



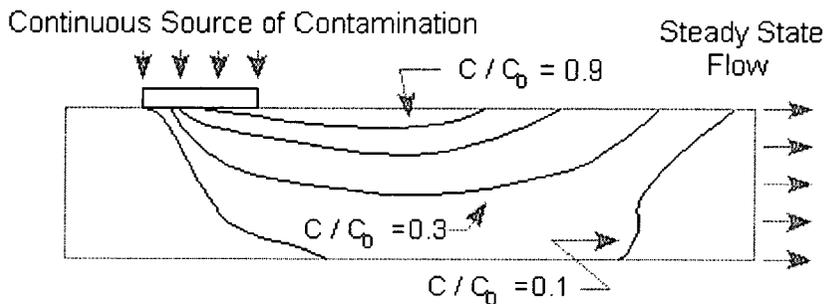
UNDERSTANDING VARIATION IN PARTITION COEFFICIENT, K_d , VALUES



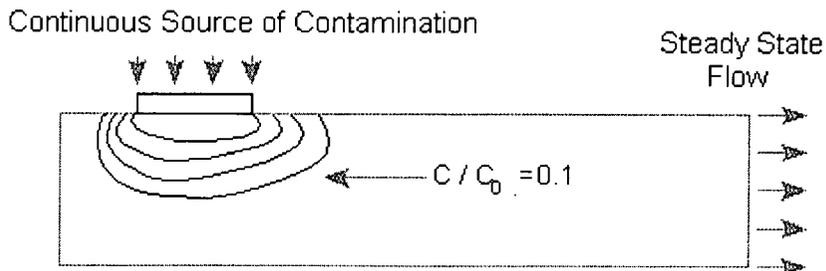
Volume II:

Review of Geochemistry and Available K_d Values for Cadmium, Cesium, Chromium, Lead, Plutonium, Radon, Strontium, Thorium, Tritium (^3H), and Uranium

Case I: $K_d = 1 \text{ ml/g}$



Case II: $K_d = 10 \text{ ml/g}$



1/14

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for Cadmium, Cesium, Chromium, Lead, Plutonium,
Radon, Strontium, Thorium, Tritium (^3H), and Uranium**

August 1999

A Cooperative Effort By:

**Office of Radiation and Indoor Air
Office of Solid Waste and Emergency Response
U.S. Environmental Protection Agency
Washington, DC 20460**

**Office of Environmental Restoration
U.S. Department of Energy
Washington, DC 20585**

NOTICE

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FOREWORD

Understanding the long-term behavior of contaminants in the subsurface is becoming increasingly more 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 two-volume report 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. 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 this two-volume document include: chromium, cadmium, cesium, lead, plutonium, radon, strontium, thorium, tritium (^3H), and uranium. This two-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 absolute 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, Volume II of this document: (1) provides a "thumb-nail sketch" of the key geochemical processes affecting the sorption of the selected contaminants; (2) provides references to related key experimental and review articles for further reading; (3) identifies the important aqueous- and solid-phase parameters controlling the sorption of these contaminants in the subsurface environment under oxidizing conditions; and (4) identifies, when possible, minimum and maximum conservative partition coefficient values for each contaminant as a function of the key geochemical processes affecting their sorption.

This publication is the result of a cooperative effort between the EPA Office of Radiation and Indoor Air, Office of Solid Waste and Emergency Response, and the Department of Energy Office of Environmental Restoration (EM-40). 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.

Stephen D. Page, Director
Office of Radiation and Indoor Air

ACKNOWLEDGMENTS

Ronald G. Wilhelm from ORIA's Center for Remediation Technology and Tools was the project lead and EPA Project Officer for this two-volume report. Paul Beam, Environmental Restoration Program (EM-40), was the project lead and sponsor for the Department of Energy (DOE). Project support was provided by both DOE/EM-40 and EPA's Office of Remedial and Emergency Response (OERR).

EPA/ORIA wishes to thank the following people for their assistance and technical review comments on various drafts of this report:

Patrick V. Brady, U.S. DOE, Sandia National Laboratories
David S. Brown, U.S. EPA, National Exposure Research Laboratory
Joe Eidelberg, U.S. EPA, Region 9
Amy Gamerdinger, Washington State University
Richard Graham, U.S. EPA, Region 8
John Griggs, U.S. EPA, National Air and Radiation Environmental Laboratory
David M. Kargbo, U.S. EPA, Region 3
Ralph Ludwig, U.S. EPA, National Risk Management Research Laboratory
Irma McKnight, U.S. EPA, Office of Radiation and Indoor Air
William N. O'Steen, U.S. EPA, Region 4
David J. Reisman, U.S. EPA, National Risk Management Research Laboratory
Kyle Rogers, U.S. EPA, Region 5
Joe R. Williams, U.S. EPA, National Risk Management Research Laboratory
OSWER Regional Groundwater Forum Members

In addition, special acknowledgment goes to Carey A. Johnston from ORIA's Center for Remediation Technology and Tools for his contributions in the development, production, and review of this document.

Principal authorship in production of this guide was provided by the Department of Energy's Pacific Northwest National Laboratory (PNNL) under the Interagency Agreement Number DW89937220-01-03. Lynnette Downing served as the Department of Energy's Project Officer for this Interagency Agreement. PNNL authors involved in this project include:

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ABSTRACT

This two-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. Volume I discusses the technical issues associated with the measurement of K_d values and its use in formulating the retardation factor, R_f . The K_d concept and methods for measurement of K_d values are discussed in detail in Volume I. 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 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 presented. The capabilities of EPA's geochemical reaction model MINTEQA2 and its different conceptual adsorption models are also reviewed. Volume II provides a "thumb-nail sketch" of the key geochemical processes affecting the sorption of selected inorganic contaminants, and a summary of K_d values given in the literature for these contaminants under oxidizing conditions. The contaminants chosen for the first phase of this project include chromium, cadmium, cesium, lead, plutonium, radon, strontium, thorium, tritium (^3H), and uranium. Important aqueous speciation, (co)precipitation/dissolution, and adsorption reactions are discussed for each contaminant. References to related key experimental and review articles for further reading are also listed.

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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_d) 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 two-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 of this volume noted, " K_d 's are the coin of the realm in this business." For better or worse, the K_d model is 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 Volume II. 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.

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.

The K_d parameter is very important in estimating the potential for the adsorption of dissolved contaminants in contact with soil. 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 errors 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 conservatism into their calculations by selecting limiting or bounding conservative K_d values. For example, the most conservative (*i.e.*, maximum) estimate from the perspective of off-site risks due to contaminant migration through the 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. Due to groundwater flow paths, site characteristics, or environmental uncertainties, 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. For those situations that are sensitive to the selected K_d value, site-specific K_d values are essential.

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. These methods include the batch laboratory method, the column laboratory method, field-batch method, field modeling method, and K_{oc} method. The summary identifies what the 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 and briefly described in Chapter 4 of Volume II. 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 is 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 Volume II 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 include cadmium, cesium, chromium, lead, plutonium, radon, strontium, thorium, tritium (^3H), and uranium. The selection of these contaminants by EPA and PNNL project staff was based on 2 criteria. First, the contaminant had to be of high priority to the 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 - cadmium, cesium, plutonium, strontium, thorium, and uranium(VI).
- ☐ Anions - chromium(VI) (as chromate) and uranium(VI).
- ☐ Radionuclides - cesium, plutonium, radon, strontium, thorium, tritium (^3H), and uranium.
- ☐ Conservatively transported contaminants - tritium (^3H) and radon.
- ☐ Nonconservatively transported contaminants - other than tritium (^3H) and radon.
- ☐ Redox sensitive elements - chromium, plutonium, 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 3 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. 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

$$K_d = \frac{\text{Mass of Adsorbate Sorbed}}{\text{Mass of Adsorbate in Solution}} = \frac{A_i}{C_i} \quad (2.1)$$

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,

$$R_f = v_p/v_c \quad (2.2)$$

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 2.8). 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

$$R_f = 1 + (p_b/n_c)K_d \quad (2.3)$$

where p_b = porous media bulk density (mass/length³)
 n_c = 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 use in 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 1 sorbate (contaminant) and 1 sorbent (soil), and (6) all adsorption sites are accessible and have equal strength. The last point is especially limiting for groundwater contaminant models because it requires that K_d values should be used only to predict transport in systems chemically identical to those used in the laboratory measurement of 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) 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 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 is presented in Volume I primarily to provide a paradigm for sorption processes.

3.0 Methods, Issues, and Criteria for Measuring K_d Values

There are 5 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. These methods and the associated technical issues are described in detail in Chapter 3 of Volume I. 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. The 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. The primary advantage of the 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).

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 1 mechanism of adsorption or desorption over another cannot be predicted *a priori* and therefore generalizing the results from 1 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.

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 organic compounds. 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. One key drawback to this technique is that it is very model dependent. Because the calculated K_d value are model dependent and highly site specific, the K_d values must 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 include: using simple versus complex systems to measure K_d values, field variability, the "gravel issue," and the "colloid issue." 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 1 or 2 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. 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 <1 percent of the soil volume but is the most chemically reactive fraction, would 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 has a $K_d = 0$ ml/g. Although this assumption is incorrect (i.e., 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 in the smaller fraction are similar to those that occur in the larger fraction.

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 appreciable different K_d values. Examples are presented in this volume.

Contaminant transport models generally treat the subsurface environment as a 2-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 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 2 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. Secondly, it is difficult to unambiguously delineate between the contaminants in the mobile-aqueous and mobile-solid phases.

Often K_d values used in transport models are selected to provide a conservative estimate of contaminant migration or health effects. However, the same K_d value would not provide a conservative estimate for clean-up calculations. 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.

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 6 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.

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.

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.

The MINTEQA2 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.

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 [chromium, cadmium, cesium, tritium (^3H), lead, plutonium, radon, strontium, thorium, and uranium], the MINTEQA2 thermodynamic database contains speciation and solubility reactions for chromium, including the valence states Cr(II), Cr(III), and Cr(VI); cadmium; lead; strontium; and uranium, including the valence states U(III), U(IV), U(V), and U(VI). Some of the thermodynamic data in the EPA version have been superseded in other users' databases by more recently published data.

The MINTEQA2 code includes 7 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 7 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. The user however 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 several waste disposal issues. The EPA in its "Soil Screening Guidance" determined MINTEQA2-estimated K_d values for barium, beryllium, cadmium, Cr(III), 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.

Chemical reaction models can be used, however, to support evaluations of K_d values and related contaminant migration and risk assessment modeling predictions. Chemical reaction codes can be used to calculate aqueous complexation to determine the ionic state and composition of the dominant 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. Chemical reaction models can be used to predict bounding, 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. Chemical reaction models can also be used to analyze initial and final geochemical conditions associated with laboratory K_d measurements to determine if the measurement had been affected by processes such as mineral precipitation which might have compromised the derived K_d values. Although chemical reaction models cannot be used to predict K_d values, they 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.

5.0 Contaminant Geochemistry and K_d Values

The important geochemical factors affecting the sorption¹ of cadmium (Cd), cesium (Cs), chromium (Cr), lead (Pb), plutonium (Pu), radon (Rn), strontium (Sr), thorium (Th), tritium (³H), and uranium (U) 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) identify, when possible, minimum and maximum conservative K_d values for each contaminant as a function key geochemical processes affecting their sorption.

5.1 General

Important chemical speciation, (co)precipitation/dissolution, and adsorption/desorption processes of 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 2 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 MINTQA2 (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 convenience as a proxy for the composition of a shallow groundwater. Obviously, there are significant differences between surface waters and groundwaters, and considerable variability in the concentrations of various constituents in surface and groundwaters. For example, the concentrations of

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 3-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 .

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 groundwaters, especially deep groundwaters, 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, 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, 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 materials. The species distributions of thorium and uranium were also modeled using pure water, free of any ligands other than hydroxyl ions, to show the effects of hydrolysis in the absence of other complexation reactions. The concentrations used for the dissolved contaminants in the species distribution calculations are presented in Table 5.2 and are further discussed in the following sections. The species distributions of cesium, radon, and tritium were not determined because only 1 aqueous species is likely to exist under the environmental conditions under consideration; namely, cesium would exist as Cs^+ , radon as $Rn^0(gas)$, and tritium as tritiated water, HTO (T = tritium, 3H).

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, the variables had include parameters that were readily available to modelers. For instance, particle size and pH are often available to modelers whereas such parameters as 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).¹

Dissolved Constituent	Total Concentration	
	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 micro g/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.

Table 5.2. Concentrations of contaminants used in the aqueous species distribution calculations.

Element	Total Conc. (micro g/l)	Reference for Concentration of Contaminant Used in Aqueous Speciation Calculations
Cd	1.0	Hem (1985, p. 142) lists this value as a median concentration of dissolved cadmium based on the reconnaissance study of Duram <i>et al.</i> (1971) of metal concentrations in surface waters in the United States.
Cs	--	Distribution of aqueous species was not modeled, because mobility of dissolved cesium is not significantly affected by complexation (see Section 5.3).
Cr	1.4	Hem (1985, p. 138) lists this value as an average concentration estimated by Kharkar <i>et al.</i> (1968) for chromium in river waters.
Pb	1.0	Hem (1985, p. 144) lists this value as an average concentration estimated by Duram <i>et al.</i> (1971) for lead in surface-water samples from north- and southeastern sections of the United States.
Pu	3.2×10^{-7}	This concentration is based on the maximum activity of $^{239,240}\text{Pu}$ measured by Simpson <i>et al.</i> (1984) in 33 water samples taken from the highly alkaline Mono Lake in California.
Rn	--	Aqueous speciation was not calculated, because radon migrates as a dissolved gas and is not affected by complexation (see Section 5.7).
Sr	110	Hem (1985, p. 135) lists this value as the median concentration of strontium for larger United States public water supplies based on analyses reported by Skougstad and Horr (1963).
Th	1.0	Hem (1985, p. 150) gives 0.01 to 1 micro g/l as the range expected for thorium concentrations in fresh waters.
^3H	--	Aqueous speciation was not calculated, because tritium (^3H) migrates as tritiated water.
U	0.1 and 1,000	Because dissolved hexavalent uranium can exist as polynuclear hydroxyl complexes, the hydrolysis of uranium under oxic conditions is therefore dependent on the concentration of total dissolved uranium. To demonstrate this aspect of uranium chemistry, 2 concentrations (0.1 and 1,000 micro g/l) of total dissolved uranium were used to model the species distributions. Hem (1985, p. 148) gives 0.1 to 10 microg/l as the range for dissolved uranium in most natural waters. For waters associated with uranium ore deposits, Hem states that the uranium concentrations may be greater than 1,000 microg/l.

5.2 Cadmium Geochemistry and K_d Values

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

The dominant cadmium aqueous species in groundwater at pH values less than 8.2 and containing moderate to low concentrations of sulfate ($<10^{-2.5}$ M SO_4^{2-}) is the uncomplexed Cd^{2+} species. The dominant cadmium solution species in groundwater at pH values greater than 8.2 are CdCO_3^0 (aq) and to a smaller extent CdCl^+ . Both precipitation/coprecipitation/dissolution and adsorption/desorption reactions control cadmium concentrations. Several researchers report that otavite (CdCO_3) limits cadmium solution concentrations in alkaline soils. The solid $\text{Cd}_3(\text{PO}_4)_2$ has also been reported to be a solubility-controlling solid for dissolved cadmium. Under low redox conditions, sulfide concentrations and the formation of CDs precipitates may play an important role in controlling the concentrations of dissolved cadmium. At high concentrations of dissolved cadmium ($>10^{-7}$ M Cd), either cation exchange or (co)precipitation are likely to control dissolved cadmium concentrations. Precipitation with carbonate is increasingly important in systems with a pH greater than 8, and cation exchange is more important in lower pH systems. At lower environmental concentrations of dissolved cadmium, surface complexation with calcite and aluminum- and iron-oxide minerals may be the primary process influencing retardation. Transition metals (*e.g.*, copper, lead, zinc) and alkaline earth (*e.g.*, calcium, magnesium) cations reduce cadmium adsorption by competition for available specific adsorption and cation exchange sites. In conclusion, the key aqueous- and solid-phase parameters influencing cadmium adsorption include pH, cadmium concentration, competing cation concentrations, redox, cation exchange capacity (CEC), and mineral oxide concentrations.

5.2.2 General Geochemistry

Cadmium (Cd) exists in the +2 oxidation state in nature. It forms a number of aqueous complexes, especially with dissolved carbonate. Its concentration may be controlled by either adsorption or precipitation/coprecipitation processes. The extent to which cadmium is associated with or bound to soils varies greatly with type of mineral, oxidation state of the system, and presence of competing cations in solution.

Cadmium concentrations in uncontaminated soils is typically less than 1 mg/kg. However, concentrations may be significantly elevated by some human activities or by the weathering of parent materials with high cadmium concentrations, *e.g.*, black shales (Jackson and Alloway, 1992). Approximately 90 percent of all the cadmium consumed goes into 4 use categories: plating (35 percent), pigments (25 percent), plastic stabilizers (15 percent), and batteries (15 percent) (Nriagu, 1980b). Cadmium may also be introduced into the environment by land applications of sewage sludge. Cadmium concentrations in sewage sludge are commonly the limiting factor controlling land disposal (Juste and Mench, 1992). Nriagu (1980a) has edited an excellent review on the geochemistry and toxicity of cadmium.

5.2.3 Aqueous Speciation

Cadmium forms soluble complexes with inorganic and organic ligands resulting in an increase of cadmium mobility in soils (McLean and Bledsoe, 1992). The distribution of cadmium aqueous species was calculated using the water composition described in Table 5.1 and a concentration of 1 micro g/l total dissolved cadmium (Table 5.2). Hem (1985, p. 142) lists this value as a median concentration of dissolved cadmium based on the reconnaissance study of Duram *et al.* (1971) of metal concentrations in surface waters in the United States. These MINTEQA2 calculations indicate that cadmium speciation is relatively simple. In groundwaters of pH values less than 6, essentially all of the dissolved cadmium is expected to exist as the uncomplexed Cd^{2+} ion (Figure 5.1). The aqueous species included in the MINTEQA2 calculations are listed in Table 5.3. As the pH increases between 6 and 8.2, cadmium carbonate species [CdHCO_3^+ and $\text{CdCO}_3^0(\text{aq})$] become increasingly important. At pH values between 8.2 and 10, essentially all of the cadmium in solution is expected to exist as the neutral complex $\text{CdCO}_3^0(\text{aq})$. The species $\text{CdSO}_4^0(\text{aq})$, CdHCO_3^+ , CdCl^+ , and CdOH^+ are also present, but at much lower concentrations. The species distribution illustrated in Figure 5.1 does not change if the concentration of total dissolved cadmium is increased from 1 to 1,000 micro g/l.

Table 5.3. Cadmium aqueous species included in the speciation calculations.

Aqueous Species
Cd^{2+}
CdOH^+ , $\text{Cd}(\text{OH})_2^0(\text{aq})$, $\text{Cd}(\text{OH})_3^-$, $\text{Cd}(\text{OH})_4^{2-}$, $\text{Cd}_2\text{OH}^{3+}$
CdHCO_3^+ , $\text{CdCO}_3^0(\text{aq})$, $\text{Cd}(\text{CO}_3)_3^{4-}$
$\text{CdSO}_4^0(\text{aq})$, $\text{Cd}(\text{SO}_4)_2^{2-}$
CdNO_3^+
CdCl^+ , $\text{CdCl}_2^0(\text{aq})$, CdCl_3^- , $\text{CdOHCl}^0(\text{aq})$
CdF^+ , $\text{CdF}_2^0(\text{aq})$

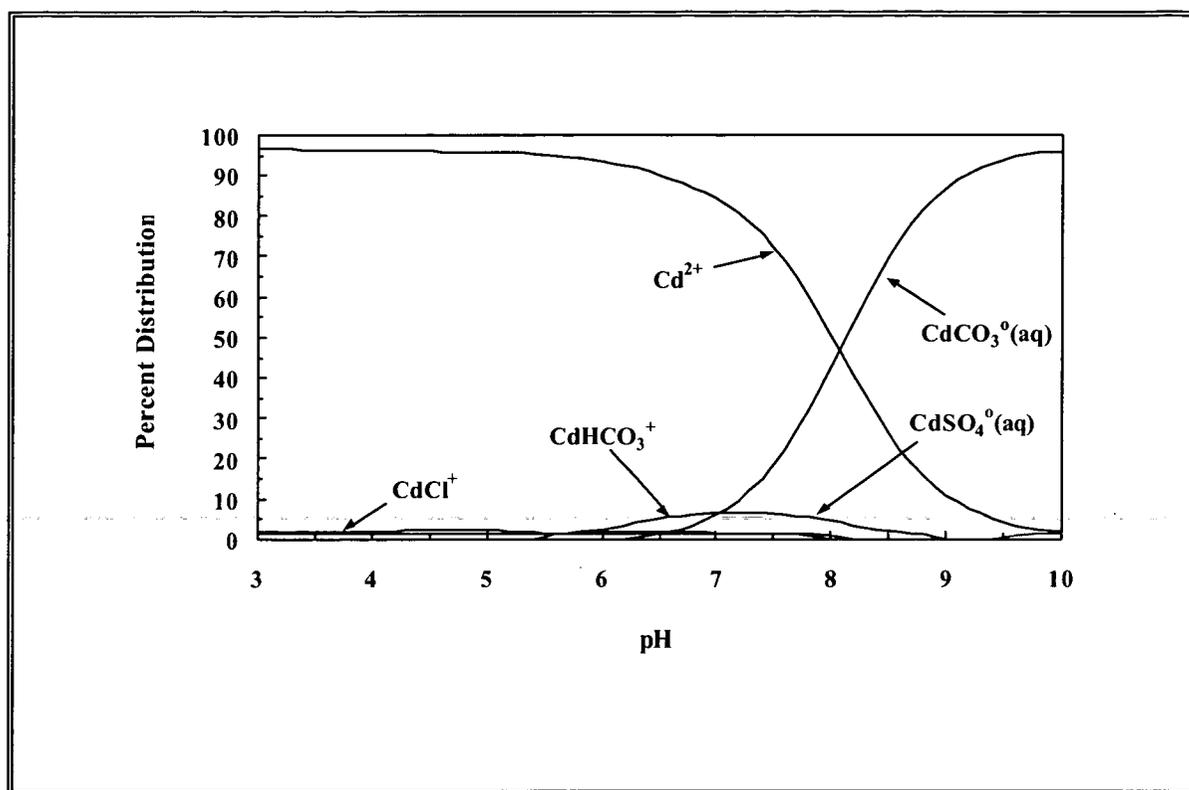


Figure 5.1. Calculated distribution of cadmium aqueous species as a function of pH for the water composition in Table 5.1. [The species distribution is based on a concentration of 1 micro g/l total dissolved cadmium and thermodynamic data supplied with the MINTEQA2 geochemical code.]

Information available in the literature regarding interactions between dissolved cadmium and naturally occurring organic ligands (humic and fulvic acids) is ambiguous. Weber and Posselt (1974) reported that cadmium can form stable complexes with naturally occurring organics, whereas Hem (1972) stated that the amount of cadmium occurring in organic complexes is generally small and that these complexes are relatively weak. Pittwell (1974) reported that cadmium is complexed by organic carbon under all pH conditions encountered in normal natural waters. Levi-Minzi *et al.* (1976) found cadmium adsorption in soils to be correlated with soil organic matter content. In a critical review of the literature, Giesy (1980) concluded that the complexation constants of cadmium to naturally occurring organic matter are weak because of competition for binding sites by calcium, which is generally present in much higher concentrations.

5.2.4 Dissolution/Precipitation/Coprecipitation

Lindsay (1979) calculated the relative stability of cadmium compounds. His calculations show that at pH values less than 7.5, most cadmium minerals are more soluble than cadmium concentrations found in oxic soils (10^{-7} M), indicating that cadmium at these concentrations is not likely to precipitate. At pH levels greater than 7.5, the solubilities of $\text{Cd}_3(\text{PO}_4)_2$ or CdCO_3 may control the concentrations of cadmium in soils. Cavallaro and McBride (1978) and McBride (1980) demonstrated that otavite, CdCO_3 , precipitates in calcareous soils ($\text{pH} > 7.8$), whereas in neutral or acidic soils, adsorption is the predominate process for removal of cadmium from solution. Jenne *et al.* (1980), working with the waters associated with abandoned lead and zinc mines and tailings piles, also indicate that the upper limits on dissolved levels of cadmium in most waters were controlled by CdCO_3 . Santillan-Medrano and Jurinak (1975) observed that the activity of dissolved cadmium in cadmium-amended soils was lowest in calcareous soils. Baes and Mesmer (1976) suggested that cadmium may coprecipitate with calcium to form carbonate solid solutions, $(\text{Ca,Cd})\text{CO}_3$. This may be an important mechanism in controlling cadmium concentrations in calcareous soils.

Although cadmium itself is not sensitive to oxidation/reduction conditions, its concentration in the dissolved phase is generally very sensitive to redox state. There are numerous studies (reviewed by Khalid, 1980) showing that the concentrations of dissolved cadmium greatly increase when reduced systems are oxidized, such as when dredged river sediments are land filled or rice paddies are drained. The following 2 mechanisms appear to be responsible for this increase in dissolved cadmium concentrations: (1) very insoluble CDs (greenockite) dissolves as sulfide [S(II)] that is oxidized to sulfate [S(VI)], and (2) organic materials binding cadmium are decomposed through oxidization, releasing cadmium into the environment (Gambrell *et al.*, 1977; Giesy, 1980). This latter mechanism appears to be important only in environments in which moderate to high organic matter concentrations are present (Gambrell *et al.*, 1977). Serne (1977) studied the effect of oxidized and reduced sediment conditions on the release of cadmium from dredged sediments collected from the San Francisco Bay. Greater than 90 percent of the cadmium in the reduced sediment [sediment incubated in the presence of low O_2 levels ($\text{Eh} < 100$ mV)] was complexed with insoluble organic matter or precipitated as sulfides. The remainder of the cadmium was associated with the oxide minerals, clay lattices, or exchangeable sites. Dissolved cadmium concentrations greatly increased when the sediments were incubated under oxidizing conditions ($\text{Eh} > 350$ mV). Cadmium concentrations released in the elutriate increased with agitation time. These data suggested that this kinetic effect was due to slow oxidation of sulfide or cadmium bound to organic matter bound in the reduced sediment prior to steady state equilibrium conditions being reached. In a similar type of experiment in which Mississippi sediments were slowly oxidized, Gambrell *et al.* (1977) reported that the insoluble organic- and sulfide-bound cadmium fractions in sediment decreased dramatically (decreased > 90 percent) while the exchangeable and water-soluble cadmium fractions increased. Apparently, once the cadmium was released from the sulfide and organic matter fractions, the cadmium entered the aqueous phase and then re-adsorbed onto other sediment phases.

A third mechanism involves pyrite that may be present in soils or sediments and gets oxidized when exposed to air.¹ The pyrite oxidizes to form FeSO_4 , which generates high amounts of acidity when reacted with water. The decrease in the pH results in the dissolution of cadmium minerals and increase in the dissolved concentration of cadmium. This process is consistent with the study by Kargbo (1993) of acid sulfate clays used as waste covers.

