125}I K_d values for the sand sediment with the groundwater solutions ranged from 4 to 15 ml/g. The K_d values for the salt solutions were 18 and 4 ml/g for the high and low salt solutions, respectively. The addition of ethylenediamine tetraacetic acid (EDTA) to the ^{125}I -spiked solution had the apparent effect of decreasing the K_d values for the measurements made with the high and low salt solutions.

Wildung *et al.* (1974) used the batch equilibration method to measure the K_d values for I^- and methyl iodide on 22 types of soils collected in Oregon, Washington, and Minnesota. The K_d values for I^- and methyl iodide range from 0.8 to 52.6 ml/g, and 0.1 to 3.1 ml/g, respectively. The sorption of I^- was determined to be correlated only to the content of silt-size particles in these soils. Wildung *et al.*

¹ Andosol (or Andept) is defined as a black or dark brown soil that is formed from volcanic material. It is characterized as being high in organic material, low in exchangeable bases, and high in exchangeable aluminum (Bates and Jackson, 1980).

(1974) found that the sorption of methyl iodide on these soils was positively correlated to clay-size soil particles, organic carbon, and cation exchange capacity, and negatively correlated to pH.

Table 5.14. Values of K_d (ml/g) measured by Muramatsu *et al.* (1990) for the sorption of I^- and IO_3^- on soil and selected soil components of an andosol.

| Soil Identification | K_d (ml/g) | CEC (meq/100 g) | Solution |
|---------------------|--------------------|-----------------|-----------------|
| Field Soil | 7,500 for I^- | 20 | Deionized Water |
| Rice Paddy Soil | 560 for I^- | 10 | Deionized Water |
| Sandy Soil | 35 for I^- | 3.9 | Deionized Water |
| Field Soil | 7,000 for IO_3^- | 20 | Deionized Water |
| Rice Paddy Soil | 430 for IO_3^- | 10 | Deionized Water |
| Sandy Soil | 32 for IO_3^- | 3.9 | Deionized Water |

5.5.5.4 *Published Compilations Containing K_d Values for Iodine*

Because the references in this section are often cited or used for comparison in other publications, the following summaries are provided for completeness. It is recommended that the reader review the original reference and the references cited therein to understand the procedures and sources of the K_d values used for each compilation. The compilations do not distinguish between oxidation states for those contaminants that are redox sensitive or consider other important factors that contribute to variability in sorption, such as pH. Moreover, in cases where very large K_d values are listed, there is a risk that the original K_d measurement may have included precipitated components.

Looney *et al.* (1987) tabulated estimates for geochemical parameters needed for environmental assessments of waste sites at DOE's Savannah River Plant in South Carolina. Looney *et al.* list K_d values for several metal and radionuclide contaminants based on values that they found in 1-5 published sources. For iodine, Looney *et al.* list a "recommended" K_d of 0.2 ml/g, and a range from 0.001 to 1 ml/g. Looney *et al.* note that their recommended values are specific to the Savannah River Plant site, and they must be carefully reviewed and evaluated prior to use in assessments at other sites.

Thibault *et al.* (1990) (also see Sheppard and Thibault, 1990) present a compilation of soil K_d values prepared to support radionuclide migration assessments for a Canadian geologic repository for spent nuclear fuel in Precambrian Shield plutonic rock. Thibault *et al.* collected K_d values from other compilations, journal articles, and government laboratory reports for important elements, such as iodine, that would be present in the nuclear fuel waste inventory. The iodine K_d values listed in Thibault *et al.* (1990) are included in Table 5.15. Thibault *et al.* (1990) describe the statistical methods used for analysis of the compiled K_d values. The range for the K_d values used to calculate the

“geometric mean” cover several orders of magnitude. Readers are cautioned against using “geometric mean” values or any other form of averaged K_d values as “default” K_d values, as such values are usually calculated from data compiled from different investigators for different soil systems. These mean or average values do not represent any particular environmental system and geochemical conditions. As discussed in Volume I (EPA, 1999b), the variation observed in the literature for K_d values for a contaminant is due to differences in sorption mechanisms, geochemical conditions, soil materials, and methods used for the measurements.

Table 5.15. Iodine K_d values (ml/g) listed in Thibault *et al.* (1990, Tables 4 to 8).

| Soil Type | K_d Values (ml/g) | | |
|-----------|---------------------|------------------------|-----------|
| | Geometric Mean | Number of Observations | Range |
| Sand | 1 | 22 | 0.04 - 81 |
| Silt | 5 | 33 | 0.1 - 43 |
| Clay | 1 | 8 | 0.2 - 29 |
| Organic | 25 | 9 | 1.4 - 368 |

McKinley and Scholtis (1993) compare radionuclide K_d sorption databases used by different international organizations for performance assessments of repositories for radioactive wastes. The iodine K_d values listed in McKinley and Scholtis (1993, Tables 1, 2, and 4) are listed in Table 5.16. The reader should refer to sources cited in McKinley and Scholtis (1993) for details regarding their source, derivation, and measurement. Radionuclide K_d values listed for cementitious environments in McKinley and Scholtis (1993, Table 3) are not included in Table 5.16. The organizations listed in the tables include: AECL, GSF, IAEA, KBS, NAGRA, NIREX, NRC, NRPB, PAGIS (CEC), PSE, RIVM, SKI, TVO, and UK DoE (acronyms defined in Section A.1.0 in Appendix A).

5.5.5.5 *K_d Studies of Iodine on Pure Mineral, Oxide, and Crushed Rock Materials*

Numerous adsorption studies have been conducted of iodine on pure minerals, oxide phases, and other geologic-related materials. The K_d values listed in these studies are not necessarily relevant to the mobility and sorption of iodine in soils. However, they are listed in Appendix F for completeness. The references cited in Appendix F are listed in the main reference list in Chapter 6. The potential value of the references that they cite and the sorption processes that they discuss is left to the reader. Many of these studies were conducted because of extensive research interest in developing getters (adsorbents) that could be added to waste streams and tailored barriers for removal and/or immobilization of dissolved iodine. The studies of iodine sorption on crushed rock were conducted typically as part of national research programs to investigate the feasibility of geological disposal of high-level radioactive waste (HLW).

Table 5.16. Iodine K_d values (ml/g) listed by McKinley and Scholtis (1993, Tables 1, 2, and 4) from sorption databases used by different international organizations for performance assessments of repositories for radioactive wastes.

| Organization | Argillaceous (Clay) | | Crystalline Rock | | Soil/Surface Sediment | |
|--------------|----------------------|--------------|----------------------------|--------------|-----------------------|--------------|
| | Sorbing Material | K_d (ml/g) | Sorbing Material | K_d (ml/g) | Sorbing Material | K_d (ml/g) |
| AECL | Bentonite-Sand | 0.0085 | Granite | 0 | Soil/Sediment | 10 |
| GSF | Sediment | 0.5 | | | | |
| IAEA | Pelagic Clay | 200 | | | | |
| KBS-3 | Bentonite | 13 | Granite | 0 | | |
| NAGRA | Bentonite | 5 | Granite | 1 | Soil/Sediment | 1 |
| | Clay | 5 | | | Soil/Sediment | 10 |
| NIREX | Clay Mudstone | 0 | | | | |
| NRC | Clay, Soil Shale | 0 | Granite | 0 | | |
| | | | Basalt | 0 | | |
| | | | Tuff | 0 | | |
| NRPB | Clay | 0 | | | Soil/Sediment | 0 |
| PAGIS | Subseabed | 100 | | | | |
| PSE | Sediment | 0 | | | | |
| RIVM | Sandy Clay | 1 | | | | |
| SKI | Bentonite | 1 | Granite | 0 | | |
| TVO | Baltic Sea Sediment | 100 | Crystalline Rock, Reducing | 0.5 | Soil/Sediment | 100 |
| | Lake Sediment | 100 | Crystalline Rock | 0.8 | | |
| UK DoE | Clay | 10 | | | Soil/Sediment | 0.8 |
| | Coastal Marine Water | 20 | | | | |

5.6 Neptunium Geochemistry and K_d Values

5.6.1 Overview: Important Aqueous- and Solid-Phase Parameters Controlling Retardation

Neptunium is a transuranic element that may exist in several valence states. Neptunium(V) (Np(V)) and Np(IV) are the most important valence states in natural waters. Over the pH range of most natural waters, Np(V) is present primarily as the cation NpO_2^+ . Neptunium(V) is considered relatively mobile, and Np(V) solids are quite soluble. If the concentrations of dissolved Np(V) are

sufficiently high, the solubility of Np(V) may be controlled by solids such as NpO_2OH , $\text{NaNpO}_2\text{CO}_3$, $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2$, and KNpO_2CO_3 . Neptunium (IV) exists in reducing (*i.e.*, low Eh) groundwater systems, and is not considered very mobile, because it forms sparingly soluble oxide and hydroxide solids. Reduction of Np(V) to Np(IV) can occur by a variety of abiotic and biotic processes.

Neptunium(V) aqueous species sorb to some extent to iron oxides and clays, but do not sorb to a major degree on most common minerals. Because NpO_2^+ does not compete favorably with dissolved Ca^{2+} and other divalent ions for adsorption sites on soils, the K_d values for Np(V) are relatively low. The adsorption of Np(V) has a strong dependence on pH. Typically, the sorption of Np(V) on minerals is negligible at pH values less than 5, and increases rapidly at pH values between 5 to 7. This pH-dependency is expected for ions present in solution primarily as cations. In carbonate-containing solutions, the adsorption of Np(V) on iron oxides has been observed to decrease at pH values greater than 7 to 9 in response to the formation of aqueous Np(VI) carbonate complexes.

5.6.2 General Geochemistry

Neptunium [Np, atomic number (Z) = 93] has 19 isotopes (Tuli, 2000). The atomic masses of these isotopes range from 225 to 244. Neptunium-237 (^{237}Np) has a half live ($t_{1/2}$) of 2.14×10^6 years and is the most important neptunium isotope from an environmental perspective. Potential sources of ^{237}Np include fallout from nuclear weapons, effluent cooling water from fission reactors, industrial processing of ^{237}Np produced in fission reactors, and ^{237}Np present as a component of high-level nuclear wastes (Thompson, 1982). Although spent nuclear fuel contains a relatively small initial concentration of ^{237}Np , its concentration increases with time from the radioactive decay of Am-241 ($t_{1/2} = 432.2$ years). Because of its long half-life, ^{237}Np will be a major contributor to the radiation inventory of nuclear waste stored in geologic repositories after approximately 100,000 years (Kaszuba and Runde, 1999).

Neptunium is a transuranic (actinide) element. Neptunium may exist in the +3, +4, +5, +6, and +7 valence states, but only the +4, +5, and possibly +6 states are relevant to natural environments. Neptunium(VI) is stable only in highly oxidizing solutions and is therefore not important under most environmental conditions. As noted in Volume II (EPA, 1999c), aqueous speciation and solubility reactions, and sorption onto minerals and soils usually differ considerably for redox-sensitive elements contaminants in their different valence states. Neptunium(V) is considered relatively mobile, because Np(V) solids are quite soluble and Np(V) aqueous species do not readily sorb on common minerals. Over the pH range of most natural waters, Np(V) will be present primarily as the neptunyl ion, NpO_2^+ . Neptunium(IV) exists in reducing (*i.e.*, low Eh) groundwater systems, and like U(IV) and Pu(IV), may form sparingly soluble oxide and hydroxide solids that limit the mobility of Np(IV) under reducing conditions. Redox-sensitive elements, such as neptunium, can be immobilized by surface-mediated, heterogeneous reduction/sorption reactions on Fe(II)-containing oxide and silicate minerals. Many of these minerals exist as coatings on soil particles and/or primary constituents of soils. The heterogeneous electrochemical reactions occur by electron transfer reactions by which the Fe(II) is oxidized to Fe(III), and the redox-sensitive contaminant, is reduced to a lower valence state, such as reduction of Np(V) to Np(IV). These reactions have recently been the subject of considerable interest because they may have a significant effect on the mobility of redox-sensitive elements in the vadose zone, aquatic sediments, and

groundwater. They are the basis for certain remediation technologies, such as permeable barriers composed of zero-valent iron particles (*i.e.*, as metallic iron) or sodium-dithionite reduced soils, which are currently being tested for immobilization of groundwater contaminants.

Surface-mediated, heterogeneous reduction/sorption reactions are reviewed in detail by White (1990), and studied experimentally by White and Yee (1985), White *et al.* (1994), and many others. Experimental studies include investigations of Fe(II)-containing silicate minerals and/or rocks in the reduction of: Np(V) (Hakanen and Lindberg, 1991; Susak *et al.*, 1983; Meyer *et al.*, 1984); Fe(III) (White and Peterson, 1996; White and Yee, 1985); Cr(VI) (White and Peterson, 1996; Eary and Rai, 1989, Ilton and Veblen, 1994); Cu(II) (White and Peterson, 1996); nitrate (Postma, 1990); and V(V) (White and Peterson, 1996). These surface-mediated, heterogeneous reduction/sorption reactions have also been observed in sorption experiments conducted with crushed rock materials. For example, Bondietti and Francis (1979) showed that Np(V) could be reduced to less soluble Np(IV) by Fe(II) in minerals in igneous rocks.

The reduction of Np(V) to Np(IV) by biotic processes has also been demonstrated. Lloyd *et al.* (2000a) conducted a biochemical study of the reduction of Np(V). Their experiments demonstrated that *Shewanella putrefaciens* reduced Np(V) to a lower valence state, possibly Np(IV). However, this reduction process was not sufficient to remove neptunium from solution. Lloyd *et al.* (2000a) were able to remove ^{237}Np and its daughter product of protactinium-233 (^{233}Pa) from solution by bioprecipitation using a combination of the two organisms *S. putrefaciens* and *Citrobacter sp.* The bioprecipitation resulted from bioreduction to Np(IV) by *S. putrefaciens* in concert with phosphate liberation by the *Citrobacter sp.* from the glycerol 2-phosphate solution.

The environmental chemistry and mobility of neptunium in surface water, groundwater, and geologic environments has been reviewed extensively by others, such as Silva and Nitsche (1995), Tanaka *et al.* (1992), Lieser and Mühlenweg (1988); Coughtrey *et al.* (1984), Thompson (1982), Onishi *et al.* (1981), and Ames and Rai (1978). Although somewhat dated, the extensive review by Coughtrey *et al.* (1984) is particularly noteworthy.

5.6.3 Aqueous Speciation

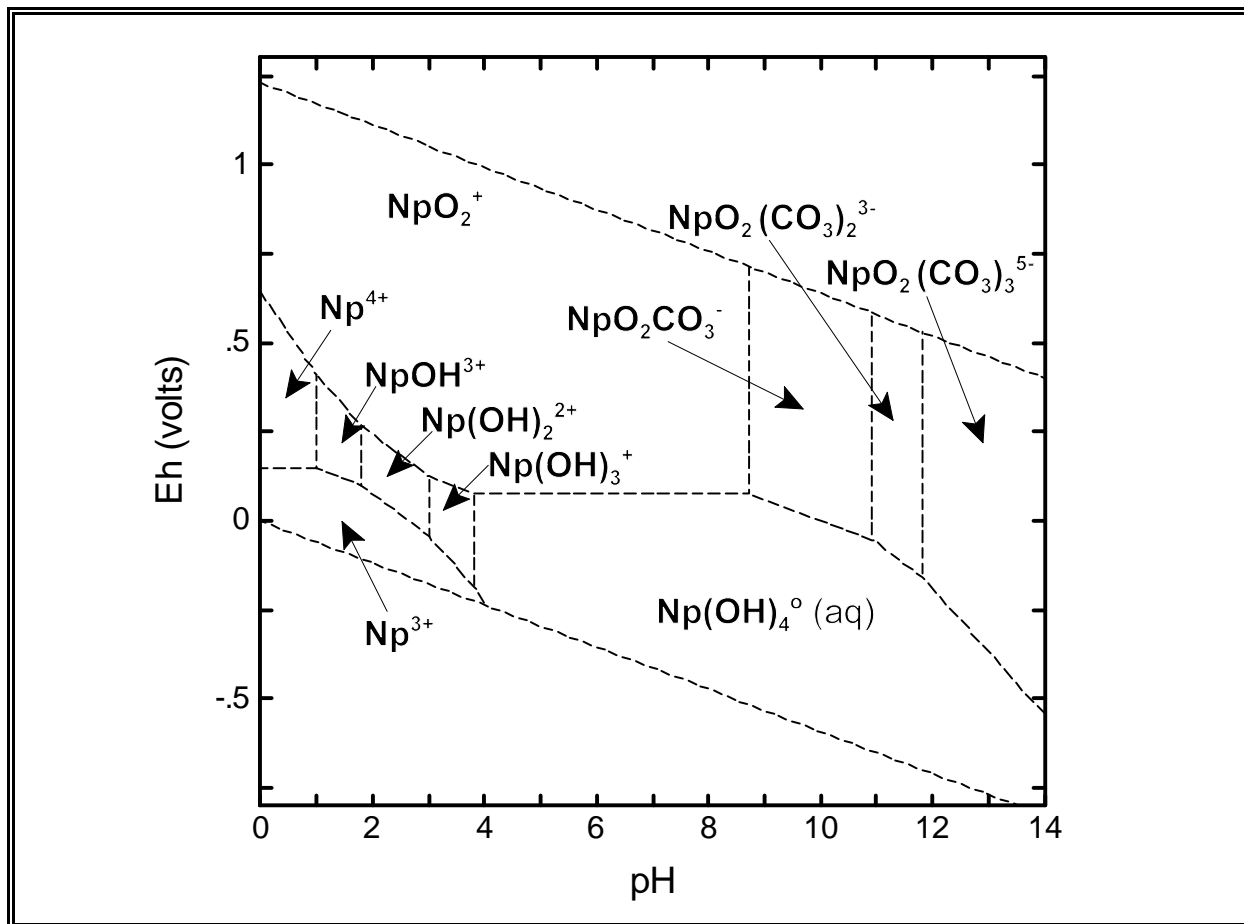
Lemire *et al.* (2001) have published an extensive, detailed review of the chemical thermodynamics of neptunium. The thermodynamic data for neptunium aqueous species and solids are limited and not well known relative to other radionuclides. Figure 5.7 is an Eh-pH diagram that shows the dominant aqueous species of neptunium as a function of pH and Eh (redox potential) at 25°C with respect to the thermodynamic stability of water.

Possible Np(V) aqueous species include those listed in Table 5.17.¹ The distribution of aqueous species for Np(V) (see Figure 5.8) as a function of pH was calculated for an oxidizing environment containing the water composition listed in Table 5.1. The speciation calculations indicate that the neptunyl ion, NpO_2^+ , is the dominant aqueous species for most environmentally-relevant pH conditions. The aqueous speciation of neptunium is dominated by NpO_2^+ over a wide range of

¹ Lemire *et al.* (2001) was published after the writing of this report had been completed. Therefore, the Np(V) species and associated thermodynamic constants from Lemire *et al.* (2001) were not included in the speciation calculations listed in this section.

environmental pH and Eh conditions. At pH conditions greater than about 8.5, aqueous Np(V) complexes, such as $\text{NpO}_2(\text{OH})^\circ(\text{aq})$ and $\text{NpO}_2(\text{CO}_3)^-$ may be more dominant.

Figure 5.7. Eh-pH stability diagram for the dominant neptunium aqueous species at 25°C. [Diagram based on a total concentration of 10^{-8} mol/l dissolved neptunium and 10^{-3} mol/l dissolved carbonate.]

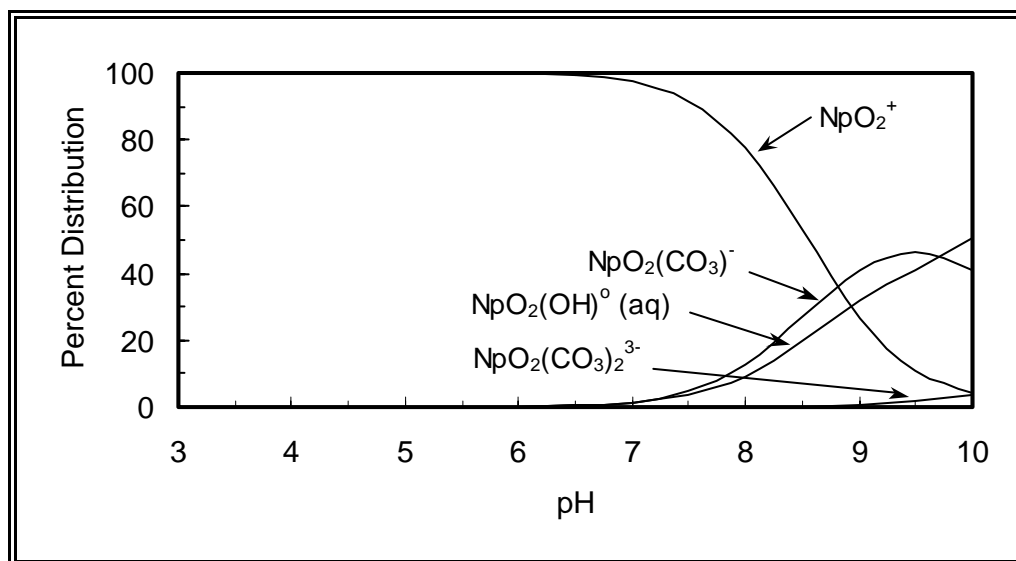


Several recent studies have been published regarding the aqueous speciation of Np(V). For example, the hydrolysis and complexation of Np(V) has been studied by Runde *et al.* (1996) and Fanghänel *et al.* (1995). Increasing carbonate at high pH increases the importance of carbonate complexes such as $\text{NpO}_2(\text{CO}_3)_3^{5-}$. Neck *et al.* (1994, 1997) has studied the complexation reactions of Np(V) in carbonate solutions. In strongly alkaline NaOH)/ Na_2CO_3 solutions, Neck *et al.* (1997) found that the mixed Np(V) hydroxo-carbonate complexes $\text{NpO}_2(\text{OH})(\text{CO}_3)_2^+$ and $\text{NpO}_2(\text{OH})_2(\text{CO}_3)^-$ may form. Morgenstern and Kim (1996) used absorption spectroscopy to confirm the formation of the Np(V) phosphate complexes $\text{NpO}_2\text{PO}_4^{2-}$ and $\text{NpO}_2\text{HPO}_4^-$. Ultrafiltration and centrifugation studies conducted with colloidal iron by Itagaki *et al.* (1991) suggest that Np(V) pseudocolloids can be formed in the pH conditions where the aqueous species $\text{NpO}_2\text{OH}^\circ(\text{aq})$ is dominant. Under reducing conditions, precipitation of amorphous $\text{NpO}_2 \cdot x\text{H}_2\text{O}$ and its colloids were found to be important to the environmental behavior of neptunium (Itagaki *et al.*, 1991).

Table 5.17. Np(V) aqueous species.

| Aqueous Species |
|--|
| NpO_2^+ , $\text{NpO}_2\text{OH}^\circ$ (aq), $\text{NpO}_2(\text{OH})_2^-$ |
| $\text{NpO}_2\text{CO}_3^-$, $\text{NpO}_2(\text{CO}_3)_2^{3-}$, $\text{NpO}_2(\text{CO}_3)_3^{5-}$, $\text{NpO}_2(\text{OH})(\text{CO}_3)_2^{4-}$, $\text{NpO}_2(\text{OH})_2(\text{CO}_3)^{3-}$. |
| $\text{NpO}_2\text{H}_2\text{PO}_4^\circ$ (aq), $\text{NpO}_2\text{HPO}_4^-$, $\text{NpO}_2\text{SO}_4^-$ |
| $\text{NpO}_2\text{Cl}^\circ$ (aq), $\text{NpO}_2\text{F}^\circ$ (aq) |

Figure 5.8. Calculated aqueous speciation for Np(V) as a function of pH. [Neptunium(V) aqueous speciation was calculated based on a total concentration of dissolved neptunium of 1×10^{-8} mol/l, the water composition in Table 5.1, and thermodynamic constants from Lemire *et al.* (1984).]



The aqueous speciation of neptunium in the presence of humic substances in natural waters conditions has been reviewed by Moulin *et al.* (1992). The complexation and reduction of Np(V) with humic substances has also been investigated by various laboratories with different experimental methods (Artinger *et al.*, 2000; Sakamoto *et al.*, 2000; Zeh *et al.*, 1999; Marquardt and Kim, 1998, 1996; Rao and Choppin, 1995; Choppin, 1992; Kim and Sekine, 1991). Zeh *et al.* (1999) used absorption spectrometry and ultrafiltration in the neutral pH range to investigate the reduction of Np(V) to Np(IV) in a groundwater containing humic substances. The data suggest that Np(IV) may form a humic colloid-born species that can be separated from water by ultrafiltration. The original dissolved Np(V) was present as NpO_2^+ , $\text{NpO}_2\text{CO}_3^-$, and/or Np(V)-humate depending on pH. If the reduction of Np(V) to Np(IV) takes place by the formation of humic colloid-born species of

Np(IV), the colloids may remain stable in groundwater and mobile in porous aquifer systems (Zeh *et al.*, 1999).

Marquardt and Kim (1998) investigated the humate complexation of NpO_2^+ over the pH range 7 to 9 with purified humic acid extracted from a groundwater from Gorleben in northern Germany. Their results indicated that the only reaction competitive with Np(V)-humate complexation was the formation of Np(V) complexes with dissolved carbonate. Their calculations suggested that humate complexation of Np(V) may play an important role in groundwater with relatively high humic acid concentrations. However, Marquardt and Kim (1998) noted that the reduction of Np(V) to Np(IV) by interaction with humic acid was another important reaction to be considered with respect to the environmental behavior of neptunium. Marquardt *et al.* (1996) studied the influence of neptunium and humic acid concentrations, pH value, ionic strength, temperature, and competing cations on the complexation of Np(V) with humic acids. The stability constant for the complex was found to increase with increasing concentration of Np(V). No effect of ionic strength between 0.001 and 0.1 M was observed, and neptunium-humate complexation decreased with increasing temperature. Calcium and magnesium competed with neptunium for the available humic ligands. Under anaerobic conditions and at very low metal concentrations, humic acid reduces Np(V) to Np(IV), and the rate of reduction was dependent on pH. Rao and Choppin (1995) used near-IR (infrared) absorption and two sources of humic acid to determine the binding constants for Np(V)-humate complexes in the pH range 4.5 to 7.5. Their results indicated that Np(V) forms a single type of complex with humate, probably a 1:1 Np(V)-carboxylate complex.

5.6.4 Dissolution/Precipitation/Coprecipitation

The solubility of Np(V) has been studied extensively for the purpose of estimating the maximum solubility concentrations of dissolved neptunium that might be released from a geologic repository for high level waste (HLW) with subsequent migration in groundwater systems (*e.g.*, Novak and Roberts, 1995; Neck *et al.*, 1994; Lemire, 1984; and others). In carbonate-free aqueous solutions with OH^- as the only complexing ligand, the maximum concentration of dissolved Np(V) is likely determined by the solubility product of solids, such as $\text{Np}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ (Eford *et al.*, 1998) or solid NpO_2OH (Al Mahamid *et al.*, 1998; Roberts *et al.*, 1996). In carbonate-rich solutions, a variety of solids, such as hydrated $\text{NaNpO}_2\text{CO}_3$ (Neck *et al.*, 1994; Lemire *et al.*, 1993), $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2$ (Al Mahamid *et al.*, 1998; Neck *et al.*, 1994; Lemire *et al.*, 1993), and KNpO_2CO_3 (Al Mahamid *et al.*, 1998; Lemire *et al.*, 1993), have been studied as possible solubility controls for the maximum concentrations of dissolved Np(V) under oxidizing conditions. Neck *et al.* (1994) studied the solid/liquid reactions of Np(V) in carbonate solutions at different ionic strength. At the conditions of his experiments, he found that $\text{NaNpO}_2\text{CO}_3$ and $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2$ formed at pH values less than 8.5 and greater than 9, respectively.

Solids such as Np(IV) hydrous oxide (Nakayama *et al.*, 1996; Rai and Ryan, 1985); amorphous $\text{NpO}_2 \cdot x\text{H}_2\text{O}$ (Rai *et al.*, 1987), and amorphous NpO_2 (Rai *et al.*, 1999) have been studied as possible solubility controls for Np(IV).

5.6.5 Adsorption/Desorption

5.6.5.1 Guidance for Screening Calculations of Adsorption

Neptunium(V) aqueous species sorb to some extent to iron oxides and clays, but do not sorb to a major degree on most common minerals. Therefore, dissolved Np(V) is considered to be relatively mobile in soil systems. Because NpO_2^+ does not compete favorably with dissolved Ca^{2+} and other divalent ions for adsorption sites on soils, the K_d values for Np(V) are relatively low (Kaplan and Serne, 2000). Coughtrey *et al.* (1984) review sorption studies published prior to 1984 for neptunium to soils and crushed rock materials. Some of these studies and more recent neptunium adsorption studies are described in the sections below.

The limited number of K_d studies identified during this review for the adsorption of Np(V) on soil precluded derivation of K_d look-up tables of conservative minimum and maximum K_d values for Np(V). Of the studies discussed below, only Routson *et al.* (1975, 1977), Serne *et al.* (1993), and Kaplan *et al.* (1996) report K_d values and corresponding pH values for Np(V) adsorption on soil. The majority of their values are limited to the pH range from 6.2 to 8.5, and only Routson *et al.* (1975, 1977) reports Np(V) K_d values for pH values less than 8.5. For the pH range from 4 to 10, it is suggested that a K_d of 0.2 ml/g be used as a minimum K_d value for screening calculations of americium migration in soils. This value was reported for pH 7.8 by Routson *et al.* (1975, 1977) and is the lowest K_d value that they gave for experiments conducted with very to moderately dilute calcium and sodium electrolyte solutions. The other K_d values reported by Routson *et al.* (1975, 1977) for these solution concentrations ranged from 0.36 ml/g at pH 7.4 to 3.51 at pH 4.1. It is likely that the conservative minimum K_d for Np(V) in the pH range from 4 to 10 is greater than this limiting value, but no additional Np(V) K_d studies substantiate this assumption. As noted previously, it is recommended that for site-specific calculations, partition coefficient values measured at site-specific conditions are absolutely essential.

Given the limited availability of K_d studies for the adsorption of Np(V) on soil, readers may want to consider using geochemical models [see Section 5 in Volume I (EPA, 1999b)] to estimate the mass of adsorbed Np(V). Kohler *et al.* (1999) and Girvin *et al.* (1991) have determined the neptunium surface complexation reactions and associated intrinsic constants for modeling Np(V) adsorption on hematite and amorphous iron oxyhydroxide, respectively. If soil characterization studies indicate that either of these iron oxides is an important constituent for soils at the site under study, geochemical models can be used to calculate the mass of Np(V) adsorbed on these oxides, and based on the iron oxide concentration in the site soils, estimate a K_d for Np(V).

5.6.5.2 General Adsorption Studies

Experimental studies indicate that the adsorption of Np(V) has a strong dependence on pH, especially for iron oxides (Kohler *et al.*, 1999; Girvin *et al.*, 1991; Allard, 1984). Typically, the sorption of Np(V) on minerals is negligible at pH values less than 5, and increases rapidly when pH is between 5 to 7. This pH-dependency is expected for ions that are present in solution primarily as cations, such as NpO_2^+ (EPA, 1999b). In carbonate-containing solutions, the adsorption of Np(V) on iron oxides has been observed to decrease at pH values greater than 7 to 9 in response to the formation of aqueous Np(VI) carbonate complexes (Kohler *et al.*, 1999). This latter behavior is

analogous to that observed for the adsorption of U(VI) in carbonate-solutions at alkaline pH values [see Section 5.11 in Volume II (EPA, 1999c)].

Table 5.18. Neptunium(V) K_d values (ml/g) measured for three sediments by Kaplan *et al.* (1996).

| Sediment Sample | K_d Values (ml/g) | |
|-------------------------------------|---------------------|---------|
| | 7 days | 77 days |
| Touchet Bed Sand (sample TBS-1) | 2.17 | 3.62 |
| Silty Loam (Sample Trench AE-3) | 2.67 | 13.48 |
| Very Coarse Sand (Sample Trench-94) | 14.17 | 19.86 |

5.6.5.3 K_d Studies for Neptunium on Soil Materials

Serne *et al.* (1993) measured K_d values for Np(V) in groundwater contacting the <2-mm size fraction of Trench-8 sediment from the DOE's Hanford Site in eastern Washington. The pH of the Hanford groundwater was 8.3. The particle size distribution for the *in situ* Trench-8 sediment contained 9.7 percent gravel, 78.6 percent sand, 6.3 percent silt, and 5.4 percent clay. The <2-mm size fraction of this sediment contained 87 percent sand, 7 percent silt, and 6 percent clay. The K_d values measured at 5 and 44 days were 13.5 ± 3 and 29.1 ± 3.6 ml/g, respectively.

Kaplan *et al.* (1996) used the batch technique to measure the K_d values for Np(V) on three sediment samples from the Hanford Site in southeastern Washington. The measurements were conducted with a groundwater (pH 8.46) taken from a well located in an uncontaminated area of the Hanford Site. The sediment samples included a Touchet bed sand (sample TBS-1), a silty loam (sample Trench AE-3), and a very coarse sand (sample Trench-94). Kaplan *et al.* (1996) observed that the K_d values increased as a function of time. The K_d values measured at 7 and 77 days for the three sediments are listed in Table 5.18.

Sheppard and Thibault (1988) studied the vertical migration of neptunium in two types of mires typical of the Precambrian Shield in Canada. Sheppard and Thibault (1988) derived *in situ* K_d values from analyses of the dried peat and pore water. The K_d values determined for neptunium ranged from 31 to 2,600 ml/g. Neptunium was quickly immobilized in the reducing environment of the mire, which was the cause for the large *in situ* neptunium K_d values.

Nishita *et al.* (1981) studied the extractability of $^{237}\text{Np(V)}$ several types of soils as a function of pH. The extractability of neptunium was considered to parallel the solubilization of insoluble aluminum, iron, and/or manganese hydrous oxides, which are important adsorbents for dissolved contaminants in soil systems (Nishita *et al.*, 1981). The Np(V) K_d values and soil characteristics determined for these soils by Nishita *et al.* (1981) are listed in Table 5.19. Nishita *et al.* (1981) concluded that Np(V) will likely be more mobile than americium, curium, and plutonium in geologic systems.

Table 5.19. Measured Np(V) K_d values (ml/l) and soil properties for soils studied by Nishita *et al.* (1981).

| Soil Type | pH ¹ | OM ² Fraction (%) | CEC (meq/100 g) | Free Fe Oxides (%) | Mn ³ Fraction (%) | Extract pH | K_d (ml/g) |
|---------------------------|-----------------|------------------------------|-----------------|--------------------|------------------------------|--------------|--------------|
| Silt Clay Loam Sharpsburg | 5.9 | 2.8 | 20 | 1.29 | 0.06 | 5.83 6.85 | 35 95 |
| Sandy Loam Malbis | 5.3 | 2.4 | 15 | 1.65 | 0.05 | 4.08 5.57 | 3 18 |
| Sandy Loam Lyman | 5.0 | 5.7 | 15 | 1.52 | 0.04 | 4.42 6.06 | 32 |
| Silty Clay Holtsville | 7.8 | 0.6 | 30 | 1.20 | 0.04 | 7.29 8.28 | 41 117 |
| Loam Aiken | 6.0 | 8.4 | 15 | 5.29 | 0.10 | 5.56 6.57 | 26 108 |
| Silt Loam Yolo | 6.7 | 2.5 | 25 | 2.41 | 0.08 | 6.13 6.83 | 52 81 |
| Muck Egbert | 7.2 | 40.8 | 60 | 1.57 | 0.10 | 6.24 7.25 | 786 929 |

¹ Saturated paste.
² Organic matter.
³ In 4 M HNO₃ extract.

Sheppard *et al.* (1979) examined the extent to which neptunium was sorbed by colloidal-size soil particles which are potentially diffusible in soil/water systems. The batch equilibration experiments were conducted with distilled water and 14 soils from Muscatine, Illinois; Hanford, Washington; Barnwell, South Carolina; Idaho Falls, Idaho; and Paradise and Placerville, California. Centrifugation measurements indicated that some ²³⁷Np was retained by the colloidal-size soil particles. The sorption of ²³⁷Np on the soil particles was not complete after four to six months, and the proportion of radionuclide retained by the colloidal-size fraction decreased with time. Sheppard *et al.* (1979) found it difficult to correlate the results with the chemical and physical properties of the soil samples. This was attributed to the lack of precise distribution ratios, competition with cation exchange reactions, and complexation with humic and fulvic acid materials. Based on these results, Sheppard *et al.* (1979) suggest that colloids of clay and humic acids are potentially important processes for the transport of actinides in soil/water systems.

Dahlman *et al.* (1976) determined the K_d values for ²³⁷Np(V) in suspensions of <2 μm-clay particles from a silt loam soil. At pH 6.5 in a 0.005 mol/l solution of dissolved calcium, the measured K_d value was 320 ml/g.

Table 5.20. Properties of soils used in K_d measurements by Routson *et al.* (1975, 1977).

| Soil | CaCO ₃ (mg/g) | Silt (%) | Clay (%) | CEC (meq/100 g) | pH |
|----------------|-----------------------------|-------------|-------------|------------------------|-----|
| Washington | 0.8 | 10.1 | 0.5 | 4.9 | 7.0 |
| South Carolina | <0.2 | 3.6 | 37.2 | 2.5 | 5.1 |

Table 5.21. Neptunium K_d values (ml/g) measured for Washington and South Carolina soil samples in Ca(NO₃)₂ and NaNO₃ solutions by Routson *et al.* (1975, 1977).

| Concentration of Electrolyte (mol/l) | K_d Values (ml/g) | |
|--|---------------------|---------------------|
| | Washington Soil | South Carolina Soil |
| Ca(NO ₃) ₂ Solution | | |
| 0.002 | 2.37 | 0.25 |
| 0.02 | 0.93 | Not Determined |
| 0.05 | 0.78 | Not Determined |
| 0.10 | 0.62 | Not Determined |
| 0.20 | 0.36 | 0.16 |
| NaNO ₃ Solution | | |
| 0.015 | 3.90 | 0.66 |
| 0.030 | 3.51 | 0.57 |
| 0.30 | 3.28 | 0.51 |
| 0.75 | 3.28 | 0.45 |
| 3.00 | 3.19 | 0.43 |

Routson *et al.* (1975, 1977) used batch equilibration experiments to measure K_d values for ²³⁷Np on two soils as a function of the concentrations of dissolved calcium and sodium. The soil samples were selected to represent a range of weathering intensities. For arid conditions in the western United States, sandy (coarse-textured), low-exchange capacity soil was selected from a low rainfall area in eastern Washington. For humid conditions in the southeastern United States, a moderate-exchange capacity soil was selected from South Carolina. Properties of the soils used for these measurements are listed in Table 5.20. The K_d values were measured in 0.002, 0.02, 0.05, 0.10, and

0.20 mol/l $\text{Ca}(\text{NO}_3)_2$ solutions, and 0.015, 0.030, 0.30, 0.75, and 3.0 mol/l NaNO_3 solutions. The pH values for selected samples of the ^{237}Np solutions in the calcium and sodium systems were 7.4 and 4.1 for the Washington soil, and 7.8 and 6.2 for the South Carolina soil. The K_d values (Table 5.21) decreased with increasing concentrations of dissolved calcium and sodium.

For the solution concentrations used in these experiments, the K_d values for ^{237}Np on the Washington soil ranged from 2.37 to 0.36 ml/g as a function of dissolved calcium, and 3.90 to 3.19 ml/g as a function of dissolved sodium. For the South Carolina soil, the K_d values for ^{237}Np ranged from 0.25 to 0.16 ml/g as a function of dissolved calcium, and 0.66 to 0.43 ml/g as a function of dissolved sodium.

5.6.5.4 Published Compilations Containing K_d Values for Neptunium

Because the references in this section are often cited or used for comparison in other publications, the following summaries are provided for completeness. It is recommended that the reader review the original reference and the references cited therein to understand the procedures and sources of the K_d values used for each compilation. The compilations do not distinguish between oxidation states of contaminants that are redox sensitive (*e.g.*, neptunium) or consider other important factors that contribute to variability in sorption, such as pH. Moreover, in cases where very large K_d values are listed, there is a risk that the original K_d measurement may have included precipitated components.

Baes and Sharp (1983) present a simple model developed for order-of-magnitude estimates for leaching constants for solutes in agricultural soils. As part of this model development, they reviewed and determined generic default values for input parameters, such as K_d . A literature review was completed to evaluate appropriate distributions for K_d values for various solutes, including neptunium. Because Baes and Sharp (1983) are cited frequently as a source of K_d values in other published K_d reviews (*e.g.*, Looney *et al.*, 1987; Sheppard and Thibault, 1990), the neptunium K_d values listed by Baes and Sharp are reported here for completeness. Based on the distribution that Baes and Sharp determined for the K_d values for cesium and strontium, they assumed a lognormal distribution for the K_d values for all other elements in their compilation. Baes and Sharp listed an estimated default K_d of 11 ml/g for neptunium based on 44 K_d values that ranged from 0.16 to 929 ml/g for agricultural soils and clays over the pH range 4.5 to 9.0. Their compiled K_d values represent a diversity of soils, pure clays (other K_d values for pure minerals were excluded), extracting solutions, measurement techniques, and experimental error.

Looney *et al.* (1987) tabulated estimates for geochemical parameters needed for environmental assessments of waste sites at DOE's Savannah River Plant in South Carolina. Looney *et al.* list K_d values for several metal and radionuclide contaminants based on values that they found in 1-5 published sources. For neptunium, Looney *et al.* list a "recommended" K_d of 10 ml/g, and a range from 0.1 to 1,000 ml/g. Looney *et al.* note that their recommended values are specific to the Savannah River Plant site, and they must be carefully reviewed and evaluated prior to use in assessments at other sites.

Table 5.22. Neptunium K_d values (ml/g) listed in Thibault *et al.* (1990, Tables 4 to 8).

| Soil Type | K_d Values (ml/g) | | |
|-----------|---------------------|------------------------|-------------|
| | Geometric Mean | Number of Observations | Range |
| Sand | 5 | 16 | 0.5 - 390 |
| Silt | 25 | 11 | 1.3 - 79 |
| Clay | 55 | 4 | 0.4 - 2,575 |
| Organic | 1,200 | 3 | 857 - 1,900 |

Thibault *et al.* (1990) (also see Sheppard and Thibault, 1990) present a compilation of soil K_d values prepared to support radionuclide migration assessments for a Canadian geologic repository for spent nuclear fuel in Precambrian Shield plutonic rock. Thibault *et al.* collected K_d values from other compilations, journal articles, and government laboratory reports for important elements, such as neptunium, that would be present in the nuclear fuel waste inventory. The neptunium K_d values in Thibault *et al.* (1990) are included in Table 5.22. Thibault *et al.* (1990) describe the statistical methods used for analysis of the compiled K_d values. The range for the K_d values used to calculate the “geometric mean” cover several orders of magnitude. Readers are cautioned against using “geometric mean” values or any other form of averaged K_d values as “default” K_d values, as such values are usually calculated from data compiled from different investigators for different soil systems. These mean or average values do not represent any particular environmental system and geochemical conditions. As discussed in Volume I (EPA, 1999b), the variation observed in the literature for K_d values for a contaminant is due to differences in sorption mechanisms, geochemical conditions, soil materials, and methods used for the measurements.

McKinley and Scholtis (1993) compare radionuclide K_d sorption databases used by different international organizations for performance assessments of repositories for radioactive wastes. The neptunium K_d values listed in McKinley and Scholtis (1993, Tables 1, 2, and 4) are listed in Table 5.23. The reader should refer to sources cited in McKinley and Scholtis (1993) for details regarding their source, derivation, and measurement. Radionuclide K_d values listed for cementitious environments in McKinley and Scholtis (1993, Table 3) are not included in Table 5.23. The organizations listed in the tables include: AECL, GSF, IAEA, KBS, NAGRA, NIREX, NRC, NRPB, PAGIS (CEC), PSE, RIVM, SKI, TVO, and UK DoE (acronyms defined in Section A.1.0 in Appendix A).

Table 5.23. Neptunium K_d values (ml/g) listed by McKinley and Scholtis (1993, Tables 1, 2, and 4) from sorption databases used by different international organizations for performance assessments of repositories for radioactive wastes.

| Organization | Argillaceous (Clay) | | Crystalline Rock | | Soil/Surface Sediment | |
|--------------|----------------------|--------------|----------------------------|--------------|-----------------------|--------------|
| | Sorbing Material | K_d (ml/g) | Sorbing Material | K_d (ml/g) | Sorbing Material | K_d (ml/g) |
| AECL | Bentonite-Sand | 30 | Granite | 80 | Soil/Sediment | 10 |
| GSF | Sediment | 30 | | | | |
| IAEA | Pelagic Clay | 5,000 | | | | |
| KBS-3 | Bentonite | 600 | Granite | 5,000 | | |
| NAGRA | Bentonite | 1,000 | Granite | 1,000 | Soil/Sediment | 10 |
| | Clay | 5,000 | | | Soil/Sediment | 1,000 |
| NIREX | Clay Mudstone | 100 | | | | |
| NRC | Clay, Soil Shale | 10 | Granite | 10 | | |
| | | | Basalt | 10 | | |
| | | | Tuff | 10 | | |
| NRPB | Clay | 30 | | | Soil/Sediment | 30 |
| PAGIS | Bentonite | 150 | | | Soil/Sediment | 500 |
| | Subseabed | 2,000 | | | | |
| PAGIS SAFIR | Clay | 200 | | | | |
| PSE | Sediment | 5 | | | | |
| RIVM | Sandy Clay | 10 | | | | |
| SKI | Bentonite | 1,000 | Granite | 5,000 | | |
| TVO | Bentonite | 1,000 | Crystalline Rock, Reducing | 200 | Soil/Sediment | 1,000 |
| | Baltic Sea Sediment | 50,000 | | | | |
| | Ocean Sediment | 50,000 | | | | |
| | Lake Sediment | 50,000 | | | | |
| UK DoE | Clay | 50 | | | Soil/Sediment | 10 |
| | Coastal Marine Water | 5,000 | | | | |

5.6.5.5 *K_d Studies of Neptunium on Pure Mineral, Oxide, and Crushed Rock Materials*

Numerous adsorption studies have been conducted of neptunium on pure minerals, oxide phases, and other geologic-related materials. The K_d values listed in these studies are not necessarily relevant to the mobility and sorption of neptunium in soils. However, they are listed in Appendix G for completeness. The references cited in Appendix G are listed in the main reference list in Chapter 6. The potential value of the references that they cite and the sorption processes that they discuss is left to the reader. Surface complexation modeling techniques have been used to understand the mechanisms of neptunium adsorption (Kohler *et al.*, 1999; Girvin *et al.*, 1991; Fujita *et al.*, 1995). Kohler *et al.* (1999) and Girvin *et al.* (1991) derived the neptunium surface complexation reactions and associated intrinsic constants to model Np(V) adsorption of hematite and amorphous iron oxyhydroxide, respectively. The studies of neptunium sorption on crushed rock were conducted typically as part of national research programs to investigate the feasibility of geological disposal of high-level radioactive waste (HLW).

5.7 Radium Geochemistry and K_d Values

5.7.1 Overview: Important Aqueous- and Solid-Phase Parameters Controlling Retardation

Radium (Ra) is an alkaline earth element, and can exist in nature only in the +2 oxidation state. In the pH range of 3 to 10, the uncomplexed ion Ra^{2+} is the dominant aqueous species for dissolved radium in natural waters. In sulfate-containing waters, precipitation and redissolution of calcium (Ca), strontium (Sr), and barium (Ba) sulfates, rather than adsorption/desorption, could control the concentrations of dissolved radium in the soil environment. Precipitation of radium is readily possible as the solid-solution solids $(\text{Ba,Ra})\text{SO}_4$ and $(\text{metal, Ra})\text{CO}_3$ in waters where the concentrations of dissolved sulfate and carbonate, respectively, are sufficiently high. This reaction, as noted by some investigators, may also be the cause for some very high adsorption values reported for radium in the literature. Very limited sorption data, especially K_d values, exist for radium on soils and sediments. The adsorption behavior of radium will be similar to that of strontium. Relative to other alkaline earth elements, radium is the most strongly sorbed by ion exchange on clay minerals. The adsorption of radium is strongly dependent on ionic strength and concentrations of other competing ions in that adsorption of radium decreases with increasing ionic strength. Radium is also strongly adsorbed to mineral oxides present in soils, especially at near neutral and alkaline pH conditions. The results of some studies also suggest that radium may be strongly adsorbed by organic material in soils.