5.2.5 Sorption/Desorption

At high solution concentrations of cadmium (>10 mg/l), the adsorption of cadmium often correlates with the CEC of the soil (John, 1971; Levi-Minzi *et al.*, 1976; McBride *et al.*, 1981; Navrot *et al.*, 1978; Petruzelli *et al.*, 1978). During cation exchange, cadmium generally exchanges with adsorbed calcium and magnesium (McBride *et al.*, 1982). The ionic radius of Cd^{2+} is comparable to that of Ca^{2+} and, to a lesser extent, Mg^{2+} . At low solution concentrations of cadmium, surface complexation to calcite (McBride, 1980) and hydrous oxides of aluminum and iron (Benjamin and Leckie, 1981) may be the most important adsorption mechanism. Both Cd^{2+} and possibly CdOH^+ may adsorb to aluminum- and iron-oxide minerals (Balistrieri and Murray, 1981; Davis and Leckie, 1978).

As with other cationic metals, cadmium adsorption exhibits pH dependency. The effect of pH on cadmium adsorption by soils (Huang *et al.*, 1977), sediment (Reid and McDuffie, 1981), and iron oxides (Balistrieri and Murray, 1982; Levy and Francis, 1976) is influenced by the solution concentration of cadmium and the presence of competing cations or complexing ligands. At low cadmium solution concentrations, sharp adsorption edges (the range of pH where solute adsorption goes from ~ 0 to ~ 100 percent) suggests that specific adsorption (*i.e.*, surface complexation via a strong bond to the mineral surface) occurs. Under comparable experimental conditions, the adsorption edge falls at pH values higher than those for lead, chromium, and zinc. Thus, in lower pH environments, these metals, based on their propensity to adsorb, would rank as follows: $\text{Pb} > \text{Cr} > \text{Zn} > \text{Cd}$. This order is inversely related to the pH at which hydrolysis of these metals occurs (Benjamin and Leckie, 1981).

Competition between cations for adsorption sites strongly influences the adsorption behavior of cadmium. The presence of calcium, magnesium, and trace metal cations reduce cadmium adsorption by soils (Cavallaro and McBride, 1978; Singh, 1979), iron oxides (Balistrieri and Murray, 1982), manganese oxides (Gadde and Laitinen, 1974), and aluminum oxides (Benjamin and Leckie, 1980). The extent of competition between cadmium and other ions depends on the relative energies of interaction between the ions and the adsorbing surface, the concentrations of the competing ions, and solution pH (Benjamin and Leckie, 1981; Sposito, 1984). The addition of copper or lead, which are more strongly adsorbed, slightly reduces cadmium adsorption by iron and aluminum oxides, suggesting that copper and lead are preferentially adsorbed by different surface sites (Benjamin and Leckie,

¹ D. M. Kargbo (1998, personal communication).

1980). In contrast, zinc almost completely displaces cadmium, indicating that cadmium and zinc compete for the same group of binding sites (Benjamin and Leckie, 1981).

Although organic matter may influence adsorption of cadmium by soils (John, 1971; Levi-Minzi *et al.*, 1976), this effect is probably due to the CEC of the organic material rather than to complexation by organic ligands (Singh and Sekhon, 1977). In fact, removal of organic material from soils does not markedly reduce cadmium adsorption and may enhance adsorption (Petruzelli *et al.*, 1978). Clay minerals with adsorbed humic acids (organo-clay complexes) do not adsorb cadmium in excess of that expected for clay minerals alone (Levy and Francis, 1976).

5.2.6 Partition Coefficient, K_d , Values

5.2.6.1 General Availability of K_d Data

A total of 174 cadmium K_d values were found in the literature and included in the data base used to create the look-up tables.¹ The cadmium K_d values as well as the ancillary experimental data are presented in Appendix C. Data included in this table were from studies that reported K_d values (not percent adsorption or Langmuir constants) and were conducted in systems consisting of natural soils (as opposed to pure mineral phases), low ionic strength (< 0.1 M), pH values between 4 and 10, low humic material concentrations (<5 mg/l), and no organic chelates (*e.g.*, EDTA). At the start of the literature search, attempts were made to identify cadmium K_d studies that reported ancillary data on aluminum/iron-oxide concentrations, calcium and magnesium solution concentrations, CEC, clay content,² pH, redox status, organic matter concentrations and sulfide concentrations. Upon reviewing the data and determining the availability of cadmium K_d studies reporting ancillary data, we selected data on clay content, pH, CEC, and total organic carbon. The selection of these parameters was based on availability of data and the possibility that the parameter may impact cadmium K_d values. Of the 174 cadmium K_d values included in the compiled data, only 62 values had associated clay content data, 174 values had associated pH data, 22 values had associated CEC data, 63 values had total organic carbon data, and 16 had associated aluminum/iron-oxide data. Descriptive statistics and a correlation coefficient matrix are presented in Appendix C.

¹ Since the completion of our review and analysis of K_d data for the selected contaminants and radionuclides, the study by Wang *et al.* (1998) was identified and may be of interest to the reader.

² Unless specified otherwise, "clay content" refers to the particle size fraction of soil that is less than 2 micro m.

5.2.6.2 Look-Up Tables

One cadmium K_d look-up table was created. The table requires knowledge of the pH of the system (Table 5.4). The pH was selected as the key independent variable because it had a highly significant ($P < 0.001$) correlation with cadmium K_d , a correlation coefficient value of 0.75. A detailed explanation of the approach used in selecting the K_d values used in the table is presented in Appendix C. Briefly, it involved conducting a regression analysis between pH and K_d values). The subsequent regression equation was used to provide central estimates. Minimum and maximum values were estimated by plotting the data and estimating where the limits of the data existed.

There is an unusually wide range of possible cadmium K_d values for each of the 3 pH categories. The cause for this is likely that there are several other soil parameters influencing the K_d in addition to pH. Unfortunately, the correlations between the cadmium K_d values and the other soil parameters in this data set were not significant (Appendix C).

5.2.6.2.1 Limits of K_d Values With Respect to Aluminum/Iron-Oxide Concentrations

The effect of iron-oxide concentrations on cadmium K_d values was evaluated using the data presented in Appendix C. Of the 174 cadmium K_d values in the data set presented in Appendix C, only 16 values had associated iron oxide concentration data. In each case iron, and not aluminum, oxide concentration data were measured. The correlation coefficient describing the linear relationship between cadmium K_d values and iron oxide concentration was 0.18, which is nonsignificant at the 5 percent level of probability. It was anticipated that there would be a positive correlation between iron or aluminum oxide concentrations and cadmium K_d values because oxide minerals provide adsorption (surface complexation) sites.

Table 5.4. Estimated range of K_d values for cadmium as a function of pH.
[Tabulated values pertain to systems consisting of natural soils (as opposed to pure mineral phases), low ionic strength (< 0.1 M), low humic material concentrations (< 5 mg/l), no organic chelates (e.g., EDTA), and oxidizing conditions.]

K_d (ml/g)	pH		
	3 - 5	5 - 8	8 - 10
Minimum	1	8	50
Maximum	130	4,000	12,600

5.2.6.2.2 Limits of K_d Values with Respect to CEC

The effect of CEC on cadmium K_d values was evaluated using the data presented in Appendix C. Of the 174 cadmium K_d values in the data set presented in Appendix C, only 22 values had associated CEC data. The correlation coefficient describing the linear relationship between cadmium K_d values and CEC was 0.40, which is nonsignificant at the 5 percent level of probability. It was anticipated that there would be a positive correlation between CEC and cadmium K_d values because cadmium can adsorb to minerals via cation exchange.

5.2.6.2.3 Limits of K_d Values with Respect to Clay Content

The effect of clay content on cadmium K_d values was evaluated using the data presented in Appendix C. Of the 174 cadmium K_d values in the data set presented in Appendix C, 64 values had associated clay content data. The correlation coefficient describing the linear relationship between cadmium K_d values and clay content was -0.04, which is nonsignificant at the 5 percent level of probability. It was anticipated that there would be a positive correlation between clay content and cadmium K_d values, because clay content is often highly correlated to CEC, which in turn may be correlated to the number of sites available for cadmium adsorption.

5.2.6.2.4 Limits of K_d Values with Respect to Concentration of Organic Matter

The effect of organic matter concentration, as approximated by total organic carbon, on cadmium K_d values was evaluated using the data presented in Appendix C. Of the 174 cadmium K_d values in the data set presented in Appendix C, 63 values had associated total organic carbon concentration data. The correlation coefficient describing the linear relationship between cadmium K_d values and total organic carbon concentration was 0.20, which is nonsignificant at the 5 percent level of probability. It was anticipated that there would be a positive correlation between total organic carbon concentration and cadmium K_d values because soil organic carbon can have extremely high CEC values, providing additional sorption sites for dissolved cadmium.

5.2.6.2.5 Limits of K_d Values with Respect to Dissolved Calcium, Magnesium, and Sulfide Concentrations, and Redox Conditions

Calcium, magnesium, and sulfide solution concentrations were rarely, if at all, reported in the experiments used to comprise the cadmium data set. It was anticipated that dissolved calcium and magnesium would compete with cadmium for adsorption sites, thereby decreasing K_d values. It was anticipated that sulfides would induce cadmium precipitation, thereby increasing cadmium K_d values. Similarly, low redox status was expected to provide an indirect measure of sulfide concentrations, which would in turn induce cadmium precipitation. Sulfides only exist in low redox environments; in high redox environments, the sulfides oxidize to sulfates that are less prone to form cadmium precipitates.

5.3 Cesium Geochemistry and K_d Values

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

The aqueous speciation of cesium in groundwater is among the simplest of the contaminants being considered in this study. Cesium forms few stable complexes and is likely to exist in groundwater as the uncomplexed Cs^+ ion, which adsorbs rather strongly to most minerals, especially mica-like clay minerals. The extent to which adsorption will occur will depend on (1) the concentration of mica-like clays in the soil, and (2) the concentration of major cations, such as K^+ which has a small ionic radius as Cs^+ , that can effectively compete with Cs^+ for adsorption sites.

5.3.2 General Geochemistry

Cesium (Cs) exists in the environment in the +1 oxidation state. Stable cesium is ubiquitous in the environment with concentrations in soils ranging between 0.3 and 25 mg/kg (Lindsay, 1979). The only stable isotope of cesium is ^{133}Cs . Fission products include 4 main cesium isotopes. Of these, only ^{134}Cs [half life ($t_{1/2}$) = 2.05 y], ^{135}Cs ($t_{1/2}$ = 3×10^6 y), and ^{137}Cs ($t_{1/2}$ = 30.23 y) are at significant concentrations 10 y after separation from nuclear fuels (Schneider and Platt, 1974).

Contamination includes cesium-containing soils and cesium dissolved in surface- and groundwaters. Of the contaminated sites considered in EPA/DOE/NRC (1993), radioactive contamination of soil, surface water, and/or groundwater by ^{134}Cs , ^{135}Cs and/or ^{137}Cs has been identified at 9 of the 45 Superfund National Priorities List (NPL) sites.

5.3.3 Aqueous Speciation

There is little, if any, tendency for cesium to form aqueous complexes in soil/water environments. Thus, the formation of inorganic complexes is not a major influence on cesium speciation and the dominant aqueous species in most groundwater is the uncomplexed Cs^+ ion. Baes and Mesmer (1976) report that cesium may be associated with OH^- ions in solution, but that the extent of this association cannot be estimated accurately. The uncomplexed Cs^+ ion forms extremely weak aqueous complexes with sulfate, chloride, and nitrate. Cesium also can form weak complexes with humic materials, as shown by the following ranking of cations by their propensity to form complexes with humic materials (Bovard *et al.*, 1970):



Further, complexation of cesium by common industrial chelates (e.g., EDTA) is believed to be poor due to their low stabilities and the presence of competing cations (e.g., Ca^{2+}) at appreciably higher concentrations than that of cesium. Therefore, aqueous complexation is not thought to greatly influence cesium behavior in most groundwater systems.

5.3.4 Dissolution/Precipitation/Coprecipitation

Neither precipitation nor coprecipitation are expected to affect the geochemistry of cesium in groundwater. The solubility of most cesium compounds in water is very high.

5.3.5 Sorption/Desorption

In general, most soils sorb cesium rather strongly (Ames and Rai, 1978). Some mica-like minerals, such as illite $\{(\text{K},\text{H}_3\text{O})(\text{Al},\text{Mg},\text{Fe})_2(\text{Si},\text{Al})_4\text{O}_{10}[(\text{OH})_2,\text{H}_2\text{O}]\}$ and vermiculite $[(\text{Mg},\text{Fe},\text{Al})_3(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_2\cdot 4\text{H}_2\text{O}]$, tend to intercalate (fix) cesium between their structural layers (Bruggenwert and Kamphorst, 1979; Douglas, 1989; Smith and Comans, 1996). These silicate minerals can be thought of as having a crystal lattice composed of continuous sheet structures. The distance between the silicate layers is controlled by the type of cation associated with the adsorption sites on the layers. Large hydrated cations, such as Na^+ , Li^+ , Ca^{2+} , and Mg^{2+} , tend to pry the layers further apart, whereas small hydrated cations, such as K^+ , have the opposite effect. The interlayer distance between the sheets of mica-like minerals excludes the adsorption of the majority of cations by size, while permitting the Cs^+ ion to fit perfectly between the layers. Consequently, these mica-like minerals commonly exhibit a very high selectivity for Cs^+ over other cations, including cations existing at much higher concentrations. Even a small amount (e.g., 1-2 weight percent) of these mica-like minerals in a soil may strongly absorb a large amount of dissolved cesium (Coleman *et al.*, 1963; Douglas, 1989). Some researchers have considered the exchange of trace cesium on these mica-like minerals to be nearly irreversible (Douglas, 1989; Routson, 1973), meaning that cesium absorbs at a much faster rate than it desorbs.

The effect of cesium concentration and pH on cesium adsorption by a calcareous soil containing mica-like minerals has been studied by McHenry (1954). The data indicate that trace cesium concentrations are essentially completely adsorbed above pH 4.0. When placed in a high-salt solution, 4 M NaCl, only up to 75 percent of the trace cesium was adsorbed, and the adsorption was essentially independent of pH over a wide range. At cesium loadings on the soil of less than 1 percent of the soil CEC, the effect of competing cations on cesium adsorption was slight. Low concentrations of dissolved cesium are typical of cesium-contaminated areas. Thus competition may not play an important role in controlling cesium adsorption in most natural groundwater environments. The results of McHenry (1954) also indicate that trace concentrations of cesium were adsorbed to a greater degree and were more difficult to displace from the soil by competing cations than when the cesium was adsorbed at higher loadings.

Cesium may also adsorb to iron oxides (Schwertmann and Taylor, 1989). Iron oxides, unlike mica-like minerals, do not "fix" cesium. Instead they complex cesium to sites whose abundance is pH dependent; *i.e.*, iron oxides have variable charge surfaces. Iron oxides dominate the adsorption capacity of many soils in semi-tropical regions, such as the southeastern United States. In these soils, many mica-like minerals have been weathered away, leaving minerals with more pH-dependent charge. As the pH decreases, the number of negatively charged complexation sites also decreases. For example, Prout (1958) reported that cesium adsorption to iron-oxide dominated soils from South Carolina decreased dramatically when the suspension pH was less than 6.

Cesium adsorption to humic materials is generally quite weak (Bovard *et al.*, 1970). This is consistent with cation ranking listed above showing that cesium forms relatively weak complexes with organic matter.

5.3.6 Partition Coefficient, K_d , Values

5.3.6.1 General Availability of K_d Data

Three generalized, simplifying assumptions were established for the selection of cesium K_d values for the look-up table. These assumptions were based on the findings of the literature review we conducted on the geochemical processes affecting cesium sorption.¹ The assumptions are as follows:

- Cesium adsorption occurs entirely by cation exchange, with the exception when mica-like minerals are present. Cation exchange capacity (CEC), a parameter that is frequently not measured, can be estimated by an empirical relationship with clay content and pH.
- Cesium adsorption into mica-like minerals occurs much more readily than desorption. Thus, K_d values, which are essentially always derived from adsorption studies, will greatly overestimate the degree to which cesium will desorb from these surfaces.
- Cesium concentrations in groundwater plumes are low enough, less than approximately 10^{-7} M, such that cesium adsorption follows a linear isotherm.

These assumptions appear to be reasonable for a wide range of environmental conditions. However, these simplifying assumptions are clearly compromised in systems with cesium concentrations greater than approximately 10^{-7} M, ionic strength levels greater than about 0.1 M, and pH levels greater than about 10.5. These 3 assumptions will be discussed in more detail in the following sections.

¹ Since the completion of our review and analysis of K_d data for the selected contaminants and radionuclides, the studies by Cygan *et al.* (1998), Fisher *et al.* (1999), and Oscarson and Hume (1998) were identified and may be of interest to the reader.

Based on the assumptions and limitation described in above, cesium K_d values and some important ancillary parameters that influence cation exchange were collected from the literature and tabulated. Data included in this table were from studies that reported K_d values (not percent adsorbed or Freundlich or Langmuir constants) and were conducted in systems consisting of: (1) low ionic strength (< 0.1 M), (2) pH values between 4 and 10.5, (3) dissolved cesium concentrations less than 10^{-7} M, (4) low humic material concentrations (< 5 mg/l), and (5) no organic chelates (*e.g.*, EDTA). Initially, attempts were made to include in the K_d data set all the key aqueous and solid phase parameters identified above. The key parameters included aluminum/iron-oxide mineral concentration, CEC, clay content, potassium concentration, mica-like mineral content, ammonium concentration, and pH. The ancillary parameters for which data could be found in the literature that were included in these tables were clay content, mica content, pH, CEC, surface area, and solution cesium concentrations. This cesium data set included 176 cesium K_d values. The descriptive statistics of the cesium K_d data set are presented in Appendix D.

5.3.6.2 Look-Up Tables

Linear regression analyses were conducted with data collected from the literature. These analyses were used as guidance for selecting appropriate K_d values for the look-up table. The K_d values used in the look-up tables could not be based entirely on statistical consideration because the statistical analysis results were occasionally nonsensible. For example, the data showed a negative correlation between pH and CEC, and pH and cesium K_d values. These trends contradict well established principles of surface chemistry. Instead, the statistical analysis was used to provide guidance as to the approximate range of values to use and to identify meaningful trends between the cesium K_d values and the solid phase parameters. Thus, the K_d values included in the look-up table were in part selected based on professional judgment. Again, only low-ionic strength solutions, such as groundwaters, were considered; thus no solution variables were included.

Two look-up tables containing cesium K_d values were created. The first table is for systems containing low concentrations of mica-like minerals: less than about 5 percent of the clay-size fraction (Table 5.5). The second table is for systems containing high concentrations of mica-like minerals (Table 5.6). For both tables, the user will be able to reduce the range of possible cesium K_d values with knowledge of either the CEC or the clay content. A detailed description of the assumptions and the procedures used in coming up with these values is presented in Appendix D.

Table 5.5. Estimated range of K_d values (ml/g) for cesium based on CEC or clay content for systems containing <5 percent mica-like minerals in clay-size fraction and $<10^{-9}$ M aqueous cesium. [Table pertains to systems consisting of natural soils (as opposed to pure mineral phases), low ionic strength (<0.1 M), low humic material concentrations (<5 mg/l), no organic chelates (e.g., EDTA), and oxidizing conditions.]

K_d (ml/g)	CEC (meq/100 g) / Clay Content (wt.%)		
	<3 / <4	3 - 10 / 4 - 20	10 - 50 / 20 - 60
Minimum	10	30	80
Maximum	3,500	9,000	26,700

Table 5.6. Estimated range of K_d values (ml/g) for cesium based on CEC or clay content for systems containing >5 percent mica-like minerals in clay-size fraction and $<10^{-9}$ M aqueous cesium. [Table pertains to systems consisting of natural soils (as opposed to pure mineral phases), low ionic strength (<0.1 M), low humic material concentrations (<5 mg/l), no organic chelates (e.g., EDTA), and oxidizing conditions.]

K_d (ml/g)	CEC (meq/100 g) / Clay Content (wt.%)		
	<3 / <4	3 - 10 / 4 - 20	10 - 50 / 20 - 60
Minimum	30	70	210
Maximum	9,000	22,000	66,700

5.3.6.2.1 Limits of K_d Values with Respect to pH

Of the 177 cesium K_d values obtained from the literature, 139 of them had associated pH values for the system under consideration (Appendix D). The average pH of the systems described in the data set was pH 7.4, ranging from pH 2.4 to 10.2. The correlation coefficient (r) between pH and cesium K_d values was 0.05. This is clearly an insignificant correlation. This poor correlation may be attributed to the fact that other soil properties having a greater impact on cesium K_d values were not held constant throughout this data set.

5.3.6.2.2 Limits of K_d Values with Respect to Potassium, Ammonium, and Aluminum/Iron-Oxides Concentrations

Potassium, ammonium, and aluminum/iron-oxide mineral concentrations were rarely, if at all, reported in the experiments used to comprise the cesium K_d data set (Appendix D). It was anticipated that dissolved potassium and ammonium would compete with cesium for adsorption sites, thereby decreasing K_d values. The presence of aluminum and/or iron oxides in the solid phase was expected to increase cesium K_d values.

5.4 Chromium Geochemistry and K_d Values

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

A plume containing high concentrations of chromium is more likely to be composed of Cr(VI) than Cr(III) because the former is less likely to adsorb or precipitate to the solid phase. Chromium(VI) is also appreciably more toxic than Cr(III). It exhibits significant subsurface mobility in neutral and basic pH environments. In acid environments, Cr(VI) may be moderately adsorbed by pH-dependent charge minerals, such as iron- and aluminum-oxide minerals. The reduction of Cr(VI) to Cr(III) by ferrous iron, organic matter, and microbes is generally quite rapid whereas the oxidation of Cr(III) to Cr(VI) by soil manganese oxides or dissolved oxygen is kinetically slower. The most important aqueous- and solid-phase parameters controlling retardation of chromium include redox status, pH, and the concentrations of aluminum- and iron-oxide minerals and organic matter.

5.4.2 General Geochemistry

Chromium is found in the environment primarily in the +3 and +6 oxidation states. The geochemical behavior and biological toxicity of chromium in these 2 oxidation states are profoundly different. Chromium(VI) tends to be soluble, forms anionic or neutral dissolved species, can be very mobile, and is acutely toxic (Nriagu and Nieboer, 1988). In contrast, Cr(III) tends to precipitate, forms cationic dissolved species, is immobile under moderately alkaline to slightly acidic conditions, and is relatively nontoxic. The primary human activities leading to the introduction of chromium into the environment are

ore processing, plating operations, and manufacturing (reviewed by Nriagu and Nieboer, 1988). Discussions of the production, uses, and toxicology of chromium have been presented by Nriagu and Nieboer (1988). Good review articles describing the geochemistry of chromium have been written by Rai *et al.* (1988), Palmer and Wittbrodt (1991), Richard and Bourg (1991), and Palmer and Puls (1994). A critical review of the thermodynamic properties for chromium metal and its aqueous ions, hydrolysis species, oxides, and hydroxides was published by Ball and Nordstrom (1998).

5.4.3 Aqueous Speciation

Chromium exists in the +2, +3, and +6 oxidation states in water, of which only the +3 and +6 states are found in the environment. Chromium(III) exists over a wide range of pH and Eh conditions, whereas Cr(VI) exists only under strongly oxidizing conditions. According to Baes and Mesmer (1976), Cr(III) exists predominantly as Cr^{3+} below pH 3.5 in a Cr(III)- H_2O system. With increasing pH, hydrolysis of Cr^{3+} yields CrOH^{2+} , $\text{Cr}(\text{OH})_2^+$, $\text{Cr}(\text{OH})_3^0(\text{aq})$, and $\text{Cr}(\text{OH})_4^-$, $\text{Cr}_2(\text{OH})_2^{4+}$, and $\text{Cr}_3(\text{OH})_4^{5+}$. At higher chromium concentrations, polynuclear species, such as $\text{Cr}_2(\text{OH})_2^{4+}$ and $\text{Cr}_3(\text{OH})_4^{5+}$, can form slowly at 25°C (Baes and Mesmer, 1976). Chromium(VI) hydrolyses extensively, forming primarily anionic species. These species are HCrO_4^- (bichromate), CrO_4^{2-} (chromate), and $\text{Cr}_2\text{O}_7^{2-}$ (dichromate) (Baes and Mesmer, 1976; Palmer and Wittbrodt, 1991; Richard and Bourg, 1991). Palmer and Puls (1994) presented some Cr(VI) speciation diagrams representative of groundwater conditions. They showed that above pH 6.5, CrO_4^{2-} generally dominates. Below pH 6.5, HCrO_4^- dominates when the total concentration of dissolved Cr(VI) is low (<30 mM). When Cr(VI) concentrations are greater than 30 mM, $\text{Cr}_2\text{O}_7^{2-}$ is the dominant aqueous species relative to HCrO_4^- at acidic conditions (Palmer and Puls, 1994). These results are consistent with those of Baes and Mesmer (1976).

5.4.4 Dissolution/Precipitation/Coprecipitation

Several investigators have presented evidence suggesting the formation of solubility-controlling solids of Cr(III) in soils. Rai and Zachara (1984) concluded that most Cr(III) solubility-controlling solids in nature are either $\text{Cr}(\text{OH})_3$ or Cr(III) coprecipitated with iron oxides. Their conclusion was supported by 3 observations: (1) the thermodynamic treatment of the data where the solubility of chromite (FeCr_2O_4) is predicted to be the lowest among the chromium minerals for which data are available (Hem, 1977), (2) the similarity of Cr(III) and Fe(III) ionic radii, and (3) the observations that aqueous Cr(III) is removed by $\text{Fe}(\text{OH})_3$ precipitation and that chromium during weathering is found to associate with ferric-rich materials (Nakayama *et al.*, 1981). Hem (1977) reported that the total chromium concentration in groundwater beneath Paradise Valley, Arizona was close to the solubility of Cr_2O_3 . Because Cr(III) minerals are sparingly soluble, the aqueous concentration of Cr(III) should be less than EPA's maximum concentration level (MCL) for chromium (0.1 mg/l) between slightly acid to moderately alkaline conditions (Palmer and Puls, 1994).

Several Cr(VI)-containing mineral phases may be present at chromium-contaminated sites. Palmer and Wittbrodt (1990) identified PbCrO_4 (crocoite), $\text{PbCrO}_4 \cdot \text{H}_2\text{O}$ (iranite), and K_2CrO_4 (tarapacaite) in

chromium sludge from a plating facility. They also reported that BaCrO_4 formed a complete solid solution with BaSO_4 . They concluded that these solid solutions can be a major impediment to the remediation of chromium-contaminated sites by pump-and-treat technologies.

Chromium(VI) is a strong oxidant and is rapidly reduced in the presence of such common electron donors as aqueous Fe(II), ferrous iron minerals, reduced sulfur, microbes, and organic matter (Bartlett and Kimble, 1976; Nakayama *et al.*, 1981). Studies indicate that Cr(VI) can be reduced to Cr(III) by ferrous iron derived from magnetite (Fe_3O_4) and ilmenite (FeTiO_3) (White and Hochella, 1989), hematite (Fe_2O_3) (Eary and Rai, 1989),¹ and pyrite (FeS_2) (Blowes and Ptacek, 1992).