5.7.2 General Geochemistry

Radium [Ra, atomic number (Z) = 88] is an alkaline earth element, and can exist in nature only in the +2 oxidation state. Radium and barium are adjacent to each other in the alkaline earth group. Due to the similarity of their ionic radii (Table 5.24), the chemical behavior of radium is very similar to that of barium.

Of the reported 34 radium isotopes, all are radioactive (Tuli, 2000). Only four radium isotopes are found naturally. These include ^{226}Ra [half life ($t_{1/2}$) = 1,600 y], ^{228}Ra ($t_{1/2}$ = 5.75 y), ^{224}Ra ($t_{1/2}$ = 3.66 d), and ^{223}Ra ($t_{1/2}$ = 11.435 d). The radium isotopes ^{226}Ra and ^{223}Ra are intermediate radioactive decay

products of the naturally occurring ^{238}U and ^{235}U decay series, respectively. ^{228}Ra and ^{224}Ra are decay products of the naturally occurring ^{232}Th decay series. The isotope ^{226}Ra is generally assumed the most important occurring radium isotopes in nature due to its long half life and the natural abundance of ^{238}U . However, King *et al.* (1982) found a relatively high proportion of ^{228}Ra in a study of groundwater geochemistry of ^{228}Ra , ^{226}Ra , and ^{222}Rn in 150 groundwater samples from a wide range of aquifer lithologies in South Carolina. The isotope ^{225}Ra ($t_{1/2} = 14.9$ d) of the ^{237}Np decay chain has not been detected in nature (Molinari and Snodgrass, 1990). All of the other radium isotopes have shorter half lives. The chemistry and radiochemistry of radium and the other elements of the uranium and thorium natural decay series are reviewed by Molinari and Snodgrass (1990). From the standpoint of health risk, ^{223}Ra , ^{224}Ra , and ^{226}Ra are also important in that they decay to produce radioactive isotopes of the noble gas radon that in turn decay by alpha particle emission [see a discussion of the geochemical and sorption behavior of radon in Section 5.7 of EPA (1999c)].

Table 5.24. Ionic radii (Å) for alkaline earth elements (Molinari and Snodgrass, 1990).

| Alkaline Earth Element | Ionic Radii (Å) | |
|------------------------|-----------------|----------|
| | Crystal | Hydrated |
| Mg^{2+} | 0.65 | 4.28 |
| Ca^{2+} | 0.99 | 4.12 |
| Sr^{2+} | 1.13 | 4.12 |
| Ba^{2+} | 1.35 | 4.04 |
| Ra^{2+} | 1.52 | 3.98 |

The fate and mobility of radium in surface water, groundwater, and geologic environments have been reviewed extensively. For example, see Beneš (1990), Frissel and Köster (1990), Dickson (1990), Onishi *et al.* (1981), Ames and Rai (1978), and others. Readers should also be aware of the detailed reviews published in *The Environmental Behavior of Radium* (IAEA, 1990) and *Radon, Radium and Uranium in Drinking Water* (Cothorn and Rebers, 1990). Chapters pertinent to this K_d review, for example, include the following reviews:

- Chemistry and radiochemistry of radium and the other elements of the uranium and thorium natural decay series (Molinari and Snodgrass, 1990)
- Relationship of radium and radon in geologic formations (Michel, 1990)
- Removal of radium from drinking water (Hanslík and Mansfeld, 1990)
- Removal of radium from uranium mining effluents and leaching from sludges (Huck and Anderson, 1990)
- Behavior of radium in soil (Frissel and Köster, 1990)
- Behavior of radium in continental surface water (Beneš, 1990)
- Behavior of radium in groundwater (Dickson, 1990).

5.7.3 Aqueous Speciation

The thermodynamic properties of radium aqueous species and solids are reviewed by Langmuir and Riese (1985). Radium exists in nature only in the +2 oxidation state. In the pH range of 3 to 10, the uncomplexed ion Ra^{2+} is expected to be the dominant aqueous species for dissolved radium. The species Ra^{2+} is the only aqueous species for radium in the thermodynamic database for the MINTEQA2 geochemical code (Allison *et al.*, 1991). Dissolved radium shows little tendency to form aqueous complexes, although the aqueous complexes RaOH^+ , RaCl^+ , RaCO_3° (aq), and RaSO_4° (aq) are known. The thermodynamic constants for such aqueous complexes however are not well established (Langmuir and Riese, 1985; Beneš *et al.*, 1982).

Beneš *et al.* (1982) studied the speciation of radium using centrifugation and free-liquid electrophoresis. The electrophoresis measurements conducted in 0.01 mol/l chloride solutions in the pH range 2 to 7 indicated that dissolved radium was present primarily as Ra^{2+} . The results of measurements conducted with solutions containing dissolved sulfate, carbonate, and bicarbonate indicated that significant concentrations of aqueous radium complexes were present.

5.7.4 Dissolution/Precipitation/Coprecipitation

In moderate to high sulfate waters, precipitation and redissolution of calcium, strontium, and barium sulfates, rather than adsorption/desorption, could control the concentrations of dissolved radium in the soil environment. Although radium is moderately soluble in natural waters and radium salts are less soluble than barium salts, the solubility of radium is unlikely controlled by pure RaSO_4 in natural waters. Precipitation of radium is possible as the solid-solution solids $(\text{Ba,Ra})\text{SO}_4^1$ and $(\text{metal,Ra})\text{CO}_3$ in waters where the concentrations of dissolved sulfate and carbonate, respectively, are sufficiently high.

The $(\text{Ba,Ra})\text{SO}_4$ coprecipitation process is well known as a preferred means for the removal of dissolved ^{226}Ra from effluents from uranium mining and milling operations (Huck and Anderson, 1990; Clifford, 1990). The addition of BaCl_2 reacts with dissolved sulfate present in the effluent to cause the almost instantaneous precipitation of $(\text{Ba,Ra})\text{SO}_4$ solid. The $(\text{Ba,Ra})\text{SO}_4$ coprecipitation process is so efficient that microcrystals of BaSO_4 have been incorporated into specific adsorbents for removal of radium from drinking water and other radium-contaminated solutions (Clifford, 1990).

The $(\text{Ba,Ra})\text{SO}_4$ coprecipitation process has also been shown to be important process in controlling the solubility of radium in natural waters (Baraniak *et al.*, 1999; Martin and Akber, 1999; Pardue and Guo, 1998; Landa and Gray, 1995; Dickson, 1990; Beneš and Strejc, 1986; Langmuir and Melchior, 1985; Beneš *et al.*, 1983; Church, 1979). Pardue and Guo (1998) studied the solubility of ^{226}Ra in contaminated sediments used integrated microcosm, geochemical modeling, and field-sampling techniques. Their results indicated that the solubility of radium was controlled by the coprecipitation of radium with barite. This conclusion was confirmed using selective extractions, solution saturation measurements, theoretical solubility calculations, and x-ray diffraction. Landa

¹ The barium end-member composition of this solid solution corresponds to the mineral known as barite (BaSO_4).

and Gray (1995) used selective extraction studies and leaching studies of components from uranium mill tailings to show that alkaline earth sulfate was an important sorption phase for ^{226}Ra .

Langmuir and Melchior (1985) investigated the geochemical controls for radium in some deep brines in north Texas. Analyses of the geochemistry of calcium, strontium, barium, and radium sulfates in these brines indicated that the concentrations of dissolved radium were likely controlled by coprecipitation of trace radium in sulfate minerals such as celestite (SrSO_4) and barite (BaSO_4). Langmuir and Melchior (1985) dismissed solid RaSO_4 as the solubility control for dissolved radium, because the brine compositions calculated to be 5 to 6 orders of magnitude undersaturated with respect to RaSO_4 . Beneš *et al.* (1983) investigated the particulate forms of radium and barium in a system consisting of uranium mine waste waters purified by coprecipitation with barium sulfate and of adjacent river waters. Results of selective dissolution analyses identified the following four particulate forms of both elements: “loosely bound,” “acid soluble,” $(\text{Ba,Ra})\text{SO}_4$, and “in crystalline detritus.” Beneš *et al.* (1983) determined that the main form of radium in the system was $(\text{Ba,Ra})\text{SO}_4$. Radium was present mainly as “acid soluble” or “in crystalline detritus” in the river water upstream of the sulfate-containing mine water discharge. In marine environments, radium is also found to be efficiently scavenged and exchanged during the diagenetic¹ formation of barite (Church, 1979).

It should be noted that under certain reducing conditions, the $(\text{Ba,Ra})\text{SO}_4$ coprecipitate is not thermodynamically stable. Sulfate-reducing bacteria can produce rapid dissolution of $(\text{Ba,Ra})\text{SO}_4$ sludge under suitable reducing conditions and appropriate carbon sources (Huck and Anderson, 1990). For example, Pardue and Guo (1998) observed that ^{226}Ra in contaminated sediment was remobilized under anaerobic, sulfate-reducing conditions.

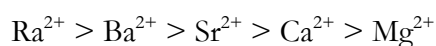
5.7.5 Adsorption/Desorption

5.7.5.1 Guidance for Screening Calculations of Adsorption

Compared to most other contaminants, very limited sorption data, especially K_d values, exist for radium on soils and sediments. Moreover, the reader is cautioned that any data that indicates very high adsorption of radium on geological materials should be suspect due to the possibility that $(\text{Ba,Ra})\text{SO}_4$ coprecipitation may have occurred during the measurements. Development of K_d look-up tables for radium is not possible given the minimal number of adsorption studies. However, as an alkaline earth element, the adsorption behavior of radium will be similar and somewhat greater to that of strontium for which extensive studies and data exist [see Section 5.8 in Volume II (EPA 1999c)]. For screening calculations of radium migration in soils, the K_d look-up table listed for strontium in Volume II can be used as general guidance for radium. Given the absence of definitive maximum and minimum K_d values for radium as a function of the key geochemical parameters, such as pH, EPA suggests that K_d values measured for radium at site-specific conditions are thus essential for site-specific contaminant transport calculations and conceptual models.

¹ Diagenetic - “caused by the chemical, physical, and biological changes undergone by a sediment after its initial deposition, and during and after its consolidation into a coherent solid rock, exclusive of surficial weathering and metamorphism” (Bates and Jackson, 1980).

Radium migrates as a cation competing with other alkaline earth cations for sorption sites in soils systems. Relative to other alkaline earth elements, the relative affinity this group of elements for ion exchange on clay minerals has been described as follows (Sposito, 1989):



The adsorption of radium has been shown to be strongly dependent on ionic strength and concentrations of other competing ions in that adsorption of radium decreases with increasing ionic strength.

The studies reviewed below indicate that radium is readily adsorbed to clays and mineral oxides present in soils, especially at near neutral and alkaline pH conditions. For the pH conditions of most natural waters, dissolved radium will be present primarily as the uncomplexed Ra^{2+} cation. Sorption studies discussed below confirm the adsorption behavior expected for Ra^{2+} as a function of pH. Radium adsorption on mineral phases is negligible at acidic pH values, and increases with increasing pH. Because adsorption of cations is coupled with a release of H^+ ions, cation adsorption is greatest at high pH and decreases with decreasing pH. For iron oxides, the increase in adsorption starts typically at pH values from 6 to 8 and is at a maximum by pH ~ 10 or less. As discussed in Volume I (EPA, 1999b), the pH range at which adsorption of cations begins to increase on mineral surfaces depends on the values of the zero point charge (PZC) (often used as a reference for how the surface charge of solids varies with pH) for each type of mineral. In general, at pH values less than PZC, the mineral surface serves as a strong adsorbent for anions. At pH values greater than the PZC, the surface strongly adsorbs dissolved cationic constituents.

Only a few studies have been conducted with respect to the adsorption of radium on organic matter. The results of these studies also suggest that radium may be strongly adsorbed by organic material in soils (Greeman *et al.*, 1999; Nathwani and Phillips, 1979a; 1979b). As noted previously, one of the major recommendations of this report is that for site-specific calculations, partition coefficient values measured at site-specific conditions are absolutely essential.

5.7.5.2 *General Adsorption Studies*

Sturchio *et al.* (2001) studied the processes that affect the mobility of radium isotopes in continuous Paleozoic carbonate aquifers in Missouri, Kansas, and Oklahoma. The concentrations of dissolved radium were correlated to the salinity and concentrations of other alkaline earth elements. The behavior of radium in the aquifers was explained by salinity-dependent sorption/desorption processes on surface mineral coatings.

Greeman *et al.* (1999) measured the abundance, chemical, and mineralogical form of ^{226}Ra , ^{238}U , and ^{232}Th in soil samples from 12 sites in the eastern United States. Selective chemical extraction and size fraction techniques were used to determine the abundance and radiometric equilibrium condition for ^{226}Ra , ^{238}U , and ^{232}Th in the following soil fractions: exchangeable cation, organic matter, “free iron oxide,” sand, silt, and clay size. Their results indicated that radium was enriched in the exchangeable cation and organic (humic) matter fractions in these soils.

Landa and Gray (1995) conducted selective extraction studies and studies of radionuclide sorption by and leaching from components of uranium mill tailings. Their results indicated that alkaline earth

sulfate and hydrous ferric oxide solids are important sorption phases for ^{226}Ra .

Willet and Bond (1995) used batch equilibration measurements to investigate the sorption of ^{226}Ra on highly weathered and sandy soils from the area near the Ranger Uranium Mine in Australia. The measurements were conducted using a background electrolyte solution of 0.0025 M MgSO_4 , and initial concentrations of dissolved ^{226}Ra of 100 Bq/l (1.2×10^{-11} mol/l), 150 Bq/l (1.8×10^{-11} mol/l), and 200 Bq/l (2.4×10^{-11} mol/l). The pH values of the soil/electrolyte suspensions ranged between 4.6 and 7. The sorption data for ^{226}Ra were fitted to the Freundlich isotherm. Willet and Bond (1995) found no clear relationship between ^{226}Ra sorption and the concentrations of organic matter and clay in the soils. Sorption of ^{226}Ra on all soils increased with increasing soil pH. For some soils, the sorption of ^{226}Ra was nearly complete. Because trace concentrations of dissolved ^{226}Ra were used for their measurements, Willet and Bond (1995) concluded that precipitation of radium salts was not likely in their experiments. The results also indicated that the ^{226}Ra was strongly sorbed to these soils. Less than 1 percent of the sorbed ^{226}Ra was remobilized by resuspension of the soils in the background electrolyte solution.

Berry *et al.* (1994) conducted diffusion experiments of the mobility of radium through sandstone. Their results indicated that the sorption of radium was affected by competitive ion effects. Radium sorption in the high ionic strength groundwater experiment was less than 50 percent of the sorption measured in the lower ionic strength groundwater solution.

Nathwani and Phillips (1979a, 1979b) used batch equilibration experiments to study ^{226}Ra adsorption by soil with different physical-chemical characteristics. The measured ^{226}Ra adsorption followed Freundlich and Langmuir adsorption isotherms over a large range of ^{226}Ra concentrations. Organic matter and clay were determined to be the dominant phases contributing to the adsorption of ^{226}Ra on these soils. Nathwani and Phillips (1979a) suggested that adsorption affinity of the organic matter and clays was primarily due to their cation exchange capacity (CEC). Their results also indicated that organic matter adsorbed approximately 10 times more ^{226}Ra than did the clays. The results of Nathwani and Phillips (1979b) show that the addition of competing alkaline earth cations to the system can greatly affect radium sorption on the clay minerals.

5.7.5.3 *K_d Studies for Radium on Soil Materials*

Compared to other contaminants and in particular to ^{90}Sr , which is another alkaline earth isotope of environmental concern, a very limited number of published K_d studies was identified for the adsorption of radium on soils. Meier *et al.* (1994) completed parametric studies with site-specific waters and crushed sedimentary rocks from strata that overly the Gorleben salt dome in Germany. In the pH range from approximately 4 to 9, the adsorption and desorption of radium increased with increasing pH. The K_d values measured for the adsorption of radium on a sandy sediment in groundwater were 6.7, 12.6, 26.3, and 26.3 ml/g at pH values of 6, 7, 8, and 9, respectively. For the same system, the desorption K_d values were 10.9, 31, 38, and 29 ml/g at pH values of 6, 7, 8, and 9, respectively. As commonly reported for the sorption of strontium (EPA, 1999c), these adsorption and desorption K_d values indicate that radium is essentially completely reversibly adsorbed.

Nathwani and Phillips (1979b) measured the adsorption of ^{226}Ra on soils as a function of calcium concentrations. All experiments were conducted with a constant total concentration of ^{226}Ra of 10 pCi/ml (4.5×10^{-8} mol/l). The dissolved concentrations of calcium varied from 0 to 0.5 mol/l. Values for K_d for ^{226}Ra estimated from those plotted in Nathwani and Phillips (1979b) are listed in Table 5.25. The characteristics of the soil samples for which K_d values are reported in Nathwani and

Phillips (1979b) are given in Table 5.26, as reported in the companion paper by Nathwani and Phillips (1979a). Nathwani and Phillips (1979b) also plot K_d values for each soil for calcium concentrations of 0.02 and 0.04 mol/l. These values, however, are not significantly different from the K_d values determined for the respective soils at calcium concentrations of 0.01 and 0.05 mol/l, and show the same trend as a function of calcium concentrations. Sorption of ^{226}Ra by all soils decreased with increasing concentrations of dissolved calcium. The K_d values reported by Nathwani and Phillips (1979b) are unusually large, and orders of magnitude greater than those reported by most researchers. This suggests that precipitation of radium may have occurred during the course of these measurements.

Serne (1974) measured K_d values for radium on four sandy, arid soil samples from Utah using a simulated river water solution. The final pH values of the soil/river water suspensions ranged from 7.6 to 8.0. The soil consisted primarily of quartz and feldspar with 2-5 percent calcite and minor amounts of muscovite and smectite. The K_d values ranged from 214 to 467 ml/g for the four soil samples (Table 5.27). Serne (1974) was able to correlate the K_d values to the cation exchange capacity (CEC) values for these soils.

Table 5.25. Radium K_d values (ml/g) as function of calcium concentration [Nathwani and Phillips, 1979b)]. [K_d values estimated from Figure 3 in Nathwani and Phillips (1979b).]

| Soil Series | K_d (ml/g) as Function of Concentration of Calcium (mol/l) | | | |
|-------------|--|-------------------|-------------------|-------------------|
| | 0 | 0.005 | 0.01 | 0.05 |
| Wendover | 9.5×10^5 | 3.1×10^5 | 2.1×10^5 | 1.1×10^5 |
| Grimsby | 1.2×10^5 | 4.0×10^4 | 3.2×10^4 | 1.9×10^4 |
| St. Thomas | 3.8×10^4 | 1.1×10^4 | 7.1×10^3 | 4.3×10^3 |

5.7.5.4 *Published Compilations Containing K_d Values for Radium*

Because the references in this section are often cited or used for comparison in other publications, the following summaries are provided for completeness. As noted previously, the reader is cautioned that any very high adsorption results, including K_d values, reported for radium should be suspect due to the possibility that $(\text{Ba,Ra})\text{SO}_4$ coprecipitation occurred during the measurements. It is recommended that the reader review the original reference and the references cited therein to understand the procedures and sources of the K_d values used for each compilation. The compilations do not typically consider important factors that contribute to variability in sorption, such as pH. Moreover, in cases where very large K_d values are listed, there is a risk that the original K_d measurement may have included precipitated components.

Table 5.26. Properties of soil samples for which K_d values are given in Nathwani and Phillips (1979b). [The soil characteristics were taken from Nathwani and Phillips (1979a).]

| Soil Series | Texture | pH | Organic Matter % | Sand % | Silt % | Clay % | CEC (meq/100 g) |
|-------------|------------|-----|------------------|--------|--------|--------|-----------------|
| Wendover | Silty Clay | 5.4 | 16.2 | 6.7 | 47.9 | 45.4 | 34.7 |
| Grimsby | Silt Loam | 4.3 | 1.0 | 43.7 | 48.9 | 7.4 | 10.4 |
| St. Thomas | Sand | 5.2 | 3.1 | 91.1 | 6.8 | 1.3 | 10.9 |

Table 5.27. Radium K_d values (ml/g) measured by Serne (1974) for sandy, arid soil samples from Utah.

| Soil Sample | Final pH | K_d (ml/g) |
|-------------|----------|--------------|
| Soil I | 7.9-8.0 | 354 ± 15 |
| Soil II | 7.6-7.7 | 289 ± 7 |
| Soil III | 7.8-7.9 | 467 ± 15 |
| Soil IV | 7.6-7.8 | 214 ± 15 |

Looney *et al.* (1987) tabulated estimates for geochemical parameters needed for environmental assessments of waste sites at DOE's Savannah River Plant in South Carolina. Looney *et al.* list K_d values for several metal and radionuclide contaminants based on values that they found in 1-5 published sources. For radium, Looney *et al.* list a "recommended" K_d of 100 ml/g, and a range from 10 to 1,000,000 ml/g. Looney *et al.* note that their recommended values are specific to the Savannah River Plant site, and they must be carefully reviewed and evaluated prior to use in assessments at other sites.

Thibault *et al.* (1990) (also see Sheppard and Thibault, 1990) present a compilation of soil K_d values prepared to support radionuclide migration assessments for a Canadian geologic repository for spent nuclear fuel in Precambrian Shield plutonic rock. Thibault *et al.* collected K_d values from other compilations, journal articles, and government laboratory reports for important elements, such as radium, that would be present in the nuclear fuel waste inventory. The radium K_d values listed in Thibault *et al.* (1990) are included in Table 5.28. Thibault *et al.* (1990) describe the statistical methods used for analysis of the compiled K_d values. The range for the K_d values used to calculate the "geometric mean" cover several orders of magnitude. Readers are cautioned against using "geometric mean" values or any other form of averaged K_d values as "default" K_d values, as such values are usually calculated from data compiled from different investigators for different soil

systems. These mean or average values do not represent any particular environmental system and geochemical conditions. As discussed in Volume I (EPA, 1999b), the variation observed in the literature for K_d values for a contaminant is due to differences in sorption mechanisms, geochemical conditions, soil materials, and methods used for the measurements.

5.7.5.5 K_d Studies of Radium on Pure Mineral, Oxide, and Crushed Rock Materials

Numerous adsorption studies have been conducted of radium on pure minerals, oxide phases, and other geologic-related materials. The K_d values listed in these studies are not necessarily relevant to the mobility and sorption of radium in soils. However, they are listed in Appendix H for completeness. The references cited in Appendix H are listed in the main reference list in Chapter 6. The potential value of the references that they cite and the sorption processes that they discuss is left to the reader. The results of the studies conducted with minerals and oxide phases demonstrate that the adsorption of radium on is dependent on pH, as expected for cations, and decreases with increasing concentrations of competing ions. The studies of radium sorption on crushed rock were conducted typically as part of national research programs to investigate the feasibility of geological disposal of high-level radioactive waste (HLW).

Table 5.28. Radium K_d values (ml/g) listed in Thibault *et al.* (1990, Tables 4 to 8).

| Soil Type | K_d Values (ml/g) | | |
|-----------|---------------------|------------------------|-----------------|
| | Geometric Mean | Number of Observations | Range |
| Sand | 500 | 3 | 57 - 21,000 |
| Silt | 36,000 | 3 | 1,262 - 530,000 |
| Clay | 9,100 | 8 | 696 - 56,000 |
| Organic | 2,400 | 1 | None Listed |

5.8 Technetium Geochemistry and K_d Values

5.8.1 Overview: Important Aqueous- and Solid-Phase Parameters Controlling Retardation

In natural environments, the most stable valence states of technetium (Tc) are +7 and +4 under oxidizing and reducing conditions, respectively. Technetium(VII) in oxic environmental systems is highly mobile (*i.e.*, K_d values are ≈ 0 ml/g). The dominant aqueous Tc(VII) species in oxic waters is the oxyanion TcO_4^- , which is highly soluble and essentially nonadsorptive. However, under reducing conditions in soil and geologic systems, Tc(IV) is expected to dominate because of biotic and abiotic reactive processes, such as surface-mediated reduction of Tc(VII) by iron (Fe)(II). In the absence of aqueous complexing agents other than OH^- , Tc(IV) is considered to be essentially immobile, because it readily precipitates as sparingly soluble hydrous oxide and forms strong surface complexes with surface sites on iron and aluminum oxides and clays.