The reduction of Cr(VI) by Fe(II) is very rapid. The reaction can go to completion in a matter of minutes (Eary and Rai, 1989). The rate of reduction of Cr(VI) increases with decreasing pH and increasing initial Cr(VI) and reductant concentrations (Palmer and Puls, 1994). Interestingly, this reaction does not appear to be slowed by the presence of dissolved oxygen (Eary and Rai, 1989). When the pH is greater than 4, Cr(III) can precipitate with Fe(III) to form a solid solution with the general composition $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3$ (Sass and Rai, 1987). The solubility of chromium in this solid solution decreases as the mole fraction of Fe(III) increases. The oxidation reaction proceeds much more slowly than the reduction reaction; the former reaction requires months for completion (Eary and Rai, 1987; Palmer and Puls, 1994). Only 2 constituents in the environment are known to oxidize Cr(III): dissolved oxygen and manganese-dioxide minerals [*e.g.*, pyrolusite ($\beta\text{-MnO}_2$)]. Eary and Rai (1987) reported that the rate of Cr(III) oxidation was much greater in the presence of manganese-dioxide minerals than dissolved oxygen.

5.4.5 Sorption/Desorption

The extent to which Cr(III) sorbs to soils is appreciably greater than that of Cr(VI) because the former exists in groundwater as a cation, primarily as Cr^{3+} (and its complexed species), whereas the latter exists as an anion, primarily as CrO_4^{2-} or HCrO_4^- . Most information on Cr(VI) adsorption comes from studies with pure mineral phases (Davis and Leckie, 1980; Griffin *et al.*, 1977; Leckie *et al.*, 1980). These studies suggest that Cr(VI) adsorbs strongly to gibbsite ($\alpha\text{-Al}_2\text{O}_3$) and amorphous iron oxide [$\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}(\text{am})$] at low to medium pH values (pH 2 to 7) and adsorbs weakly to silica (SiO_2) at all but very low pH values (Davis and Leckie, 1980; Griffin *et al.*, 1977; Leckie *et al.*, 1980). These results can be explained by considering the isoelectric points (IEP)² of these minerals. When the pH of the system is greater than the isoelectric point, the mineral has a net negative charge. When the pH is

¹ Eary and Rai (1989) attributed the reduction of Cr(VI) to Cr(III) by hematite (Fe_2O_3) as containing having trace quantities of Fe(II).

² The isoelectric point (IEP) of a mineral is the pH at which it has a net surface charge of zero. More precisely, it is the pH at which the particle is electrokinetically uncharged.

below the isoelectric point, the mineral has a net positive charge. Hence, anion adsorption generally increases as the pH becomes progressively lower than the isoelectric point. The isoelectric point of gibbsite ($\alpha\text{-Al}_2\text{O}_3$) is 9.1, amorphous iron oxide [$\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$ (am)] is 8.1, and silica is 2.0 (Stumm and Morgan, 1981).

The presence of competing and, less commonly, complexing ions may significantly alter chromate adsorption. Although sulfate is adsorbed less strongly on $\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$ (am) than chromate, sulfate may compete for adsorption sites when present in higher concentration (Leckie *et al.*, 1980). Phosphate exhibits a greater competitive effect on chromate adsorption (MacNaughton, 1977), reducing sorption by around 50 percent when present at equal normality. Information on effects of complexing ions on Cr(VI) sorption is almost nonexistent, though adsorption of ion pairs [*e.g.*, $\text{CaCrO}_4^0(\text{aq})$ and $\text{KHCrO}_4^0(\text{aq})$] is suggested as 1 possible mechanism for removal of Cr(VI) by $\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$ (am) (Leckie *et al.*, 1980).

Adsorption of Cr(III) to soils has received only a nominal amount of research attention. The reason for this may be that sorption of Cr(III) by soil is commonly ascribed to solid phase formation.

Chromium(III) rapidly hydrolyzes, and precipitates as the hydroxide $\text{Cr}(\text{OH})_3$ and/or coprecipitates with $\text{Fe}(\text{OH})_3$ (Artiola and Fuller, 1979; Hem, 1977). Adsorption may be an especially important mechanism of sorption at lower pH (pH <4.5) and total chromium concentrations ($<10^{-6}$ M). Limited studies infer that Cr(III), like other +3 cationic metals, is strongly and specifically adsorbed by soil iron and manganese oxides (Korte *et al.*, 1976). However, when Cr(III) is present in solution at high concentrations, it may undergo exchange reactions with aluminosilicates (Griffin *et al.*, 1977).

Chromium(III) adsorption may also be influenced by the presence of manganese-oxide minerals. Manganese oxides may catalyze oxidation to Cr(VI), thereby decreasing the tendency for chromium to adsorb to the soils (Bartlett and James, 1979; Nakayama *et al.*, 1981).

5.4.6 Partition Coefficient, K_d , Values

5.4.6.1 General Availability of K_d Data

The review of chromium K_d data obtained for a number of soils (Appendix E) indicated that a number of factors influence the adsorption behavior of chromium. These factors and their effects on chromium adsorption on soils were used as the basis for generating a look-up table. These factors are:

- Concentrations of Cr(III) in soil solutions are typically controlled by dissolution/precipitation reactions.
- Increasing pH decreases adsorption (decrease in K_d) of Cr(VI) on minerals and soils. The data are quantified for only a limited number of soils.

- The redox state of the soil affects chromium adsorption. Ferrous iron associated with iron oxide/hydroxide minerals in soils can reduce Cr(VI) which results in precipitation (higher K_d). Soils containing Mn oxides oxidize Cr(III) into Cr(VI) form thus resulting in lower K_d values. The relation between oxide/hydroxide contents of iron and manganese and their effects on K_d have not been adequately quantified except for a few soils.
- The presence of competing anions reduce Cr(VI) adsorption. These effects have been quantified as a function of pH for only 2 soils.

The factors which influence chromium adsorption were identified from studies by Leckie *et al.* (1980), Davis and Leckie (1980), Griffin *et al.* (1977), and Rai *et al.* (1986), and studies discussed below. A description and assessment of these data are provided in Appendix E.

Adsorption data also show that iron and manganese oxide contents of soils significantly affect the adsorption of Cr(VI) on soils (Korte *et al.*, 1976). However, these investigators did not publish either K_d values or any correlative relationships between K_d and the oxide contents. Studies by Stollenwerk and Grove (1985) and Sheppard *et al.* (1987) using soils showed that K_d decreases as a function of increasing equilibrium concentration of Cr(VI). Another study conducted by Rai *et al.* (1988) on 4 different soils confirmed that K_d values decrease with increasing equilibrium Cr(VI) concentration. The adsorption data obtained by Rai *et al.* (1988) also showed that quantities of sodium dithionite-citrate-bicarbonate (DCB) extractable iron content of soils is a good indicator of a soil's ability to reduce Cr(VI) to the Cr(III) oxidation state. The reduced Cr has been shown to coprecipitate with ferric hydroxide. Therefore, observed removal of Cr(VI) from solution when contacted with chromium-reductive soils may stem from both adsorption and precipitation reactions. Similarly, Rai *et al.* (1988) also showed that certain soils containing manganese oxides may oxidize Cr(III) to Cr(VI). Depending on solution concentrations, the oxidized form (+6) of chromium may also precipitate in the form of $Ba(S,Cr)O_4$. Such complex geochemical behavior chromium in soils implies that depending on the properties of a soil, the measured K_d values may reflect both adsorption and precipitation reactions.

Adsorption studies have shown that competing anions such as SO_4^{2-} , CO_3^{2-}/HCO_3^- , HPO_4^{2-} , $H_2PO_4^-$, NO_3^- and Cl⁻, significantly reduce Cr(VI) adsorption on oxide minerals and soils (Leckie *et al.*, 1980; MacNaughton, 1977; Rai *et al.*, 1986; Rai *et al.*, 1988; Stollenwerk and Grove, 1985).

The data regarding the effects of soil organic matter on Cr(VI) adsorption are rather sparse. In 1 study (Stollenwerk and Grove, 1985) which evaluated the effects of soil organic matter on adsorption of Cr(VI), the results indicated that organic matter did not influence Cr(VI) adsorption properties (see Appendix E).

5.4.6.2 K_d Look-Up Tables

Among all available data for Cr(VI) adsorption on soils, the most extensive data set was developed by Rai *et al.* (1988). These investigators studied the adsorption behavior of 4 different well-characterized subsurface soil samples. They investigated the adsorption behavior of Cr(VI) on these 4 soil samples as a function of pH. Additionally, they also investigated the effects of competing anions such as SO_4^{2-} , and $\text{CO}_3^{2-}/\text{HCO}_3^-$. The adsorption data developed by these investigators was used to calculate the K_d values (Appendix E). These K_d values were used as the basis to develop the look-up Table 5.7.

5.4.6.2.1 Limits of K_d Values with Respect to pH

Natural soil pH typically ranges from about 4 to 11 (Richards, 1954). The 2 most common methods of measuring soil pH are either using a soil paste or a saturation extract. The standard procedure for obtaining saturation extracts from soils has been described by Rhoades (1996). The saturation extracts are obtained by saturating and equilibrating the soil with distilled water followed by collection using vacuum filtration. Saturation extracts are usually used to determine the pH, the electrical conductivity, and dissolved salts in soils.

The narrow pH ranges in the look-up table (Table 5.7) were selected from the observed rate of change of K_d with pH. The K_d values for all 4 soils were observed to decline with increasing pH and at pH values beyond about 9, K_d values for Cr(VI) are ≤ 1 ml/g (see Appendix E).

5.4.6.2.2 Limits of K_d Values with Respect to Extractable Iron Content

The soil characterization data provided by Rai *et al.* (1988) indicate the soils with DCB extractable iron contents above ~ 0.3 mmol/g can reduce Cr(VI) to Cr(III). Therefore the measured K_d values for such soils reflect both redox-mediated precipitation and adsorption phenomena. The data also show that soils with DCB extractable iron contents of about 0.25 mmol/g or less do not appear to reduce Cr(VI). Therefore, 3 ranges of DCB extractable iron contents were selected which represent the categories of soils that definitely reduce (≥ 0.3 mmol/g), probably reduce (0.26 - 0.29 mmol/g), and do not reduce (≤ 0.25 mmol/g) Cr(VI) to Cr(III) form.

5.4.6.2.3 Limits of K_d Values with Respect to Competing Anion Concentrations

The adsorption data (Rai *et al.*, 1988) show that when total sulfate concentration in solution is about 2×10^{-3} M (191.5 mg/l), the chromium K_d values are reduced by about an order of magnitude as compared to a noncompetitive condition. Therefore, a sulfate concentration of about 2×10^{-3} M (191.5 mg/l) has been used as a limit at which an order of magnitude reduction in K_d values are expected. Four ranges of soluble sulfate concentrations (0 - 1.9, 2 - 18.9, 19 - 189, and ≥ 190 mg/l) have been used to develop the look-up table. The soluble sulfate concentrations in soils can be assessed from saturation extracts (Richards, 1954).

Table 5.7. Estimated range of K_d values for chromium (VI) as a function of soil pH, extractable iron content, and soluble sulfate. (Data analysis and generation of the table of K_d values are described in Appendix E.)

Soluble Sulfate Conc (mg/l)	K_d (ml/g)	pH											
		4.1 - 5.0			5.1 - 6.0			6.1 - 7.0			≥ 7.1		
		DCB Extractable Fe (mmol/g)			DCB Extractable Fe (mmol/g)			DCB Extractable Fe (mmol/g)			DCB Extractable Fe (mmol/g)		
		≤ 0.25	0.26 - 0.29	≥ 0.30	≤ 0.25	0.26 - 0.29	≥ 0.30	≤ 0.25	0.26 - 0.29	≥ 0.30	≤ 0.25	0.26 - 0.29	≥ 0.30
0 - 1.9	Min	25	400	990	20	190	390	8	70	80	0	0	1
	Max	35	700	1770	34	380	920	22	180	350	7	30	60
2 - 18.9	Min	12	190	460	10	90	180	4	30	40	0	0	1
	Max	15	330	820	15	180	430	10	80	160	3	14	30
19 - 189	Min	5	90	210	4	40	80	2	15	20	0	0	0
	Max	8	150	380	7	80	200	5	40	75	2	7	13
≥ 190	Min	3	40	100	2	20	40	1	7	8	0	0	0
	Max	4	70	180	3	40	90	2	20	35	1	3	6

5.5 Lead Geochemistry and K_d Values

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

Lead has 3 known oxidation states, 0, +2, and +4, and the most common redox state encountered in the environment is the divalent form. Total dissolved lead concentrations in natural waters are very low ($\sim 10^{-8}$ M). Dissolved lead in natural systems may exist in free ionic form and also as hydrolytic and complex species. Speciation calculations show that at pH values exceeding 7, aqueous lead exists mainly as carbonate complexes [$\text{PbCO}_3^0(\text{aq})$, and $\text{Pb}(\text{CO}_3)_2^{2-}$]. Important factors that control aqueous speciation of lead include pH, the types and concentrations of complexing ligands and major cationic constituents, and the magnitude of stability constants for lead-ligand aqueous complexes.

A number of studies and calculations show that under oxidizing conditions depending on pH and ligand concentrations, pure-phase lead solids, such as PbCO_3 , $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$, PbSO_4 , $\text{Pb}_5(\text{PO}_4)_3(\text{Cl})$, and $\text{Pb}_4\text{SO}_4(\text{CO}_3)_2(\text{OH})_2$, may control aqueous lead concentrations. Under reducing conditions, galena (PbS) may regulate the concentrations of dissolved lead. It is also possible that lead concentrations in some natural systems are being controlled by solid solution phases such as barite ($\text{Ba}_{(1-x)}\text{Pb}_x\text{SO}_4$), apatite [$\text{Ca}_{(1-x)}\text{Pb}_x(\text{PO}_4)_3\text{OH}$], calcite ($\text{Ca}_{(1-x)}\text{Pb}_x\text{CO}_3$), and iron sulfides ($\text{Fe}_{(1-x)}\text{Pb}_x\text{S}$).

Lead is known to adsorb onto soil constituent surfaces such as clay, oxides, hydroxides, oxyhydroxides, and organic matter. In the absence of a distinct lead solid phase, natural lead concentrations would be controlled by adsorption/desorption reactions. Adsorption data show that lead has very strong adsorption affinity for soils as compared to a number of first transition metals. Lead adsorption studies on bulk soils indicate that the adsorption is strongly correlated with pH and the CEC values of soils. Properties that affect CEC of soils, such as organic matter content, clay content, and surface area, have greater affect on lead adsorption than soil pH.

5.5.2 General Geochemistry

Lead is an ubiquitous heavy metal and its concentration in uncontaminated soil ranges from 2 to 200 mg/kg and averages 16 mg/kg (Bowen, 1979). Annual anthropogenic lead input into soils has been estimated to be from 0.04 to 4 micro g/kg (Ter Haar *et al.*, 1967). In contaminated soils, lead concentrations may be as high as 18 percent by weight (Mattigod and Page, 1983; Ruby *et al.*, 1994). Lead in nature occurs in 4 stable isotopic forms (^{204}Pb , ^{206}Pb , ^{207}Pb , and ^{208}Pb). The isotopes, ^{206}Pb , ^{207}Pb , and ^{208}Pb are the stable end products of the ^{238}U , ^{235}U , and ^{232}Th thorium decay series, respectively (Robbins, 1980). Additionally, heavier isotopes of lead (^{210}Pb , ^{211}Pb , ^{212}Pb , and ^{214}Pb) are known to occur in nature as intermediate products of uranium and thorium decay (Robbins, 1978).
The

most common valence state of lead encountered in the environment is the divalent form (Baes and Mesmer, 1976). Extensive studies of lead biogeochemistry have been conducted due to its known adverse effects on organisms (Hammond, 1977). Comprehensive descriptions of environmental chemistry of lead have been published by Boggess and Wixson (1977) and Nriagu (1978).

5.5.3 Aqueous Speciation

Lead exhibits typical amphoteric¹ metal ion behavior by forming hydrolytic species (Baes and Mesmer, 1976). Formation of monomeric hydrolytic species, such as PbOH^+ , $\text{Pb(OH)}_2^{\circ}(\text{aq})$ and Pb(OH)_3^- , is well established. Although several polymeric hydrolytic species such as $\text{Pb}_2\text{OH}^{3+}$, $\text{Pb}_3(\text{OH})_3^{3+}$, $\text{Pb}_4(\text{OH})_4^{4+}$, and $\text{Pb}_6(\text{OH})_8^{4+}$ are known to form at high lead concentrations, calculations show that these types of species are unlikely to form at concentrations of dissolved lead ($\sim 10^{-9}$ M) typically encountered even in contaminated environments (Rickard and Nriagu, 1978). These investigators also showed that computation models of speciation of dissolved lead in fresh- or seawater predicted that at pH values exceeding about 6.5, the dominant species are lead-carbonate complexes. Lead is known to form aqueous complexes with inorganic ligands such as carbonate, chloride, fluoride, nitrate, and sulfate.

To examine the distribution of dissolved lead species in natural waters, MINTEQA2 model calculations were completed using the water composition described in Table 5.1. The total lead concentration was assumed to be 1 micro g/l based on the data for natural waters tabulated by Duram *et al.* (1971) and Hem (1985). A total of 21 aqueous species (uncomplexed Pb^{2+} , and 20 complex species, listed in Table 5.8) were used in the computation. Results of the computation are plotted as a species distribution diagram (Figure 5.2). The data show that, under low pH (<6) conditions, free ionic Pb^{2+} appears to be the dominant species, and the neutral species, $\text{PbSO}_4^{\circ}(\text{aq})$, accounts for about 5 percent of the total dissolved lead. Within the pH range of 6.5 to 7.5, the main species of lead appear to be free ionic species, Pb^{2+} , and the neutral complex species, $\text{PbCO}_3^{\circ}(\text{aq})$ with minor percentage of the species consisting of PbHCO_3^+ (about 15 percent), $\text{PbSO}_4^{\circ}(\text{aq})$ (<5 percent), and PbOH^+ (<5 percent). Between the pH range 7 to 9, the neutral complex species $\text{PbCO}_3^{\circ}(\text{aq})$ dominates dissolved lead speciation. At pH values exceeding 9, in addition to $\text{PbCO}_3^{\circ}(\text{aq})$, a significant fraction of soluble lead is present as the anionic carbonate complex, $\text{Pb(CO}_3)_2^{2-}$. These calculations also confirm Rickard and Nriagu's (1978) observation that polymeric species are not significant in the chemistry of lead in natural waters. The species distribution illustrated in Figure 5.2 does not change if the concentration of total dissolved lead is increased from 1 to 1,000 micro g/l.

This speciation calculation demonstrates that the important factors that control aqueous speciation of lead include pH and the types of complexing ligands. Aqueous speciation of lead has a direct bearing

¹ Amphoteric behavior is the ability of an aqueous complex or solid material to have a negative, neutral, or positive charge.

on dissolution/precipitation of lead-solid phases and the adsorption/desorption reactions. Complexation enhances the solubility of lead-bearing solid phases. This enhancement in solubility is dependent on the strength of complexation [indicated by the magnitude of stability constant] and the total concentrations of complexing ligands. Also, as will be discussed shortly, adsorption of lead is affected by the type, charge, and the concentration of lead complexes present in solution. Cationic lead species, especially Pb^{2+} and its hydrolysis species, adsorb more commonly than anionic lead complexes.

5.5.4 Dissolution/Precipitation/Coprecipitation

Lead solids in the environment may occur in a number of mineral forms (Rickard and Nriagu 1978; Mattigod *et al.*, 1986; Zimdahl and Hassett, 1977). However, these authors have identified a limited number of secondary lead minerals that may control the concentrations of dissolved lead in soil/water environments. If the concentration of dissolved lead in a pore water or groundwater exceeds the solubility of any of these phases, the lead-containing solid phase will precipitate and thus control the maximum concentration of lead that could occur in the aqueous phase. According to Rickard and Nriagu (1978), under oxidizing conditions, depending on pH and ligand concentrations, cerussite ($PbCO_3$), hydrocerussite [$Pb_3(OH)_2(CO_3)_2$], anglesite ($PbSO_4$), or chloropyromorphite [$Pb_5(PO_4)_3Cl$] may control aqueous lead concentrations. A review paper by McLean and Bledsoe (1992) included data which showed that lead concentrations in a calcareous soil was controlled by lead-phosphate compounds at lower pH and by mixed mineral phases at pH values exceeding 7.5. A study conducted by Mattigod *et al.* (1986) indicated that the mineral leadhillite [$Pb_4SO_4(CO_3)_2(OH)_2$] may be the solubility controlling solid for lead in a mine-waste contaminated soil.

Table 5.8. Lead aqueous species included in the speciation calculations.

Aqueous Species
Pb^{2+}
PbOH^+ , $\text{Pb}(\text{OH})_2^{\circ}(\text{aq})$, $\text{Pb}(\text{OH})_3^-$, $\text{Pb}(\text{OH})_4^{2-}$ $\text{Pb}_2(\text{OH})_3^+$, $\text{Pb}_3(\text{OH})_3^{3+}$
$\text{PbCO}_3^{\circ}(\text{aq})$, $\text{Pb}(\text{CO}_3)_2^{2-}$, PbHCO_3^+
$\text{PbSO}_4^{\circ}(\text{aq})$, $\text{Pb}(\text{SO}_4)_2^{2-}$
PbNO_3^+
PbCl^+ , $\text{PbCl}_2^{\circ}(\text{aq})$, PbCl_3^- , PbCl_4^{2-}
PbF^+ , $\text{PbF}_2^{\circ}(\text{aq})$, PbF_3^- , PbF_4^{2-}

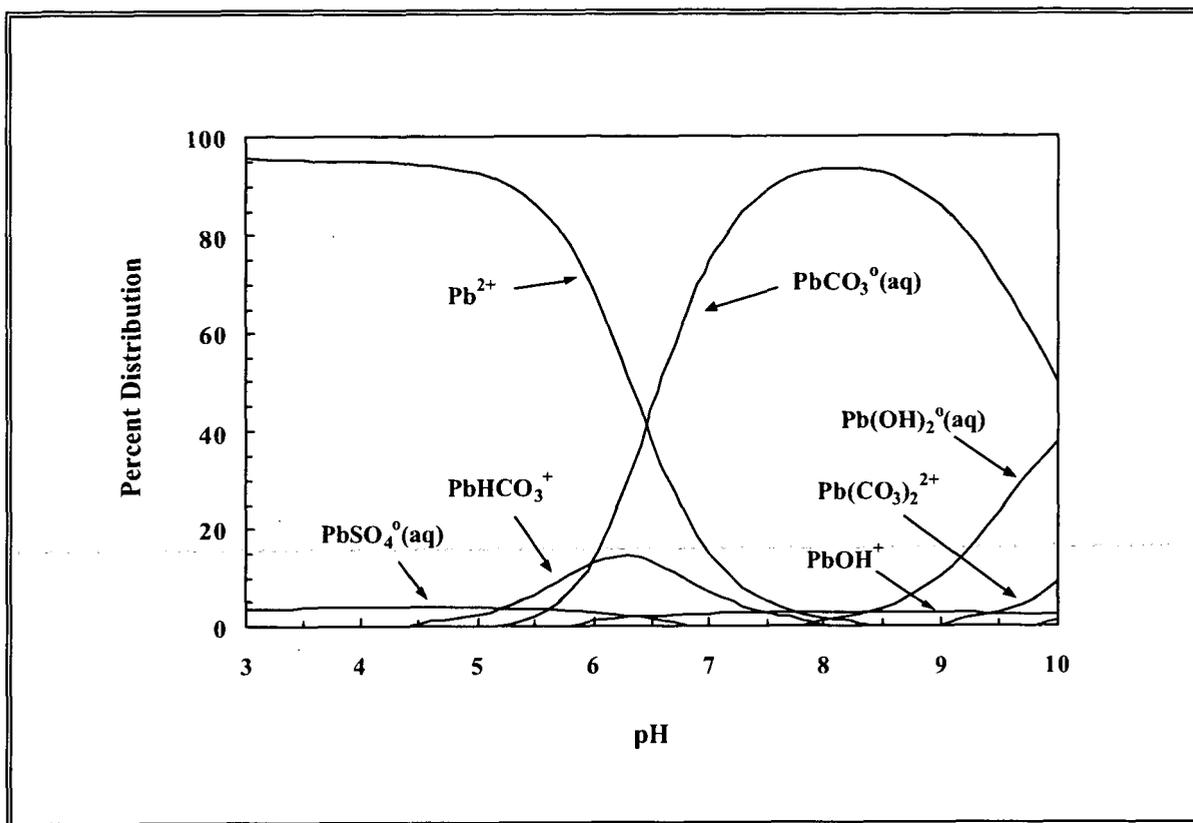


Figure 5.2. Calculated distribution of lead aqueous species as a function of pH for the water composition in Table 5.1. [The species distribution is based on a concentration of 1 micro g/l total dissolved lead.]

Lead may also exist in soils as solid-solution phases. Solid solutions are defined as solid phases in which a minor element will substitute for a major element in the mineral structure. Depending on the degree of substitution and the overall solubility of the solid-solution phase, the equilibrium solubility of the minor element in the solid solution phase will be less than the solubility of the solid phase containing only the minor element (pure phase). For instance, lead may occur as a minor replacement in barite [$\text{Ba}_{(1-x)}\text{Pb}_x\text{SO}_4$], apatite [$\text{Ca}_{(1-x)}\text{Pb}_x(\text{PO}_4)_3\text{OH}$], calcite [$\text{Ca}_{(1-x)}\text{Pb}_x\text{CO}_3$], and iron sulfides, [$\text{Fe}_{(1-x)}\text{Pb}_x\text{S}$] (Driesens, 1986; Goldschmidt, 1954; Nriagu and Moore, 1984; Rickard and Nriagu, 1978). Consequently, the equilibrium solubility of lead controlled by these phases will be less than the concentrations controlled by corresponding pure phases, namely PbSO_4 , $\text{Pb}_5(\text{PO}_4)_3\text{OH}$, PbCO_3 , and PbS , respectively.

Under reducing conditions, galena (PbS) may control the lead concentrations in the environment. Rickard and Nriagu (1978) calculated that, within the pH range of 6-9, the equilibrium solubility of galena would control total lead concentrations at levels less than approximately 10^{-10} M (<21 ng/l). Therefore, if galena is present in a soil under reducing conditions, the aqueous concentrations of lead will be controlled at extremely low concentrations.

5.5.5 Sorption/Desorption

Lead is known to adsorb onto soil constituent surfaces such as clays, oxides, hydroxides, oxyhydroxides, and organic matter. Ion exchange reactions of lead on a number of clay minerals such as montmorillonite, kaolinite, illite, and vermiculite have been studied by a number of investigators. These studies showed that lead was preferentially adsorbed by exchange on clays, readily replacing calcium and potassium (Bittel and Miller, 1974; Overstreet and Krishnamurthy, 1950). Studies conducted by Lagerwerff and Brower (1973) on montmorillonitic, illitic, and kaolinitic soils confirmed that lead would preferentially exchange for calcium. Another clay mineral, vermiculite, is also known to exhibit very high ion exchange selectivity for lead (Rickard and Nriagu, 1978). Based on a number of studies Rickard and Nriagu (1978) also concluded that beyond neutral pH, precipitation reactions may control lead concentrations in solution rather than ion exchange and adsorption reactions involving clay mineral surfaces.

Experimental data show that only hydrogen ions and unhydrolyzed aluminum ions are capable of displacing lead from exchange sites on clay minerals (Lagerwerff and Brower, 1974; Zimdahl and Hassett, 1977). Clay minerals also differ in their exchange preference for lead. Bittel and Miller (1974) showed that the exchange preference for lead varies in the sequence,

kaolinite > illite > montmorillonite.