5.8.2 General Geochemistry

Technetium [Tc, atomic number (Z) = 43] exists in valence states from +7 to -1. In natural environments, the most stable valence states of technetium are +7 and +4 under oxidizing and reducing conditions, respectively. Other valence states are encountered chiefly in complex compounds. The chemical behavior of technetium in these two oxidation states differs drastically. In the +7 valence state, dissolved technetium exists as pertechnetate anion, TcO_4^- , over the complete pH range of natural waters. Because the pertechnetate anion is highly soluble and is not strongly sorbed, it is highly mobile in most oxidizing systems. In the +4 valence state, technetium exists as the tetravalent cation and is relatively immobile in the absence of strongly complexing ligands. Tc(IV) is highly sorbed, and forms the sparingly soluble $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ solid. There are 34 reported isotopes of technetium (Tuli, 2000). Of the few technetium isotopes having long half lives, ^{99}Tc ($t_{1/2} = 2.11 \times 10^5$ yr) is a long lived fission product generated during the irradiation of uranium-containing nuclear fuels and is the primary isotope of environmental interest. Most of the other technetium isotopes have half lives of hours or less.

The behavior of technetium in environmental systems has been reviewed extensively by others. Reviews include Lieser (1993), Gu and Schulz (1991), Sparks and Long (1987), Meyer *et al.* (1985a), Beasley and Lorz (1984), Coughtrey *et al.* (1983), Onishi *et al.* (1981), Wildung *et al.* (1979), Ames and Rai (1978), and others. Huges and Rossotti (1987) review in detail the solution chemistry of technetium.

5.8.3 Aqueous Speciation

Rard *et al.* (1999) have published an extensive, detailed review of the chemical thermodynamics of technetium. Figure 5.9 is an Eh-pH diagram that shows the dominant aqueous species of technetium as a function of pH and Eh (redox potential) at 25°C with respect to the thermodynamic stability of water. Technetium is present in +7 and +4 valence states under oxidizing and reducing conditions, respectively. The predominate Tc(VII) aqueous species is the pertechnetate oxyanion TcO_4^- . The TcO_4^- ion is stable over the complete pH range of natural waters, and its not known to form any strong aqueous complexes. Although the thermodynamic stability of TcO_4^- is well established, thermodynamic data for technetium aqueous species and solids in its various valence states is extremely limited.

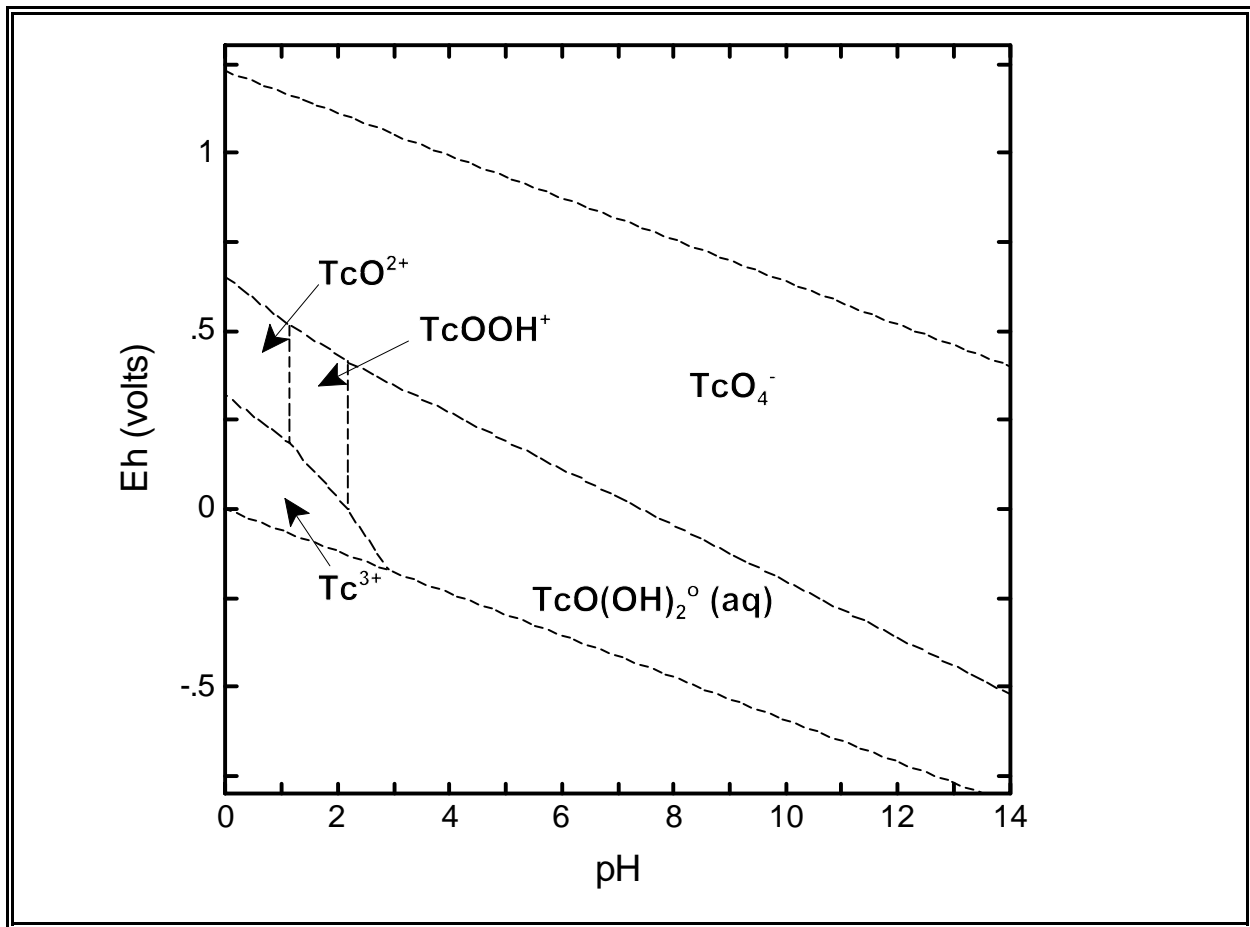
5.8.4 Dissolution/Precipitation/Coprecipitation

Technetium(VII), TcO_4^- , is highly soluble, and does not form solubility-controlling phases in soil systems. Technetium(VII) can be reduced to Tc(IV) by biotic and abiotic processes. This reduction usually results in the immobilization of technetium under reducing conditions via the formation of the sparingly soluble solid $\text{TcO}_2 \cdot n\text{H}_2\text{O}$. The solubility of Tc(IV) has been studied experimentally by Eriksen *et al.* (1992), Meyer *et al.* (1991b), Guppy *et al.* (1989), and others.

The reduction of Tc(VII) to Tc(IV) by surface-mediated processes has been the subject of extensive studies [*e.g.*, Wharton *et al.* (2000); Byegård *et al.* (1992); Eriksen and Cui (1991); Haines *et al.* (1987); Bondietti and Francis (1979)]. Such reactions have recently been the subject of considerable interest because they could have a significant affect on the mobility of technetium in waste streams, vadose

zones, aquatic sediments, and groundwater. They are the basis for certain remediation technologies, such as permeable barriers composed of zero-valent iron particles (*i.e.*, as metallic iron) or sodium-dithionite reduced soils, which are currently being tested for immobilization of groundwater contaminants.

Figure 5.9. Eh-pH stability diagram for the dominant technetium aqueous species at 25°C. [Diagram based on a total concentration of 10^{-8} mol/l dissolved technetium.]



Cui and Eriksen (1996b) studied the surface-mediated reduction of TcO_4^- by Fe(II)-containing mineral material collected from granite fractures and by hornblende and magnetite at neutral to alkaline pH conditions. Batch equilibration experiments were conducted using anoxic synthetic groundwater and perchlorate solutions. The Eh values for the various mineral/water systems studied ranged from +60 to -150 mV. Cui and Eriksen (1996b) determined that magnetite was at least 1 order of magnitude more effective than hornblende in the reduction of Tc(VII). Hornblende, on the other hand, was slightly less effective than crushed granite and the fracture filling materials with respect to Tc(VII) reduction. Desorption experiments conducted by Cui and Eriksen (1996b) with anoxic and oxic groundwater solutions over 6 and 21 days, respectively, indicated that remobilization of the reduced/sorbed technetium was a slow process. A desorption experiment conducted with the addition of a high concentration of H_2O_2 resulted in a sudden

increase of remobilized dissolved technetium. Cui and Eriksen suggested that the addition of H_2O_2 consumed the reductive capacity of the solids which permitted the reoxidation and dissolution of the sorbed hydrous Tc(IV) oxide precipitate.

Byegård *et al.* (1992) studied the sorption of technetium on magnetite in groundwater solutions under oxic and anoxic conditions. The solutions used in the laboratory experiments included a synthetic groundwater (pH 8.2) and a natural groundwater solutions (pH 8.8). For some experiments, 6 ppm dissolved Fe(II) was added to the synthetic groundwater solution. Under anoxic conditions, 95 percent of the initial concentration of dissolved technetium was sorbed within 48 hours on the magnetite reacted with the Fe(II)-augmented synthetic groundwater. However, only 16 and 15 percent of the technetium was sorbed in the magnetite systems reacted with Fe(II)-free synthetic and natural groundwater, respectively. Under oxic conditions at 48 hours, the amounts of sorbed technetium were 9, 4, and 4 percent, respectively, for magnetite reacted with Fe(II)-augmented synthetic, Fe(II)-free synthetic, and natural groundwater. Byegård *et al.* (1992) also observed a significant decrease in the concentration of dissolved technetium in experiments conducted with Fe(II)-augmented synthetic groundwater under anoxic conditions in the absence of magnetite.

Haines *et al.* (1987) used Fourier transform infrared (FTIR) spectroscopy to study the sorption of Tc(VII) at room temperature on synthetic magnetite and hematite particles that were contacted with dissolved TcO_4^- and nitrogen-purged pH 6 water. Their experiments indicated that, under these geochemical conditions, sorption of Tc(VII) on magnetite occurred by a surface-mediated reduction/precipitation mechanism. Based on pH_{ZPC} values reported by others for hematite and magnetite of 8.5 ± 0.5 and 6.5 ± 0.2 , respectively, hematite and, to a lesser degree, magnetite, were expected to have a positive surface charge and thus capable of anion adsorption in these pH 6 solutions. Haines *et al.* (1987) proposed that the sorption of Tc(VII) at pH values less than pH_{ZPC} is initiated by electrostatic attraction of the TcO_4^- anion by the magnetite surface. The sorbed Tc(VII) is then reduced to Tc(IV) by Fe(II) centers on the magnetite surface to simultaneously both precipitate sparingly soluble Tc(IV) oxide and oxidize Fe(II) to Fe(III) to form an Fe(III) oxide on the magnetite surface.

Microbial reduction of Tc(VII) has been suggested as a potential mechanism for removal of technetium from contaminated groundwater and waste streams [*e.g.*, Lovley (1993, 1995); Lloyd *et al.* (1997, 2000b)]. Dissimilatory metal reducing bacteria (Lloyd and Macaskie, 1996; Wildung *et al.*, 2000) and the sulfate reducing bacterium *Desulfovibrio desulfuricans* [Lloyd *et al.*, 1998, 1999] are capable of coupling the oxidation of organic carbon or hydrogen to the reduction of Tc(VII). Wildung *et al.* (2000) examined the influence of electron donor and the presence of dissolved bicarbonate on the rate and extent of enzymatic reduction of TcO_4^- by the subsurface metal-reducing bacterium *Shewanella putrefaciens* CN32 under anoxic conditions. Using a variety of analytical methods and geochemical modeling techniques, these studies indicated that the dominant solid-phase reduction product in both saline (0.85 percent NaCl) and bicarbonate (30mM NaHCO_3) systems was amorphous Tc(IV) hydrous oxide. However, the reduced technetium in saline systems was associated principally with the cell surface, whereas Tc(IV) in bicarbonate systems was present primarily in extracellular particulates.

5.8.5 Adsorption/Desorption

5.8.5.1 Guidance for Screening Calculations of Adsorption

The dominant aqueous Tc(VII) species under oxidizing conditions is the oxyanion TcO_4^- , which is highly soluble and essentially nonadsorptive. For soils with low contents of organic material, the reported K_d values range from 0 to approximately 0.5 ml/g, although most values are less than 0.1 ml/g (see studies reviewed below). The very low K_d values measured for Tc(VII) and the limited availability of K_d values as a function of key geochemical parameters, such as pH, preclude derivation of meaningful look-up tables for Tc(VII) K_d values. For screening calculations of off-site migration of Tc(VII), a K_d of 0 ml/g is suggested as a conservative minimum value for low organic soils under oxidizing conditions at pH values greater than 5. As an anion, the adsorption of TcO_4^- is expected to increase with decreasing pH at pH values less than 5. Values of K_d measured by Kaplan *et al.* (2000a) for a wetland sediment ranged from approximately 0 ml/g at pH 4.6 to 0.29 at pH 3.2. The maximum K_d value that they determined for an upland sediment was 0.11 ml/g at pH 3. As noted previously, however, one of the major recommendations of this report is that for site-specific calculations, partition coefficient values measured at site-specific conditions are absolutely essential.

The sorption of TcO_4^- has been found to be positively correlated to the organic carbon content of soils (Wildung *et al.*, 1974; 1984). However, studies of the effect that organic material has on the sorption of Tc(VII) in soils are limited. As an extreme example, Sheppard and Thibault (1988) reported K_d values of greater than 2 ml/g based *in situ* K_d values derived from analyses of the dried peat and pore water from the Precambrian Shield in Canada. Measurable adsorption of Tc(VII) observed in experiments conducted with organic material as well as with crushed rock and Fe(II)-containing minerals has been attributed to the reduction of Tc(VII) to Tc(IV). Technetium(IV) is essentially immobile, because it readily precipitates as sparingly soluble hydrous oxides and forms strong complexes with surface sites on iron and aluminum oxides and clays. Studies by Landa *et al.* (1977) however suggest that anaerobic conditions may not be a prerequisite to technetium sorption by soils, and that the living and nonliving organic fraction of soil may have a role in technetium sorption.

5.8.5.2 General Adsorption Studies

Winkler *et al.* (1988) studied the sorption of technetium on several sands and single mineral phases using batch-equilibration, recirculation column and flow-through column experiments. The studies were conducted under anoxic conditions using simulated calcium-bicarbonate groundwater containing 13.6 meq/l salt. No significant sorption of technetium was observed in the experiments conducted with the sands (K_d values less than 0.2 ml/g). Little or no sorption was measured in experiments conducted with pure quartz or smectite. Significant sorption, however, was observed in the pyrite experiments, and appeared to be a function of time even at low concentrations (*i.e.*, 1 wt. percent) of pyrite. In a flow-through column experiment containing a 1:99 mixture (by wt. percent) of pyrite to quartz, rapid and complete sorption of technetium was observed. The sorbed technetium was localized in the first 50 mm of the 200-mm long columns. The pH and Eh values for this flow-through experiment were, respectively, 7 and +400 mV.

Lieser and Bauscher (1987) conducted batch equilibration experiments to study the sorption and desorption of technetium under oxic and anoxic conditions on five sediments and

five corresponding groundwater samples from Gorleben, Federal Republic of Germany. The sediments consisted mainly of quartz and minor concentrations of calcite, dolomite, anhydrite, kaolinite, illite, and montmorillonite. Low sorption of technetium (*i.e.*, K_d values of 0.1-0.3 ml/g) was observed in those experiments conducted under oxic conditions. Technetium sorption decreased with increasing salinity, and was found to be reversible. Under anoxic conditions, high sorption values were measured for technetium on these water/sediment systems. Technetium sorption did not depend on salinity and was not reversible under these anoxic conditions. However, at higher salinity values, steady-state sorption of technetium was attained more quickly. When the Eh was increased, Lieser and Bauscher (1987) determined that the sorption behavior changed abruptly from high to low adsorption at Eh of 170 ± 60 mV and pH of 7.0 ± 0.5 . In all experiments, analysis of the dissolved technetium indicated the presence of only Tc(VII) and no colloidal size technetium was detected by ultrafiltration.

5.8.5.3 *K_d Studies for Technetium on Soil Materials*

Kaplan and coworkers have conducted a series of laboratory studies on the adsorption of TcO_4^- on soils and mineral phases. Kaplan *et al.* (2000a) measured K_d values for TcO_4^- as a function of pH on two sediments from the Savannah River Site at Aiken, South Carolina. The K_d values ranged from 0.29 to -0.13 ml/g. Their measurements also indicate that the K_d values increased with decreasing pH as would be expected for dissolved anionic contaminants. Kaplan *et al.* (1998b) suggested that the negative K_d values measured for technetium were due to anion exclusion effects.

Kaplan *et al.* (1998a) used the batch equilibration technique to measure the K_d values for technetium under oxic conditions on 20 sediment samples from the Hanford formation at the Hanford Site in southeastern Washington. The sediment samples were taken from 1 borehole, and included material from 3 layers of the Hanford formation. Each sediment sample was equilibrated with uncontaminated groundwater from the Hanford Site, which was spiked with ^{99}Tc prior to the K_d measurements. The groundwater solution had a low ionic strength and a pH of 8.4 [see Table 1 in Kaplan *et al.* (1998a)]. The mean K_d values of 3 replicates measured for technetium on each Hanford sediment sample are listed in Table 5.29, and ranged from -0.04 to 0.01 ml/g. The measurements indicated essentially no sorption of technetium on Hanford sediments under these conditions.

Kaplan *et al.* (1998b) studied the effects of ionic strength and high pH on the sorption of technetium under oxic conditions on sediments from the Hanford Site in Washington. Batch sorption experiments were completed using the <2-mm size fraction of sediment collected from Trench AE-3 in the 200 Area of the Hanford Site. The sediment was characterized as a silty loam with cation exchange capacity (CEC) of 6.4 meq/100 g. The carbonate content of the sediment is primarily calcite. Based on analyses reported by Kaplan *et al.* (1996) for a sediment from a nearby location, the Trench AE-3 sample was expected to contain approximately 0.2-0.5 wt. percent amorphous Fe_2O_3 (Kaplan *et al.* (1998b)). The <2-mm size fraction contained 41 percent sand, 50 percent silt, and 9 percent clay. The clay fraction of the sediment contained primarily smectite (57 percent), illite (19 percent), and vermiculite (14 percent). The groundwater selected for the sorption studies was an uncontaminated groundwater from the Hanford Site with a low ionic strength and pH of 8.4 [see Table 2 in Kaplan *et al.* (1998b)]. The effect of ionic strength on the sorption of technetium was investigated by adding 0.05, 0.10, 0.50, and 1.00 M NaClO_4 solutions to the groundwater. To study the effect of high pH on the sorption of technetium, NaOH was added

to separate samples of groundwater to adjust the pH to 8.1, 9.9, 10.2, 11.0, and 11.9. The sediment was equilibrated with these amended groundwater solutions. Based on the experimental conditions and geochemical modeling calculations, the dissolved technetium was assumed to be TcO_4^- . The mean K_d values of three replicates measured for technetium in the ionic strength and pH experiments are listed in Table 5.29. Kaplan *et al.* (1998a) noted that negative K_d values had usually been attributed to experiment error associated with measuring the concentration of a nonadsorbing solute.

However, based on the results of Kaplan and Serne (1998), Kaplan *et al.* (1998b) suggested that the negative K_d values measured for technetium were due to anion exclusion effects. The reason for the high K_d value (3.94 ml/g) measured for technetium in the 1.00 M NaClO_4 solution was not known. Kaplan *et al.* (1998b) speculated that the higher ionic strength allowed greater interaction of the technetium with the mineral surfaces by decreasing the double layer around the sediment particles. The K_d values determined for technetium (*i.e.*, 1.04 to 1.07 ml/g) at pH values greater than 8.8 in the NaOH-amended solutions were greater than expected. The reason for these greater-than-expected values was not known.

Kaplan and Serne (1998) [also see Kaplan *et al.* (1996)] used the batch technique to measure the K_d values for technetium, as TcO_4^- , on three sediment samples from the Hanford Site in southeastern Washington. The measurements were conducted with a groundwater sample (pH 8.3) taken from a well located in an uncontaminated area of the Hanford Site. The sediment samples included a loamy sand (sample TSB-1), a silty loam (sample Trench AE-3), and a very coarse sand (sample Trench-94). The K_d values at 266 days of contact time were very low for all sediments, and ranged from 0.11 to -0.18 mg/l.

Kaplan *et al.* (1996) measured the K_d values for TcO_4^- on sediment samples from the 200 Areas at the Hanford Site. The sorption measurements were conducted under oxidizing conditions using uncontaminated groundwater (pH=8.46) from Hanford Site Well S3-25. The sorption values for TcO_4^- were determined for three sediment samples, Trench 94, Trench AE-3, and TSB-1, using the batch equilibration method. As with previous sorption studies of Hanford Site sediments at oxidizing conditions, no significant sorption of TcO_4^- was observed. The average K_d values measured after 30 days of contact for Trench 94 and Trench AE-3 sediments were -0.02 ml/g and -0.05 ml/g, respectively. The effect of contact time (7-398 days) on the sorption of TcO_4^- to these sediments was also studied by Kaplan *et al.* (1996). The K_d values for all three sediments varied from slightly negative at short contact times to slightly positive at contact times greater than 300 days. The values ranged from -0.18 to 0.11 ml/g.

Table 5.29. Technetium K_d values (ml/g) measured for Hanford sediments under oxidizing conditions (Kaplan *et al.* (1998a, 1998b).

| pH | K_d (ml/g) | CEC (meg/100 g) | Solution | Soil Identification | Reference and Comments |
|------|---------------------|--------------------|-------------|-------------------------------|------------------------------|
| 8.54 | -0.01 ± 0.02 | 5.07 | Groundwater | Hanford Sediment B8500-07A | Kaplan <i>et al.</i> (1998a) |
| 8.80 | -0.02 ± 0.03 | 4.73 | Groundwater | Hanford Sediment B8500-10A | Kaplan <i>et al.</i> (1998a) |
| 8.77 | 0.01 ± 0.00 | 4.60 | Groundwater | Hanford Sediment B8500-12A | Kaplan <i>et al.</i> (1998a) |
| 8.73 | -0.01 ± 0.03 | 4.62 | Groundwater | Hanford Sediment B8500-14A | Kaplan <i>et al.</i> (1998a) |
| 8.75 | 0.00 ± 0.02 | 4.11 | Groundwater | Hanford Sediment B8500-15A | Kaplan <i>et al.</i> (1998a) |
| 8.77 | -0.01 ± 0.02 | 2.32 | Groundwater | Hanford Sediment B8500-16A | Kaplan <i>et al.</i> (1998a) |
| 8.52 | -0.04 ± 0.01 | 4.98 | Groundwater | Hanford Sediment B8500-17A | Kaplan <i>et al.</i> (1998a) |
| 8.50 | -0.02 ± 0.02 | 4.72 | Groundwater | Hanford Sediment B8500-19A | Kaplan <i>et al.</i> (1998a) |
| 8.52 | 0.00 ± 0.01 | 4.67 | Groundwater | Hanford Sediment B8500-20A | Kaplan <i>et al.</i> (1998a) |
| 8.56 | 0.00 ± 0.02 | 4.56 | Groundwater | Hanford Sediment B8500-21A | Kaplan <i>et al.</i> (1998a) |
| 8.94 | 0.00 ± 0.02 | 7.33 | Groundwater | Hanford Sediment B8500-22A | Kaplan <i>et al.</i> (1998a) |
| 8.82 | -0.01 ± 0.03 | 8.41 | Groundwater | Hanford Sediment B8500-23A | Kaplan <i>et al.</i> (1998a) |
| 8.81 | 0.00 ± 0.02 | 9.03 | Groundwater | Hanford Sediment B8500-24A | Kaplan <i>et al.</i> (1998a) |
| 8.89 | 0.01 ± 0.01 | 6.63 | Groundwater | Hanford Sediment B8500-25A | Kaplan <i>et al.</i> (1998a) |
| 8.88 | 0.00 ± 0.01 | 8.36 | Groundwater | Hanford Sediment B8500-27A | Kaplan <i>et al.</i> (1998a) |

Continuation of Table 5.29

| pH | K_d (ml/g) | CEC (meg/100 g) | Solution | Soil Identification | Reference and Comments |
|------|---------------------|--------------------|--|---------------------------------|------------------------------|
| 8.84 | -0.01 ± 0.03 | 7.77 | Groundwater | Hanford Sediment B8500-29A | Kaplan <i>et al.</i> (1998a) |
| 8.56 | -0.03 ± 0.04 | 10.98 | Groundwater | Hanford Sediment B8500-31A | Kaplan <i>et al.</i> (1998a) |
| 8.93 | -0.01 ± 0.01 | 8.39 | Groundwater | Hanford Sediment B8500-32A | Kaplan <i>et al.</i> (1998a) |
| 8.92 | -0.02 ± 0.01 | 6.21 | Groundwater | Hanford Sediment B8500-34A | Kaplan <i>et al.</i> (1998a) |
| 8.89 | -0.02 ± 0.01 | 6.65 | Groundwater | Hanford Sediment B8500-35A | Kaplan <i>et al.</i> (1998a) |
| 7.74 | -0.16 ± 0.04 | 6.4 | 0.05 M NaClO ₄ + Groundwater | Hanford Trench AE-3 Sediment | Kaplan <i>et al.</i> (1998b) |
| 7.76 | -0.13 ± 0.00 | 6.4 | 0.1 M NaClO ₄ + Groundwater | Hanford Trench AE-3 Sediment | Kaplan <i>et al.</i> (1998b) |
| 7.73 | -0.28 ± 0.01 | 6.4 | 0.5 M NaClO ₄ + Groundwater | Hanford Trench AE-3 Sediment | Kaplan <i>et al.</i> (1998b) |
| 7.70 | 3.95 ± 0.99 | 6.4 | 1.0 M NaClO ₄ + Groundwater | Hanford Trench AE-3 Sediment | Kaplan <i>et al.</i> (1998b) |
| 8.1 | -0.02 ± 0.01 | 6.4 | Groundwater + NaOH | Hanford Trench AE-3 Sediment | Kaplan <i>et al.</i> (1998b) |
| 9.9 | 1.04 ± 0.06 | 6.4 | Groundwater + NaOH | Hanford Trench AE-3 Sediment | Kaplan <i>et al.</i> (1998b) |
| 10.2 | 1.05 ± 0.02 | 6.4 | Groundwater + NaOH | Hanford Trench AE-3 Sediment | Kaplan <i>et al.</i> (1998b) |
| 11.0 | 1.07 ± 0.05 | 6.4 | Groundwater + NaOH | Hanford Trench AE-3 Sediment | Kaplan <i>et al.</i> (1998b) |
| 11.9 | 1.07 ± 0.03 | 6.4 | Groundwater + NaOH | Hanford Trench AE-3 Sediment | Kaplan <i>et al.</i> (1998b) |

Serne *et al.* (1993) measured the K_d values for TcO₄ on three samples of sediment from the Hanford Formation at the Hanford Site. The sediment samples included two loamy sands (samples TBS-1 and Trench-8) and one sand (sample CGS-1). The measurements were conducted using an uncontaminated groundwater (pH 8.14) sample from the Hanford site. Characterization of the sediment samples indicated that they contained very little amorphous or poorly crystalline hydrous Al, Mn, and Fe oxides (determined by hydroxylamine-hydrochloride extraction) and very low organic carbon contents. The sorption measurements were conducted using the batch-equilibration

method under oxidizing conditions. After 35 days of contact, the pH values for the CGS-1, TBS-1, and Trench-8 sediment suspensions were 7.9-8.4., 8.0-8.4, and 8.22, respectively. Under the conditions studied, no significant sorption of Tc was measured. The K_d values for TcO_4^- were 0.1 ml/g for CGS-1 sediment at 35 days, 0.1 ml/g for TBS-1 sediment at 35 days, and 0.2 ml/g for Trench-8 sediment at 44 days.

Sheppard and Thibault (1988) studied the vertical migration of technetium in two types of mires typical of the Precambrian Shield in Canada. Sheppard and Thibault (1988) derived *in situ* K_d values from analyses of the dried peat and pore water. The K_d values determined for technetium were greater than 2 ml/g. Technetium was quickly immobilized in the reducing environment of the mire, which was the cause for the observed *in situ* technetium K_d values.

Table 5.30. Average technetium K_d values (ml/g) (based on three replicates) for technetium on Hanford sediments after 21.5 days from Gee and Campbell (1980).

| Solution Sample Number | Silty Sediment | | Surface Sand | |
|------------------------|----------------|--------------|--------------|--------------|
| | pH | K_d (ml/g) | pH | K_d (ml/g) |
| 1 | 8.26 | -2.77 | 8.14 | 0.07 |
| 2 | 8.07 | -1.13 | 8.00 | -1.62 |
| 3 | 8.52 | -0.04 | 8.25 | -0.31 |
| 4 | 7.78 | 0.57 | 7.63 | 0.06 |
| 5 | 7.90 | 0.54 | 7.57 | 0.52 |
| 6 | 7.75 | -0.51 | 7.44 | 0.38 |

Gee and Campbell (1980) conducted batch equilibration and unsaturated flow column studies of the sorption behavior of technetium using two Hanford Site sediments and a series of synthetic groundwater solutions. The sediments include a sample from the Ringold Formation (deep, old sediment) and a surface soil sample at the Hanford Site. Except for the degree of crystallinity of the clay minerals, the two sediments were similar with respect to their clay mineralogy. The compositions of the synthetic groundwater solutions were developed to simulate the composition of a solution as it changes in response to its initial contact and saturation of arid sediment and its progressive percolation through the arid sediment. Gee and Campbell (1980) found low sorption of technetium, and no relationship in the technetium K_d values with respect to soil type, solution composition, pH, and contact time. The technetium K_d values for the two sediment samples ranged from -2.34 to 1.27 ml/g at 8.5 days, and -2.77 to 0.57 ml/g at 21.5 days. The average batch K_d values determined for the technetium-spiked sediments equilibrated with the six synthetic groundwater solutions at 21.5 days are listed in Table 5.30. Although there was general agreement

between the sorption measured by the batch and unsaturated column studies, Gee and Campbell noted that the K_d values measured for technetium, using the unsaturated column studies were less variable and better defined.

Wildung *et al.* (1974) used the batch equilibration method to measure the K_d values for TcO_4^- on 22 types of soils collected in Oregon, Washington, and Minnesota. The K_d values for TcO_4^- ranged from 0.007 to 2.8 ml/g. Wildung *et al.* (1974) determined that the sorption of TcO_4^- was positively correlated to soil organic carbon, and negatively correlated to pH.

Routson *et al.* (1975, 1977) used batch equilibration experiments to measure K_d values for ^{99}Tc on soil as a function of the concentrations of dissolved calcium bicarbonate. The soil sample was a moderate-exchange capacity soil from South Carolina. The soil contained <0.2 mg/g $CaCO_3$, 3.6 percent silt, 37.2 percent clay, and had a cation exchange capacity (CEC) of 2.5 meq/100 g and saturated paste pH equal to 5.1. The measurements indicated that ^{99}Tc did not sorb to the South Carolina soil sample. The measured K_d values for ^{99}Tc were +0.019, -0.052, -0.033, and +0.010 ml/g for 0.002, 0.008, 0.020, and 0.200 M $NaHCO_3$ solutions.

5.8.5.4 Published Compilations Containing K_d Values for Technetium

Because the references in this section are often cited or used for comparison in other publications, the following summaries are provided for completeness. It is recommended that the reader review the original reference and the references cited therein to understand the procedures and sources of the K_d values used for each compilation. The compilations do not distinguish between oxidation states for those contaminants that are redox sensitive or consider other important factors that contribute to variability in sorption, such as pH. Moreover, in cases where very large K_d values are listed, there is a risk that the original K_d measurement may have included precipitated components.

Baes and Sharp (1983) present a simple model developed for order-of-magnitude estimates for leaching constants for solutes in agricultural soils. As part of this development, they reviewed and determined generic default values for input parameters, such as K_d . A literature review was completed to evaluate appropriate distributions for K_d values for various solutes, including technetium. Because Baes and Sharp (1983) are cited frequently as a source of K_d values in other published K_d reviews (*e.g.*, Looney *et al.*, 1987; Sheppard and Thibault, 1990), the technetium K_d values listed by Baes and Sharp are reported here for completeness. Based on the distribution that Baes and Sharp determined for the K_d values for cesium and strontium, they assumed a lognormal distribution for the K_d values for all other elements in their compilation. Baes and Sharp listed an estimated default K_d of 0.033 ml/g for technetium based on 24 K_d values that range from 0.0029 to 0.28 ml/g for agricultural soils and clays over the pH range 4.5 to 9.0. The 24 K_d values were taken from Gast *et al.* (1979) which was not available for our review. Their compiled K_d values represent a diversity of soils, pure clays (other K_d values for pure minerals were excluded), extracting solutions, measurement techniques, and experimental error.

Looney *et al.* (1987) tabulated estimates for geochemical parameters needed for environmental assessments of waste sites at DOE's Savannah River Plant in South Carolina. Looney *et al.* list K_d values for several metal and radionuclide contaminants based on values that they found in 1-5 published sources. For technetium, Looney *et al.* list a "recommended" K_d of 0.001 ml/g, and a range from 0.001 to 100 ml/g. Looney *et al.* note that their recommended values are specific to the

Savannah River Plant site, and they must be carefully reviewed and evaluated prior to use in assessments at other sites.

Thibault *et al.* (1990) (also see Sheppard and Thibault, 1990) present a compilation of soil K_d values prepared to support radionuclide migration assessments for a Canadian geologic repository for spent nuclear fuel in Precambrian Shield plutonic rock. Thibault *et al.* collected K_d values from other compilations, journal articles, and government laboratory reports for important elements, such as technetium, that would be present in the nuclear fuel waste inventory. The technetium K_d values listed in Thibault *et al.* (1990) are included in Table 5.31. Thibault *et al.* (1990) describe the statistical methods used for analysis of the compiled K_d values. The range for the K_d values used to calculate the “geometric mean” cover several orders of magnitude. Readers are cautioned against using “geometric mean” values or any other form of averaged K_d values as “default” K_d values, as such values are usually calculated from data compiled from different investigators for different soil systems. These mean or average values do not represent any particular environmental system and geochemical conditions. As discussed in Volume I (EPA, 1999b), the variation observed in the literature for K_d values for a contaminant is due to differences in sorption mechanisms, geochemical conditions, soil materials, and methods used for the measurements.

Table 5.31. Technetium K_d values (ml/g) listed in Thibault *et al.* (1990, Tables 4 to 8).

| Soil Type | K_d Values (ml/g) | | |
|-----------|---------------------|------------------------|-------------|
| | Geometric Mean | Number of Observations | Range |
| Sand | 0.1 | 19 | 0.01 - 16 |
| Silt | 0.1 | 10 | 0.01 - 0.4 |
| Clay | 1 | 4 | 1.16 - 1.32 |
| Organic | 1 | 24 | 0.02 - 340 |

McKinley and Scholtis (1993) compare radionuclide K_d sorption databases used by different international organizations for performance assessments of repositories for radioactive wastes. The technetium K_d values listed in McKinley and Scholtis (1993, Tables 1, 2, and 4) are listed in Table 5.32. The reader should refer to sources cited in McKinley and Scholtis (1993) for details regarding their source, derivation, and measurement. Radionuclide K_d values listed for cementitious environments in McKinley and Scholtis (1993, Table 3) are not included in Table 5.32. The organizations listed in the tables include: AECL, GSF, IAEA, KBS, NAGRA, NIREX, NRC, NRPB, PAGIS (CEC), PSE, RIVM, SKI, TVO, and UK DoE (acronyms defined in Section A.1.0 in Appendix A).

Table 5.32. Technetium K_d values (ml/g) listed by McKinley and Scholtis (1993, Tables 1, 2, and 4) from sorption databases used by different international organizations for performance assessments of repositories for radioactive wastes.

| Organization | Argillaceous (Clay) | | Crystalline Rock | | Soil/Surface Sediment | |
|--------------|----------------------|--------------|----------------------------|--------------|-----------------------|--------------|
| | Sorbing Material | K_d (ml/g) | Sorbing Material | K_d (ml/g) | Sorbing Material | K_d (ml/g) |
| AECL | Bentonite-Sand | 0.09 | Granite | 26 | Soil/Sediment | 0.03 |
| GSF | Sediment | 7 | | | | |
| IAEA | Pelagic Clay | 100 | | | | |
| KBS-3 | Bentonite | 2 | Granite | 50 | | |
| NAGRA | Bentonite | 250 | Granite | 250 | Soil/Sediment | 5 |
| | Clay | 250 | | | Soil/Sediment | 1 |
| NIREX | Clay Mudstone | 0 | | | | |
| NRC | Clay, Soil Shale | 0.4 | Granite | 0.4 | | |
| | | | Basalt | 0.4 | | |
| | | | Tuff | 0.4 | | |
| NRPB | Clay | 0 | | | Soil/Sediment | 0 |
| PAGIS | Bentonite | 20 | | | Soil/Sediment | 1.7 |
| | Subseabed | 0 | | | | |
| PAGIS SAFIR | Clay | 19 | | | | |
| PSE | Sediment | 1 | | | | |
| RIVM | Sandy Clay | 1 | | | | |
| SKI | Bentonite | 50 | Granite | 5 | | |
| TVO | Lake Sediment | 100 | Crystalline Rock, Reducing | 50 | Soil/Sediment | 1,000 |
| | | | Crystalline Rock | 0 | Soil/Sediment | 10 |
| UK DoE | Clay | 40 | | | Soil/Sediment | 0.03 |
| | Coastal Marine Water | 100 | | | | |

5.8.5.5 *K_d Studies of Technetium on Pure Mineral, Oxide, and Crushed Rock Materials*

Numerous adsorption studies have been conducted of technetium on pure minerals, oxide phases, and other geologic-related materials. The K_d values listed in these studies are not necessarily relevant to the mobility and sorption of technetium in soils. However, they are listed in Appendix I for completeness. The references cited in Appendix I are listed in the main reference list in Chapter 6. The potential value of the references that they cite and the sorption processes that they discuss is left to the reader. Like those for iodine, many of the studies that used on pure mineral and oxide materials were conducted because of extensive research interest in developing getters (adsorbents) that could be added to waste streams and tailored barriers for removal and/or immobilization of dissolved iodine. The studies of technetium sorption on crushed rock were conducted typically as part of national research programs to investigate the feasibility of geological disposal of high-level radioactive waste (HLW).

5.9 Conclusions

One objective of this volume report is to provide a “thumb-nail sketch” of the geochemistry of americium, arsenic, curium, iodine, neptunium, radium, and technetium. These contaminants represent six nonexclusive contaminant categories: radionuclides, cations, anions, redox-sensitive, non-retarded (non-attenuated) contaminants, and retarded (attenuated) contaminants (Table 5.33). By categorizing the contaminants in this manner, general geochemical behaviors of one contaminant may be extrapolated by analogy to other contaminants in the same category. For example, anions, such as NO_3^- and Cl^- , commonly adsorb to geological materials to a limited extent. This is also the case observed for the sorption behavior of anionic iodide.

Important solution speciation, coprecipitation/dissolution, and adsorption reactions were discussed for each contaminant. Where relevant, the distributions of aqueous species for certain contaminants were calculated using the chemical equilibria code MINTQA2 (Version 3.11, Allison *et al.*, 1991) for the water composition described in Table 5.1. The purpose of these calculations was to identify the compositions of the dominant aqueous species that might exist in an oxidizing groundwater for the contaminants reviewed in Volume III. A summary of the results of these calculations is presented in Table 5.34. The aqueous speciation of iodide, iodate, radium, and pertechnetate does not change in the pH range of 3 and 10 under oxidizing conditions; they exist as I^- , IO_3^- , Ra^{2+} , and TcO_4^- , respectively. Americium(III), As(V), and Np(V) have two or three different dominant species across this pH range. The aqueous speciation of arsenic, iodine, neptunium, and technetium is especially complicated, because these contaminants may exist in multiple oxidation states over the range of pH-Eh conditions of natural waters.

One general conclusion that can be made from the calculations in Table 5.34 is that, as the pH increases, the aqueous complexes tend to become increasingly more negatively charged. For example, americium and neptunium are cationic at pH 3. At pH values greater than 7, they exist predominantly as either neutral or anionic species. Negatively charged complexes tend to adsorb less to soils than their respective cationic species. This rule-of-thumb stems from the fact that most minerals in soils have a net negative charge in the range of pH values of most natural waters. Conversely, the solubility of several of these contaminants decreases dramatically as pH increases. Therefore, the net contaminant concentration in solution does not necessarily increase as the dominant aqueous species becomes more negatively charged.

Table 5.33. Selected chemical and transport properties of the contaminants.

| Element | Radio-nuclide ¹ | Primary Species at pH 7 and Oxidizing Conditions | | | Redox Sensitive ² | Transport Through Soils at pH 7 | |
|---------|----------------------------|--|---------|---------|------------------------------|---------------------------------|------------------------------------|
| | | Cationic | Anionic | Neutral | | Not Retarded ³ | Retarded ³ (Attenuated) |
| Am | x | x | | | | | x |
| As | | | x | | x | | x (limited) |
| Cm | x | x | | | | | x |
| I | x | | x | | x | | x (limited) |
| Np | x | x | | | x | | x (limited) |
| Ra | x | x | | | | | x |
| Tc | x | | x | | x | x | |

¹ Contaminants that are primarily a health concern as a result of their radioactivity are identified in this column.

² The redox status column identifies contaminants (As, I, and Tc) that have variable oxidation states within the pH and Eh limits commonly found in the environment.

³ Retarded or attenuated (nonconservative) transport means that the contaminant moves slower than water through geologic material. Nonretarded or nonattenuated (conservative) transport means that the contaminant moves at the same rate as water.

Another objective of this report is to identify the important chemical, physical, and mineralogical characteristics controlling sorption of these contaminants. There are several aqueous- and solid-phase characteristics that can influence contaminant sorption. These characteristics commonly have an interactive effect on contaminant sorption, such that the effect of one parameter on sorption varies as the magnitude of other parameters changes. A list of some of the more important chemical, physical, and mineralogical characteristics affecting contaminant sorption are listed in Table 5.35.

Table 5.34. Distribution of dominant aqueous species for each contaminant at three pH values for an oxidizing water described in Table 5.1¹.

| Element | pH 3 | | pH 7 | | pH 10 | |
|----------------------|---|----------------|---|------------------------|--|--------------------|
| | Species | % | Species | % | Species | % |
| Am(III) | Am ³⁺ AmF ²⁺ AmSO ₄ ⁻ | 65 20 14 | AmCO ₃ ⁺ Am(OH) ²⁺ Am(CO ₃) ₂ ⁻ Am ³⁺ AmF ²⁺ | 88 4 3 2 2 | Am(OH) ₃ ^o (aq) Am(CO ₃) ₂ ⁻ AmCO ₃ ⁺ | 56 42 2 |
| As(V) | H ₂ AsO ₄ ⁻ H ₃ AsO ₄ ^o (aq) | 86 14 | HAsO ₄ ²⁻ H ₂ AsO ₄ ⁻ | 66 34 | HAsO ₄ ²⁻ AsO ₄ ³⁻ | 97 3 |
| Cm(III) ² | Cm ³⁺ | 100 | CmCO ₃ ⁺ Cm ³⁺ Cm(OH) ²⁺ | 43 42 15 | Cm(OH) ₂ ⁺ CmCO ₃ ⁺ Cm(OH) ²⁺ Cm(CO ₃) ₂ ⁻ | 86 8 4 2 |
| I(-I) | I ⁻ | 100 | I ⁻ | 100 | I ⁻ | 100 |
| I(V) | IO ₃ ⁻ | 100 | IO ₃ ⁻ | 100 | IO ₃ ⁻ | 100 |
| Np(V) | NpO ₂ ⁺ | 100 | NpO ₂ ⁺ NpO ₂ (CO ₃) ⁻ NpO ₂ (OH) ^o (aq) | 97 1 1 | NpO ₂ (OH) ^o (aq) NpO ₂ (CO ₃) ⁻ NpO ₂ ⁺ NpO ₂ (CO ₃) ₂ ³⁻ | 51 41 4 4 |
| Ra | Ra ²⁺ | 100 | Ra ²⁺ | 100 | Ra ²⁺ | 100 |
| Tc(VII) | TcO ₄ ⁻ | 100 | TcO ₄ ⁻ | 100 | TcO ₄ ⁻ | 100 |

¹ Only species comprising 1 percent or more of the total contaminant distribution are presented. Hence, the total of the percent distributions presented in table may not always equal 100 percent.
² Thermodynamic constants for aqueous species and solids containing curium are extremely limited. By analogy, the aqueous speciation of curium is expected to be very similar to Am(III). Aqueous speciation calculated for Cm(III) is based on a limited set of constants.

The effect of pH on both adsorption and (co)precipitation of contaminants is pervasive. The pH influences a number of aqueous and solid phase properties that directly affect the sorption to some degree of each contaminant reviewed in Volumes II and III. These effects are summarized in Volume I (EPA, 1999b), and discussed in greater detail for each contaminant in the individual geochemistry review sections in Volumes II and III. As discussed above, pH has a significant effect on the aqueous speciation of most contaminants (Table 5.34). The adsorption behavior of each contaminant depends on the ionic charge and composition of its important aqueous species present in the environmental system being studied. Additionally, pH affects the number of adsorption sites on variable-charged minerals (aluminum- and iron-oxide minerals), partitioning of contaminants to organic matter, CEC, formation of aqueous complexes, oxidation state of contaminants and complexing/precipitating ligands, and H⁺/OH⁻-competition for anionic or cationic adsorption sites.

Table 5.35 lists some of the more important aqueous- and solid phase parameters affecting contaminant sorption.

Table 5.35. Some of the more important aqueous- and solid-phase parameters affecting contaminant sorption.

| Element | Important Aqueous- and Solid-Phase Parameters Influencing Contaminant Sorption ¹ |
|---------|--|
| Am | Clay Minerals, Iron-/Aluminum-Oxide Minerals, pH |
| As | Clay Minerals, Dissolved Phosphate, Iron-/Aluminum-Oxide Minerals, pH, Redox |
| Cm | Clay Minerals, Iron-/Aluminum-Oxide Minerals, pH |
| I | Dissolved Halides, Organic Matter, Redox, Volatilization, pH |
| Np | Clay Minerals, Iron-/Aluminum-Oxide Minerals, pH |
| Ra | BaSO ₄ Coprecipitation, Dissolved Alkaline Earth Elements, Cation Exchange Capacity, Clay Minerals, Ionic Strength, Iron-/Aluminum-Oxide Minerals, Organic Matter, pH |
| Tc | Organic Matter, Redox |

¹ Parameters listed in alphabetical order.

Unlike most ancillary parameters, the redox status of a system also dramatically influences the sorption of several contaminants included in this study. If the bulk redox potential of a soil/water system is above the potential of the specific element redox reaction, the oxidized form of the redox sensitive element will exist. Below this critical value, the reduced form of the element will exist. Such a change in redox state can alter K_d values by several orders of magnitude, and can have direct and indirect effects on contaminant coprecipitation. The direct effect occurs with contaminants like technetium where the oxidized species form more soluble solid phases than the reduced species. The indirect effects occur when the contaminants adsorb to redox sensitive solid phases or precipitate with redox sensitive ligands. An example of the former involves the reductive dissolution of ferric oxide minerals, which can adsorb (complex) metals strongly. As the ferric oxide minerals dissolve, the adsorption potential of the soil is decreased. Another indirect effect of redox on contaminant sorption involves sulfur-ligand chemistry. Under reducing conditions, S(VI) (SO_4^{2-} , sulfate) will convert into S(II) (S^{2-} , sulfide) and then the S(II) may form sparingly soluble sulfide minerals. Thus, these two redox sensitive reactions may have off-setting net effects on total contaminant sorption (sulfide precipitates may sequester some of the contaminants previously bound to ferric oxides).

The greatest limitation of using a K_d value to calculate a retardation term for contaminant transport modeling is that it is only applicable to a single set of environmental conditions. The K_d values reported in the literature for any given contaminant may vary by as much as *six orders of magnitude*. One of the major recommendations of this three-volume report is that for site-specific calculations,

K_d values measured at site-specific conditions are absolutely essential. To select appropriate K_d value(s) for contaminant transport modeling, it is incumbent upon technical staff to understand (1) the strengths, weaknesses, and underlying assumptions of the different K_d methods (see EPA, 1999b); and (2) the important geochemical processes and knowledge of the important ancillary parameters affecting the sorption chemistry of each contaminant of interest. This volume, which is an extension of Volume II (EPA, 1999c), provides “thumb-nail sketches” of the important aqueous speciation, (co)precipitation/dissolution, and adsorption processes affecting the sorption of americium, arsenic, curium, iodine, neptunium, radium, and technetium under oxidizing conditions.