These studies also showed that, in neutral to high pH conditions, lead can preferentially exchange for calcium, potassium, and cadmium. Under low pH conditions, hydrogen ions and aluminum ions would displace lead from mineral exchange sites.

Studies of lead adsorption on oxide, hydroxide, and oxyhydroxide minerals show that the substrate properties, such as the specific surface and degree of crystallinity, control the degree of adsorption (Rickard and Nriagu, 1978). Experimental data by Forbes *et al.* (1976) showed that goethite (FeOOH) has higher adsorption affinity for lead than zinc, cobalt, and cadmium. Data show that manganese-oxide minerals also adsorb lead ions (Rickard and Nriagu, 1978). These investigators concluded that the high specificity of lead adsorption on oxide and hydroxide surfaces and the relative lack of desorbability (<10 percent) of adsorbed lead indicated that lead upon adsorption forms solid solutions with oxide or hydroxide surfaces. Therefore, this lack of reversibility indicated that the reaction is not a true adsorption phenomenon.

A number of studies have confirmed that many natural and synthetic organic materials adsorb lead. Data showing significant correlations between concentrations of organic matter and lead in soils indicate that soil organic matter has a higher affinity for lead adsorption as compared soil minerals.

A number of lead adsorption studies on bulk soils indicate that the adsorption is strongly correlated with pH and the CEC values of soils (Zimdahl and Hassett, 1977). A multiple regression analysis by Hassett (1974) of lead adsorption data indicated that properties that affect CEC of soils, such as organic matter content, clay content, and surface area, have a greater effect on lead adsorption than soil pH. The results of a number of studies of lead adsorption on a variety of soil and mineral surfaces were summarized by McLean and Bledsoe (1992). These data show that lead has very strong adsorption affinity as compared to a number of first row transition metals (cobalt, nickel, copper, and zinc). According to a recent study (Peters and Shem, 1992), the presence of very strong chelating organic ligands dissolved in solution will reduce adsorption of lead onto soils. These data show that the adsorption of lead in the environment is influenced by a number of factors such as the type and properties of adsorbing substrate, pH, the concentrations of lead, and the type and concentrations of other competing cations and complex forming inorganic and organic ligands.

5.5.6 Partition Coefficient, K_d , Values

5.5.6.1 General Availability of K_d Data

The review of lead K_d data reported in the literature for a number of soils (Appendix F) led to the following important conclusions regarding the factors which influence lead adsorption on minerals and soils.¹ These principles were used to evaluate available quantitative data and generate a look-up table. These conclusions are:

- Lead may precipitate in soils if soluble concentrations exceed about 4 mg/l at pH 4 and about 0.2 mg/l at pH 8. In the presence of phosphate and chloride, these solubility limits may be as low as 0.3 mg/l at pH 4 and 0.001 mg/l at pH 8. Therefore, in experiments in which concentrations of lead exceed these values, the calculated K_d values may reflect precipitation reactions rather than adsorption reactions.
- Anionic constituents such as phosphate, chloride, and carbonate are known to influence lead reactions in soils either by precipitation of minerals of limited solubility or by reducing adsorption through complex formation.

¹ Since the completion of our review and analysis of K_d data for the selected contaminants and radionuclides, the studies by Azizian and Nelson (1998) and Yong and MacDonald (1998) were identified and may be of interest to the reader.

- ~ A number of adsorption studies indicate that within the pH range of soils (4 to 11), lead adsorption increases (as does precipitation) with increasing pH.
- ~ Adsorption of lead increases with increasing organic matter content of soils.
- ~ Increasing equilibrium solution concentrations correlates with decreasing lead adsorption (decrease in K_d).

The factors which influence lead adsorption were identified from the following sources of data. A description and assessment of these data are provided in Appendix F. Lead adsorption behavior on soils and soil constituents (clays, oxides, hydroxides, oxyhydroxides, and organic matter) has been studied extensively. However, calculations by Rickard and Nriagu (1978) show that the solution lead concentrations used in a number of adsorption studies may be high enough to induce precipitation. For instance, their calculations show that lead may precipitate in soils if soluble concentrations exceed about 4 mg/l at pH 4 and about 0.2 mg/l at pH 8. In the presence of phosphate and chloride, these solubility limits may be as low as 0.3 mg/l at pH 4 and 0.001 mg/l at pH 8. Therefore, in experiments in which concentrations of lead exceed these values, the calculated K_d values may reflect precipitation reactions rather than adsorption reactions.

Lead adsorption studies on manganese and iron oxides and oxyhydroxides indicate irreversible adsorption which was attributed to the formation of solid solution phases (*i.e.*, coprecipitation) (Forbes *et al.*, 1976; Grasselly and Hetenyi, 1971; Rickard and Nriagu, 1978). No correlations however have been established between the type and content of oxides in soil and the lead adsorption characteristics of soil.

Anionic constituents such as phosphate, chloride, and carbonate are known to influence lead reactions in soils either by precipitation of minerals of limited solubility or by reducing adsorption through complex formation (Rickard and Nriagu, 1978). Presence of synthetic chelating ligands, such as EDTA, has been shown to reduce lead adsorption on soils (Peters and Shem, 1992). These investigators showed that the presence of strongly chelating EDTA in concentrations as low as 0.01 M reduced K_d for lead by about 3 orders of magnitude. By comparison quantitative data is lacking on the effects of more common inorganic ligands (phosphate, chloride, and carbonate) on lead adsorption on soils.

A number of adsorption studies indicate that within the pH range of soils (4 to 11), lead adsorption increases with increasing pH (Braids *et al.*, 1972; Bittel and Miller, 1974; Griffin and Shimp, 1976; Haji-Djafari *et al.*, 1981; Hildebrand and Blum, 1974; Overstreet and Krishnamurthy, 1950; Scudato and Estes, 1975; Zimdahl and Hassett, 1977). Griffin and Shimp (1976) also noted that clay minerals adsorbing increasing amounts of lead with increasing pH may also be attributed to the formation of lead carbonate precipitates which was observed when the solution pH values exceeded 5 or 6.

Solid organic matter such as humic material in soils is known to adsorb lead (Rickard and Nriagu, 1978; Zimdahl and Hassett, 1977). Additionally, soluble organic matter such as fulvates and amino acids are known to chelate soluble lead and affect its adsorption on soils (Rickard and Nriagu, 1978). Correlative relationships between the organic matter content of soils and its effect on lead adsorption have been established by Gerritse *et al.* (1982) and Soldatini *et al.* (1976).

Lead adsorption by a subsurface soil sample from Hanford, Washington was investigated by Rhoads *et al.* (1992). Adsorption data from these experiments showed that K_d values increased with decreasing lead concentrations in solution (from 0.2 mg/l to 0.0062 mg/l).

5.5.6.2 K_d Look-Up Tables

Among all available data, Gerritse *et al.* (1982) obtained adsorption data at lead concentrations (0.0001 - 0.01 mg/l) which apparently precluded precipitation reactions. Also, these concentrations are within the range of lead concentrations most frequently encountered in ground waters (Chow, 1978). Additionally, data obtained by Rhoads *et al.* (1992) indicated that K_d values vary log-linearly as a function of equilibrium lead concentrations within the range of 0.00001 to 0.2 mg/l. The data generated by Gerritse *et al.* (1982) and Rhoads *et al.* (1992) were used to develop a look-up table (Table 5.9) of K_d as a function of soil pH and equilibrium lead concentrations.

5.5.6.2.1 Limits of K_d Values with Respect to pH

The pH ranges in the look-up table (Table 5.9) were selected from the rate of change that we noted in the K_d data as a function of pH. The K_d values within this pH range increase with increasing pH, and are greatest at the maximum pH limit (pH \approx 11) of soils.

Table 5.9. Estimated range of K_d values for lead as a function of soil pH, and equilibrium lead concentrations.

Equilibrium Lead Concentration (micro g/l)	K_d (ml/g)	Soil pH		
		4.0 - 6.3	6.4 - 8.7	8.8 - 11.0
0.1 - 0.9	Minimum	940	4,360	11,520
	Maximum	8,650	23,270	44,580
1.0 - 9.9	Minimum	420	1,950	5,160
	Maximum	4,000	10,760	20,620
10 - 99.9	Minimum	190	900	2,380

	Maximum	1,850	4,970	9,530
100 - 200	Minimum	150	710	1,880
	Maximum	860	2,300	4,410

5.5.6.2.2 Limits of K_d Values with Respect to Equilibrium Lead Concentrations

The limits of equilibrium lead concentrations (0.0001 mg/l to about 0.2 mg/l) were selected based on the experimental data generated by Gerritse *et al.* (1982) and Rhoads *et al.* (1992). These investigators showed that within the range of initial lead concentrations used in their experiments the principal lead removal reaction from solution was adsorption and not precipitation. Four concentration ranges were selected to develop the K_d values.

5.6 Plutonium Geochemistry and K_d Values

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

In the ranges of pH and conditions typically encountered in the environment, plutonium can exist in all 4 oxidation states, namely +3, 4, +5, and +6. Under oxidizing conditions, Pu(IV), Pu(V), and Pu(VI) are common, whereas, under reducing conditions, Pu(III) and Pu(IV) would exist. Dissolved plutonium forms very strong hydroxy-carbonate mixed ligand complexes, therefore, its adsorption and mobility is strongly affected by these complex species. Under conditions of low pH and high concentrations of dissolved organic carbon, it appears that plutonium-organic complexes may be control adsorption and mobility of plutonium in the environment.

If plutonium is present as a distinct solid phase (amorphous or partly crystalline $\text{PuO}_2 \cdot x\text{H}_2\text{O}$) or as a solid solution, the upper limits of aqueous plutonium concentrations would be in the 10^{-12} to 10^{-9} M range. Dissolved plutonium in the environment is typically present at $\leq 10^{-15}$ M levels indicating that adsorption may be the principal phenomenon that regulates the mobility of this actinide.

Plutonium can adsorb on geologic material from low to extremely high affinities with K_d values ranging from 11 to 300,000 ml/g. Plutonium in the higher oxidation state adsorbed on iron oxide surfaces may be reduced to the tetravalent state by Fe(II) present in the iron oxides.

Two factors that influence the mobilization of adsorbed plutonium under environmental pH conditions (>7) are the concentrations of dissolved carbonate and hydroxyl ions. Both these ligands form very strong mixed ligand complexes with plutonium, resulting in desorption and increased mobility in the environment.

5.6.2 General Geochemistry

Plutonium is produced by fissioning uranium fuel and is used in the construction of nuclear weapons. Plutonium has entered the environment either through accidental releases or through disposal of wastes generated during fuel processing and the production and detonation of nuclear weapons. Plutonium has 15 isotopes, but only 4 of these isotopes namely, ^{238}Pu [$t_{1/2}$ (half life) = 86 y], ^{239}Pu ($t_{1/2}$ = 24,400 y), ^{240}Pu ($t_{1/2}$ = 6,580 y), ^{241}Pu ($t_{1/2}$ = 13.2 y), are of environmental concern due to their abundances and long-half lives.

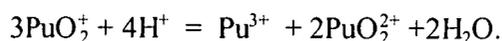
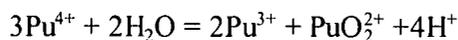
In the range of pH and redox conditions typically encountered in the environment, plutonium can exist in 4 oxidation states, namely +3, +4, +5, and +6 (Allard and Rydberg, 1983). Plutonium oxidation states are influenced by factors such as pH, presence of complexants and reductants, radiolysis, and temperature (Choppin, 1983). Observations indicate that under very low plutonium concentrations and oxidizing environmental conditions, the disproportionation¹ reactions of plutonium are not significant (Cleveland, 1979). Under reducing conditions, Pu(III) species would be dominant up to pH values approaching about 8.5, beyond which the Pu(IV) species are known to be the dominant species. However, under oxidizing conditions and at pH values greater than 4.0, plutonium can exist in +4, +5, and +6 oxidation states (Keeney-Kennicutt and Morse, 1985). A number of investigators believe that under oxidizing conditions, the +5 state to be the dominant redox state (Aston, 1980; Bondietti and Trabalka, 1980; Nelson and Orlandini, 1979; Rai *et al.*, 1980b).

Of the contaminated sites considered in EPA/DOE/NRC (1993), radioactive contamination by ^{238}Pu , ^{239}Pu , and/or ^{240}Pu has been identified at 9 of the 45 Superfund National Priorities List (NPL) sites. The reported contamination includes airborne particulates, plutonium-containing soils, and plutonium dissolved in surface- and groundwaters.

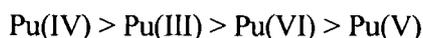
5.6.3 Aqueous Speciation

Dissolved plutonium forms complexes with various inorganic ligands such as hydroxyl, carbonate, nitrate, sulfate, phosphate, chloride, bromide, and fluoride; with many naturally occurring organic ligands such as acetate, citrate, formate, fulvate, humate, lactate, oxalate, and tartrate; and with

¹ 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:



synthetic organic ligands such as EDTA and 8-hydroxyquinoline derivatives (Cleveland, 1979). Plutonium(IV) hydrolyzes more readily than all other redox species of plutonium (Baes and Mesmer, 1976). The order of hydrolysis of plutonium redox species follows the sequence



(Choppin, 1983). Plutonium hydrolytic species may have up to 4 coordinated hydroxyls. The tendency of plutonium in various oxidation states to form complexes depends on the ionic potential defined as the ratio (z/r) of the formal charge (z) to the ionic radius (r) of an ion. Among plutonium redox species, Pu(IV) exhibits the highest ionic potential and therefore forms the strongest complexes with various ligands. Based on the equilibrium constants ($K_{r,298}^{\circ}$) for the plutonium complexation reactions, ligands, such as chloride and nitrate, form weak complexes ($\log K_{r,298}^{\circ}$ of 1 to 2) with plutonium, whereas fluoride, sulfate, phosphate, citrate, and oxalate form stronger complexes ($\log K_{r,298}^{\circ}$ of 6 to 30). Among the strongest complexes of plutonium are the hydroxy-carbonate mixed ligand complexes [e.g., $\text{Pu(OH)}_2(\text{CO}_3)_2^-$] (Tait *et al.*, 1995; Yamaguchi *et al.*, 1994). Additionally, dissolved organic matter (fulvic and humic material) may also form complexes with plutonium. Although the nature of these complexes and their stability constants have not been fully characterized, it is believed that humic complexes of plutonium may be the dominant soluble species in natural environments at lower pH (below 5 to 6) values (Allard and Rydberg, 1983).

Because dissolved plutonium can exist in multiple redox states and form hydrolytic and complex species in solution, it is useful to assess the probable dominant plutonium aqueous species that may exist in typical ground water. Therefore, the aqueous speciation of dissolved plutonium was calculated as a function of pH using the MINTEQA2 code and a concentration of 3.2×10^{-10} mg/l (1.36×10^{-15} M) total dissolved plutonium. This concentration is based on the maximum activity of $^{239,240}\text{Pu}$ measured by Simpson *et al.* (1984) in 33 water samples taken from the highly alkaline Mono Lake in California. The species distribution was calculated assuming that multiple plutonium valence states might be present based on thermodynamic equilibrium considerations. This calculation is dependent on redox conditions as well as the pH and composition of the water. Therefore, a set of oxic conditions that might be associated with surface or near-surface disposal facilities or contaminated sites were selected for these illustrative calculations. These redox conditions are based on an experimentally determined pH/Eh relationship described in Lindsay (1979) for suspensions of sandy loam and distilled water. In a series of acid and base titrations, the pH/Eh response of the soil/water suspension was determined to vary according to the equation

$$\text{pe} + \text{pH} = 15.23 \quad (5.1)$$

where pe = negative log of the electron activity.¹

¹ The electron activity is defined as unity for the standard hydrogen electrode.

The pe is related to Eh by the equation

$$pe = (2.303RT / F) pe \quad (5.2)$$

where R = universal gas constant (1.9872 cal/mol·K)

T = temperature in degrees kelvin

F = Faraday constant (96,487 coulombs/equivalent).

At 25.0°C (298 K),

$$Eh(\text{mV}) = 5.92 pe \quad (5.3)$$

Using Equations 5.1 and 5.3, an Eh value was calculated for each pH value used as an input for the MINTEQA2 calculations of plutonium aqueous speciation. The plutonium aqueous species that were included in the computation scheme are tabulated in Table 5.10. Thermodynamic data for these species were taken primarily from Lemire and Tremaine (1980) and other secondary sources and database modifications described by Krupka and Serne (1996).

Results are plotted as a species distribution diagram (Figure 5.3). The data show that, under very low pH (~3 - 3.5) conditions, PuF_2^{2+} and PuO_2^+ are the dominant species of plutonium. The free ionic species, PuO_2^+ appears to be the dominant form within the pH range of 4 to 5. Within the pH range of 5.5 to 6.5, the main species of plutonium appear to be PuO_2^+ , and $\text{Pu}(\text{OH})_2(\text{CO}_3)_2^{2-}$, with minor species being the neutral hydrolytic species $\text{Pu}(\text{OH})_4^0(\text{aq})$ and the phosphate complex $\text{Pu}(\text{HPO}_4)_4^{4-}$. At pH values exceeding 6.5, the bulk of the dissolved plutonium (~90 percent) would be comprised of the $\text{Pu}(\text{OH})_2(\text{CO}_3)_2^{2-}$ species with a minor percentage of $\text{Pu}(\text{OH})_4^0(\text{aq})$. These illustrative computations indicate that, under pH conditions that typically exist in surface and groundwaters (>6.5), the dominant form of dissolved plutonium would be the tetravalent complex species, $\text{Pu}(\text{OH})_2(\text{CO}_3)_2^{2-}$.

Polymeric species of plutonium may not occur under environmental conditions because the total plutonium concentrations in nature are at least 7 orders of magnitude less than the concentrations required for the formation of such species (Choppin, 1983). It is important to note that the speciation of plutonium would change significantly with changing redox conditions, pH, the types and total concentrations of complexing ligands and major cationic constituents.

5.6.4 Dissolution/Precipitation/Coprecipitation

Allard and Rydberg (1983) calculated that the aqueous concentrations of plutonium in nature may be controlled by the solubility of the solid phase $\text{PuO}_2 \cdot x\text{H}_2\text{O}$. Many observations show that plutonium associated with soils and particulate organic matter is present in tetravalent oxidation state (Nelson and Lovett, 1980; Nelson *et al.*, 1987; Silver, 1983). Calculations by Allard and Rydberg (1983) based on available thermodynamic data show that, under reducing conditions, the solubility of dissolved

plutonium would be limited by the solid phase PuO_2 at pH values greater than 8, and by the solid phase $\text{Pu}_2(\text{CO}_3)_3$ of trivalent plutonium at lower pH values.

Table 5.10. Plutonium aqueous species included in the speciation calculations.

Redox State	Aqueous Species
Pu(III)	$\text{Pu}^{3+}, \text{PuOH}^{2+}, \text{Pu}(\text{OH})_2^+, \text{Pu}(\text{OH})_3^{\circ}(\text{aq})$ $\text{PuCO}_3^+, \text{Pu}(\text{CO}_3)_2^-, \text{Pu}(\text{CO}_3)_3^{3-}$ $\text{PuSO}_4^+, \text{Pu}(\text{SO}_4)_2^-$ $\text{PuH}_2\text{PO}_4^{2+}, \text{PuCl}^+$
Pu(IV)	$\text{Pu}^{4+}, \text{PuOH}^{3+}, \text{Pu}(\text{OH})_2^{2+}, \text{Pu}(\text{OH})_3, \text{Pu}(\text{OH})_4^{\circ}(\text{aq})$ $\text{Pu}(\text{OH})_4(\text{CO}_3)_2^{4+}, \text{Pu}(\text{OH})_2(\text{CO}_3)_2^{2-}$ $\text{PuSO}_4^{2+}, \text{Pu}(\text{SO}_4)_2^{\circ}(\text{aq}), \text{PuHPO}_4^{2+}, \text{Pu}(\text{HPO}_4)_2^{\circ}(\text{aq}),$ $\text{Pu}(\text{HPO}_4)_3^{2+}, \text{Pu}(\text{HPO}_4)_4^{4+}$ $\text{PuCl}^+, \text{PuF}^{3+}, \text{PuF}_2^{2+}, \text{PuF}_3^+, \text{PuF}_4^{\circ}(\text{aq})$
Pu(V)	$\text{PuO}_2^+, \text{PuO}_2\text{OH}^{\circ}(\text{aq}), (\text{PuO}_2)_2\text{OH}^+$
Pu(VI)	$\text{PuO}_2^{2+}, \text{PuO}_2\text{OH}^+, \text{PuO}_2(\text{OH})_2^{\circ}(\text{aq}),$ $\text{PuO}_2(\text{OH})_3^-, (\text{PuO}_2)_2(\text{OH})_2^{2+}, (\text{PuO}_2)_3(\text{OH})_5^+$ $\text{PuO}_2\text{CO}_3^{\circ}(\text{aq}), \text{PuO}_2(\text{CO}_3)_2^{2-}, \text{PuO}_2(\text{CO}_3)_3^{4-}$ $\text{PuO}_2\text{Cl}^+, \text{PuO}_2\text{F}^+, \text{PuO}_2\text{F}_2^{\circ}(\text{aq}), \text{PuO}_2\text{F}_3^-, \text{PuO}_2\text{F}_4^{2-}$ $\text{PuO}_2\text{SO}_4^{\circ}(\text{aq}), \text{PuO}_2\text{H}_2\text{PO}_4^+$

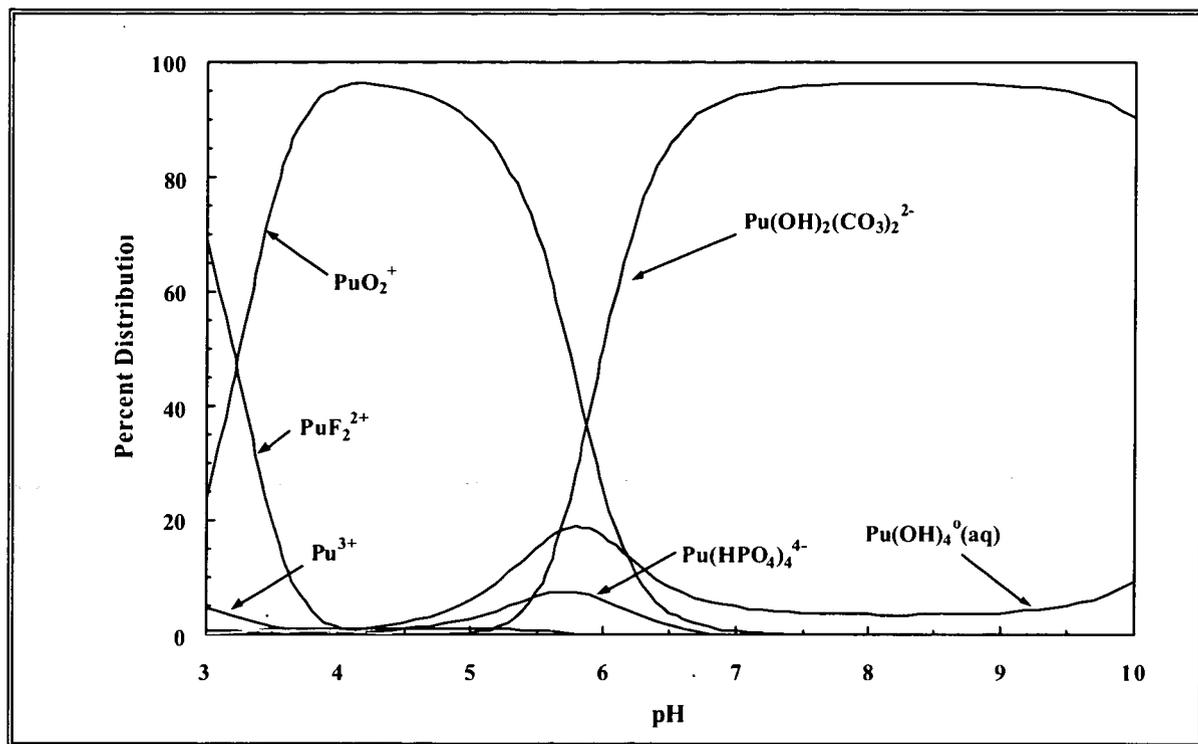


Figure 5.3. Calculated distribution of plutonium aqueous species as a function of pH for the water composition in Table 5.1. [The species distribution is based on a concentration of 3.2×10^{-10} mg/l (1.36×10^{-15} M) total dissolved plutonium.]

Laboratory studies conducted by Rai *et al.* (1980a), Delegard (1987), and Yamaguchi *et al.* (1994) indicated that a freshly precipitated amorphous $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ phase controls the equilibrium solubility of plutonium. Solubility on aged precipitates by Rai *et al.* (1980a) and Delegard (1987) also showed that equilibrium plutonium concentrations would be controlled by a partially crystallized $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ phase at concentrations about 2 orders of magnitude less than that of amorphous $\text{PuO}_2 \cdot x\text{H}_2\text{O}$. Therefore, under oxidizing conditions, amorphous $\text{PuO}_2 \cdot x\text{H}_2\text{O}$, if present in soils, may control soluble plutonium concentrations near 10^{-8} M. Under alkaline conditions with high dissolved carbonate concentrations, dissolved plutonium concentrations may increase to micromolar levels. When dissolved carbonate is not present, $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ may control plutonium concentrations at about 10^{-10} M (Rai *et al.*, 1980a).

5.6.5 Sorption/Desorption

Plutonium is known to adsorb onto soil components such as clays, oxides, hydroxides, oxyhydroxides, aluminosilicates and organic matter. Depending on the properties of the substrate, pH, and the composition of solution, plutonium would adsorb with affinities varying from low ($K_d = 11$ ml/g) to extremely high ($K_d = 300,000$ ml/g) (Baes and Sharp, 1983; Coughtrey *et al.*, 1985; Thibault *et al.*, 1990).

A number of studies indicate that iron hydroxides adsorb and reduce penta- and hexavalent plutonium to its tetravalent state at the solid surface. Experimental data showed that tetra- and pentavalent plutonium aqueous species oxidize to hexavalent form upon adsorption onto manganese dioxide surfaces whereas, pentavalent plutonium adsorbed on goethite disproportionate into tetra and hexavalent forms (Keeney-Kennicutt and Morse, 1985). Subsequently, the hexavalent form of plutonium was observed to have been reduced to tetravalent state. Additionally, these reactions were found to occur faster under light conditions than under dark conditions suggesting photochemical catalysis of adsorbed plutonium redox change reactions.

Laboratory studies have indicated that increasing carbonate concentrations decreased adsorption of tetra- and pentavalent plutonium on goethite surfaces (Sanchez *et al.*, 1985). Phenomenon similar to the reduction and suppression of plutonium adsorption in the presence of carbonate ions have also been observed for other actinides which also form strong hydroxy-carbonate mixed ligand aqueous species. These data suggest that plutonium would be most mobile in high pH carbonate-rich groundwaters.

Some studies indicate that the mass of plutonium retarded by soil may not be easily desorbed from soil mineral components. For example, Bunzl *et al.* (1995) studied the association of $^{239+240}\text{Pu}$ from global fallout with various soil components. They determined the fractions of plutonium present as readily exchangeable, bound to carbonates, bound to iron and manganese oxides, bound to organic matter, and residual minerals. For soils at their study site in Germany, the results indicated that 30-40 y after deposition of the plutonium, the readily exchangeable fraction of plutonium was less than 1 percent. More than 57 percent of the plutonium was sorbed to organic matter and a considerable mass sorbed to the oxide and mineral fractions.