6.0 References

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APPENDIX A

Acronyms, Abbreviations, Symbols, and Notation

Appendix A

Acronyms, Abbreviations, Symbols, and Notation

A.1 Acronyms and Abbreviations

| | |
|--------------|---|
| AA | Atomic absorption |
| AEC | Anion exchange capacity |
| AECL | Atomic Energy of Canada Limited |
| ASCII | American Standard Code for Information Interchange |
| ASTM | American Society for Testing and Materials |
| CCM | Constant capacitance (adsorption) model |
| CDTA | Trans-1,2-diaminocyclohexane tetra-acetic acid |
| CEAM | Center for Exposure Assessment Modeling (at EPA's Environmental Research Laboratory in Athens, Georgia) |
| CEC | Commission of European Communities |
| CEC | Cation exchange capacity |
| DDLDM | Diffuse double layer (adsorption) model |
| DIRM | Dissimilatory iron-reducing bacteria |
| DLM | Diffuse (double) layer (adsorption) model |
| DOE | U.S. Department of Energy |
| DTPA | Diethylenetriaminepentacetic acid |
| EDTA | Ethylenediaminetriacetic acid |
| EDS | Energy dispersive spectroscopy |
| EDX | Energy dispersive x-ray analysis |
| EPA | U.S. Environmental Protection Agency |
| EXAFS | X-ray absorption fine structure spectroscopy |
| GSF | Gesellschaft für Strahlen- und Umweltforschung m.b.H., Germany |
| GTLM | Generalized two-layer surface complexation model |
| HEDTA | N-(2-hydroxyethyl) ethylenedinitrilotriacetic acid |
| HFO | Hydrous ferric oxide |
| HLW | High-level radioactive waste |
| IAEA | International Atomic Energy Agency, Vienna, Austria |
| ICP | Inductively coupled plasma |
| ICP/MS | Inductively coupled plasma/mass spectroscopy |
| IEP (or iep) | Isoelectric point |
| IR | Infrared |
| KBS | Swedish Nuclear Safety Board |
| LANL | Los Alamos National Laboratory |
| LLNL | Lawrence Livermore National Laboratory |
| LLW | Low-level radioactive waste |
| MCL | Maximum Contaminant Level |
| MEPAS | Multimedia Environmental Pollutant Assessment System |
| MS-DOS® | Microsoft® disk operating system (Microsoft and MS-DOS are registered trademarks of Microsoft Corporation.) |

| | |
|-------------|--|
| NAGRA | Nationale Genossenschaft für die Lagerung radioaktiver AbfälleSwiss (National Cooperation for Storage of Radioactive Waste), Switzerland |
| NEA | OECD Nuclear Energy Agency, France |
| NBS | U.S. National Bureau of Standards |
| NIREX | United Kingdom Nirex Ltd. |
| NIST | U.S. National Institute of Standards and Technology |
| NPL | Superfund National Priorities List |
| NRC | U.S. Nuclear Regulatory Commission |
| NRPB | National Radiological Protection Board, United Kingdom |
| NWWA | National Water Well Association |
| OECD | Organisation for Economic Co-operation and Development, France |
| PAGIS | Performance Assessment of Geological Isolation Systems, Commission of the European Communities (CEC), Belgium |
| PAGIS SAFIR | PAGIS Safety Assessment and Feasibility Interim Report |
| PC | Personal computers (operating under the MS-DOS® and Microsoft® Windows operating systems, Microsoft® Windows is a trademark of Microsoft Corporation.) |
| PNL | Pacific Northwest Laboratory. In 1995, DOE formally changed the name of the Pacific Northwest Laboratory to the Pacific Northwest National Laboratory. |
| PNNL | Pacific Northwest National Laboratory |
| PSE | Projekt Sicherheitsstudien Entsorgung, Germany |
| REE | Rare earth element |
| RIVM | Rijksinstituut voor Volksgezondheid en Milieuhygiene (National Institute of Public Health and Environment Protection), Netherlands |
| SCM | Surface complexation model |
| SDMP | NRC's Site Decommissioning Management Plan |
| SEM | Scanning electron microscopy |
| SKI | Statens Kärnkraftinspektion (Swedish Nuclear Power Inspectorate) |
| TDS | Total dissolved solids |
| TLM | Triple-layer adsorption model |
| TOC | Total organic carbon |
| TVO | Teollisuuden Voima Oy (Industrial Power Company), Finland |
| UK | United Kingdom (UK) |
| UK DoE | United Kingdom Department of the Environment |
| UNSCEAR | United Nations Scientific Committee on the Effects of Atomic Radiation |
| USDA | U.S. Department of Agriculture |
| WHO | World Health Organization |
| XANES | X-ray absorption near-edge structure spectroscopy |

A.2 List of Symbols for the Elements and Corresponding Names

| Symbol | Element | Symbol | Element | Symbol | Element |
|--------|-------------|--------|--------------|--------|--------------|
| Ac | Actinium | Ge | Germanium | Pr | Praseodymium |
| Ag | Silver | H | Hydrogen | Pt | Platinum |
| Al | Aluminum | He | Helium | Pu | Plutonium |
| Am | Americium | Hf | Hafnium | Ra | Radium |
| Ar | Argon | Hg | Mercury | Rb | Rubidium |
| As | Arsenic | Ho | Holmium | Re | Rhenium |
| At | Astatine | I | Iodine | Rh | Rhodium |
| Au | Gold | In | Indium | Rn | Radon |
| B | Boron | Ir | Iridium | Ru | Ruthenium |
| Ba | Barium | K | Potassium | S | Sulfur |
| Be | Beryllium | Kr | Krypton | Sb | Antimony |
| Bi | Bismuth | La | Lanthanum | Sc | Scandium |
| Bk | Berkelium | Li | Lithium | Se | Selenium |
| Br | Bromine | Lu | Lutetium | Si | Silicon |
| C | Carbon | Lr | Lawrencium | Sm | Samarium |
| Ca | Calcium | Md | Mendelevium | Sn | Tin |
| Cd | Cadmium | Mg | Magnesium | Sr | Strontium |
| Ce | Cerium | Mn | Manganese | Ta | Tantalum |
| Cf | Californium | Mo | Molybdenum | Tb | Terbium |
| Cl | Chlorine | N | Nitrogen | Tc | Technetium |
| Cm | Curium | Na | Sodium | Te | Tellurium |
| Co | Cobalt | Nb | Niobium | Th | Thorium |
| Cr | Chromium | Nd | Neodymium | Ti | Titanium |
| Cs | Cesium | Ne | Neon | Tl | Thallium |
| Cu | Copper | Ni | Nickel | Tm | Thulium |
| Dy | Dysprosium | No | Nobelium | U | Uranium |
| Er | Erbium | Np | Neptunium | V | Vanadium |
| Es | Einsteinium | O | Oxygen | W | Tungsten |
| Eu | Europium | Os | Osmium | Xe | Xenon |
| F | Fluorine | P | Phosphorus | Y | Yttrium |
| Fe | Iron | Pa | Protactinium | Yb | Ytterbium |
| Fm | Fermium | Pb | Lead | Zn | Zinc |
| Fr | Francium | Pd | Palladium | Zr | Zirconium |
| Ga | Gallium | Pm | Promethium | | |
| Gd | Gadolinium | Po | Polonium | | |

A.3 List of Symbols and Notation

| | |
|-------------------|--|
| ρ_b | Porous media bulk density (mass/length ³) |
| Å | Ångström, 10 ⁻¹⁰ meters |
| ads | Adsorption or adsorbed |
| AEC | Anion exchange capacity |
| A_i | Concentration of adsorbate (or species) <i>i</i> on the solid phase at equilibrium |
| am | Amorphous |
| aq | Aqueous |
| CEC | Cation exchange capacity |
| Ci | Curie |
| d | Day |
| dpm | Disintegrations per minute |
| e ⁻ | Free electron |
| Eh | Redox potential of an aqueous system relative to the standard hydrogen electrode |
| F | Faraday constant, 23,060.9 cal/V·mol |
| g | Gram |
| ³ H | Tritium |
| h | Hour |
| I | Ionic strength |
| IAP | Ion activity product |
| IEP | Isoelectric point |
| K_d | Concentration-based partition (or distribution) coefficient |
| $K_{r,298}$ | Equilibrium constant at 298 K |
| $K_{r,T}$ | Equilibrium constant at temperature T |
| l | Liter |
| M | Molar |
| m | Meter |
| mCi | Millicurie, 10 ⁻³ Curies |
| meq | Milliequivalent |
| mi | Mile |
| ml | Milliliter |
| mol | Mole |
| mV | Millivolt |
| N | Constant in the Freundlich isotherm model |
| n | Total porosity |
| n_e | Effective porosity |
| pCi | Picocurie, 10 ⁻¹² Curies |
| pE | Negative common logarithm of the free-electron activity |
| pH | Negative logarithm of the hydrogen ion activity |
| pH _{zpc} | pH for zero point of charge |
| ppm | Parts per million |
| R | Ideal gas constant, 1.9872 cal/mol |
| R_f | Retardation factor |
| s | Solid phase species |
| sec | Second |

| | |
|-----------|--|
| SI | Saturation index, as defined by $\log (IAP/K_{r,T})$ |
| T | Absolute temperature, usually in Kelvin unless otherwise specified |
| t | Time |
| $t_{1/2}$ | Half life |
| TDS | Total dissolved solids |
| TU | Tritium unit which is equivalent to 1 atom of ^3H (tritium) per 10^{18} atoms of ^1H (protium) |
| v_c | Velocity of contaminant through a control volume |
| v_p | Velocity of the water through a control volume |
| y | Year |
| Z | Valence state |
| z | Charge of ion |
| { } | Activity |
| [] | Concentration |

APPENDIX B

Definitions

Appendix B

Definitions

Adsorption - partitioning of a dissolved species onto a solid surface.

Adsorption Edge - the pH range where solute adsorption sharply changes from ~10 percent to ~90 percent.

Actinon - name occasionally used, especially in older documents, to refer to ^{219}Rn which forms from the decay of actinium.

Activity - the effective concentration on an ion that determines its behavior to other ions with which it might react. An activity of ion is equal to its concentration only in infinitely dilute solutions. The activity of an ion is related to its analytical concentration by an activity coefficient, γ .

Alkali Metals - elements in the 1A Group in the periodic chart. These elements include lithium, sodium, potassium, rubidium, cesium, and francium.

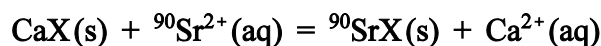
Alpha Particle - particle emitted from nucleus of atom during 1 type of radioactive decay. Particle is positively charged and has 2 protons and 2 neutrons. Particle is physically identical to the nucleus of the ^4He atom (Bates and Jackson 1980).

Alpha Recoil - displacement of an atom from its structural position, as in a mineral, resulting from radioactive decay of the release an alpha particle from its parent isotope (*e.g.*, alpha decay of ^{222}Rn from ^{226}Ra).

Amphoteric Behavior - the ability of the aqueous complex or solid material to have a negative, neutral, or positive charge.

Basis Species - see component species.

Cation Exchange - reversible adsorption reaction in which an aqueous species exchanges with an adsorbed species. Cation exchange reactions are approximately stoichiometric and can be written, for example, as



where X designates an exchange surface site.

Cation Exchange Capacity (CEC) - the sum total of exchangeable cations per unit mass of soil/sediment that a soil can adsorb.

Chernozem - A great soil group of the 1938 USDA classification system. It is a group of zonal soils whose surface horizon is dark and highly organic, below which is a lighter-colored horizon and accumulation of lime. The soil group is developed under conditions of temperate to cool subhumid climate (USDS, 1938).

Clay Content - particle size fraction of soil that is less than 2 μm (unless specified otherwise).

Code Verification - test of the accuracy with which the subroutines of the computer code perform the numerical calculations.

Colloid - any fine-grained material, sometimes limited to the particle-size range of <0.00024 mm (*i.e.*, smaller than clay size), that can be easily suspended. In its original sense, the definition of a colloid included any fine-grained material that does not occur in crystalline form.

Complexation (Complex Formation) - any combination of dissolved cations with molecules or anions containing free pairs of electrons.

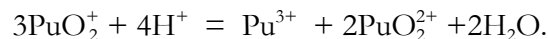
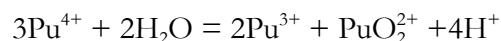
Component Species - “basis entities or building blocks from which all species in the system can be built” (Allison et al. 1991). They are a set of linearly independent aqueous species in terms of which all aqueous speciation, redox, mineral, and gaseous solubility reactions in the MINTEQA2 thermodynamic database are written.

Detrital Mineral - “any mineral grain resulting from mechanical disintegration of parent rock” (Bates and Jackson 1980).

Deuterium (D) - stable isotope ^2H of hydrogen.

Diagenetic - “caused by the chemical, physical, and biological changes undergone by a sediment after its initial deposition, and during and after its consolidation into a coherent solid rock, exclusive of surficial weathering and metamorphism” (Bates and Jackson 1980).

Disproportionation - is a chemical reaction in which a single compound serves as both oxidizing and reducing agent and is thereby converted into more oxidized and a more reduced derivatives (Sax and Lewis 1987). For the reaction to occur, conditions in the system must be temporarily changed to favor this reaction (specifically, the primary energy barrier to the reaction must be lowered). This is accomplished by a number of ways, such as adding heat or microbes, or by radiolysis occurring. Examples of plutonium disproportionation reactions are:



Electron Activity - unity for the standard hydrogen electrode.

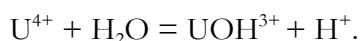
Evaporite - A sedimentary rock composed principally of minerals precipitated from a saline solution as a result of extensive or total evaporation of the solution.

Far Field - the portion of a contaminant plume that is far from the point source and whose chemical composition is not significantly different from that of the uncontaminated portion of the aquifer.

Fulvic Acids - breakdown products of cellulose from vascular plants (also see humic acids). Fulvic acids are the alkaline-soluble portion which remains in solution at low pH and is of lower molecular weight (Gascoyne 1982).

Humic Acids - breakdown products of cellulose from vascular plants (also see fulvic acids). Humic acids are defined as the alkaline-soluble portion of the organic material (humus) which precipitates from solution at low pH and are generally of high molecular weight (Gascoyne 1982).

Hydrolysis - a chemical reaction in which a substance reacts with water to form two or more new substances. For example, the first hydrolysis reaction of U^{4+} can be written as



Hydrolytic Species - an aqueous species formed from a hydrolysis reaction.

Ionic Potential - ratio (z/r) of the formal charge (z) to the ionic radius (r) of an ion.

Isoelectric Point (iep) - pH at which a mineral's surface has a net surface charge of zero. More precisely, it is the pH at which the particle is electrokinetically uncharged.

Lignite - a coal that is intermediate in coalification between peat and subbituminous coal.

Marl - an earthy substance containing 35 to 65 percent clay and 65 to 5 percent carbonate formed under marine or freshwater conditions

Mass Transfer - transfer of mass between 2 or more phases that includes an aqueous solution, such as the mass change resulting from the precipitation of a mineral or adsorption of a metal on a mineral surface.

Mass Transport - time-dependent movement of 1 or more solutes during fluid flow.

Methylation - a chemical process for introducing a methyl group (CH_3-) into a species

Mire - a small piece of marshy, swampy, or boggy ground.

Model Validation - integrated test of the accuracy with which a geochemical model and its thermodynamic database simulate actual chemical processes.

Monomeric Species - an aqueous species containing only one center cation (as compared to a polymeric species).

Near Field - the portion of a contaminant plume that is near the point source and whose chemical composition is significantly different from that of the uncontaminated portion of the aquifer.

Peat - an unconsolidated deposit of semicarbonized plant remains in a water saturated environment.

pH_{zpc} - As the pH increases, mineral surfaces become increasingly more negatively charged. The pH where the surface is uncharged (*i.e.*, zero net charge) is referred to as the pH of zero-point-of-charge, pH_{zpc}.

Polynuclear Species - an aqueous species containing more than one central cation moiety, *e.g.*, (UO₂)₂CO₃(OH)₃⁻ and Pb₄(OH)₄⁴⁺.

Podzol - A great soil group of the 1938 USDA classification system. It is a group of zonal soils having an organic mat and a very thin organic-mineral layer overlying gray, leached A2 horizon and a dark brown, illuvial B horizon enriched in iron oxide, alumina, and organic matter. It develops under coniferous or mixed forests or under heath, in a cool to temperate moist climate (USDA, 1938).

Protium (H) - stable isotope ¹H of hydrogen.

Retrograde Solubility - solubility that decreases with increasing temperature, such as those of calcite (CaCO₃) and radon. The solubility of most compounds (*e.g.*, salt, NaCl) increases with increasing temperature.

Species - actual form in which a dissolved molecule or ion is present in solution.

Specific Adsorption - surface complexation via a strong bond to a mineral surface. For example, several transition metals and actinides are specifically adsorbed to aluminum- and iron-oxide minerals.

Sol - a homogeneous suspension or dispersion of colloidal matter in a fluid.

Solid Solution - a solid material in which a minor element is substituted for a major element in a mineral structure.

Thoron - name occasionally used, especially in older documents, to refer to ²²⁰Rn which forms from the decay of thorium.

Tritium (T) - radioactive isotope ³H of hydrogen.

Tritium Units - units sometimes used to report tritium concentrations. A tritium unit (TU) is equivalent to 1 atom of ³H (tritium) per 10¹⁸ atoms of ¹H (protium). In natural water that produces 7.2 x 10⁻³ disintegrations per minute per milliliter (dpm/ml) of tritium, 1 TU is approximately equal to 3.2 picocuries/milliliter (pCi/ml).

zpc (zero-point-of-charge) - see pH_{zpc}.

APPENDIX C

Americium Adsorption Studies

Appendix C

Americium Adsorption Studies

The K_d values listed in the following pure mineral/oxide and crushed rock studies are not necessarily relevant to the mobility and sorption of americium in soils. However, the studies and associated references are listed below for completeness. The potential value of these references and the sorption processes that were investigated is left to the reader. The references cited in this appendix are listed in the main reference list in Chapter 6.

C.1 Adsorption Studies of Americium on Single Mineral Phases

Several studies have been conducted for the adsorption of americium on pure mineral and oxide phases. Some of these studies are listed in Tables C.1a and C.1b.

Degueldre *et al.* (1994) investigated the role of dissolved carbonate concentrations on the sorption and desorption of americium on montmorillonite, illite, and hematite colloids. Strong adsorption of americium on the mineral colloids was observed. They concluded that in addition to the uncomplexed aqueous ion Am^{3+} , americium hydroxyl, carbonate, and carbonate-hydroxyl complexes also sorbed to the minerals. A small decrease in americium adsorption was observed at pH 8 in experiments conducted with greater than 0.02 M total dissolved carbonate. Under these pH/carbonate conditions, the anion $\text{Am}(\text{CO}_3)_3^{3-}$ dominates the speciation of dissolved americium. Degueldre *et al.* (1994) concluded that the formation of americium carbonate and hydroxyl-carbonate aqueous complexes compete with the formation of americium surface complexes on the mineral colloids. At pH 10, this decreasing trend ends due to the formation and adsorption of strong aqueous americium hydroxyl complexes.

Samadfam *et al.* (2000) studied the sorption of Am(III) on kaolinite as a function of pH from 3.5 to 10 and humic acid concentrations over the range 0 to 20 ppm in 0.1 M NaClO_4 solutions. In the absence of humic acid, the adsorption of Am(III) increased with pH from 3.5 to 10. The presence of humic acid increased the adsorption of Am(III) to kaolinite at pH values less than 5 and decreased adsorption at higher pH values.

Beall *et al.* (1978) determined the sorption behavior of Am(III) on attapulgite, montmorillonite, and kaolinite in NaCl brines buffered at pH 5. Their results indicated that the Am(III) adsorption on these minerals decreased with increasing ionic strength.

Table C.1 Americium adsorption studies on pure mineral and oxide phases.

| Mineral/Oxide | References |
|-------------------------|---|
| Albite | Allard (1984) |
| Almandine | Allard (1984) |
| Anhydrite | Allard (1984) |
| Anorthite | Allard (1984) |
| Apatite | Allard (1984), Andersson <i>et al.</i> (1982) |
| Attapulgite | Allard (1984), Andersson <i>et al.</i> (1982), Beall <i>et al.</i> (1978) |
| Augite | Allard (1984) |
| Bentonite | Nagasaki <i>et al.</i> (1994) |
| Beryl | Allard (1984) |
| Biotite | Ticknor <i>et al.</i> (1996), Allard (1984), Andersson <i>et al.</i> (1982) |
| Bytownite | Allard (1984) |
| Calcite | Allard (1984), Andersson <i>et al.</i> (1982) |
| Chalcopyrite | Allard (1984) |
| Chalcocite | Allard (1984) |
| Clay (abyssal red clay) | Erickson (1980) |
| Clinoptolite | Triay <i>et al.</i> (1991) |
| Corundum | Allard (1984) |
| Dolomite | Brady <i>et al.</i> (1999), Allard (1984) |
| Epidote | Allard (1984) |
| Fluorite | Allard (1984), Andersson <i>et al.</i> (1982) |
| Galena | Allard (1984) |
| Gibbsite | Allard (1984) |
| Goethite | Ticknor <i>et al.</i> (1996) |

Continuation of Table C.1

| Mineral/Oxide | References |
|-----------------|---|
| Halloysite | Allard (1984) |
| Hematite | Degueldre <i>et al.</i> (1994), Allard (1984) |
| Hornblende | Allard (1984) |
| Illite | Degueldre <i>et al.</i> (1994) |
| Kaolinite | Samadfam <i>et al.</i> (2000), Allard (1984), Beall <i>et al.</i> (1978) |
| Limonite | Allard (1984) |
| Magnetite | Allard (1984), Andersson <i>et al.</i> (1982) |
| Microcline | Allard (1984) |
| Molybdenite | Allard (1984) |
| Monazite | Allard (1984) |
| Montmorillonite | Ticknor <i>et al.</i> (1996), Degueldre <i>et al.</i> (1994), Allard (1984), Andersson <i>et al.</i> (1982), Beall <i>et al.</i> (1978) |
| Muscovite | Allard (1984) |
| Olivine | Allard (1984), Andersson <i>et al.</i> (1982) |
| Pyrite | Allard (1984) |
| Quartz | Ticknor <i>et al.</i> (1996), Allard (1984), Andersson <i>et al.</i> (1982) |
| Romanechite | Triay <i>et al.</i> (1991) |
| Serpentine | Allard (1984) |
| Sphene | Allard (1984) |
| Zircon | Allard (1984) |

Degueldre *et al.* (1994) investigated the role of dissolved carbonate concentrations on the sorption and desorption of americium on montmorillonite, illite, and hematite colloids. Strong adsorption of americium on the mineral colloids was observed. Degueldre *et al.* (1994) concluded that in addition to the uncomplexed aqueous ion Am^{3+} , americium hydroxyl, carbonate, and carbonate-hydroxyl complexes also sorbed to the minerals. A small decrease in americium adsorption was observed at pH 8 in experiments conducted with greater than 0.02 M total dissolved carbonate. Under these pH/carbonate conditions, the anion $\text{Am}(\text{CO}_3)_3^{3-}$ dominates the speciation of dissolved americium. Degueldre *et al.* (1994) concluded that the formation of americium carbonate and hydroxyl-carbonate aqueous complexes compete with the formation of americium surface complexes on the

mineral colloids. At pH 10, this decreasing trend ends due to the formation and adsorption of strong aqueous americium hydroxyl complexes.

Samadfam *et al.* (2000) studied the sorption of Am(III) on kaolinite as a function of pH from 3.5 to 10 and humic acid concentrations over the range 0 to 20 ppm in 0.1 M NaClO₄ solutions. In the absence of humic acid, the adsorption of Am(III) increased with pH from 3.5 to 10. The presence of humic acid increased the adsorption of Am(III) to kaolinite at pH values less than 5 and decreased adsorption at higher pH values.