5.6.6 Partition Coefficient, K_d , Values

5.6.6.1 General Availability of K_d Data

A number of studies have focused on the adsorption behavior of plutonium on minerals, soils, and other geological materials.¹ A review of data from diverse sources of literature indicated that K_d values for plutonium typically range over 4 orders of magnitude (Thibault *et al.*, 1990). Also, based on a review of these data, a number of factors which influence the adsorption behavior of plutonium have been identified. These factors and their effects on plutonium adsorption on soils were used as the basis for generating a look-up table. These factors are:

- ~ Typically, in many experiments, the oxidation state of plutonium in solution was not determined or controlled. Therefore it would be inappropriate to compare the K_d data obtained from different investigations.
- ~ In natural systems with organic carbon concentrations exceeding ~10 mg/kg, plutonium exists mainly in trivalent and tetravalent redox states. If initial plutonium concentrations exceed $\sim 10^{-7}$ M, the measured K_d values would reflect mainly precipitation reactions and not adsorption reactions.
- ~ Adsorption data show that the presence of ligands influence plutonium adsorption onto soils. Increasing concentrations of ligands decrease plutonium adsorption.
- ~ If no complexing ligands are present plutonium adsorption increases with increasing pH (between 5.5 and 9.0).
- ~ Plutonium is known to adsorb onto soil components such as aluminum and iron oxides, hydroxides, oxyhydroxides, and clay minerals. However, the relationship between the amounts of these components in soils and the measured adsorption of plutonium has not been quantified.

The factors which influence plutonium adsorption were identified from the following sources of data. A description and assessment of these data are provided in Appendix G. Because plutonium in nature can exist in multiple oxidation states (III, IV, V, and VI), soil redox potential would influence the Pu redox state and its adsorption on soils. However, our literature review found no plutonium adsorption studies which included soil redox potential as a variable. Studies conducted by Nelson *et al.* (1987) and Choppin and Morse (1987) indicated that the oxidation state of dissolved plutonium under natural

¹ Since the completion of our review and analysis of K_d data for the selected contaminants and radionuclides, the studies by Duff *et al.* (1999) and Fisher *et al.* (1999) were identified and may be of interest to the reader.

conditions depended on the colloidal organic carbon content in the system. Additionally, Nelson et al (1987) also showed that plutonium precipitation occurred if the solution concentration exceeded 10^{-7} M.

Plutonium complexation by ligands, such as acetate (Nishita, 1978; Rhodes, 1957), oxalate (Bensen, 1960), and fulvate (Bondietti *et al.*, 1975), are known to reduce adsorption of plutonium. Studies of suspended particles from natural water systems also showed that increasing concentrations of dissolved organic carbon decreased plutonium adsorption (Nelson *et al.*, 1987). Experiments using synthetic ligands such as EDTA (1 mmol/l), DTPA (1 mmol/l), and HEDTA (100 mmol/l) have shown that plutonium adsorption onto soils was reduced due to complexing effects of these ligands (Delegard *et al.*, 1984; Relyea and Brown, 1978). However, it is unlikely that such concentrations of these synthetic ligands would exist in soils. The effects of carbonate ions on Pu(IV) adsorption on goethite have been quantified by Sanchez *et al.* (1985). They found that carbonate concentrations exceeding 100 mmol/l significantly reduced adsorption of Pu(IV) on goethite. In contrast, under soil saturation extract conditions in which carbonate concentrations typically range from 0.1 to 6 mmol/l HCO_3^- , Pu(IV) adsorption appears to increase with increasing carbonate concentration (Glover *et al.*, 1976).

Rhodes (1957) and Prout (1958) conducted studies of plutonium adsorption as a function of pH. Both these studies indicated that Pu exhibited an adsorption maxima between pH values 6.5 to 8.5. These data however are unreliable because initial plutonium concentrations of 6.8×10^{-7} to 1×10^{-6} M used in the experiments may have resulted in precipitation reactions thus confounding the observations.

Even though the adsorption behavior of plutonium on soil minerals such as glauconite (Evans, 1956), montmorillonite (Billon, 1982; Bondietti *et al.*, 1975), attapulgite (Billon, 1982), and oxides, hydroxides, and oxyhydroxides (Evans, 1956; Charyulu *et al.*, 1991; Sanchez *et al.*, 1985; Tamura, 1972; Ticknor, 1993; Van Dalen *et al.*, 1975) has been studied, correlative relationships between the type and quantities of soil minerals in soils and the overall plutonium adsorption behavior of the soils have not been established.

Plutonium adsorption data for 14 soils have been collected by Glover *et al.* (1976) along with a number of soil properties that included soil organic matter content. A multiple regression analyses of these data showed that compared to other soil parameters such as clay mineral content, dissolved carbonate concentration, electrical conductivity and pH, soil organic matter was not a significant variable.

These criteria were used to evaluate and select plutonium adsorption data in developing a look-up table. Only 2 adsorption studies using soils in which the initial concentrations of Pu(IV) used were less than the concentration that would trigger precipitation reactions. Barney (1984) conducted adsorption experiments in which initial plutonium concentrations of 10^{-11} to 10^{-9} M were used to examine plutonium adsorption on to basalt interbed sediments from Hanford, Washington. Glover *et al.* (1976) conducted a set of experiments using 10^{-8} M initial concentration to study the adsorption behavior of Pu(IV) on

14 different soil samples from 7 DOE sites. A number of soil properties were also measured thus providing a basis to correlate the adsorption behavior with a number of soil parameters. This is the best available data set for Pu(IV) adsorption on a number of well characterized soils therefore, it was used to develop correlative relationships and a look-up table for K_d values.

5.6.6.2 K_d Look-Up Table

The look-up table for plutonium K_d values (Table 5.11) was generated using the a piece-wise regression model with clay content and dissolved carbonate as the independent variables (See Appendix G for details).

5.6.6.2.1 Limits of K_d Values with Respect to Clay Content

The clay contents of the soils used for developing the regression relationship ranged from 3 to 64 percent by weight. Therefore the range of clay contents for the look-up table was set between 0 and 70 percent. Extending the regression relationship for high clay soils (>70 percent) would result in a higher degree of uncertainty for predicted K_d values. Clay contents of soils are typically measured as part of textural analysis of soil. Clay content of a soil is defined as the mass of soil particles with average particle size of ≤ 2 micro m.

Table 5.11. Estimated range of K_d values for plutonium as a function of the soluble carbonate and soil clay content values.

K_d (ml/g)	Clay Content (wt.%)								
	0 - 30			31 - 50			51 - 70		
	Soluble Carbonate (meq/l)			Soluble Carbonate (meq/l)			Soluble Carbonate (meq/l)		
	0.1 - 2	3 - 4	5 - 6	0.1 - 2	3 - 4	5 - 6	0.1 - 2	3 - 4	5 - 6
Minimum	5	80	130	380	1,440	2,010	620	1,860	2,440
Maximum	420	470	520	1,560	2,130	2,700	1,980	2,550	3,130

5.6.6.2.2 Limits of K_d Values with Respect to Dissolved Carbonate Concentrations

The dissolved carbonate content of the soils used for the regression relationships ranged from about 0.1 to 6 meq/l (0.1 to 6 mmol/l of HCO_3^-). The dissolved carbonate values were measured on saturation extracts obtained from these soils. The standard procedure for obtaining saturation extracts from soils has been described by Rhoades (1996). The saturation extracts are obtained by saturating and equilibrating the soil with distilled water followed by vacuum filtration to collect the extract. Saturation extracts are usually used to determine the pH, the electrical conductivity, and dissolved salts in soils. For soils with pH values less than 8.5, the saturation extracts typically contain less than 8 mmol/l of dissolved carbonate (Richards, 1954).

The regression relationship indicates that within the range of 0.1 to 6 mmol/l of dissolved carbonate, the K_d values increase with increasing dissolved carbonate values. Adsorption experiments conducted by Sanchez *et al.* (1985) showed however that very high concentrations (100 to 1,000 meq/l) of dissolved carbonate in matrix solution decreases Pu adsorption on goethite. The dissolved carbonates in soil saturation extracts are 3 to 4 orders of magnitude less than the concentrations used in experiments by Sanchez *et al.* (1985). The data by Glover *et al.* (1976) show that within very low concentration range of dissolved carbonate (0.1 to 6 mmol/l) found soil saturation extracts, K_d values for Pu increase as a function of dissolved carbonate. This correlation may be strictly serendipitous and a more likely variable that would lead to an increased K_d would be increasing pH.

5.7 Radon Geochemistry and K_d Values

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

The migration of radon, an inert gas, in soil/water systems is not affected itself by aqueous speciation, precipitation/dissolution, or adsorption/desorption processes. Therefore, the mobility of radon is not affected by issues associated with the selection of appropriate "adsorption" K_d values for modeling contaminant transport and risks in soil/water systems. Radon is soluble in water, and the hydrostatic pressure on ground water below the water table is sufficient to keep dissolved radon in solution.

The generation of radon is however affected by the concentrations of its parent elements which, along with radon's decay products, are of regulatory concern. Because aqueous speciation, precipitation/dissolution, or adsorption/desorption processes can affect the movement of radon's parents and decay products in soils, these processes should be considered when modeling contaminant transport in a total environmental system, including air transport pathways.

5.7.2 General Geochemistry

Radon is a colorless, odorless, essentially inert gas. All radon isotopes are radioactive. The longest-lived isotope of radon is ^{222}Rn which has a half life ($t_{1/2}$) of 3.8 d. The main health risk is from inhalation of radon gas and its daughter products which are usually adsorbed on dust in the air. Detailed descriptions of the geologic controls, migration, and detection of radon have been included in published proceedings such as Graves (1987), Gesell and Lowder (1980), and elsewhere. Of the 45 Superfund National Priorities List (NPL) sites considered in EPA/DOE/NRC (1993), radioactive contamination of air, soil, surface water, and/or groundwater by ^{220}Rn and/or ^{222}Rn has been identified at 23 sites.

Twenty isotopes of radon are known (Weast and Astle, 1980). Environmental radon contamination typically results from radioactive decay of isotopes in the uranium-thorium series. These include the formation of:

- ^{222}Rn by alpha decay from ^{226}Ra in the ^{238}U decay series
- ^{220}Rn ($t_{1/2}=54$ sec) by alpha decay from ^{224}Ra in the ^{232}Th decay series
- ^{219}Rn ($t_{1/2}=3.9$ sec) by alpha decay from ^{223}Ra in the ^{235}U decay series.

The final, stable daughter products in these 3 decay series are ^{206}Pb , ^{208}Pb , and ^{207}Pb , respectively.

Some noble gases (*i.e.*, krypton, xenon, and radon) have very limited chemical reactivity with other elements. The chemical reactivity of radon is difficult to assess because of its short half life.

Geologic and hydrogeologic processes that might influence radon mobility are discussed in detail by Tanner (1980). As an inert gas, radon is not immobilized by precipitation processes along migration pathways. According to data cited by Tanner (1980), the ratio (*i.e.*, solubility distribution coefficient) of ^{222}Rn in a water phase to that in a gas phase ranges from 0.52 at 0°C to 0.16 at 40°C . This ratio has been used, for example, for the solubility of radon in water in mathematical models designed to calculate radon diffusion coefficients in soils (*e.g.*, Nielson *et al.*, 1984). The solubility of radon in organic liquids is greater than that in water.

5.7.3 Aqueous Speciation

The existence of radon aqueous species was not identified in any of the references reviewed for this study. Given the inertness of radon and the short half life ($t_{1/2}=3.8$ d) for ^{222}Rn , aqueous speciation and complexation of dissolved radon would not be expected to be important.

However, as noted above, radon is soluble in water. The hydrostatic pressure on ground water below the water table is sufficient to keep dissolved radon in solution. Above the water table, the radon

present in vadose zone pore water will exsolve from solution, enter the vapor phase, and migrate as part of the air through the open rock and soil pore spaces.

5.7.4 Dissolution/Precipitation/Coprecipitation

Because radon exists as a dissolved gas, dissolution/precipitation processes are not important relative to the geochemical behavior of radon and its movement through aqueous environments. These processes are, however, important relative to the geochemical behavior of radon's parent elements (*e.g.*, radium) and associated mechanisms by which the radon gas escapes from the solid phases into ground- and soil waters.

Rama and Moore (1984) studied the mechanism for the release of ^{222}Rn and ^{220}Rn from solid aquifer material. They determined that radon and other decay products from the U-Th series were released by alpha recoil¹ from the walls of nanometer-size pores in the aquifer solids. Radon diffused into the intergranular water for release to the atmosphere or decay to more long-lived products. These decay products may in turn diffuse from the intergranular water and become adsorbed onto the walls of the nanometer-size pores.

5.7.5 Adsorption/Desorption

Adsorption processes are not expected to be important relative to the geochemical behavior of gaseous radon and its movement through aqueous environments. The lack of importance of sorption processes is also supported by studies conducted at cryogenic temperatures (Tanner, 1980). However, as noted by Tanner (1980), "adsorption effects on the release of radon isotopes from geologic materials have not been studied sufficiently to determine unambiguously whether they are an important factor."

5.7.6 Partition Coefficient, K_d , Values

Because adsorption processes are not important relative to the movement of gaseous radon through aqueous environments, a review of K_d values for radon was not conducted. Compilations, such as Thibault *et al.* (1990), do not list any K_d values for radon. A K_d value of zero should be considered for radon.

¹ Alpha recoil refers to the 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).

5.8 Strontium Geochemistry and K_d Values

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

Strontium in solution is expected to be predominantly present as the uncomplexed Sr^{2+} ion. Only in highly alkaline soils could strontianite (SrCO_3) control strontium concentrations in solutions. The extent to which strontium partitions from the aqueous phase to the solid phase is expected to be controlled primarily by the CEC of the solid phase. In environments with a pH greater than 9 and dominated by carbonates, coprecipitation with CaCO_3 and/or precipitation as SrCO_3 may become an increasingly important mechanism controlling strontium removal from solution (Lefevre *et al.*, 1993). A direct correlation between solution pH and strontium K_d has been reported (Prout, 1958; Rhodes, 1957). This trend is likely the result of hydrogen ions competing with Sr^{2+} for exchange sites and the result of pH increasing the CEC. Strontium K_d values may decrease from 100 to 200 ml/g in low ionic strength solutions to less than 5 ml/g in high ionic strength solutions (Routson *et al.*, 1980). Calcium is an important competing cation affecting ^{90}Sr K_d values (Kokotov and Popova, 1962; Schulz, 1965). The most important ancillary parameters affecting strontium K_d values are CEC, pH, and concentrations of calcium and stable strontium.

5.8.2 General Geochemistry

Strontium exists in nature only in the +2 oxidation state. The ionic radius of Sr^{2+} is 1.12 Å, very close to that of Ca^{2+} at 0.99 Å (Faure and Powell, 1972). As such, strontium can behave chemically as a calcium analog, substituting for calcium in the structure of a number of minerals. Strontium has 4 naturally occurring isotopes: ^{84}Sr (0.55 percent), ^{86}Sr (9.75 percent), ^{87}Sr (6.96 percent), and ^{88}Sr (82.74 percent). The other radioisotopes of strontium are between ^{80}Sr and ^{95}Sr . Only ^{90}Sr [half life ($t_{1/2}$) = 28.1 y], a fission product, is of concern in waste disposal operations and environmental contamination. The radionuclide ^{89}Sr also is obtained in high yield, but the half-life is too short ($t_{1/2}$ = 52 d) to create a persistent environmental or disposal problem. Because of atmospheric testing of nuclear weapons, ^{90}Sr is distributed widely in nature. The average ^{90}Sr activity in soils in the United States is approximately 100 mCi/mi². As a calcium analog, ^{90}Sr tends to accumulate in bone (UNSCEAR, 1982).

Contamination includes airborne particulates, strontium-containing soils and strontium dissolved in surface- and groundwaters. Of the contaminated sites considered in EPA/DOE/NRC (1993), radioactive contamination by ^{90}Sr has been identified at 11 of the 45 Superfund National Priorities List (NPL).

5.8.3 Aqueous Speciation

There is little tendency for strontium to form complexes with inorganic ligands (Faure and Powell, 1972). The solubility of the free Sr^{2+} ion is not greatly affected by the presence of most inorganic anions. Dissolved strontium forms only weak aqueous complexes with carbonate, sulfate, chloride, and nitrate. For example, Izrael and Rovinskii (1970) used electro dialysis to study the chemical state of strontium leached by groundwater from rubble produced in a nuclear explosion. They found that 100 percent of the strontium existed as uncomplexed Sr^{2+} , with no colloidal or anionic strontium present in the leachate. Stevenson and Fitch (1986) concluded that strontium should not form strong complexes with fulvic or humic acids based on the assumptions that strontium would exhibit similar stability with organic ligands as calcium and that strontium could not effectively compete with calcium for exchange sites because calcium would be present at much greater concentrations. Thus, organic and inorganic complexation is not likely to greatly affect strontium speciation in natural groundwaters.

Species distribution of strontium was calculated using the water composition described in Table 5.1 and a concentration of 0.11 mg/l total dissolved strontium. Hem (1985, p. 135) lists this value as a median concentration of dissolved strontium for larger United States public water supplies based on analyses from Skougstad and Horr (1963). The strontium aqueous species included in the speciation calculations are listed in Table 5.12. These MINTEQA2 calculations support the contention that strontium will exist in groundwaters predominantly as the uncomplexed Sr^{2+} ion. The Sr^{2+} ion dominates the strontium speciation throughout the pH range of 3 to 10. Between pH 3 and 8.5, the Sr^{2+} species constitutes approximately 98 percent of the total dissolved strontium. The remaining 2 percent is composed of the neutral species $\text{SrSO}_4^0(\text{aq})$. Between pH 9 and 10, $\text{SrCO}_3^0(\text{aq})$ is calculated to be between 2 and 12 percent of the total dissolved strontium. As the pH increases above 9, the $\text{SrCO}_3^0(\text{aq})$ complex becomes increasingly important. The species distribution for strontium does not change if the concentration of total dissolved cadmium is increased from 1 to 1,000 micro g/l.

5.8.4 Dissolution/Precipitation/Coprecipitation

Strontium is an alkaline-earth element, which also includes beryllium, magnesium, calcium, strontium, barium and radium, and can form similar solid phases as calcium. For instance, the 2 most prevalent strontium minerals, celestite (SrSO_4) and strontianite (SrCO_3), have calcium counterparts, anhydrite (CaSO_4), and calcite (CaCO_3). In an acidic environment, most of the strontium solids will be highly soluble, and, if the activity of Sr^{2+} in solution exceeds approximately 10^{-4} mol/l, celestite may precipitate to form a stable phase. However, in alkaline conditions, strontianite would be the stable solid phase and could control strontium concentrations in soil solutions. However, the dissolved strontium concentrations in most natural waters are generally well below the solubility limit of strontium-containing minerals.

Table 5.12. Strontium aqueous species included in the speciation calculations.

Aqueous Species
Sr^{2+} , SrOH^+
$\text{SrCO}_3^{\circ}(\text{aq})$, $\text{SrSO}_4^{\circ}(\text{aq})$, SrNO_3^+
SrCl^+ , SrF^+
SrPO_3 , $\text{SrHPO}_4^{\circ}(\text{aq})$, $\text{SrH}_2\text{PO}_4^+$, $\text{SrP}_2\text{O}_7^{2-}$

Because strontium generally exists in nature at much lower concentration than calcium, it commonly does not form pure phases (Faure and Powell, 1972). Instead it forms coprecipitates (solid solutions) with calcite and anhydrite. Calcite can allow the substitution of several hundred parts per million strontium before there is any tendency for strontianite to form. Strontium can also coprecipitate with barium to form $(\text{Ba}_{(1-x)}, \text{Sr}_x)\text{SO}_4$ in more-alkaline environments (Ainsworth and Rai, 1987; Felmy *et al.*, 1993).

5.8.5 Adsorption/Desorption

A great deal of research has been directed at understanding and measuring the extent to which strontium adsorbs to soils [reviewed by Ames and Rai (1978) and Streng and Peterson (1989)]. The primary motivation for this research is the need to understand the environmental fate and mobility of ^{90}Sr , particularly as it relates to site remediation and risk assessment. The mechanism by which

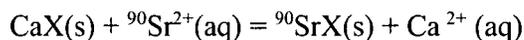
strontium partitions from the dissolved phase to the solid phase at pH values less than 9 is commonly believed to be cation exchange¹ (Ames and Rai, 1978; Lefevre *et al.*, 1993; McHenry, 1958).

Among the most important environmental parameters affecting the magnitude of a strontium K_d value is the soil CEC (Ames and Rai, 1978; Lefevre *et al.*, 1993; McHenry, 1958). This finding is consistent with cation exchange proposed as the mechanism generally controlling strontium adsorption. The results of Serne and LeGore (1996) also indicate that strontium adsorption is largely controlled by cation exchange. They reported that ^{90}Sr adsorption was reversible; that is, strontium could be easily desorbed (exchanged) from the surfaces of soils. Natural soils that had been in contact with ^{90}Sr for approximate 27 y could be leached of adsorbed ^{90}Sr as readily as similar soils containing recently adsorbed strontium, indicating that ^{90}Sr does not become more recalcitrant to leaching with time. Furthermore, these studies suggested that cation exchange, and not (co)precipitation, was responsible for ^{90}Sr sorption because the latter would leach at a much slower rate.

Some studies indicate that a fraction of some ^{90}Sr sorbed to soil components may not be readily exchanged [see review in Brady *et al.* (1999)]. For example, Schulz and Riedel (1961) studied the influence of aging on the sorption of carrier-free ^{90}Sr into nonexchangeable forms by three soils. They observed that less than 10% of the total applied carrier-free ^{90}Sr was not easily exchanged which they attributed to adsorption onto solid-phase carbonates or phosphates. A study by Wiklander (1964) indicated that after 4 y, only 90 percent of the ^{90}Sr added to the soil could be displaced by repeated acidic ammonium acetate (pH 4.6) extractions. Wiklander proposed that the retention of ^{90}Sr was due to strontium substituting for calcium into or adsorbing onto calcium-bearing minerals. Studies by Roberts and Menzel (1961) and Taylor (1968) showed that as much as 50% of the ^{90}Sr in some acidic soils was not readily exchangeable. In sediments sampled from the White Oak Creek watershed at DOE's Oak Ridge Site, Cerling and Spalding (1982) determined that the majority of the ^{90}Sr present in the sediments was weakly adsorbed and exchangeable, but substantial mass was fixed in the sediments. They found that approximately 80-90 percent of ^{90}Sr present in these sediments was extracted by warm 1N NaCl or NH_4OAC solutions and quantitative extraction required hot 8 N nitric acid.

Some important ancillary soil properties include the natural strontium and calcium concentrations in the aqueous and solid phases (Kokotov and Popova, 1962; Schulz, 1965), mineralogy (Ames and Rai,

¹ Cation exchange is a 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. Adsorption phenomena are discussed in more detail in Volume I of this report.

1978), pH (Juo and Barber, 1970; Prout, 1958; Rhodes, 1957), and solution ionic strength (Rhodes, 1957; Routson *et al.*, 1980). Numerous studies have been conducted to elucidate the effects of competing cations on strontium adsorption [reviewed by Ames and Rai (1978) and Strenge and Peterson (1989)]. These experiments consistently show that, on an equivalence basis, strontium will dominate most Group 1A and 1B elements (alkaline and alkaline earth elements) in competition for exchange sites.

A ranking of the most common groundwater cations by their ability to displace strontium from an exchange site is:

$$\text{Stable Sr} > \text{Ca} > \text{Mg} > \text{K} \geq \text{NH}_4 > \text{Na} \quad (5.4)$$

(Kokotov and Popova, 1962). Calcium exists in groundwaters at concentrations typically 2 orders of magnitude greater than stable strontium and typically more than 12 orders of magnitude greater than ^{90}Sr (Table 5.1). Consequently, mass action would improve the likelihood of calcium out competing ^{90}Sr for exchange sites.

Rhodes (1957) showed the effect of solution pH and ionic strength on the adsorption of strontium on soils containing carbonate minerals and montmorillonite. The pH of the system was adjusted with NaOH or HCl and the ionic strength was adjusted by adding 4 M NaNO₃. For a dilute solution, the strontium K_d increased from 5 ml/g at pH 6 to 10 ml/g at pH 8, and 120 ml/g at pH 10. Above pH 10, strontium adsorption began to level off, and the sodium added in the NaOH used for pH adjustment began to compete for exchange sites with the strontium. In 4 M NaNO₃ (an extremely high ionic strength solution with respect to natural environments), strontium adsorption was much less affected by pH. At pH 8, for example, the strontium K_d was about 5 ml/g and increased to about 10 ml/g at pH 10. Using kaolinitic soils from South Carolina, Prout (1958) reported very similar pH and ionic strength effects as Rhodes (1957). A maximum strontium adsorption was reached at about pH 10, although this maximum was much higher ($K_d = 700$ to 800 ml/g) than that reported by Rhodes (1957). Prout (1958) also reported only a slight pH effect on strontium K_d values in high ionic strength solutions. Rhodes (1957) and Prout (1958) reported that increases in ionic strength resulted in lower strontium K_d values.

5.8.6 Partition Coefficient, K_d , Values

5.8.6.1 General Availability of K_d Data

Two simplifying assumptions underlying the selection of strontium K_d values included in the look-up table were made. Strontium adsorption: (1) occurs by cation exchange, and (2) follows a linear isotherm. These assumptions appear to be reasonable for a wide range of environmental conditions. However, these simplifying assumptions are compromised in systems with strontium concentration

greater than about 10^{-4} M, humic substance concentration greater than about 5 mg/l, ionic strength levels greater than about 0.1 M, and pH levels greater than about 12.

Based on these assumptions and limitation, strontium K_d values and some important ancillary parameters that influence cation exchange were collected from the literature and tabulated (Appendix H).¹ Data included in this table, were from studies that reported K_d values (not percent adsorbed or Freundlich or Langmuir constants) and were conducted in systems consisting of (1) natural soils (as opposed to pure mineral phases), (2) low ionic strength (<0.1 M), (3) pH values between 4 and 10, (4) strontium concentrations less than 10^{-4} M, (5) low humic material concentrations (<5 mg/l), and (6) no organic chelates (*e.g.*, as EDTA). Initially, attempts were made to include in the K_d data set all the key aqueous- and solid-phase parameters identified above. These parameters included CEC, pH, calcium concentration, stable strontium concentration, and carbonate concentration.

The ancillary parameters for which data could be found that was included in these tables were clay content, pH, CEC, surface area, solution calcium concentrations, and solution strontium concentrations. This table described 63 strontium K_d values. A second table containing strontium K_d values for soils as well as pure mineral phases was prepared at the same time and this table contained 166 entries. These data are included in Appendix H but were not used to provide guidance regarding the selection of K_d values to be included in the look-up table.

5.8.6.2 Look-Up Table

The look-up table requires knowledge of the CEC (or clay content) and pH of the system in order to select the appropriate strontium K_d value (Table 5.13). A detailed explanation of the approach used in selecting these K_d values is presented in Appendix H. Briefly, it involves tabulating the K_d and ancillary data found in the literature and then conducting regression analysis of the data with strontium K_d as the dependent variable. Selection of independent variables used in the final look-up tables was based in part on their correlation coefficients. Perhaps more importantly, the independent variables had to be a parameter that is readily available to modelers. For instance, particle size and pH are often available to modelers whereas such parameters as iron oxide or surface area are not as frequently available. The estimated ranges for the minimum and maximum K_d values were based on regression estimates of the 95 percent error ($P < 0.05$). The central estimates were based primarily on values calculated using the appropriate regression equations.