Beall *et al.* (1978) determined the sorption behavior of Am(III) on attapulgite, montmorillonite, and kaolinite in NaCl brines buffered at pH 5. Their results indicated that the Am(III) adsorption on these minerals decreased with increasing ionic strength.

C.2 *K_d* Studies of Americium on Crushed Rock Materials

Some studies have been conducted for the sorption of americium on crushed rock as part of national research programs to investigate the feasibility of geological disposal of high-level radioactive waste (HLW). Some of these studies are listed in Table C.2.

Table C.2 Americium adsorption studies on crushed rock and related materials.

| Geologic Material | References |
|--------------------------|---|
| Basalt | Allard (1984), Salter <i>et al.</i> , 1981a), Ames and McGarrah, 1980)), Silva <i>et al.</i> , 1979), |
| Diabase | Andersson <i>et al.</i> (1982) |
| Gneiss | Andersson <i>et al.</i> (1982) |
| Granite | Ticknor <i>et al.</i> (1996), Allard (1984), Andersson <i>et al.</i> (1982), Silva <i>et al.</i> (1979) |
| Sandstone | Barney (1982) |
| Shale | Silva <i>et al.</i> (1979) |
| Tuff | Triay <i>et al.</i> (1991), Barney (1982) |

APPENDIX D

Arsenic Adsorption Studies

Appendix D

Arsenic Adsorption Studies

The K_d values listed in the following pure mineral/oxide and crushed rock studies are not necessarily relevant to the mobility and sorption of arsenic in soils. However, the studies and associated references are listed below for completeness. The potential value of these references and the sorption processes that were investigated is left to the reader. The references cited in this appendix are listed in the main reference list in Chapter 6.

Several studies have been conducted on the adsorption to arsenic on pure mineral and oxide phases. Some of these studies are listed in Table D.1a and D1.b.

Table D.1 Arsenic adsorption studies on pure mineral and oxide phases.

| Mineral/Oxide | References |
|--------------------------------|---|
| Alumina (activated) | Gupta and Chen (1978) |
| Aluminum hydroxide (amorphous) | Manning and Goldberg [1997a, As(III)], Davis (1978), Anderson <i>et al.</i> (1976) |
| Bauxite (activated) | Gupta and Chen (1978) |
| Biotite (Hydroxy Al-coated) | Huang (1975) |
| Corundum | Halter and Pfeider [2001, As(V)] |
| Ettringite | Myneni <i>et al.</i> [1997, As(V)] |
| Ferrihydrite | Jain <i>et al.</i> [1999, As(V) and As(III)], Raven <i>et al.</i> [1998, As(V) and As(III)], Fuller <i>et al.</i> [1993, As(III)], Waychunas <i>et al.</i> [1992, As(V)], Davis <i>et al.</i> [1989, As(V)] |
| Gibbsite | Ladeira <i>et al.</i> (2001) |
| Goethite | O'Reilly <i>et al.</i> [2001, As(V)], Manning <i>et al.</i> [1998, As(III)], Sun and Doner [1998, As(III)], Fendorf <i>et al.</i> [1997, As(V)] |
| Hydrous iron oxide | Wilkie and Hering [1996, As(V) and As(III)], Hsi <i>et al.</i> (1994) |
| Illite | Manning and Goldberg [1997a, As(III)] |

Continuation of Table D.1.

| Mineral/Oxide | References |
|-------------------------------|---|
| Iron oxyhydroxide (amorphous) | Belzile and Tessier (1990), Benjamin and Bloom (1981), Pierce and Moore [1982, As(V) and As(III)], Leckie <i>et al.</i> (1980) |
| Kaolinite | Lin and Puls [2000, As(V) and As(III)], Takahashi <i>et al.</i> [1999, As(V)], Manning and Goldberg [1997a, As(III)], Frost and Griffin [1977, As(V) and As(III)] |
| Montmorillonite | Manning and Goldberg [1997a, As(III)], Frost and Griffin [1977, As(V) and As(III)] |
| Muscovite (Hydroxy Al-coated) | Huang (1975) |
| Silica (amorphous) | Takahashi <i>et al.</i> [1999, As(V)] |

APPENDIX E

Curium Adsorption Studies

Appendix E

Curium Adsorption Studies

The K_d values listed in the following pure mineral/oxide and crushed rock studies are not necessarily relevant to the mobility and sorption of curium in soils. However, the studies and associated references are listed below for completeness. The potential value of these references and the sorption processes that were investigated is left to the reader. The references cited in this appendix are listed in the main reference list in Chapter 6.

E.1 Adsorption Studies of Curium on Single Mineral Phases

Few studies have been conducted on the adsorption of curium on pure mineral, oxide phases, and other geologic-related materials. Some of these studies are listed in Table E.1.

Samadfam *et al.* (2000) studied the sorption of Cm(III) on kaolinite as a function of pH over the range 3.5 to 10 and humic acid concentrations over the range 0 to 20 ppm in 0.1 M NaClO₄ solutions. In the absence of humic acid, the adsorption of Cm(III) increased with pH over the range 3.5 to 10. The presence of humic acid increased the adsorption of Cm(III) to kaolinite at pH values less than 5, and decreased adsorption at high pH values.

Beall *et al.* (1978) determined the sorption behavior of Cm(III) on attapulgite, montmorillonite, and kaolinite in NaCl brines buffered at pH 5. Their results indicated that the Cm(III) adsorption on these minerals decreased with increasing ionic strength.

Table E.1 Curium adsorption studies on pure mineral and oxide phases.

| Mineral/Oxide | References |
|-------------------------|--|
| Attapulgite | Beall <i>et al.</i> (1978) |
| Bentonite | Baston <i>et al.</i> (1997) |
| Clay (abyssal red clay) | Erickson (1980) |
| Goethite | Alberts <i>et al.</i> (1986) |
| Montmorillonite | Beall <i>et al.</i> (1978) |
| Kaolinite | Samadfam <i>et al.</i> (2000), Alberts <i>et al.</i> (1986), Beall <i>et al.</i> (1978) |
| Silica gel | Alberts <i>et al.</i> (1986) |

E.2 K_d Studies of Curium on Crushed Rock Materials

Few studies have been conducted for the sorption of curium on crushed rocks. Studies identified were conducted as part of national research programs to investigate the feasibility of geological disposal of high-level radioactive waste (HLW). Some of these studies are listed in Table E.2.

Table E.2 Curium adsorption studies on crushed rock and related materials.

| Geologic Material | References |
|--------------------------|-----------------------------|
| Basalt | Silva <i>et al.</i> (1979) |
| Granite | Silva <i>et al.</i> (1979) |
| Granodiorite | Baston <i>et al.</i> (1997) |
| Shale | Silva <i>et al.</i> (1979) |
| Tuff | Baston <i>et al.</i> (1997) |

APPENDIX F

Iodine Adsorption Studies

Appendix F

Iodine Adsorption Studies

The K_d values listed in the following pure mineral/oxide and crushed rock studies are not necessarily relevant to the mobility and sorption of iodine in soils. However, the studies and associated references are listed below for completeness. The potential value of these references and the sorption processes that were investigated is left to the reader. The references cited in this appendix are listed in the main reference list in Chapter 6.

F.1 Adsorption Studies of Iodine on Single Mineral Phases

Numerous studies have been conducted of the adsorption of iodine on pure mineral, oxide phases, and other geologic-related materials. Many of these studies were conducted because of extensive research interest in developing getters (adsorbents) that could be added to waste streams and tailored barriers for removal and/or immobilization of dissolved iodine. Some of these studies are listed in Tables F.1a, F.1b, and F.1c.

Balsley *et al.* (1996) used potentiometric titrations to investigate the sorption of I^- on cinnabar (HgS) and chalcocite (Cu_2S) in 1, 0.1, 0.01, and 0.001 mol/l NaCl solutions. The surfaces of cinnabar and chalcocite are negatively charged at pH values greater than 3. Despite the anionic nature of the surfaces of these 2 metal sulfides, I^- sorbs strongly to both minerals. Measured K_d values far exceed those reported for all other minerals with maximal K_d values of 1,375 and 3,080 ml/g, respectively, for chalcocite and cinnabar between pH values of 4 and 5. Adsorption was substantial at all pH values from 4 to 10. Balsley *et al.* (1996) suggest that I^- sorption apparently occurs by exchange of hydroxyls attached to H and Cu sites.

Ticknor *et al.* (1996) studied the effects of fulvic acid on the sorption of ^{125}I (oxidation state not specified) on crushed granite, biotite, goethite, and montmorillonite. Batch sorption experiments with 28-day reaction times were conducted under aerobic conditions using synthetic groundwater solutions with pH values ranging from 7.6 to 7.8. Low sorption was measured for iodine on montmorillonite in the presence of dissolved organic material. The K_d values for iodine sorbed to montmorillonite ranged from 1.9 to 4.0 ml/g. No sorption (K_d values less than 1) was measured for iodine on the other solids. Ticknor *et al.* (1996) noted that if the sorbed iodine was associated with the organic directly, then sorption of iodine on goethite should have been observed because the goethite sorbed more fulvic acid than did the montmorillonite.

Table F.1 Iodine adsorption studies on pure minerals and oxide phases.

| Mineral/Oxide | References |
|--------------------------------|--|
| AgCl | Andersson <i>et al.</i> (1982), Allard <i>et al.</i> (1980) |
| Al(OH) ₃ | Andersson <i>et al.</i> (1982), Allard <i>et al.</i> (1980) |
| Al ₂ O ₃ | Hakem <i>et al.</i> (1996, colloidal-size), Muramatsu <i>et al.</i> (1990), Ticknor and Cho (1990, I ⁻ and IO ₃ ⁻) |
| Allophane | Sazarashi <i>et al.</i> (1994,1995) |
| Anhydrite | Strickert <i>et al.</i> (1980) |
| Apatite | Strickert <i>et al.</i> (1980) |
| Argentite | Kaplan <i>et al.</i> (2000a) |
| Attapulgitite | Sazarashi <i>et al.</i> (1994,1995), Raçon (1988), Allard <i>et al.</i> (1980) |
| Bauxite | Raçon (1988) |
| Bentonite | Muramatsu <i>et al.</i> (1990), Raçon (1988) |
| Biotite | Ticknor <i>et al.</i> (1996) |
| Bornite | Strickert <i>et al.</i> (1980) |
| Bournonite | Strickert <i>et al.</i> (1980) |
| Calcite | Kaplan <i>et al.</i> (2000b), Kaplan <i>et al.</i> (1999), Ticknor and Cho (1990, I ⁻ and IO ₃ ⁻) |
| Cerussite | Raçon (1988) |
| Chalcopyrite | Sazarashi <i>et al.</i> (1995,1994), Raçon (1988), Andersson <i>et al.</i> (1982), Strickert <i>et al.</i> (1980), Allard <i>et al.</i> (1980) |
| Chalcocite | Kaplan <i>et al.</i> (2000a), Balsley <i>et al.</i> (1996,1997) |
| Chalcopyrite | Kaplan <i>et al.</i> (2000a), Huie <i>et al.</i> (1988) |
| Chlorite | Kaplan <i>et al.</i> (2000b), Kaplan <i>et al.</i> (1999), Ticknor and Cho (1990, I ⁻ and IO ₃ ⁻) |
| Chrysocolla | Raçon (1988), Strickert <i>et al.</i> (1980) |
| Cinnabar | Kaplan <i>et al.</i> (2000a), Balsley <i>et al.</i> (1996, 1997), Sazarashi <i>et al.</i> (1994,1995), Ikeda <i>et al.</i> (1994), Andersson <i>et al.</i> (1982), Allard <i>et al.</i> (1980) |

Continuation of Table F.1.

| Mineral/Oxide | References |
|--------------------------------|--|
| Clinoptilolite | Rançon (1988) |
| Coals (sub-bituminous) | Balsley <i>et al.</i> (1997) |
| Covellite | Balsley <i>et al.</i> (1997) |
| Cu (metal) | Haq <i>et al.</i> (1980) |
| Cu ₂ O | Haq <i>et al.</i> (1980) |
| CuO | Haq <i>et al.</i> (1980) |
| Dolomite | Strickert <i>et al.</i> (1980) |
| Enargite | Strickert <i>et al.</i> (1980) |
| Epidote | Ticknor and Cho (1990, I ⁻ and IO ₃ ⁻) |
| Fe ₂ O ₃ | Muramatsu <i>et al.</i> (1990) |
| Ferric hydroxide | Andersson <i>et al.</i> (1982), Allard <i>et al.</i> (1980) |
| Galena | Kaplan <i>et al.</i> (2000a), Huie <i>et al.</i> (1988), Rançon (1988), Strickert <i>et al.</i> (1980), Allard <i>et al.</i> (1980) |
| Goethite | Kaplan <i>et al.</i> (2000b), Kaplan <i>et al.</i> (1999), Ticknor <i>et al.</i> (1996), Ticknor and Cho (1990, I ⁻ and IO ₃ ⁻), Rançon (1988) |
| Gypsum | Ticknor and Cho (1990, I ⁻ and IO ₃ ⁻) |
| Halloysite | Allard <i>et al.</i> (1980) |
| Hematite | Ticknor and Cho (1990, I ⁻ and IO ₃ ⁻), Huie <i>et al.</i> (1988, rare-earth hematite), Rançon (1988) |
| Illite | Kaplan <i>et al.</i> (2000b), Kaplan <i>et al.</i> (1999), Rançon (1988) |
| Imogolite-bearing soil | Balsley <i>et al.</i> (1997) |
| Kaolinite | Muramatsu <i>et al.</i> (1990), Ticknor and Cho (1990, I ⁻ and IO ₃ ⁻), Rançon (1988) |
| Laterite | Rançon (1988) |

Continuation of Table F.1.

| Mineral/Oxide | References |
|-----------------------------------|---|
| Lignite | Balsley <i>et al.</i> (1997) |
| Limonite | Rançon (1988), Allard <i>et al.</i> (1980) |
| Molybdenite | Huie <i>et al.</i> (1988) |
| Montmorillonite | Kaplan <i>et al.</i> (2000b), Kaplan <i>et al.</i> (1999), Ticknor <i>et al.</i> (1996), Sazarashi <i>et al.</i> (1994,1995), Allard <i>et al.</i> (1980) |
| Muscovite | Ticknor and Cho (1990, I ⁻ and IO ₃ ⁻) |
| Olivine | Andersson <i>et al.</i> (1982), Allard <i>et al.</i> (1980) |
| PbOH | Andersson <i>et al.</i> (1982). Allard <i>et al.</i> (1980) |
| Pyrite | Huie <i>et al.</i> (1988), Strickert <i>et al.</i> (1980) |
| Quartz | Kaplan <i>et al.</i> (2000b), Kaplan <i>et al.</i> (1999), Ticknor <i>et al.</i> (1996), Muramatsu <i>et al.</i> (1990), Ticknor and Cho (1990, I ⁻ and IO ₃ ⁻), Rançon (1988), Allard <i>et al.</i> (1980) |
| Sepiolite | Rançon (1988) |
| Serpentine | Andersson <i>et al.</i> (1982), Allard <i>et al.</i> (1980) |
| Siderite | Rançon (1988) |
| SiO ₂ (colloidal size) | Hakem <i>et al.</i> (1996) |
| Stibnite | Kaplan <i>et al.</i> (2000a), Huie <i>et al.</i> (1988) |
| Tennantite | Strickert <i>et al.</i> (1980) |
| Tetrahedrite | Strickert <i>et al.</i> (1980) |
| Tiemannite | Zhuang <i>et al.</i> (1995) |
| TiO ₂ (colloidal size) | Hakem <i>et al.</i> (1996) |
| Vermiculite | Kaplan <i>et al.</i> (2000b), Kaplan <i>et al.</i> (1999), Rançon (1988) |
| Witherite | Strickert <i>et al.</i> (1980) |
| Zinc hydrotalcite | Balsley <i>et al.</i> (1997) |
| Zeolite | Rançon (1988) |

Ticknor and Cho (1990) studied the extent of sorption of I^- and IO_3^- on bentonite and minerals found in fractures in granite. The batch equilibration experiments were conducted using synthetic groundwater (pH 7.7) and samples of crushed calcite, chlorite, epidote, goethite, gypsum, hematite, kaolinite, muscovite, and quartz. Ticknor and Cho found no measurable sorption of I^- or IO_3^- on bentonite. No detectable sorption was measured for I^- on any of the minerals selected for study. Sorption of IO_3^- was observed with chlorite and hematite over the range of conditions used for their study, and with kaolinite, epidote, goethite, and quartz at some of the experimental conditions. There was no detectable sorption of IO_3^- on calcite, gypsum, and muscovite. Inorganic I^- was not sorbed by any of the minerals under any of the conditions used in their study.

Couture and Seitz (1983) measured the sorption of I^- , IO_3^- , and IO_4^- (periodate) on hematite and kaolinite, and the sorption of IO_3^- by pelagic red clay in buffer solutions and sea water. Iodate was strongly sorbed by hematite at pH values up to 9. Hematite is more effective than kaolinite as a sorbent for IO_3^- , and IO_3^- is more strongly sorbed than I^- by kaolinite and hematite. Periodate (IO_4^-) was more strongly sorbed by hematite than IO_3^- , and I^- appears to be less strongly sorbed. At pH 4, pure kaolinite (free of hematite and goethite) sorbs IO_3^- only slightly and I^- not all. Couture and Seitz (1983) determined that the sorption of IO_3^- was reversible upon change in pH. Because IO_3^- and IO_4^- were sorbed to a greater extent than I^- by a number of minerals, especially iron oxides, the apparent sorption of I^- may be due to the sorption of oxidized iodine species. Based on their measurements, Couture and Seitz (1983) suggest that results from published iodine sorption experiments should be questioned unless the oxidation state of the iodine adsorbate and the mineralogical purity of the adsorbents were established.

F.2 K_d Studies of Iodine on Crushed Rock Materials

Numerous studies have been conducted of the sorption of iodine on crushed rock as part of national research programs to investigate the feasibility of geological disposal of high-level radioactive waste (HLW). Some of these studies are listed in Table F.2.

Table F.2. Iodine adsorption studies on crushed rock and related materials.

| Geologic | Materials References |
|--|---|
| Basalt | Strickert <i>et al.</i> (1980), Salter <i>et al.</i> (1981a), Ames and McGarrah (1980) |
| Basalt secondary mineral assemblage from vesicles, vugs, and fractures | Salter <i>et al.</i> (1981b) [assemblage consists of approximately 98 percent smectite clay and trace amounts of amorphous iron oxide, calcite, quartz, opal (or α -cristobalite), and zeolites] |
| Chalk | Strickert <i>et al.</i> (1980) |
| Granite | Strickert <i>et al.</i> (1980) |
| Limestone | Strickert <i>et al.</i> (1980) |
| Shale | Strickert <i>et al.</i> (1980) |
| Siltstone | Strickert <i>et al.</i> (1980) |
| Tuff | Strickert <i>et al.</i> (1980) |

APPENDIX G

Neptunium Adsorption Studies

Appendix G

Neptunium Adsorption Studies

The K_d values listed in the following pure mineral/oxide and crushed rock studies are not necessarily relevant to the mobility and sorption of neptunium in soils. However, the studies and associated references are listed below for completeness. The potential value of these references and the sorption processes that were investigated is left to the reader. The references cited in this appendix are listed in the main reference list in Chapter 6.

G.1 Adsorption Studies of Neptunium on Single Mineral Phases

Several studies have been conducted for the adsorption of Np(V) on pure mineral and oxide phases. Some of these studies are listed in Tables G.1a and G.1b.

Table G.1 Neptunium adsorption studies on pure mineral and oxide phases.

| Mineral/Oxide | References(s) |
|---------------|--|
| Albite | Torstenfelt <i>et al.</i> (1988), Beall <i>et al.</i> (1980) |
| Anorthite | Torstenfelt <i>et al.</i> (1988) |
| Apatite | Andersson <i>et al.</i> (1982) |
| Aragonite | Keeney-Kennicutt <i>et al.</i> (1984) |
| Attapulgit | Andersson <i>et al.</i> (1982) |
| Bentonite | Torstenfelt <i>et al.</i> (1988) |
| Biotite | Nakayama and Sakamoto (1991), Andersson <i>et al.</i> (1982), Beall <i>et al.</i> (1980) |
| Böhmite | Kung and Triay (1994), Nakayama and Sakamoto (1991) |
| Bytownite | Beall <i>et al.</i> (1980) |
| Calcite | Ticknor (1993), Keeney-Kennicutt <i>et al.</i> (1984), Andersson <i>et al.</i> (1982) |
| Chlorite | Ticknor (1993) |
| Clay | Hart <i>et al.</i> (1994), Keeney-Kennicutt <i>et al.</i> (1984) |
| Corundum | Nakayama and Sakamoto (1991) |
| Dolomite | Brady <i>et al.</i> (1999) |

Continuation of Table G.1.

| Mineral/Oxide | References(s) |
|-------------------------------|--|
| Epidote | Ticknor (1993) |
| Fluorite | Andersson <i>et al.</i> (1982) |
| Gibbsite | Del Nero <i>et al.</i> (1997) |
| Goethite | Fujita <i>et al.</i> (1995), Tochiyama <i>et al.</i> (1995), Kung and Triay (1994), Ticknor (1993), Combes <i>et al.</i> (1992), Nakayama and Sakamoto (1991), Keeney-Kennicutt <i>et al.</i> (1984) |
| Gypsum | Ticknor (1993) |
| Hematite | Nakata <i>et al.</i> (2000), Kohler <i>et al.</i> (1999), Tochiyama <i>et al.</i> (1995), Ticknor (1993), Nakayama and Sakamoto (1991), Allard (1984) |
| Hornblende | Torstenfelt <i>et al.</i> (1988) |
| Hydrargillite | Del Nero <i>et al.</i> (1997) |
| Illite | Nagasaki <i>et al.</i> (1998), Ticknor (1993), Torstenfelt <i>et al.</i> (1988) |
| Iron oxyhydroxide (amorphous) | Girvin <i>et al.</i> (1991) |
| Kaolinite | Ticknor (1993), Relyea and Martin (1982) |
| Lepidocrocite | Nakayama and Sakamoto (1991) |
| Magnetite | Nakata <i>et al.</i> (2000), Fujita <i>et al.</i> (1995), Tochiyama <i>et al.</i> (1995), Nakayama and Sakamoto (1991), Allard (1984), Andersson <i>et al.</i> (1982) |
| Microcline | Torstenfelt <i>et al.</i> (1988), Beall <i>et al.</i> (1980) |
| MnO ₂ | Keeney-Kennicutt <i>et al.</i> (1984) |
| Montmorillonite | Nagaski and Tanaka (2000), Andersson <i>et al.</i> (1982) |
| Muscovite | Ticknor (1993) |
| Olivine | Andersson <i>et al.</i> (1982) |
| Quartz | Kohler <i>et al.</i> (1999), Ticknor (1993), Pratopo <i>et al.</i> (1991), Nakayama <i>et al.</i> (1988), Andersson <i>et al.</i> (1982), Beall <i>et al.</i> (1980) |
| SiO ₂ (amorphous) | Kung and Triay (1994) |
| Smectite | Kozai <i>et al.</i> (1996) |

Kung and Triay (1994) used the batch sorption technique to investigate the effect of naturally occurring organic materials on the sorption of Np(V) on synthetic goethite, böhmite [also known as boehmite, AlO(OH)], amorphous silica oxides, and crushed tuff¹ material. The presence of the model amino acid and fulvic acids did not affect the sorption of neptunium on tuff material or on iron or aluminum oxides. The interaction between organic material and mineral surfaces in the natural environment is important to mineral surface geochemistry. Sorption of organic material onto mineral surfaces will affect not only the solubility and charge of organics in solution but also mineral surface properties. These changes may affect the reactivity of the mineral to other metal ions. Sorption of neptunium on iron oxides was 10 times greater than that on aluminum oxides. Sorption of neptunium on crushed tuff material was much lower than that on the oxide surfaces. Presence of model organic materials did not influence the sorption of neptunium on tuff or on iron or aluminum oxides, suggesting that the dissolved model organics did not readily complex neptunium or change the surface properties of the adsorbents.

Table G.2 Measured Np(V) K_d values (ml/l) for fracture-coating minerals as a function of total dissolved solids (TDS) and normal versus low oxygen conditions (Ticknor, 1993).

| Mineral | Normal Oxygen Conditions | | | Low Oxygen Conditions | | |
|-----------|--------------------------|------------|------------|-----------------------|------------|------------|
| | 1,850 TDS | 2,830 TDS | 12,580 TDS | 1,850 TDS | 2,830 TDS | 12,580 TDS |
| Calcite | <i>≥49¹</i> | <i>≥48</i> | 6.5 | <i>≥66</i> | <i>≥64</i> | 15 |
| Chlorite | <i>≥57</i> | <i>≥38</i> | 12 | <i>≥58</i> | 13 | 9.5 |
| Epidote | 2.2 | 1.1 | 0.6 | 13 | 9.1 | 3.6 |
| Goethite | <i>≥55</i> | <i>≥39</i> | 16 | <i>≥62</i> | <i>≥47</i> | 20 |
| Gypsum | 1.2 | 1.4 | 0.6 | 5.1 | 5.1 | 3.0 |
| Hematite | <i>≥69</i> | <i>≥68</i> | <i>≥68</i> | <i>≥84</i> | <i>≥80</i> | <i>≥72</i> |
| Illite | <i>≥57</i> | <i>≥39</i> | 7.8 | <i>≥79</i> | <i>≥76</i> | 25 |
| Kaolinite | 2.6 | 1.4 | 2.0 | 4.1 | 2.1 | 2.6 |
| Muscovite | 1.6 | 0.5 | 0.9 | 6.3 | 5.3 | 3.0 |
| Quartz | 0 | 0 | 0 | 1.3 | 0.8 | 3.7 |

¹ K_d values listed in italics are based on minimum analytical detection limit values for concentrations of dissolved neptunium.

Ticknor (1993) completed batch equilibration experiments to study the sorption of ²³⁷Np in three synthetic groundwater solutions on minerals present as fracture coatings in granitic rock. The minerals included calcite, chlorite, epidote, goethite, gypsum, hematite, illite, kaolinite, muscovite,

¹ Tuff is a general term for a rock formed of consolidated clastic (principally broken fragments) material that originated from volcanic explosion or aerial expulsion from a volcanic vent (Bates and Jackson 1980).

and quartz. Under the experimental conditions, Np(V) was the most probable oxidation state. The pH of each solution was adjusted to 7.5 using NaOH. The three saline solutions differed in their content of total dissolved solids (TDS). At the end of the contact period (27 to 30 days), the measured pH under normal oxygen conditions was 8.0 to 8.5 for all mineral/solution combination except for the kaolinite experiments which had a final pH between 6.5 to 7.0. The pH of the mineral/solution experiments conducted under low oxygen conditions was 9.5. Ticknor (1993) suggested the competition for sorption sites by increases in TDS may account for the decrease of neptunium sorption on some mineral surfaces (Table G.2).

Combes *et al.* (1992) studied the sorption of dissolved Np(V) on goethite (crystalline α -FeOOH) using synchrotron-based, extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) spectroscopies. The sorption experiments consisted of reacting high-surface area goethite with a pH 7.2, 0.08 M NaNO₃ solution containing 1.3x10⁻⁵ M Np(V). Their results indicate that Np(V) sorbs on goethite as a mononuclear, inner-sphere complex. The surface complex may also contain hydroxide or carbonate ligands. There was no indication that the Np(V) sorption on goethite occurred as an ordered neptunium oxide or hydroxide or as a coprecipitate with iron oxide/hydroxide solid.

Nakayama and Sakamoto (1991) studied the sorption of neptunium on several minerals in 0.1 M NaNO₃ solution at pH values between 4 and 11. The minerals included samples of naturally occurring hematite, magnetite, goethite, lepidocrocite, biotite, böhmite, and corundum. The sorption of neptunium on goethite differed as a function of pH relative to that for hematite, magnetite, and biotite. The experiments indicated strong sorption of neptunium on goethite at pH values greater than 6, while sorption on hematite, magnetite, and biotite increased at pH values above 9. The pH dependence of neptunium sorption on lepidocrocite and boehmite was similar to that of goethite, and neptunium sorption on corundum was similar to that for hematite. Nakayama and Sakamoto (1991) attributed the difference in neptunium sorption between the various minerals to the pH_{zpc} ¹ surface charge density, and the pH dependency of the different neptunium aqueous species.

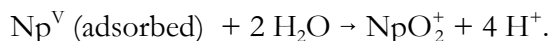
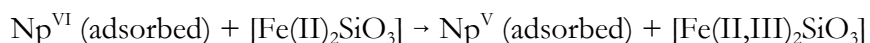
Although others have reported the enhanced adsorption of neptunium by Fe(II)-containing minerals by surface-mediated heterogeneous reduction and sorption reactions, Nakayama and Sakamoto (1991) observed no significant difference in the retardation by the Fe(II)-containing biotite and magnetite versus that for Fe(III)-containing hematite.

Torstenfelt *et al.* (1988) used batch experiments to measure neptunium K_d values for several minerals in groundwater as a function of pH. Natural groundwater containing a total concentrations of 10⁻⁷ M ²³⁷Np was equilibrated under aerobic conditions with crushed samples of granite from three sites and six minerals which included hornblende, three feldspar minerals (albite, anorthite, microcline), and two clays (illite and bentonite). The groundwater contained 143 mg/l HCO₃⁻, and its pH was adjusted to values between approximately 2 and 11 using NaOH or HCl solutions. Torstenfelt *et al.* (1988) observed greater sorption of Np(V) at higher pH than at lower pH values.

¹ As the pH increases, mineral surfaces become increasingly more negatively charged. The pH where the surface is uncharged (*i.e.*, zero net charge) is referred to as the pH of zero-point-of-charge, pH_{zpc} .

The results plotted¹ by Torstenfelt *et al.* (1988) typically indicated that the K_d values for Np(V) were near 0 ml/g measured at pH values near 2 for all solids, generally ranged from 50 to 100 ml/g for the granite and clay samples at pH values near 7 to 8, and varied between 200 and 300 ml/g for most of the mineral specimens at high pH values. At pH values from approximately 2 to 4, the K_d values measured for the feldspar minerals were typically in the region of 10 to 30 ml/g.

For the experiments conducted with hornblende, the K_d values ranged from 200 to 250 ml/g at pH 8.1 and 290 to 350 ml/g at pH 11.2. Because hornblende contains Fe(II), Torstenfelt *et al.* (1988) speculated that these high K_d values might be affected by surface-mediated heterogeneous reduction and sorption reactions on this Fe(II)-containing silicate mineral. For example, autoradiography conducted by Beall *et al.* (1980) indicate that the sorption of Np-237(V) on a fresh surface of granite in aerated groundwater shows a strong correlation to the Fe(II)-containing minerals (pyrite and biotite) in the granite. Studies by Susak *et al.* (1983) and Meyer *et al.* (1984) indicate that Fe(II)-containing geologic materials are able to reduce the concentrations of dissolved neptunium and increase the concentrations of dissolved and sorbed Np(IV). Susak *et al.* (1983) investigated the reduction of Np(VI) in the presence of olivine [$(\text{Fe(II),Mg})_2\text{SiO}_3$]. Susak *et al.* proposed the following sequence of reactions for the reduction and subsequent retardation of neptunium:



Nakayama *et al.* (1988) used high performance liquid chromatography to study the migration of Np(V) in columns packed with quartz. The distribution coefficient derived for Np(V) from these column experiments decreased with increasing ionic strength and increased with increasing pH.

Keeney-Kennicutt *et al.* (1984) studied the sorption of Np(V) on several minerals in dilute aqueous solutions and seawater. When normalized to the amount of adsorption per unit solid surface area, their results indicated that Np(V) sorbs on the following minerals with decreasing affinity in the sequence



Their measured dissolved/adsorbed ratios were constant over the range of 10^{-13} to 10^{-7} M Np(V). Contrary to speculation at that time, their results indicated that Np(V) did not behave as a simple monovalent ion with a low affinity for surfaces.

Relyea and Martin (1982) studied the adsorption of Np-237 on kaolinite over a range of concentrations, pH, electrolyte strengths, and time. The adsorption of ²³⁷Np was determined to be strongly affected by pH. Adsorption of Np-237 on kaolinite was weak at pH values less than pH 5, but increased rapidly from pH 5 to 7.5. At pH values greater than 7.5, the adsorption of Np-237 was approximately 100 percent.

¹ The coarse scale used for K_d axes by Torstenfelt *et al.* (1988) precluded interpolation of accurate values for the experimentally-determined K_d values for each solid type.

G.2 K_d Studies of Neptunium on Crushed Rock Materials

Numerous studies have been conducted for the sorption of neptunium on crushed rock as part of national research programs to investigate the feasibility of geological disposal of high-level radioactive waste (HLW). Some of these studies are listed in Table G.2.

Table G.3 Neptunium adsorption studies on crushed rock and related materials.

| Geologic Material | References |
|--|--|
| Basalt | Meyer <i>et al.</i> , (1984, 1983, 1985a, 1985b), Susak <i>et al.</i> (1983), Barney <i>et al.</i> (1983), Salter <i>et al.</i> (1981a), Ames <i>et al.</i> (1981), Ames and McGarrah (1980) |
| Basalt secondary mineral assemblage from vesicles, vugs, and fractures | Salter <i>et al.</i> (1981b) |
| Diabase | Andersson <i>et al.</i> (1982) |
| Gneiss | Andersson <i>et al.</i> (1982) |
| Granite | Torstenfelt <i>et al.</i> (1988), Andersson <i>et al.</i> (1982), Beall <i>et al.</i> (1980), Allard (1979) |
| Sandstone | Barney (1982) |
| Tuff | Baston <i>et al.</i> (1997), Kung and Triay (1994), Barney (1982) |

APPENDIX H

Radium Adsorption Studies

Appendix H

Radium Adsorption Studies

The K_d values listed in the following pure mineral/oxide and crushed rock studies are not necessarily relevant to the mobility and sorption of radium in soils. However, the studies and associated references are listed below for completeness. The potential value of these references and the sorption processes that were investigated is left to the reader. The references cited in this appendix are listed in the main reference list in Chapter 6.

H.1 Adsorption Studies of Radium on Single Mineral Phases

Several studies have been conducted for the adsorption of radium on pure mineral and oxide phases. These studies and the references they cite may be useful to the reader. Some of these studies are listed in Table H.1.

The results of these studies demonstrate that the adsorption of radium on minerals and oxide phases is dependent on pH, as expected for cations, and decreases with increasing concentrations of competing ions. For example, Tachi *et al.* (2001) used batch sorption experiments to study the sorption of radium on bentonite and purified smectite as a function of pH, ionic strength, and liquid-to-solid ratio. The measured K_d values ranged from 10^2 to more than 10^4 ml/g, and were dependent on ionic strength and pH. Tachi *et al.* (2001) found that most of the sorbed radium was desorbed by a 1 mol/l KCl solution. Modeling results indicated that radium sorption on the smectite was dominated by ion exchange at layer sites of smectite and may increase at the higher pH values from surface complexation at edge sites. Radium sorption on bentonite was explained as being due to ion exchange with smectite, and its pH dependency resulted from changes in calcium concentrations caused from dissolution and precipitation of calcite.

Koulouris (1995) used batch and column techniques to investigate the sorption of Ra-226 on MnO_2 . Radium sorption was studied as a function of initial Ra-226 concentrations, pH, chemical species, and contact time. Koulouris (1995) observed no dependency in Ra-226 sorption on MnO_2 as a function of pH at values greater than 3.6. Radium sorption was essentially constant at approximately 50 to 60 percent over the pH range 3.6 to 12.0, and decreased from 50 at pH 3.6 to 18 percent at pH 2.7. Koulouris (1995) attributed the decrease in Ra-226 sorption to a low pH_{zpc} for the MnO_2 material used in the experiments. Essentially no dependency was observed in Ra-226 sorption on MnO_2 as a function of initial Ra-226 concentrations and chemical species.

Table H.1 Radium adsorption studies on pure mineral and oxide phases.

| Mineral/Oxide | References |
|-------------------------------|---|
| Amorphous ferric oxyhydroxide | Ames <i>et al.</i> (1983c) |
| Anhydrite | Maiti <i>et al.</i> (1989) |
| Bentonite | Tachi <i>et al.</i> (2001), Hanslík and Mansfeld (1990) |
| Biotite | Hanslík and Mansfeld (1990), Ames <i>et al.</i> (1983a) |
| Calcite | Maiti <i>et al.</i> (1989) |
| Clinoptilolite | Ames <i>et al.</i> (1983b) |
| Dolomite | Maiti <i>et al.</i> (1989) |
| Feldspar | Hanslík and Mansfeld (1990), Beneš <i>et al.</i> (1986) |
| Ferric hydroxide | Beneš <i>et al.</i> (1984), |
| Glauconite | Ames <i>et al.</i> (1983b) |
| Illite | Ames <i>et al.</i> (1983b) |
| Kaolinite | Hanslík and Mansfeld (1990), Beneš <i>et al.</i> (1985), Ames <i>et al.</i> (1983b), Relyea and Martin (1982), Riese (1982) |
| MnO ₂ | Koulouris (1995) |
| Montmorillonite | Beneš <i>et al.</i> (1985), Ames <i>et al.</i> (1983b) |
| Muscovite | Beneš <i>et al.</i> (1986), Ames <i>et al.</i> (1983a) |
| Nontronite | Ames <i>et al.</i> (1983b) |
| Opal | Ames <i>et al.</i> (1983b) |
| Phlogopite | Hanslík and Mansfeld (1990) |
| Quartz | Beneš <i>et al.</i> (1984), Riese (1982) |
| Silica | Hanslík and Mansfeld (1990) |
| Smectite | Tachi <i>et al.</i> (2001) |

Beneš and his co-investigators have studied the sorption of radium on sediments (Beneš and Strejc, 1986), ferric hydroxide (Beneš *et al.*, 1984), feldspar (Beneš *et al.*, 1986), kaolinite (Beneš *et al.*, 1985), montmorillonite (Beneš *et al.*, 1985), muscovite (Beneš *et al.*, 1986), and quartz (Beneš *et al.*, 1984). Beneš and Strejc (1986) studied the adsorption and desorption of radium on stream sediments. They determined that the radium adsorption on the sediment could not easily be predicted from the composition and other properties of the sediments. No simple correlations could be made

regarding the extent of radium sorption and the specific surface area, organic matter, mineral oxide coatings, or other sediment components. As previously noted, Beneš and Strejc (1986) observed however that in the presence of dissolved sulfate, a strong dependency existed between the uptake of radium by the sediment and the barite content of the sediments. Beneš and his co-investigators also indicated that the adsorption of radium was also strongly dependent on pH (Beneš *et al.*, 1984). For example, the maximum adsorption of radium on ferric hydroxide occurred at pH values of 7 and greater, and radium adsorption decreased to almost negligible values at pH values less than 6. The pH dependency of radium adsorption on kaolinite was less than that determined for ferric hydroxide and quartz, and radium sorbed to a significant extent on kaolinite at pH values less than 6.

Riese (1982) studied the adsorption of radium on quartz and kaolinite. His measurements indicated that radium was 50 percent adsorbed on quartz at pH 6 and 50 percent adsorbed on kaolinite at pH 5. The adsorption of radium on quartz and kaolinite was also found to decrease with increasing concentrations of dissolved calcium. Results from Riese (1982), as shown on p. 386 of Langmuir (1997), for the adsorption of radium on kaolinite at 25°C in 0.01 M NaNO₃ solution containing 10⁻⁴ M calcium indicate that significant adsorption of radium occurs on kaolinite over the pH range 3 to 9. The adsorption of radium increases with increasing pH, especially at pH values greater than 6.

Lowson and Evans (1984) measured the adsorption of radium in a 0.1 M NaNO₃ solution on alumina, kaolinite, montmorillonite, and illite. The adsorption of radium on alumina and kaolinite was low at pH values less than 7, but increased rapidly at pH values greater than 8. Montmorillonite and illite were found to be stronger adsorbents for radium than alumina and kaolinite. Montmorillonite and illite exhibited significant adsorption (about 20 percent) for radium at pH 3, and the adsorption of radium on these two minerals increased approximately at a linear rate with increasing pH at higher pH values.

H.2 *K_d* Studies of Radium on Crushed Rock Materials

Numerous studies have been conducted for the sorption of radium on crushed rock as part of national research programs to investigate the feasibility of geological disposal of high-level radioactive waste (HLW). Some of these studies are listed in Table H.2. Because elevated temperatures will exist in the near vicinity of the waste canisters and repository in general, many of these studies were conducted over a range temperatures above ambient to determine the extent of radionuclide adsorption as a function of temperature and with respect to changes in groundwater chemistry (*e.g.*, pH and Eh) and mineralogy that will occur with increasing temperature.

Table H.2 Radium adsorption studies on crushed rock and related materials.

| Geologic Material | References |
|--|--|
| Basalt | Puls <i>et al.</i> (1987), Salter <i>et al.</i> (1981a), Ames <i>et al.</i> (1981), Ames and McGarrah (1980) |
| Basalt secondary mineral assemblage from vesicles, vugs, and fractures | Salter <i>et al.</i> (1981b) |
| Sandstone | Barney <i>et al.</i> (1982) |
| Tuff | Barney <i>et al.</i> (1982) |

APPENDIX I

Technetium Adsorption Studies

Appendix I

Technetium Adsorption Studies

The K_d values listed in the following pure mineral/oxide and crushed rock studies are not necessarily relevant to the mobility and sorption of technetium in soils. However, the studies and associated references are listed below for completeness. The potential value of these references and the sorption processes that were investigated is left to the reader. The references cited in this appendix are listed in the main reference list in Chapter 6.

1.1 Adsorption Studies of Technetium on Single Mineral Phases

Numerous technetium adsorption studies have been conducted of technetium on pure mineral, oxide phases, and other geologic-related materials. Like those for iodine, many of these studies were conducted because of extensive research interest in developing getters (adsorbents) that could be added to waste streams and tailored barriers for removal and/or immobilization of dissolved iodine [*e.g.*, see Zhang *et al.* (2000), Balsley *et al.* (1997), Gu and Dowlen (1997), and others]. High sorption of technetium is typically observed for minerals, such as sulfide minerals (*e.g.*, chalcopyrite, pyrite), that have the capacity to reduce Tc(VII) to Tc(IV). For example, Strickert *et al.* (1980) measured K_d values in the range 100 to 2,000 ml/g for sorption of technetium on sulfide minerals such as bournonite, chalcopyrite, pyrite, tennantite, and tetrahedrite. Technetium K_d values were however less than 1 ml/g for non-sulfide materials, such as anhydrite, basalt, granite, and tuff. Sorption studies for technetium on single mineral phases and the references they cite may be useful to the reader. Some of these studies are listed in Tables I.1a and I.1b.

1.2 K_d Studies of Technetium on Crushed Rock Materials

Numerous studies have been conducted for the sorption of technetium on crushed rock as part of national research programs to investigate the feasibility of geological disposal of high-level radioactive waste (HLW). Some of these studies are listed in Table I.2.

Table I.1 Technetium adsorption studies on pure mineral and oxide phases.

| Mineral/Oxide | References |
|------------------|---|
| Almandine | Bock <i>et al.</i> (1989) |
| Anhydrite | Strickert <i>et al.</i> (1980) |
| Apatite | Strickert <i>et al.</i> (1980) |
| Augite | Palmer and Meyer (1981) |
| Bentonite | Baston <i>et al.</i> (1995) |
| Biotite | Ticknor <i>et al.</i> (1996), Amaya <i>et al.</i> (1995), Meyer <i>et al.</i> (1983), Palmer and Meyer (1981) |
| Bornite | Strickert <i>et al.</i> (1980) |
| Bournonite | Strickert <i>et al.</i> (1980) |
| Chalcopyrite | Huie <i>et al.</i> (1988), Strickert <i>et al.</i> (1980) |
| Chrysocolla | Strickert <i>et al.</i> (1980) |
| Dolomite | Strickert <i>et al.</i> (1980) |
| Enargite | Strickert <i>et al.</i> (1980) |
| Fe(II) Silicates | Bock <i>et al.</i> (1989) |
| Ferrihydrite | Walton <i>et al.</i> (1986) |
| Galena | Bock <i>et al.</i> (1989), Huie <i>et al.</i> (1988), Meyer <i>et al.</i> (1983), Palmer and Meyer (1981), Strickert <i>et al.</i> (1980) |
| Goethite | Ticknor <i>et al.</i> (1996), Walton <i>et al.</i> (1986), Meyer <i>et al.</i> (1984) |
| Hematite | Huie <i>et al.</i> (1988), Haines <i>et al.</i> (1987), Walton <i>et al.</i> (1986), Meyer <i>et al.</i> (1984, 1985a). Palmer and Meyer (1981) |
| Hornblende | Palmer and Meyer (1981) |
| Hypersthene | Bock <i>et al.</i> (1989) |
| Ilmenite | Bock <i>et al.</i> (1989), Meyer <i>et al.</i> (1984, 1985a), Palmer and Meyer (1981) |
| Limonite | Meyer <i>et al.</i> (1984), Palmer and Meyer (1981) |

Continuation of Table I.1.

| Mineral/Oxide | References |
|--------------------------|---|
| Löllingite (Loellingite) | Bock <i>et al.</i> (1989) |
| Magnetite | Byegård <i>et al.</i> (1992), Bock <i>et al.</i> (1989), Lieser and Bauscher (1988), Haines <i>et al.</i> (1987), Meyer <i>et al.</i> (1984), Palmer and Meyer (1981) |
| Microcline | Meyer <i>et al.</i> (1984, 1985a) |
| Molybdenite | Huie <i>et al.</i> (1988) |
| Montmorillonite | Ticknor <i>et al.</i> (1996) |
| Mordenite | Meyer <i>et al.</i> (1985a) |
| Olivine | Bock <i>et al.</i> (1989), Palmer and Meyer (1981) |
| Plagioclase | Amaya <i>et al.</i> (1995) |
| Potassium Feldspar | Amaya <i>et al.</i> (1995) |
| Pyrite | Bock <i>et al.</i> (1989), Lieser and Bauscher (1988), Huie <i>et al.</i> (1988), Meyer <i>et al.</i> (1983), Palmer and Meyer (1981), Strickert <i>et al.</i> (1980) |
| Pyrrhotite | Bock <i>et al.</i> (1989), Lieser and Bauscher (1988) |
| Quartz | Ticknor <i>et al.</i> (1996), Amaya <i>et al.</i> (1995), Winkler <i>et al.</i> (1988) |
| Smectite | Winkler <i>et al.</i> (1988) |
| Stibnite | Zhuang <i>et al.</i> (1995), Bock <i>et al.</i> (1989), Huie <i>et al.</i> (1988) |
| Tennantite | Strickert <i>et al.</i> (1980) |
| Tetrahedrite | Strickert <i>et al.</i> (1980) |
| Tiemannite | Zhuang <i>et al.</i> (1995) |
| Witherite | Strickert <i>et al.</i> (1980) |

Table I.2 Technetium adsorption studies on crushed rock and related materials.

| Geologic Material | References |
|--|--|
| Alluvium | Erdal <i>et al.</i> (1979) |
| Argillite | Erdal <i>et al.</i> (1979) |
| Basalt | Wood <i>et al.</i> (1987), Meyer <i>et al.</i> (1984, 1985), Barney <i>et al.</i> (1983), Palmer and Meyer (1981), Salter <i>et al.</i> (1981a), Ames <i>et al.</i> (1981), Strickert <i>et al.</i> (1980), Ames and McGarrah (1980) |
| Basalt secondary mineral assemblage from vesicles, vugs, and fractures | Salter <i>et al.</i> (1981b) |
| Chalk | Strickert <i>et al.</i> (1980) |
| Gabbro | Vandergraaf <i>et al.</i> (1984) |
| Granite | Ticknor <i>et al.</i> (1996), Amaya <i>et al.</i> (1995), Eriksen and Cui (1991), Vandergraaf <i>et al.</i> (1984), Strickert <i>et al.</i> (1980), Allard <i>et al.</i> (1979a, 1979b) |
| Granodiorite | Baston <i>et al.</i> (1995) |
| Limestone | Strickert <i>et al.</i> (1980) |
| Sandstone | Bradbury and Stephen (1985), Barney (1982) |
| Shale | Ho (1992), Strickert <i>et al.</i> (1980) |
| Siltstone | Strickert <i>et al.</i> (1980) |
| Tuff | Amaya <i>et al.</i> (1995), Baston <i>et al.</i> (1995), Barney (1982), Strickert <i>et al.</i> (1980), Erdal <i>et al.</i> (1979) |