5.8.6.2.1 Limits of K_d Values with Respect to pH, CEC and Clay Content Values

¹ Since the completion of our review and analysis of K_d data for the selected contaminants and radionuclides, the studies by Chen *et al.* (1998), Fisher *et al.* (1999), Oscarson and Hume (1998), and Wang *et al.* (1998) were identified and may be of interest to the reader.

A full factorial table was created that included 3 pH categories and 3 CEC categories, resulting in 9 cells (Table 5.13). Each cell contains an estimated minimum and maximum K_d value. As the pH or the CEC of a system increases, so does the strontium K_d values.

A second table was created based on Table 5.13, in which clay content replaced CEC as an independent variable (subset of Table 5.13). This second table was created because it is likely that clay content data will be more readily available for modelers than CEC data. To accomplish this, clay contents associated with the CEC values used to delineate the different categories were calculated using regression equations (see Appendix H) for additional details).

5.8.6.2.2 Limits of K_d Values with Respect to Dissolved Calcium Concentrations

Of the 63 experiments reporting strontium K_d values, 32 also reported dissolved calcium concentrations (Appendix H). The mean calcium concentration in this data set was 56 mg/l, with a minimum of 0 mg/l and a maximum of 400 mg/l. Calcium concentration had a correlation with strontium K_d values, $r = -0.17$. Although this correlation is insignificant, it does show that the relationship between these 2 parameters is negative. This inverse relationship can be attributed to calcium competing with strontium for adsorption sites on the solid phase.

Table 5.13. Look-up table for estimated range of K_d values for strontium based on CEC (meq/100 g), clay content (wt.%), and pH. [Tabulated values pertain to systems consisting of natural soils (as opposed to pure mineral phases), low ionic strength (< 0.1 M), low humic material concentrations (< 5 mg/l), no organic chelates (e.g., EDTA), and oxidizing conditions.]

K_d (ml/g)	CEC (meq/100 g) / Clay Content (wt.%)								
	3 / < 4			3 - 10 / 4 - 20			10 - 50 / 20 - 60		
	pH			pH			pH		
	< 5	5 - 8	8 - 10	< 5	5 - 8	8 - 10	< 5	5 - 8	8 - 10
Minimum	1	2	3	10	15	20	100	200	300
Maximum	40	60	120	150	200	300	1,500	1,600	1,700

5.8.6.2.3 Limits of K_d Values with Respect to Dissolved Stable Strontium and Carbonate Concentrations

Of the 63 experiments reporting strontium K_d values, none reported stable strontium or carbonate concentrations (Appendix H). It was anticipated that the presence of stable strontium would compete with the ^{90}Sr for exchange sites, thereby decreasing ^{90}Sr K_d values. The presence of dissolved carbonate would likely decrease ^{90}Sr K_d values due to formation of the weaker strontium-carbonate aqueous complex.

5.9 Thorium Geochemistry and K_d Values

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

Thorium occurs only in the +4 oxidation state in nature. In aqueous solutions, especially in natural waters, the concentrations of dissolved thorium are very low. Dissolved thorium forms a variety of hydroxyl species, and undergoes extensive chemical interaction with water and most anions. Thorium can form various aqueous complexes with inorganic anions such as dissolved carbonate, fluoride, phosphate, chloride, and nitrate. The formation of these complexes will increase the concentrations of total dissolved thorium in soil- and groundwaters. Recent studies of carbonate complexation of dissolved thorium indicate that the speciation of dissolved thorium may be dominated by mixed thorium

carbonate and hydroxyl-carbonate complexes, such as $\text{Th}(\text{OH})_3\text{CO}_3^-$, at pH values greater than 7.5. Species distributions calculated using the stability constants for thorium citrate, oxalate, and ethylenediamine complexes indicate that thorium organic complexes likely predominate over inorganic complexes in organic-rich waters and soils. This would have an important effect on the solubility and adsorption of thorium in such waters.

Thorium-containing minerals, such as thorite, thorianite, monazite, and zircon, do not dissolve readily in low-temperature surface- and groundwaters. Because these minerals form at temperature and pressure conditions associated with igneous and metamorphic rocks, it is unlikely that the concentration of thorium in soil/water environments is controlled by the solubility of any of these minerals. The rate at which thorium is released to the environment may however be controlled by the rates of dissolution of 1 or more of these phases. The maximum possible concentration of thorium dissolved in low-temperature aqueous systems can however be predicted with the solubility of hydrous thorium oxide, because the solubility of this compound will result in higher concentrations of dissolved thorium than will likely occur from the kinetically-hindered dissolution of resistant primary thorium minerals. Moreover, hydrous thorium oxide solid is known to precipitate in laboratory experiments (*i.e.*, short time periods) conducted at low temperature, oversaturated conditions.

The concentrations of dissolved thorium in surface and groundwaters may also be controlled to low values by adsorption processes. Humic substances are considered particularly important in the adsorption of thorium. The available partition coefficient, K_d , data indicates significant retention of thorium by most soil types.

5.9.2 General Geochemistry

Twelve isotopes of thorium are known. Their atomic masses range from 223 to 234, and all are unstable (or radioactive) (Weast and Astle, 1980). Of these, 6 thorium isotopes exist in nature. These include:

- ^{238}U decay series: ^{234}Th [$t_{1/2}$ (half life) = 24.1 d] and ^{230}Th ($t_{1/2}$ = 8.0×10^4 y)
- ^{232}Th decay series: ^{232}Th ($t_{1/2}$ = 1.41×10^{10} y) and ^{228}Th ($t_{1/2}$ = 1.913 y)
- ^{235}U decay series: ^{231}Th ($t_{1/2}$ = 25.5 h) and ^{227}Th ($t_{1/2}$ = 18.5 d).

Natural thorium consists of essentially 1 isotope, ^{232}Th , with trace quantities of the other isotopes. Thorium is fertile nuclear material in that the principal isotope ^{232}Th can be converted by capture of a thermal neutron and 2 beta decays to fissionable ^{233}U which does not exist in nature. The application of thorium as a reactor fuel in the ThO_2 ceramic form is described in detail by Belle and Berman (1984).

Thorium occurs only in the +4 oxidation state in nature. The Th^{4+} ion is the largest tetravalent cation known with a radius of approximately 1.0 Å. Although the Th^{4+} ion is more resistant to hydrolysis than other tetravalent ions, it forms a variety of hydroxyl species at pH values above 3 (Baes and Mesmer,

1976; Cotton and Wilkinson, 1980). The thorium content in natural water is very low. The concentration range in natural fresh water rarely exceeds 1 micro g/l (0.1 pCi/l ^{232}Th), although mg/l concentrations of ^{232}Th have been detected in high-acid groundwaters beneath uranium tailings sites (Langmuir and Herman, 1980).

Although the normal ranges of thorium concentrations in igneous, metamorphic, and sedimentary rocks are less than 50 ppm, thorium concentrations can be as high as 30 and 300 ppm, respectively, in oceanic sand/clays and marine manganese nodules (Gascoyne, 1982). These anomalously high concentrations of thorium have been explained by the tendency of thorium to strongly adsorb on clay and oxyhydroxide phases (Langmuir and Herman, 1980).

The mineralogy of thorium-containing minerals is described by Frondel (1958). Most thorium-containing minerals are considered fairly insoluble and resistant to erosion. There are few minerals in which thorium is an essential structural constituent. Important thorium minerals include thorite [(Th,U,Ce,Fe,*etc.*) SiO_4] and thorianite (crystalline ThO_2). Thorite is found in pegmatites, gneisses, granites, and hydrothermal deposits. Thorianite is chiefly found in pegmatitic rocks, but is best known as a detrital mineral.¹ Thorium also occurs, however, as variable, trace concentrations in solid solution in many rare-earth, zirconium, and uranium minerals. The 2 most important minerals of this type include monazite [(Ce,La,Th) PO_4] and zircon (ZrSiO_4). Monazite and zircon are widely disseminated as accessory minerals in igneous and metamorphic rocks. They also occur in commercial quantities in detrital sands derived from regions of these rocks due to their resistance to erosion (Deer *et al.*, 1967; Frondel, 1958). Concentrations of thorium can be several weight percent in these deposits.

Because of their long half lives, ^{228}Th ($t_{1/2} = 1.913$ y), ^{230}Th ($t_{1/2} = 8.0 \times 10^4$ y), and ^{232}Th ($t_{1/2} = 1.41 \times 10^{10}$ y), which are all alpha-particle emitters, pose long-term health risks and are therefore environmentally important. Contamination includes thorium-containing soils and thorium dissolved in surface- and groundwaters. Of the contaminated sites considered in EPA/DOE/NRC (1993), radioactive contamination of soil, surface water, and/or groundwater by ^{228}Th , ^{230}Th , and/or ^{232}Th has been identified at 21 of the 45 Superfund National Priorities List (NPL) sites and 23 of the 38 NRC Site Decommissioning Management Plan (SDMP) sites. Some of the contamination resulted from the separation and processing of uranium and from the use of monazite and zircon sands as source materials for metallurgical processes.

5.9.3 Aqueous Speciation

Thorium occurs only in the +4 oxidation state in natural soil/water environments. Dissolved thorium forms a variety of hydrolytic species, and, as a small, highly charged ion, undergoes extensive chemical

¹ A detrital mineral is defined as "any mineral grain resulting from mechanical disintegration of parent rock" (Bates and Jackson, 1980).

interaction with water and most anions. The available thermodynamic data for thorium-containing aqueous species and solids have been compiled and critically reviewed by Langmuir and Herman (1980) for an analysis of the mobility of thorium in low-temperature, natural waters.

Thorium undergoes hydrolysis in aqueous solutions at pH values above 3. The distribution of thorium hydrolytic species, shown in Figure 5.4, was calculated as a function of pH using the MINTQA2 code and the thermodynamic data tabulated in Langmuir and Herman (1980). The aqueous species included in the speciation calculations are listed in Table 5.14. The species distribution in Figure 5.4 was determined for a concentration of 1 micro g/l total dissolved thorium for a water free of any complexing ligands other than hydroxide ions. The chosen thorium concentration is based on Hem (1985, p. 150) who gives 0.01 to 1 micro g/l as the range expected for thorium concentrations in fresh waters. The calculated species distribution shows that the uncomplexed ion Th^{4+} is the dominant ion at pH values less than ~ 3.5 . At pH values greater than 3.5, the hydrolysis of thorium is dominated, in order of increasing pH, by the aqueous species $\text{Th}(\text{OH})_2^{2+}$, $\text{Th}(\text{OH})_3^+$, and $\text{Th}(\text{OH})_4^0(\text{aq})$. The latter 2 hydrolytic complexes have the widest range of stability with pH.

The large effective charge of the Th^{4+} ion can induce hydrolysis to the point that polynuclear complexes may form (Baes and Mesmer, 1976). Present knowledge of the formation of polynuclear hydrolyzed species is poor because there is no unambiguous analytical technique to determine these species. However, polynuclear species are believed to play a role in mobility of thorium in soil/water systems. Langmuir and Herman (1980) list estimated thermodynamic values for the thorium polynuclear hydrolyzed species $\text{Th}_2(\text{OH})_2^{6+}$, $\text{Th}_4(\text{OH})_8^{8+}$, and $\text{Th}_6(\text{OH})_{15}^{9+}$ based on the review of Baes and Mesmer (1976).

Table 5.14. Thorium aqueous species included in the speciation calculations.

Aqueous Species
Th^{4+} , ThOH^{3+} , $\text{Th}(\text{OH})_2^{2+}$, $\text{Th}(\text{OH})_3^+$, $\text{Th}(\text{OH})_4^{\circ}(\text{aq})$, $\text{Th}_2(\text{OH})_2^{6+}$, $\text{Th}_4(\text{OH})_8^{8+}$, $\text{Th}_6(\text{OH})_{15}^{9+}$
$\text{Th}(\text{OH})_3\text{CO}_3^-$ and $\text{Th}(\text{CO}_3)_5^{6-}$
ThF^{3+} , ThF_2^{2+} , ThF_3^+ , $\text{ThF}_4^{\circ}(\text{aq})$
ThCl^{3+} , ThCl_2^{2+} , ThCl_3^+ , $\text{ThCl}_4^{\circ}(\text{aq})$
ThSO_4^{2+} , $\text{Th}(\text{SO}_4)_2^{\circ}(\text{aq})$, $\text{Th}(\text{SO}_4)_3^{2-}$, $\text{Th}(\text{SO}_4)_4^{4-}$
$\text{ThH}_3\text{PO}_4^{4+}$, $\text{ThH}_2\text{PO}_4^{3+}$, $\text{Th}(\text{H}_2\text{PO}_4)_2^{2+}$, $\text{Th}(\text{HPO}_4)_2^{\circ}(\text{aq})$, $\text{Th}(\text{HPO}_4)_3^{2-}$

In addition to hydrolytic complexes, thorium can also form various aqueous complexes with inorganic anions such as dissolved fluoride, phosphate, chloride, and nitrate. Studies (*e.g.*, LaFamme and Murray, 1987) completed since the review by Langmuir and Herman (1980) indicate the presence of dissolved thorium carbonate complexes and their importance to the solution chemistry of thorium. Due to the lack of available data, no thorium carbonate species were listed by Langmuir and Herman (1980). Östhols *et al.* (1994) have recently published thermodynamic constants for the thorium carbonate complexes $\text{Th}(\text{OH})_3\text{CO}_3^-$ and $\text{Th}(\text{CO}_3)_5^{6-}$ that are based on their solubility studies of microcrystalline ThO_2 at different partial pressures of CO_2 in aqueous media.

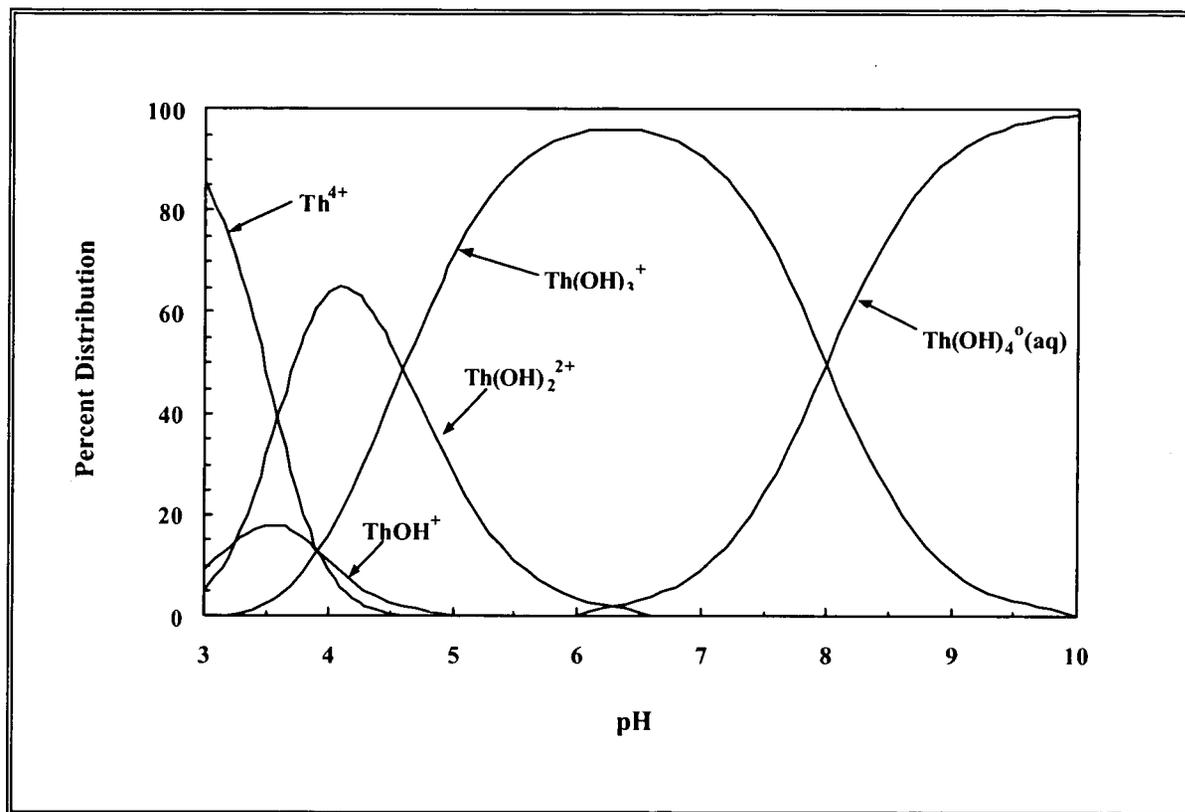


Figure 5.4. Calculated distribution of thorium hydrolytic species as a function of pH. [The species distribution is based on a concentration of 1 micro g/l total dissolved thorium in pure water (*i.e.*, absence of complexing ligands other than OH) and thermodynamic data from Langmuir and Herman (1980).]

The distribution of thorium aqueous species (Figure 5.5) was also calculated as a function of pH using the MINTQA2 for a concentration of 1 micro g/l total dissolved thorium and the water composition in Table 5.1. The thermodynamic data were principally from Langmuir and Herman (1980). The thermodynamic constants for the aqueous species $\text{Th(OH)}_3\text{CO}_3^-$ and $\text{Th(CO}_3)_2^{6-}$ from Östholms *et al.* (1994) were also included in these speciation calculations. Below pH 5, dissolved thorium is dominated by thorium fluoride complexes. Between pH 5 and 7, dissolved thorium is predicted to be dominated by thorium phosphate complexes. Although phosphate complexation is expected to have a role in the mobility of thorium in this range of pH values, the adequacy of the thermodynamic constants tabulated for thorium phosphate complexes in Langmuir and Herman (1980) are suspect, and may over predict the stability of these complexes. At pH values greater than 7.5, more than 95 percent of the dissolved thorium is predicted to be present as $\text{Th(OH)}_3\text{CO}_3^-$. The species distribution illustrated in

Figure 5.5 changes slightly in the pH range from 5 to 7 if the concentration of total dissolved thorium is increased from 1 to 1,000 micro g/l. At the higher concentration of dissolved thorium, the stability of $\text{Th}(\text{OH})_3\text{CO}_3$ extends to a pH of approximately 5, the hydrolytic species $\text{Th}(\text{OH})_3$ becomes an important species (about 30 percent of the dissolved thorium), and the thorium phosphate species are no longer dominant.

Thorium organic complexes likely have an important effect on the mobility of thorium in soil/water systems. Langmuir and Herman (1980) used citrate ($\text{C}_6\text{H}_5\text{O}_7^{3-}$), oxalate ($\text{C}_2\text{O}_4^{2-}$), and ethylenediamine tetra-acetic acid (EDTA) ($\text{C}_{10}\text{H}_{12}\text{O}_8\text{N}_2^{4-}$) to show the possible role of organic complexes in the mobility of thorium in natural waters. Based on the stability constants available for thorium citrate, oxalate, and ethylenediamine complexes, calculations by Langmuir and Herman (1980) indicate that thorium organic complexes likely predominate over inorganic complexes in organic-rich waters and soils. For the concentrations considered by Langmuir and Herman (1980), the $\text{ThEDTA}^\circ(\text{aq})$ complex dominates all other thorium aqueous species over the pH range from 2 to 8. This would in turn have an important effect on the solubility and adsorption of thorium in such waters.

5.9.4 Dissolution/Precipitation/Coprecipitation

The main thorium-containing minerals, thorite $[(\text{Th},\text{U},\text{Ce},\text{Fe},\text{etc.})\text{SiO}_4]$, thorianite (crystalline ThO_2), monazite $[(\text{Ce},\text{La},\text{Th})\text{PO}_4]$ and zircon (ZrSiO_4), are resistant to chemical weathering and do not dissolve readily at low-temperature in surface and groundwaters. Because these minerals form at temperature and pressure conditions associated with igneous and metamorphic rocks, it is unlikely that the thermodynamic *equilibrium* solubilities (where the rate of precipitation equals the rate of dissolution) of these minerals will control the concentration of dissolved thorium in low-temperature soil/water environments. The rate at which thorium is released to the environment, as might be needed in a source-term component of a performance assessment model, may however be controlled by the kinetic rates of aqueous dissolution (*i.e.*, *non-equilibrium* conditions) of 1 or more of these phases.

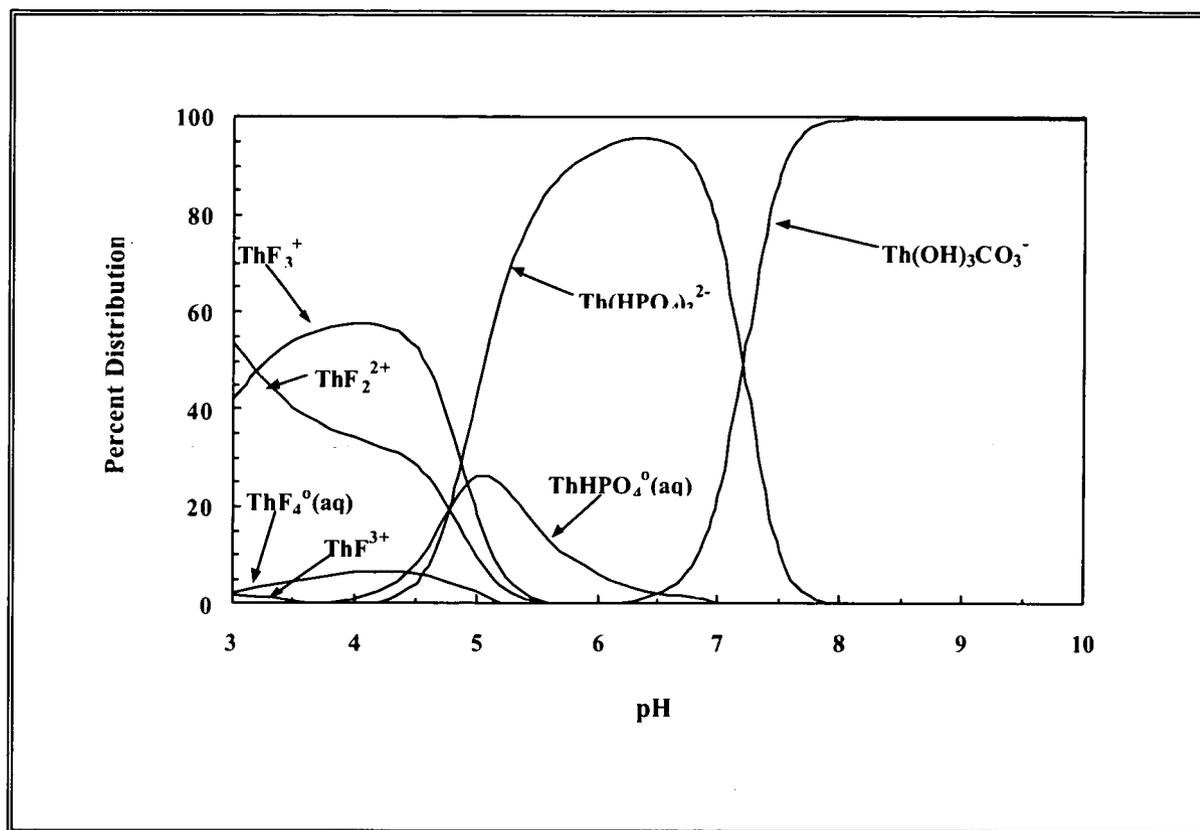


Figure 5.5. Calculated distribution of thorium aqueous species as a function of pH for the water composition in Table 5.1. [The species distribution is based on a concentration of 1 micro g/l total dissolved thorium and thermodynamic data from Langmuir and Herman (1980) and Östhols *et al.* (1994, for $\text{Th}(\text{OH})_3\text{CO}_3^-$ and $\text{Th}(\text{CO}_3)_5^{6-}$). The thermodynamic database used for these speciation calculations did not include the constants for thorium humic acid complexes.]

The maximum concentration of dissolved thorium that may occur in a low-temperature aqueous system can be predicted with the solubility of hydrous thorium oxide. This solid is known to precipitate in laboratory experiments conducted at low temperature, oversaturated conditions over several weeks. If this solid precipitates in a natural environment, it will likely alter with time to a more crystalline solid that has a lower solubility. The solubility of hydrous thorium oxide has been studied experimentally by Rai and coworkers (Felmy *et al.*, 1991; Rai *et al.*, 1995; Ryan and Rai, 1987). In 0.1 M NaClO_4 solutions, the measured solubility of hydrous thorium oxide ranges from about $10^{-8.5}$ mol/l (0.0007 mg/l)

to less than 10^{-9} mol/l (0.0002 mg/l) in the pH range from 5 to 10 (Ryan and Rai, 1987). The concentration of dissolved thorium increases to approximately $10^{-2.6}$ mol/l (600 mg/l) as pH decreases from 5.0 to 3.2.

Felmy *et al.* (1991) determined that the solubility of hydrous thorium oxide increases with increasing ionic strength. At pH values above 7 in 3.0 M NaCl solutions, the solubility of hydrous thorium oxide increased by approximately 2 to 3 orders of magnitude compared to that determined in 0.1 M NaClO₄ solutions. Moreover, the pH at which hydrous thorium oxide exhibits rapid increases in solubility with decreasing pH changes from pH 5 in 0.1 M NaClO₄ to approximately pH 7 in 3.0 M NaCl. In studies conducted at high hydroxide and carbonate concentrations, Rai *et al.* (1995) determined that the solubility of hydrous thorium oxide increases dramatically in high carbonate solutions and decreases with increases in hydroxide concentration at fixed carbonate concentrations. This supports the assertion that soluble thorium-carbonate complexes likely dominate the aqueous speciation of thorium dissolved in natural waters having basic pH values.

5.9.5 Adsorption/Desorption

Thorium concentrations in surface- and groundwaters may also be controlled to very low levels (\leq few micro g/l) by adsorption processes. Humic substances are considered particularly important in the adsorption of thorium (Gascoyne, 1982). Thibault *et al.* (1990) conducted a critical compilation and review of published K_d data by soil type needed to model radionuclide migration from a nuclear waste geological disposal vault to the biosphere. Thibault *et al.* list K_d values for thorium that range from 207 to 13,000,000 ml/g. The range of thorium K_d values listed for organic soil was 1,579 to 1.3×10^7 ml/g. Based on our experience, the very high K_d values reported for thorium should be viewed with caution. The studies resulting in these values should be examined to determine if the initial concentrations of thorium used for these K_d measurements were too great and precipitation of a thorium solid (*e.g.*, hydrous thorium oxide) occurred during the equilibration of the thorium-spiked soil/water mixtures. As noted in the letter report for Subtask 1B, precipitation of solids containing the contaminant of interest results in K_d values that are erroneously too high.

The adsorption of thorium on pure metal-oxide phases has also been studied experimentally in conjunction with surface complexation models.¹ Östhols (1995) studied the adsorption of thorium on amorphous colloidal particles of silica (SiO₂). Their results indicate that the adsorption of thorium on silica will only be important in the pH range from 3 to 6. In neutral and alkaline pH values, silica surface sites are not expected to be efficient adsorbents for thorium.

Iron and manganese oxides are expected to be more important adsorbents of thorium than silica. Hunter *et al.* (1988) studied the adsorption of thorium on goethite (α -FeOOH) and nsutite (γ -MnO₂)

¹ Surface complexation models are discussed in Volume I of this report.

in marine electrolyte solutions. Their experiments indicate that adsorption of thorium increases from approximately 0 percent at pH 2.5-3.5 to 90-100 percent at pH 5-6.5. The adsorption of thorium decreased with the addition of sulfate as a result of the formation of competitive aqueous complexes with dissolved thorium. The addition of organic ligands EDTA and trans-1,2-diaminocyclohexane tetra-acetic acid (CDTA) shifted the adsorption edges for γ -MnO₂ to higher pH values by more than 5-6 pH units, such that 100 percent adsorption of thorium was not observed until pH 12. LaFlamme and Murray (1987) experimentally studied the effects of pH, ionic strength and carbonate alkalinity on the adsorption of thorium by goethite. The adsorption edge (*i.e.*, range in pH where metal adsorption goes from 0 percent to approximately 90-100 percent) was measured to be in the pH range from 2 to 5. For conditions considered in their study, ionic strength was found to have no effect on the adsorption of thorium on goethite. LaFlamme and Murray did however observe a strong influence of carbonate alkalinity on thorium adsorption. In their experiments at pH 9.0±0.6, they observed a decrease of thorium adsorption with the addition of 100 meq/l carbonate alkalinity, and no measurable adsorption of thorium at carbonate alkalinity greater than 300 meq/l. At the low particle concentrations used in their experiments, LaFlamme and Murray attributed this reduction to the competition for surface sites by CO₃²⁻ and HCO₃⁻ and the formation of soluble thorium-carbonate complexes with a net negative charge.

5.9.6 Partition Coefficient, K_d , Values

5.9.6.1 General Availability of K_d Data

Two generalized, simplifying assumptions were established for the selection of thorium K_d values for the look-up table. These assumptions were based on the findings of the literature review conducted on the geochemical processes affecting thorium sorption. The assumptions are as follows:

- Thorium precipitates at concentrations greater than 10⁻⁹ M. This concentration is based on the solubility of Th(OH)₄ at pH 5.5. Although (co)precipitation is usually quantified with the solubility construct, a very large K_d value will be used in the look-up table to approximate thorium behavior in systems with high thorium concentrations.
- Thorium adsorption occurs at concentrations less than 10⁻⁹ M. The extent of thorium adsorption can be estimated by soil pH.

These assumptions appear to be reasonable for a wide range of environmental conditions. However, these simplifying assumptions are clearly compromised in systems containing high alkaline (LaFlamme and Murray, 1987), carbonate (LaFlamme and Murray, 1987), or sulfate (Hunter *et al.*, 1988) concentrations, and high or low pH values (pH: 3 < x > 8: Hunter *et al.*, 1988; LaFlamme and Murray 1987; Landa *et al.*, 1995). These assumptions will be discussed in more detail in the following sections.

Based on the assumptions and limitations described above, thorium K_d values and some important ancillary parameters that influence sorption were collected from the literature and tabulated (Appendix I). Data included in this table, were from studies that reported K_d values (not percent adsorbed or Freundlich or Langmuir constants) and were conducted in systems consisting of:

- Low ionic strength (< 0.1 M)
- pH values between 4 and 10.5
- Dissolved thorium concentrations less than 10^{-9} M
- Low humic material concentrations (< 5 mg/l)
- No organic chelates (*e.g.*, EDTA)

These aqueous chemistry constraints were selected to limit the thorium K_d values evaluated to those that would be expected to exist in a far-field. The ancillary parameters included in these tables were clay content, calcite concentration, pH, and CEC. Attempts were also made to include in the data set the concentration of organic carbon and aluminum/iron oxides in the solid phase. However, these latter ancillary parameters, which were identified above, were rarely included in the reports evaluated to compile the data set. The data set included 17 thorium K_d values for soils and pure phase minerals.

5.9.6.2 Look-Up Tables

Linear regression analyses were conducted with data collected from the literature (described in Appendix I). These analyses were used as guidance for selecting appropriate K_d values for the look-up table. The K_d values used in the look-up tables could not be based entirely on statistical consideration because the statistical analysis results were occasionally nonsensical. For example, the data showed a negative correlation between clay content and thorium K_d values. This trend contradicts well established principles of surface chemistry. Instead, the statistical analysis was used to provide guidance as to the approximate range of values to use and to identify meaningful trends between the thorium K_d values and the solid phase parameters. Thus, the K_d values included in the look-up table were in part selected based on professional judgment. Again, only low-ionic strength solutions, similar to that expected in far-field groundwaters, were considered in these analyses.

The look-up table for thorium K_d values was based on plume thorium concentrations and pH. These 2 parameters have an interrelated effect on thorium K_d values. The maximum concentration of dissolved thorium may be controlled by the solubility of hydrous thorium oxides (Felmy *et al.*, 1991; Rai *et al.*, 1995; Ryan and Rai, 1987). The dissolution of hydrous thorium oxides may in turn vary with pH. Ryan and Rai (1987) reported that the solubility of hydrous thorium oxide is $\sim 10^{-8.5}$ to $\sim 10^{-9}$ in the pH range of 5 to 10. The concentration of dissolved thorium increases to $\sim 10^{-2.6}$ M (600 mg/L) as pH decreases from 5.0 to 3.2. Thus, 2 categories based on thorium solubility were included in the look-up table, pH 3 to 5, and pH 5 to 10. Although precipitation is typically quantified by the solubility construct, a very large K_d value was used in the look-up table to describe high thorium concentrations

(Table 5.15). See Appendix I for a detailed account of the process used to select the K_d values in Table 5.15.

5.9.6.2.1 Limits of K_d Values with Respect to Organic Matter and Aluminum/Iron-Oxide Concentrations

Of the 17 entries in the thorium K_d data set (Appendix I), none of them had accompanying organic matter or aluminum- and iron-oxide mineral concentration data. It was anticipated that the presence of organic matter would decrease thorium K_d values by forming thorium-organic matter complexes. These complexes would be less prone to adsorb to surface than the uncomplexed thorium species. Conversely, it was anticipated that the presence of aluminum- and/or iron-oxides would increase thorium K_d values by increasing the number of adsorption (surface complexation) sites.

5.9.6.2.2 Limits of K_d Values with Respect to Dissolved Carbonate Concentrations

Of the 17 entries in the thorium K_d data set (Appendix I), none of them had accompanying carbonate concentration data. However, 5 entries had calcite (CaCO_3) mineral concentrations. It was anticipated that calcite concentrations could be used as an indirect measure, albeit poor measure, of the amount of dissolved carbonate in the aqueous phase. Calcite concentrations had a correlation coefficient (r) with thorium K_d value of 0.76 (Appendix I). Although this is a relatively high correlation value, it is not significant at the 5 percent level of probability due to the small number of observations (5 observations). Furthermore, it was anticipated that the presence of dissolved carbonate would decrease thorium K_d values due to formation of the weaker forming carbonate-thorium complexes.

Table 5.15. Look-up table for thorium K_d values (ml/g) based on pH and dissolved thorium concentrations. [Tabulated values pertain to systems consisting of low ionic strength (< 0.1 M), low humic material concentrations (< 5 mg/l), no organic chelates (*e.g.*, EDTA), and oxidizing conditions.]

K_d (ml/g)	pH					
	3 - 5		5 - 8		8 - 10	
	Dissolved Th, M		Dissolved Th, M		Dissolved Th, M	
	$< 10^{-2.6}$	$> 10^{-2.6}$	$< 10^{-9}$	$> 10^{-9}$	$< 10^{-9}$	$> 10^{-9}$
Minimum	62	300,000	1,700	300,000	20	300,000
Maximum	6,200	300,000	170,000	300,000	2,000	300,000

5.10 Tritium Geochemistry And K_d Values

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

Tritium, a radioactive isotope of hydrogen with a half life ($t_{1/2}$) of 12.3 y, readily combines with oxygen to form water. Its behavior in aqueous systems is controlled by hydrologic processes and it migrates at essentially the same velocity as surface- and groundwaters. Aqueous speciation, precipitation, and sorption processes are not expected to affect the mobility of tritium in soil/water systems.

5.10.2 General Geochemistry

Tritium (^3H) is a radioactive isotope of hydrogen. Three isotopes of hydrogen are known. These include the 2 stable isotopes ^1H (protium or H) and ^2H (deuterium or D), and the radioactive isotope ^3H (tritium or T). Tritium has a half life ($t_{1/2}$) of 12.3 y, and disintegrates into helium-3 (^3He) by emission of a weak beta (β^-) particle (Rhodehamel *et al.*, 1971). Tritium is formed by natural and man-made processes (Cotton and Wilkinson, 1980). Tritium is formed in the upper atmosphere mainly by the nuclear interaction of nitrogen with fast neutrons induced by cosmic ray reactions. The relative abundances of ^1H , ^2H , and ^3H in natural water are 99.984, 0.016, and $0\text{-}10^{-15}$ percent, respectively (Freeze and Cherry, 1979). Tritium can also be created in nuclear reactors as a result of processes such as thermal neutron reactions with ^6Li .

As an isotope of hydrogen, tritium in soil systems behaves like hydrogen and will exist in ionic, gaseous, and liquid forms (*e.g.*, tritiated water, HTO). Ames and Rai (1978) discuss the geochemical behavior of tritium, and summarize field and laboratory studies of the mobility of tritium in soil systems. Because tritium readily combines with oxygen to form water, its behavior in aqueous systems is controlled by hydrologic processes. Because of these properties and its moderately long half life, tritium has been used as an environmental isotopic indicator to study hydrologic flow conditions. Rhodehamel *et al.* (1971) present an extensive bibliography (more than 1,200 references) and summarize the use of tritium in hydrologic studies through 1966. Tritium has been used to study recharge and pollution of groundwater reservoirs; permeability of aquifers; velocity, flow patterns, and stratification of surface- and groundwater bodies; dispersion and mixing processes in surface- and groundwaters; movement of soil moisture; chemisorption of soils and water-containing materials; biological uptake and release of water; and secondary recovery techniques for petroleum resources. IAEA (1979) published the proceedings from a 1978 conference dealing with the behavior of tritium in the environment. The conference was designed to provide information on the residence time and distribution of tritium in environmental systems and the incorporation of tritium into biological materials and its transfer along the food chain.

Tritium-contamination may include surface- and groundwater, soil, sediment, and air components at a site. Of the contaminated sites considered in EPA/DOE/NRC (1993), tritium contamination has been identified at 12 of the 45 Superfund National Priorities List (NPL) sites and 1 of the 38 NRC Site Decommissioning Site Plan (SDMP) sites.

5.10.3 Aqueous Speciation

Because tritium oxidizes rapidly to form isotopic water, aqueous speciation reactions do not affect the mobility of tritium in soil/water systems.

5.10.4 Dissolution/Precipitation/Coprecipitation

Neither precipitation or coprecipitation processes affect the mobility of tritium in soil/water systems.

5.10.5 Adsorption/Desorption

Because tritium readily combines with oxygen to form water, its behavior in aqueous systems is controlled by hydrologic processes and it migrates at essentially the same velocity as surface and groundwaters. Sorption processes are therefore not expected to be important relative to the movement of tritium through aqueous environments. Typically, a partition coefficient, K_d , of 0 ml/g is used to model the migration of tritium in soil and groundwater environments. As an exception, Thibault *et al.* (1990), based on a review of published studies, list 0.04 to 0.1 ml/g as the range for K_d values for tritium in sandy soils. Although tritium may substitute for hydrogen in water on clays and other hydrated soil constituents, Ames and Rai (1978) indicate that this reaction is not important relative to the mobility of tritium based on their review of published laboratory and field studies. Some laboratory studies considered in their review describe fixation of isotopic water on clays and other hydrated minerals, while others indicate minimal fixation. All field studies reviewed by Ames and Rai indicate that tritium migrates at the same velocity as surface- and groundwaters.

5.10.6 Partition Coefficient, K_d , Values

A review of the literature pertaining to K_d values for tritium was not conducted given the limited availability of K_d values for tritium (see section above) and limited importance of sorption processes relative to the mobility of tritium in aqueous environments.

5.11 Uranium Geochemistry and K_d Values

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

In essentially all geologic environments, +4 and +6 are the most important oxidation states of uranium.

Uranium(VI) species dominate in oxidizing environments. Uranium(VI) retention by soils and rocks in alkaline conditions is poor because of the predominance of neutral or negatively charged species. An increase in CO₂ pressure in soil solutions reduces U(VI) adsorption by promoting the formation of poorly sorbing carbonate complexes. Uranium(IV) species dominate in reducing environments. Uranium(IV) tends to hydrolyze and form strong hydrolytic complexes. Uranium(IV) also tends to form sparingly soluble precipitates that commonly control U(IV) concentrations in groundwaters. Uranium(IV) forms strong complexes with naturally occurring organic materials. Thus, in areas where there are high concentrations of dissolved organic materials, U(IV)-organic complexes may increase U(IV) solubility. There are several ancillary environmental parameters affecting uranium migration. The most important of these parameters include redox status, pH, ligand (carbonate, fluoride, sulfate, phosphate, and dissolved carbon) concentrations, aluminum- and iron-oxide mineral concentrations, and uranium concentrations.

5.11.2 General Geochemistry

Uranium (U) has 14 isotopes; the atomic masses of these isotopes range from 227 to 240. All uranium isotopes are radioactive. Naturally-occurring uranium typically contains 99.283 percent ²³⁸U, 0.711 percent ²³⁵U, and 0.0054 percent ²³⁴U by weight. The half-lives of these isotopes are 4.51 x 10⁹ y, 7.1 x 10⁸ y, and 2.47 x 10⁵ y, respectively. Uranium can exist in the +3, +4, +5, and +6 oxidation states, of which the +4 and +6 states are the most common states found in the environment.

The mineralogy of uranium-containing minerals is described by Frondel (1958). Uranium in the +4 and +6 oxidation states exists in a variety of primary and secondary minerals. Important U(IV) minerals include uraninite (UO₂ through UO_{2.25}) and coffinite [USiO₄] (Frondel, 1958; Langmuir, 1978). Aqueous U(IV) is inclined to form sparingly soluble precipitates, adsorb strongly to mineral surfaces, and partition into organic matter, thereby reducing its mobility in groundwater. Important U(VI) minerals include carnotite [(K₂(UO₂)₂(VO₄)₂), schoepite (UO₃·2H₂O), rutherfordine (UO₂CO₃), tyuyamunite [Ca(UO₂)₂(VO₄)₂], autunite [Ca(UO₂)₂(PO₄)₂], potassium autunite [K₂(UO₂)₂(PO₄)₂], and uranophane [Ca(UO₂)₂(SiO₃OH)₂] (Frondel, 1958; Langmuir, 1978). Some of these are secondary phases which may form when sufficient uranium is leached from contaminated wastes or a disposal system and migrates downstream. Uranium is also found in phosphate rock and lignite¹ at concentrations that can be commercially recovered. In the presence of lignite and other sedimentary carbonaceous substances, uranium enrichment is believed to be the result of uranium reduction to form insoluble precipitates, such as uraninite.

Contamination includes airborne particulates, uranium-containing soils, and uranium dissolved in surface- and groundwaters. Of the contaminated sites considered in EPA/DOE/NRC (1993), radioactive contamination by ²³⁴U, ²³⁵U, and/or ²³⁸U has been identified at 35 of the 45 Superfund

¹ Lignite is a coal that is intermediate in coalification between peat and subbituminous coal.

National Priorities List (NPL) sites and 26 of the 38 NRC Site Decommissioning Site Plan (SDMP) sites.

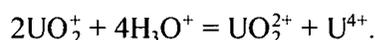
5.11.3 Aqueous Speciation

Because of its importance in nuclear chemistry and technology, a great deal is known about the aqueous chemistry of uranium [reviewed by Baes and Mesmer (1976), Langmuir (1978), and Wanner and Forest (1992)]. Uranium can exist in the +3, +4, +5, and +6, oxidation states in aqueous environments. Dissolved U(III) easily oxidizes to U(IV) under most reducing conditions found in nature. The U(V) aqueous species (UO_2^+) readily disproportionates to U(IV) and U(VI).¹ Consequently, U(IV) and U(VI) are the most common oxidation states of uranium in nature. Uranium will exist in the +6 and +4 oxidation states, respectively, in oxidizing and more reducing environments.

Both uranium species, UO_2^{2+} and U^{4+} , hydrolyze readily. The U^{4+} ion is more readily hydrolyzed than UO_2^{2+} , as would be expected from its higher ionic charge. Langmuir (1978) calculated U(IV) speciation in a system containing typical natural water concentrations of chloride (10 mg/l), fluoride (0.2 mg/l), phosphate (0.1 mg/l), and sulfate (100 mg/l). Below pH 3, UF_2^{2+} was the dominant uranium species. The speciation of dissolved U(IV) at pH values greater than 3 is dominated by hydrolytic species such as $\text{U}(\text{OH})_3^+$ and $\text{U}(\text{OH})_4^0(\text{aq})$. Complexes with chloride, fluoride, phosphate, and sulfate were not important above pH 3. The total U(IV) concentration in solution is generally quite low, between 3 and 30 $\mu\text{g/l}$, because of the low solubility of U(IV) solid phases (Bruno *et al.*, 1988; Bruno *et al.*, 1991). Precipitation is discussed further in the next section.

Dissolved U(VI) hydrolyses to form a number of aqueous complexes. The distribution of U(VI) species is presented in Figures 5.6a-b and 5.7. The distribution of uranyl hydrolytic species (Figures 5.6a-b) was calculated as a function of pH using the MINTEQA2 code. The U(VI) aqueous species included in the speciation calculations are listed in Table 5.16. The thermodynamic data for these aqueous species were taken primarily from Wanner and Forest (1992). Because dissolved uranyl ions can be present as polynuclear² hydroxyl complexes, the hydrolysis of uranyl ions under oxic conditions is therefore dependent on the concentration of total dissolved uranium. To demonstrate this aspect of uranium chemistry, 2 concentrations of total dissolved uranium, 0.1 and 1,000 $\mu\text{g/l}$, were used in these calculations. Hem (1985, p. 148) gives 0.1 to 10 $\mu\text{g/l}$ as the range for dissolved uranium in

¹ Disproportionation is defined in the glossary at the end of this letter report. This particular disproportionation reaction can be described as:



² A polynuclear species contains more than 1 central cation moiety, *e.g.*, $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$ and $\text{Pb}_4(\text{OH})_4^{4+}$.

most natural waters. For waters associated with uranium ore deposits, Hem states that the uranium concentrations may be greater than 1,000 $\mu\text{g/l}$.

In a U(VI)-water system, the dominant species were UO_2^{2+} at pH values less than 5, $\text{UO}_2(\text{OH})_2^0$ (aq) at pH values between 5 and 9, and $\text{UO}_2(\text{OH})_3^-$ at pH values between 9 and 10. This was true for both uranium concentrations, 0.1 $\mu\text{g/l}$ (Figure 5.6a) and 1,000 $\mu\text{g/l}$ dissolved U(VI) (Figure 5.6b). At 1,000 $\mu\text{g/l}$ dissolved uranium, some polynuclear species, $(\text{UO}_2)_3(\text{OH})_5^+$ and $(\text{UO}_2)_2(\text{OH})_2^{2+}$, were calculated to exist between pH 5 and 6. Morris *et al.* (1994) using spectroscopic techniques provided additional proof that an increasing number of polynuclear species were formed in systems containing higher concentrations of dissolved uranium.

A large number of additional uranyl species (Figure 5.7) are likely to exist in the chemically more complicated system such as the water composition in Table 5.1 and 1,000 $\mu\text{g/l}$ dissolved U(VI). At pH values less than 5, the UO_2F^+ species dominates the system, whereas at pH values greater than 5, carbonate complexes [UO_2CO_3^0 (aq), $\text{UO}_2(\text{CO}_3)_2^{2-}$, $\text{UO}_2(\text{CO}_3)_3^{4-}$] dominate the system. These calculations clearly show the importance of carbonate chemistry on U(VI) speciation. For this water composition, complexes with chloride, sulfate, and phosphate were relatively less important. Consistent with the results in Figure 5.7, Langmuir (1978) concluded that the uranyl complexes with chloride, phosphate, and sulfate were not important in a typical groundwater. The species distribution illustrated in Figure 5.7 changes slightly at pH values greater than 6 if the concentration of total dissolved uranium is decreased from 1,000 to 1 $\mu\text{g/l}$. At the lower concentration of dissolved uranium, the species $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$ is no longer present as a dominant aqueous species.

Sandino and Bruno (1992) showed that UO_2^{2+} -phosphate complexes [$\text{UO}_2\text{HPO}_4^0$ (aq) and UO_2PO_4^-] could be important in aqueous systems with a pH between 6 and 9 when the total concentration ratio $\text{PO}_4(\text{total})/\text{CO}_3(\text{total})$ is greater than 0.1. Complexes with sulfate, fluoride, and possibly chloride are potentially important uranyl species where concentrations of these anions are high. However, their stability is considerably less than the carbonate and phosphate complexes (Wanner and Forest, 1992).

Organic complexes may also be important to uranium aqueous chemistry. The uncomplexed uranyl ion has a greater tendency to form complexes with fulvic and humic acids than many other metals with a +2 valence (Kim, 1986). This has been attributed to the greater "effective charge" of the uranyl ion compared to other divalent metals. The effective charge has been estimated to be about +3.3 for U(VI) in UO_2^{2+} . Kim (1986) concluded that, in general, +6 actinides, including U(VI), would have approximately the same tendency to form humic- or fulvic-acid complexes as to hydrolyze or form carbonate complexes. This suggests that the dominant reaction with the uranyl ion that will take place in a groundwater will depend largely on the relative concentrations of hydroxide, carbonate, and organic material concentrations. He also concluded, based on comparison of stability constants, that the tendency for U^{4+} to form humic- or fulvic-acid complexes is less than its tendency to hydrolyze or form carbonate complexes. Importantly, U(IV) and U(VI) can form stable organic complexes, thereby increasing their solubility and mobility.

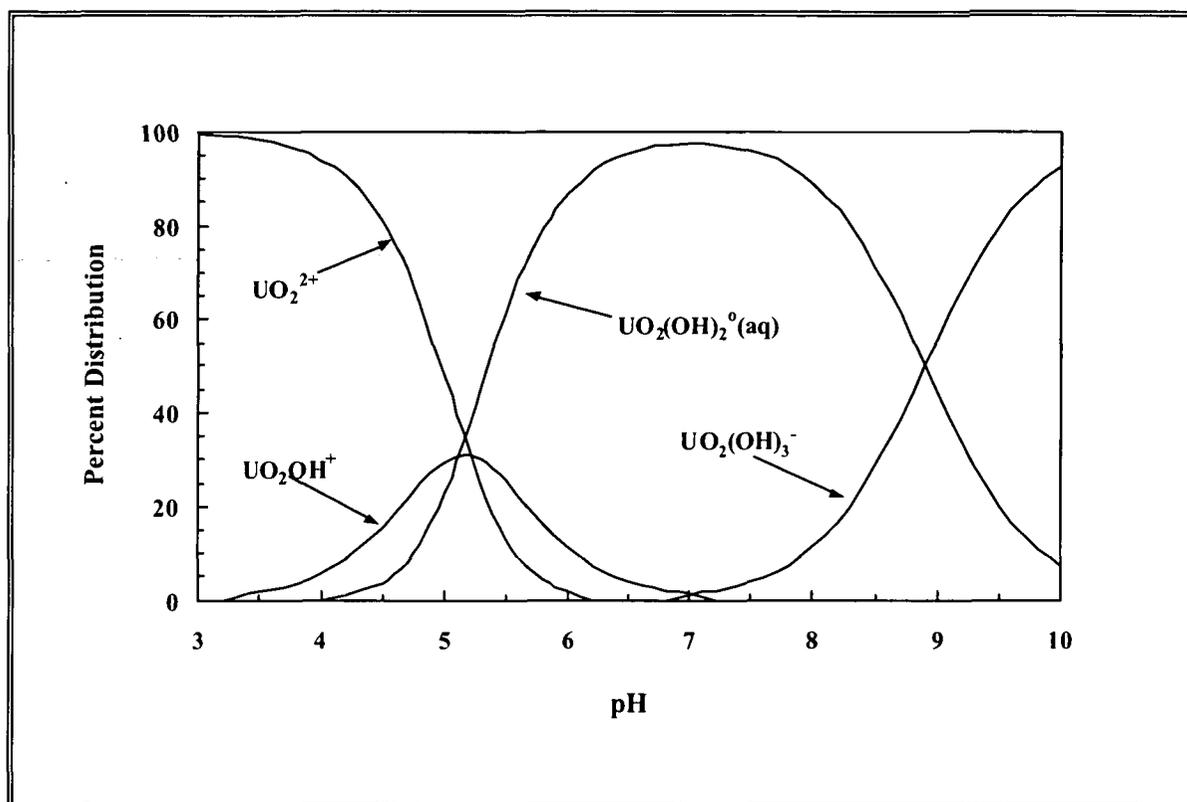
Table 5.16. Uranium(VI) aqueous species included in the speciation calculations.

Aqueous Species
UO_2^{2+} , UO_2OH^+ , $UO_2(OH)_2^0(aq)$, $UO_2(OH)_3^-$, $UO_2(OH)_4^{2-}$, $(UO_2)_2OH^{3+}$, $(UO_2)_2(OH)_2^{2+}$, $(UO_2)_3(OH)_4^{4+}$, $(UO_2)_3(OH)_5^+$, $(UO_2)_3(OH)_7^-$, $(UO_2)_4(OH)_7^+$, $U_6(OH)_{15}^{9+}$
$UO_2CO_3^0(aq)$, $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$, $UO_2(CO_3)_3^{5-}$, $(UO_2)_3(CO_3)_6^{6-}$, $(UO_2)_{11}(CO_3)_6(OH)_{12}^{2-}$, $(UO_2)_2CO_3(OH)^3-$
$UO_2PO_4^-$, $UO_2HPO_4^0(aq)$, $UO_2H_2PO_4^+$, $UO_2H_3PO_4^{2+}$, $UO_2(H_2PO_4)_2^0(aq)$, $UO_2(H_2PO_4)(H_3PO_4)^+$,
$UO_2SO_4^0(aq)$, $UO_2(SO_4)_2^{2-}$
$UO_2NO_3^+$
UO_2Cl^+ , $UO_2Cl_2^0(aq)$, UO_2F^+ , $UO_2F_2^0(aq)$, $UO_2F_3^-$, $UO_2F_4^{2-}$
$UO_2SiO(OH)_3^+$

5.11.4 Dissolution/Precipitation/Coprecipitation

Dissolution, precipitation, and coprecipitation have a much greater effect on the concentrations of U(IV) than on the concentration of U(VI) in groundwaters. In most cases, these processes will likely not control the concentration of U(VI) in oxygenated groundwaters far from a uranium source. Near a uranium source, or in reduced environments, these processes tend to become increasingly important and several (co)precipitates may form depending on the environmental conditions (Falck, 1991; Frondel, 1958). Reducing conditions may exist in deep aquifers, marsh areas, or engineered barriers that may cause U(IV) to precipitate. Important U(IV) minerals include uraninite (compositions ranging from UO_2 to $UO_{2.25}$), coffinite ($USiO_4$), and ningyoite [$CaU(PO_4)_2 \cdot 2H_2O$] (Frondel, 1958; Langmuir, 1978). Important U(VI) minerals include carnotite [$(K_2(UO_2)_2(VO_4)_2)$], schoepite ($UO_3 \cdot 2H_2O$), rutherfordine (UO_2CO_3), tyuyamunite [$Ca(UO_2)_2(VO_4)_2$], autunite [$Ca(UO_2)_2(PO_4)_2$], potassium autunite [$K_2(UO_2)_2(PO_4)_2$], and uranophane [$Ca(UO_2)_2(SiO_3OH)_2$] (Frondel, 1958; Langmuir, 1978). Carnotite, a U(VI) mineral, is found in the oxidized zones of uranium ore deposits and uraninite, a

U(IV) mineral, is a primary mineral in reducing ore zones (Fron del, 1958). The best way to model the concentration of precipitated uranium is not with the K_d construct, but through the use of solubility



constants.

Figure 5.6a. Calculated distribution of U(VI) hydrolytic species as a function of pH at 0.1 $\mu\text{g/l}$ total dissolved U(VI). [The species distribution is based on U(VI) dissolved in pure water (*i.e.*, absence of complexing ligands other than OH) and thermodynamic data from Wanner and Forest (1992).]

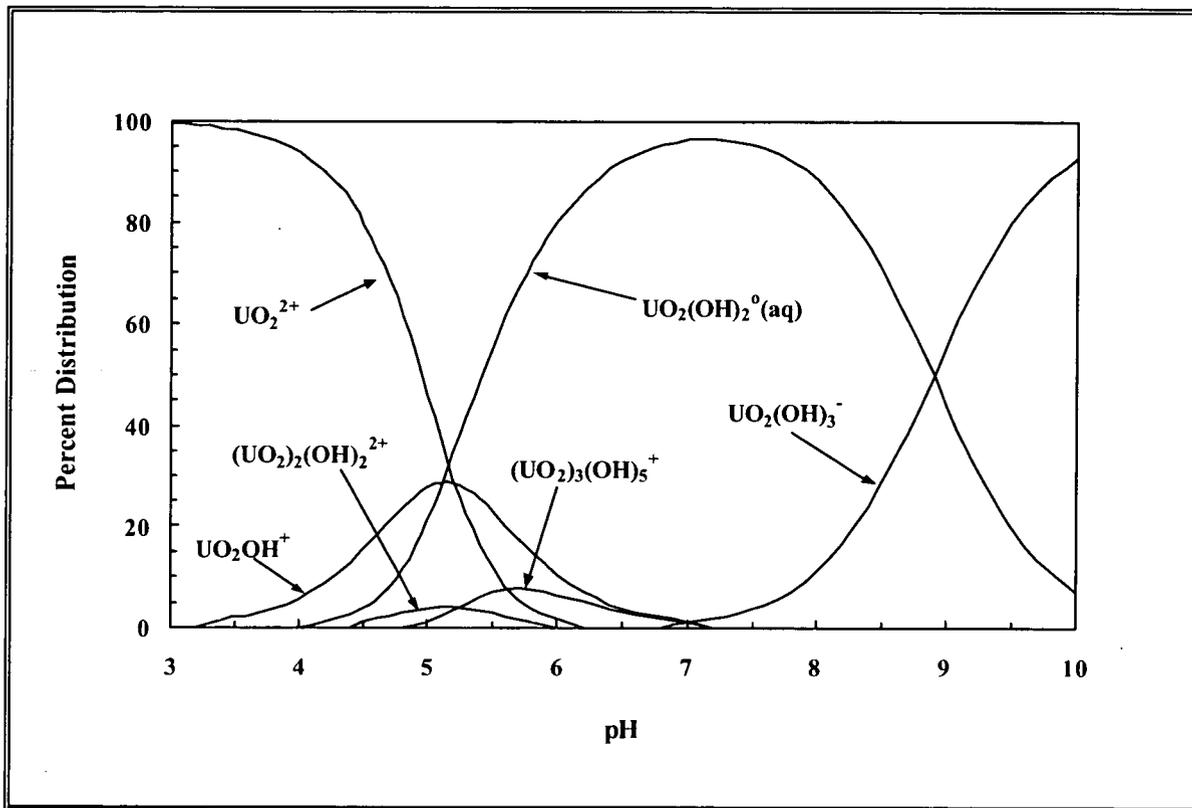


Figure 5.6b. Calculated distribution of U(VI) hydrolytic species as a function of pH at 1,000 $\mu\text{g/l}$ total dissolved U(VI). [The species distribution is based on U(VI) dissolved in pure water and thermodynamic data from Wanner and Forest (1992).]

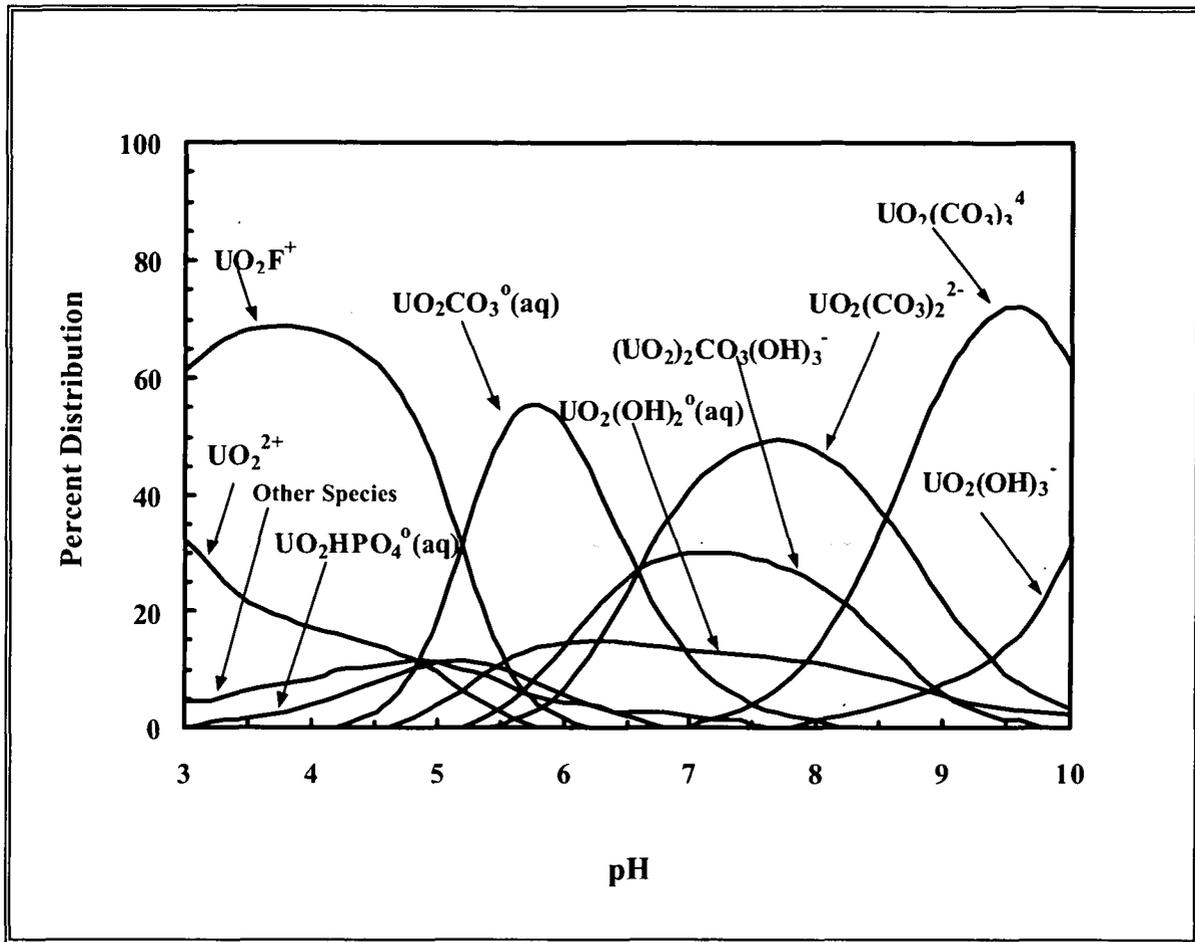


Figure 5.7. Calculated distribution of U(VI) aqueous species as a function of pH for the water composition in Table 5.1. [The species distribution is based on a concentration of 1,000 $\mu\text{g/l}$ total dissolved U(VI) and thermodynamic data from Wanner and Forest (1992).]

5.11.5 Sorption/Desorption

In low ionic strength solutions with low U(VI) concentrations, dissolved uranyl concentrations will likely be controlled by cation exchange and adsorption processes. The uranyl ion and its complexes adsorb onto clays (Ames *et al.*, 1982; Chisholm-Brause *et al.*, 1994), organics (Borovec *et al.*, 1979; Read *et al.*, 1993; Shanbhag and Choppin, 1981), and oxides (Hsi and Langmuir, 1985; Waite *et al.*, 1994). As the ionic strength of an oxidized solution increases, other ions, notably Ca^{2+} , Mg^{2+} , and K^+ , will displace the uranyl ion from soil exchange sites, forcing it into solution. For this reason, the uranyl

ion is particularly mobile in high ionic-strength solutions. Not only will other cations dominate over the uranyl ion in competition for exchange sites, but carbonate ions will form strong soluble complexes with the uranyl ion, further lowering the activity of this ion while increasing the total amount of uranium in solution (Yeh and Tripathi, 1991).

Some of the sorption processes to which uranyl ion is subjected are not completely reversible. Sorption onto iron and manganese oxides can be a major process for extraction of uranium from solution (Hsi and Langmuir, 1985; Waite *et al.*, 1994). These oxide phases act as a somewhat irreversible sink for uranium in soils. Uranium bound in these phases is not generally in isotopic equilibrium with dissolved uranium in the same system, suggesting that the reaction rate mediating the transfer of the metal between the 2 phases is slow.

Naturally occurring organic matter is another possible sink for U(VI) in soils and sediments. The mechanisms by which uranium is sequestered by organic matter have not been worked out in detail. One possible process involves adsorption of uranium to humic substances through rapid ion-exchange and complexation processes with carboxylic and other acidic functional groups (Boggs *et al.*, 1985; Borovec *et al.*, 1979; Idiz *et al.*, 1986; Shanbhag and Choppin, 1981; Szalay, 1964). These groups can coordinate with the uranyl ion, displacing waters of hydration, to form stable complexes. A process such as this probably accounts for a significant fraction of the organically bound uranium in surface and subsurface soils. Alternatively, sedimentary organics may act to reduce dissolved U(VI) species to U(IV) (Nash *et al.*, 1981).

Uranium sorption to iron oxide minerals and smectite clay has been shown to be extensive in the absence of dissolved carbonate (Ames *et al.*, 1982; Hsi and Langmuir, 1985; Kent *et al.*, 1988). However, in the presence of carbonate and organic complexants, sorption has been shown to be substantially reduced or severely inhibited (Hsi and Langmuir, 1985; Kent *et al.*, 1988).

Aqueous pH is likely to have a profound effect on U(VI) sorption to solids. There are 2 processes by which it influences sorption. First, it has a great impact on uranium speciation (Figures 5.6a-b and 5.7) such that poorer-adsorbing uranium species will likely exist at pH values between about 6.5 and 10. Secondly, decreases in pH reduce the number of exchange sites on variable charged surfaces, such as iron-, aluminum-oxides, and natural organic matter.

5.11.6 Partition Coefficient, K_d , Values

5.11.6.1 General Availability of K_d Values

More than 20 references (Appendix J) that reported K_d values for the sorption of uranium onto soils, crushed rock material, and single mineral phases were identified during this review.¹ These studies were typically conducted to support uranium migration investigations and safety assessments associated with the genesis of uranium ore deposits, remediation of uranium mill tailings, agriculture practices, and the near-surface and deep geologic disposal of low-level and high-level radioactive wastes (including spent nuclear fuel). These studies indicated that pH and dissolved carbonate concentrations are the 2 most important factors influencing the adsorption behavior of U(VI).

The uranium K_d values listed in Appendix J exhibit large scatter. This scatter increases from approximately 3 orders of magnitude at pH values below pH 5, to approximately 3 to 4 orders of magnitude from pH 5 to 7, and approximately 4 to 5 orders of magnitude at pH values from pH 7 to 9. At the lowest and highest pH regions, it should be noted that 1 to 2 orders of the observed variability actually represent uranium K_d values that are less than 10 ml/g. At pH values less than 3.5 and greater than 8, this variability includes K_d values of less than 1 ml/g.

Uranium K_d values show a trend as a function of pH. In general, the adsorption of uranium by soils and single-mineral phases in carbonate-containing aqueous solutions is low at pH values less than 3, increases rapidly with increasing pH from pH 3 to 5, reaches a maximum in adsorption in the pH range from pH 5 to 8, and then decreases with increasing pH at pH values greater than 8. This trend is similar to the *in situ* K_d values reported by Serkiz and Johnson (1994), and percent adsorption values measured for uranium on single mineral phases such as those reported for iron oxides (Hsi and Langmuir, 1985; Tripathi, 1984; Waite *et al.*, 1992, 1994), clays (McKinley *et al.*, 1995; Turner *et al.*, 1996; Waite *et al.*, 1992), and quartz (Waite *et al.*, 1992). This pH-dependent behavior is related to the pH-dependent surface charge properties of the soil minerals and complex aqueous speciation of dissolved U(VI), especially near and above neutral pH conditions where dissolved U(VI) forms strong anionic uranyl-carbonato complexes with dissolved carbonate.

5.11.6.2 Look-Up Table

Solution pH was used as the basis for generating a look-up table for the range of estimated minimum and maximum K_d values for uranium. Given the orders of magnitude variability observed for reported

¹ Since the completion of our review and analysis of K_d data for the selected contaminants and radionuclides, the studies by Pabalan *et al.* (1998), Payne *et al.* (1998), Redden *et al.* (1998), Rosentreter *et al.* (1998), and Thompson *et al.* (1998) were identified and may be of interest to the reader.

uranium K_d values, a subjective approach was used to estimate the minimum and maximum K_d values for uranium as a function of pH. These values are listed in Table 5.17. For K_d values at non-integer pH values, especially given the rapid changes in uranium adsorption observed at pH values less than 5 and greater than 8, the reader should assume a linear relationship between each adjacent pair of pH- K_d values listed in Table 5.17.

Table 5.17. Look-up table for estimated range of K_d values for uranium based on pH.

K_d (ml/g)	pH							
	3	4	5	6	7	8	9	10
Minimum	<1	0.4	25	100	63	0.4	<1	<1
Maximum	32	5,000	160,000	1,000,000	630,000	250,000	7,900	5

The boundary representing the minimum limit for uranium K_d values is based on values calculated for quartz from data given in Waite *et al.* (1992) and the K_d values reported by Kaplan *et al.* (1996, 1998), Lindenmeier *et al.* (1995), and Serne *et al.* (1993). It is unlikely that actual K_d values for U(VI) can be much lower than those represented by this lower boundary. At the pH extremes along this curve, the uranium K_d values are very small. Moreover, if one considers potential sources of error resulting from experimental methods, it is difficult to rationalize uranium K_d values much lower than this lower boundary.

The curve representing the maximum limit for uranium K_d values is based on K_d values calculated for ferrihydrite and kaolinite from data given in Waite *et al.* (1992). It is estimated that this maximum limit is biased high, possibly by an order of magnitude or more especially at pH values greater than 5. This estimate is partially based on the distribution of measured K_d values listed in Appendix J, and the assumption that some of the very large K_d measurements may have included precipitation of uranium-containing solids due to starting uranium solutions being oversaturated. Moreover, measurements of uranium adsorption onto crushed rock materials may include U(VI)/U(IV) redox/precipitation reactions resulting from contact of dissolved U(VI) with Fe(II) exposed on the fresh mineral surfaces.

5.11.6.2.1 Limits of K_d Values with Respect to Dissolved Carbonate Concentrations

As noted in several studies summarized in Appendix J and in surface complexation studies of uranium adsorption by Tripathi (1984), Hsi and Langmuir (1985), Waite *et al.* (1992, 1994), McKinley *et al.* (1995), Duff and Amrhein (1996), Turner *et al.* (1996), and others, dissolved carbonate has a significant effect on the aqueous chemistry and solubility of dissolved U(VI) through the formation of

strong anionic carbonate complexes. In turn, this complexation affects the adsorption behavior of U(VI) at alkaline pH conditions.

No attempt was made to statistically fit the K_d values summarized in Appendix J as a function of dissolved carbonate concentrations. Typically carbonate concentrations were not reported and/or discussed, and one would have to make assumptions about possible equilibrium between the solutions and atmospheric or soil-related partial pressures of CO_2 or carbonate phases present in the soil samples. Given the complexity of these reaction processes, it is recommended that the reader consider the application of geochemical reaction codes, and surface complexation models in particular, as the best approach to predicting the role of dissolved carbonate in the adsorption behavior of uranium and derivation of U(VI) K_d values when site-specific K_d values are not available.

5.11.6.2.2 Limits of K_d Values with Respect to Clay Content and CEC

No attempt was made to statistically fit the K_d values summarized in Appendix J as a function of clay content or CEC. The extent of clay content and CEC data, as noted from information compiled during this review, is limited to a few studies that cover somewhat limited geochemical conditions. Moreover, Serkiz and Johnson (1994) found no correlation between their uranium *in situ* K_d values and the clay content or CEC of their soils. Their systems covered the pH conditions from 3 to 7.

However, clays have an important role in the adsorption of uranium in soils. Attempts have been made (e.g., Borovec, 1981) to represent this functionality with a mathematical expression, but such studies are typically for limited geochemical conditions. Based on studies by Chisholm-Brause (1994), Morris *et al.* (1994), McKinley *et al.* (1995), Turner *et al.* (1996), and others, uranium adsorption onto clay minerals is complicated and involves multiple binding sites, including exchange and edge-coordination sites. The reader is referred to these references for a detailed treatment of the uranium adsorption on smectite clays and application of surface complexation modeling techniques for such minerals.

5.11.6.2.3 Use of Surface Complexation Models to Predict Uranium K_d Values

As discussed in Chapter 4 and in greater detail in Volume I of this report, electrostatic surface complexation models (SCMs) incorporated into chemical reaction codes, such as EPA's MINTEQA2, may be used to predict the adsorption behavior of some radionuclides and other metals and to derive K_d values as a function of key geochemical parameters, such as pH and carbonate concentrations. Typically, the application of surface complexation models is limited by the availability of surface complexation constants for the constituents of interest and competing ions that influence their adsorption behavior.

The current state of knowledge regarding surface complexation constants for uranium adsorption onto important soil minerals, such as iron oxides, and development of a mechanistic understanding of these reactions is probably as advanced as those for any other trace metal. In the absence of site-specific K_d

values for the geochemical conditions of interest, the reader is encouraged to apply this technology to predict bounding uranium K_d values and their functionality with respect to important geochemical parameters.

5.12 Conclusions

One objective of this report is to provide a "thumb-nail sketch" of the geochemistry of cadmium, cesium, chromium, lead, plutonium, radon, strontium, thorium, tritium, and uranium. These contaminants represent 6 nonexclusive contaminant categories: cations, anions, radionuclides, non-attenuated contaminants, attenuated contaminants, and redox-sensitive contaminants (Table 5.18). By categorizing the contaminants in this manner, general geochemical behaviors of 1 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 Cr(VI).

Important solution speciation, (co)precipitation/dissolution, and adsorption reactions were discussed for each contaminant. The species distributions for each contaminant were calculated using the chemical equilibria code MINTEQA2 (Version 3.11, Allison *et al.*, 1991) for the water composition described in Tables 5.1 and 5.2. The purpose of these calculations was to illustrate the types of aqueous species that might exist in a groundwater. A summary of the results of these calculations are presented in Table 5.19. The speciation of cesium, radon, strontium, and tritium does not change between the pH range of 3 and 10; they exist as Cs^+ , Rn^0 , Sr^{2+} , and HTO, respectively (Ames and Rai, 1978; Rai and Zachara, 1984). Chromium (as chromate, CrO_4^{2-}), cadmium, and thorium have 2 or 3 different species across this pH range. Lead, plutonium, and uranium have several species. Calculations show that lead forms a large number of stable complexes. The aqueous speciation of plutonium is especially complicated because it may exist in groundwaters in multiple oxidation states [Pu(III), Pu(IV), Pu(V), and Pu(VI)] and it forms stable complexes with a large number of ligands. Because of redox sensitivity, the speciation of uranium exhibits a large number of stable complexes. Uranium(VI) also forms polynuclear complex species [complexes containing more than 1 mole of uranyl [*e.g.*, $(\text{UO}_2)_2\text{CO}_3\text{OH}^-$]].

One general conclusion that can be made from the results in Table 5.19 is that, as the pH increases, the aqueous complexes tend to become increasingly more negatively charged. For example, lead, plutonium, thorium, and uranium 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. 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 5.18. 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
Cd		x			x		x
Cs	x	x					x
Cr			x		x	x	x
Pb		x	x		x		x
Pu	x		x	x	x		x
Rn	x			x		x	
Sr	x	x					x
Th	x		x				x
³ H	x			x		x	
U	x		x	x	x		x

¹ Contaminants that are primarily a health concern as a result of their radioactivity are identified in this column. Some of these contaminants also exist as stable isotopes (*e.g.*, cesium and strontium).

² The redox status column identifies contaminants (Cr, Pu, and U) that have variable oxidation states within the pH and Eh limits commonly found in the environment and contaminants (Cd and Pb) whose transport is affected by aqueous complexes or precipitates involving other redox-sensitive constituents (*e.g.*, dissolved sulfide).

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.

Table 5.19. Distribution of dominant contaminant species at 3 pH values for an oxidizing water described in Tables 5.1 and 5.2.¹

Element	pH 3		pH 7		pH 10	
	Species	%	Species	%	Species	%
Cd	Cd ²⁺	97	Cd ²⁺ CdHCO ₃ ⁺ CdCO ₃ ⁰ (aq)	84 6 6	CdCO ₃ ⁰ (aq)	96
Cs	Cs ⁺	100	Cs ⁺	100	Cs ⁺	100
Cr	HCrO ₄ ⁻	99	CrO ₄ ²⁻ HCrO ₄ ⁻	78 22	CrO ₄ ²⁻	99
Pb	Pb ²⁺ PbSO ₄ ⁰ (aq)	96 4	PbCO ₃ ⁰ (aq) Pb ²⁺ PbHCO ₃ ⁺ PbOH ⁺	75 15 7 3	PbCO ₃ ⁰ (aq) Pb(CO ₃) ₂ ²⁻ Pb(OH) ₂ ⁰ (aq) Pb(OH) ⁺	50 38 9 3
Pu	PuF ₂ ²⁺ PuO ₂ ²⁺ Pu ³⁺	69 24 5	Pu(OH) ₂ (CO ₃) ₂ ²⁻ Pu(OH) ₄ ⁰ (aq)	94 5	Pu(OH) ₂ (CO ₃) ₂ ²⁻ Pu(OH) ₄ ⁰ (aq)	90 10
Rn	Rn ⁰	100	Rn ⁰	100	Rn ⁰	100
Sr	Sr ²⁺	99	Sr ²⁺	99	Sr ²⁺ SrCO ₃ ⁰ (aq)	86 12
Th	ThF ₂ ²⁺ ThF ₃ ⁺	54 42	Th(HPO ₄) ₃ ²⁻ Th(OH) ₃ CO ₃	76 22	Th(OH) ₃ CO ₃	99
³ H	HTO	100	HTO	100	HTO	100
U 0.1 µg/l	UO ₂ F ⁺ UO ₂ ²⁺ UO ₂ F ₂ ⁰ (aq)	62 31 4	UO ₂ (CO ₃) ₂ ²⁻ UO ₂ (OH) ₂ ⁰ (aq) UO ₂ CO ₃ ⁰ (aq) UO ₂ PO ₄	58 19 17 3	UO ₂ (CO ₃) ₃ ⁺ UO ₂ (OH) ₃ UO ₂ (CO ₃) ₂ ²⁻	63 31 4
U 1,000 µg/l	UO ₂ F ⁺ UO ₂ ²⁺ UO ₂ F ₂ ⁰ (aq)	61 33 4	UO ₂ (CO ₃) ₂ ²⁻ (UO ₂) ₂ CO ₃ (OH) ₃ UO ₂ (OH) ₂ ⁰ (aq) UO ₂ CO ₃ ⁰ (aq)	41 30 13 12	UO ₂ (CO ₃) ₃ ⁺ UO ₂ (OH) ₃ UO ₂ (CO ₃) ₂ ²⁻	62 32 4

¹ Only species comprising 3 percent or more of the total contaminant distribution are presented. Hence, the total of the percent distributions presented in table will not always equal 100 percent.

Another objective of this report is to identify the important chemical, physical, and mineralogical characteristics controlling sorption of these contaminants. These key aqueous- and solid-phase parameters were used to assist in the selection of appropriate minimum and maximum K_d values. 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 1 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 5.20.

Sorption of all the contaminants, except tritium and radon, included in this study is influenced to some degree by pH. The effect of pH on both adsorption and (co)precipitation is pervasive. The pH, per se, typically has a small direct effect on contaminant adsorption. However, it has a profound effect on a number of aqueous and solid phase properties that in turn have a direct effect on contaminant sorption. The effects of pH on sorption are discussed in greater detail in Volume I. As discussed above, pH has a profound effect on aqueous speciation (Table 5.19), which may affect adsorption. 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 polynuclear complexes, oxidation state of contaminants and complexing/precipitating ligands, and H^+ -competition for adsorption sites.

The redox status of a system also influences the sorption of several contaminants included in this study (Table 5.20). Like pH, redox has direct and indirect effects on contaminant (co)precipitation. The direct effect occurs with contaminants like uranium and chromium where the oxidized species form more soluble solid phases than the reduced species. Redox conditions also have a direct effect on the sorption of plutonium, but the effects are quite complicated. 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 cadmium and lead precipitates. Thus, these 2 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).

Unlike most ancillary parameters, the effect of redox on sorption can be quite dramatic. 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 (Ames and Rai, 1978; Rai and Zachara, 1984).

Table 5.20. Some of the more important aqueous- and solid-phase parameters affecting contaminant sorption.¹

Element	Important Aqueous- and Solid-Phase Parameters Influencing Contaminant Sorption ²
Cd	[Aluminum/Iron-Oxide Minerals], [Calcium], Cation Exchange Capacity, [Clay Mineral], [Magnesium], [Organic Matter], pH, Redox, [Sulfide]
Cs	[Aluminum/Iron-Oxide Minerals], [Ammonium], Cation Exchange Capacity, [Clay Mineral], [Mica-Like Clays], pH, [Potassium]
Cr	[Aluminum/Iron-Oxide Minerals], [Organic Matter], pH, Redox
Pb	[Aluminum/Iron-Oxide Minerals], [Carbonate, Fluoride, Sulfate, Phosphate], [Clay Mineral], [Organic Matter], pH, Redox
Pu	[Aluminum/Iron-Oxide Minerals], [Carbonate, Fluoride, Sulfate, Phosphate], [Clay Mineral], [Organic Matter], pH, Redox
Rn	None
Sr	Cation Exchange Capacity, [Calcium], [Carbonate], pH, [Stable Strontium]
Th	[Aluminum/Iron-Oxide Minerals], [Carbonate], [Organic Matter], pH
³ H	None
U	[Aluminum/Iron-Oxide Minerals], [Carbonate, Fluoride, Sulfate, Phosphate], [Clay Mineral], [Organic Matter], pH, Redox, [U]
¹ For groundwaters with low ionic strength and low concentrations of contaminant, chelating agents (<i>e.g.</i> , EDTA), and natural organic matter.	
² Parameters listed in alphabetical order. Square brackets represent concentration.	

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