
**Pacific Northwest
National Laboratory**

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**Geochemical Data Package
for the 2005 Hanford
Integrated Disposal Facility
Performance Assessment**

K. M. Krupka
R. J. Serne
D. I. Kaplan

September 2004



Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RL01830

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Richland, Washington 99352

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Summary

CH2M HILL Hanford Group, Inc. (CH2M HILL) is designing and assessing the performance of an integrated disposal facility (IDF) to receive low-level waste (LLW), mixed low-level waste (MLLW), immobilized low-activity waste (ILAW), and failed or decommissioned melters. The CH2M HILL project to assess the performance of this disposal facility is the Hanford IDF Performance Assessment (PA) activity. The goal of the Hanford IDF PA activity is to provide a reasonable expectation that the disposal of the waste is protective of the general public, groundwater resources, air resources, surface-water resources, and inadvertent intruders. Achieving this goal will require predicting contaminant migration from the facilities. This migration is expected to occur primarily through the movement of water through the facilities and the consequent transport of dissolved contaminants through the vadose zone to groundwater, where contaminants may be reintroduced to receptors via drinking water wells or mixing in the Columbia River.

Pacific Northwest National Laboratory (PNNL) assists CH2M HILL in their performance assessment activities. One of PNNL's tasks is to provide estimates of the geochemical properties of the materials comprising the IDF, the disturbed region around the facility, and the physically undisturbed sediments below the facility (including the vadose zone sediments and the aquifer sediments in the upper unconfined aquifer). The geochemical properties are expressed as parameters that quantify the adsorption of contaminants and the solubility constraints that might apply for those contaminants that may exceed solubility limits. Solubility constraints are used for conditions in which the calculated total concentration of the radionuclide and its stable isotopes is believed to exceed the solubility of an assumed controlling phase predicted from available thermodynamic data. The common parameters used to quantify adsorption and solubility are the distribution coefficient (K_d) and the thermodynamic solubility product (K_{sp}), respectively. In this data package, we approximate the solubility of contaminants using a more simplified construct, called the empirical solubility concentration limit, a constant value. For the 2005 IDF PA, little site/waste form/engineered barrier solubility work has been done to identify the solubility-controlling solids. When the controlling solid cannot be identified but empirical solubility tests clearly indicate that some unidentified phase is controlling solution concentration, an empirical solubility concentration limit is used.

The K_d values and empirical solubility concentration limits for each contaminant are direct inputs to subsurface flow and transport codes used to predict the performance of the IDF system. In addition to the best-estimate K_d values, a reasonable conservative value and a range are provided. The data package does not list estimates for the range in empirical solubility concentration limits or their uncertainties; the data package does provide values for both the K_d values and empirical solubility concentration limits for different spatial zones in and surrounding the IDF system and does supply time-varying K_d values for cement solidified waste. The K_d values and empirical solubility concentration limits presented for each contaminant were presented in an earlier version of this report prepared by Kaplan and Serne (2000) for the 2001 ILAW PA and have been updated to include applicable data from investigations completed since that report was issued and our understanding of the geochemistry specific to Hanford has improved.

A discussion is also included on the evolution of the K_d values recommended from the original 1999 ILAW PA through the 2001 ILAW and 2003 Supplemental PAs to the current values to be used for the

2005 IDF PA for the key contaminants of concern: Cr(VI), nitrate, ^{129}I , ^{79}Se , ^{99}Tc , and U(VI). This discussion provides the rationale for why some K_d values have changed with time.

Reference

Kaplan DI and RJ Serne. 2000. *Geochemical Data Package for the Hanford Immobilized Low-Activity Tank Waste Performance Assessment (ILAW PA)*. PNNL 13037 Rev. 1, Pacific Northwest National Laboratory, Richland, WA.

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1.0 Introduction

The Hanford Integrated Disposal Facility Performance Assessment (IDF PA) examines the long-term environmental and human health effects associated with the planned disposal of the vitrified low-activity fraction of waste, i.e., immobilized low-activity waste (ILAW), contained within Hanford Site tanks, as well as low-level waste (LLW), mixed low-level waste (MLLW), and failed or decommissioned melters used for waste vitrification. Greater than 200,000 m³ of tank waste have been created as a result of separating nuclear materials from irradiated nuclear fuels. This waste has been stored in 18 underground tank farms within which are 177 individual tanks. The tank waste is to be retrieved, separated into low-activity and high-level fractions, and then immobilized by private vendors. The high-level fraction, which will be of low volume but will contain most of the radionuclides, will be vitrified at the Waste Treatment Plant (WTP), then stored at Hanford until a national geologic repository is approved. The low-activity fraction will be disposed of as vitrified waste in the 200 East Area in the IDF.

The current PA for the IDF is the *Hanford Immobilized Low-Activity Waste Performance Assessment: 2001 Version* (ILAW PA) (Mann et al. 2001). The ILAW PA is updated annually, most recently as Mann (2003a). The 2001 ILAW PA was prepared assuming that only ILAW would be disposed at the IDF. Mann (2003) acknowledges the anticipated changes in the waste types to be disposed at the facility. A risk assessment for the IDF was prepared recently that considers the combined disposal of ILAW, LLW, MLLW, and failed or decommissioned melters in a single facility (Mann et al. 2003). That risk assessment used information from the ILAW PA (Mann et al. 2001), and the performance assessments completed for the Hanford solid waste burial grounds (Wood et al. 1995, 1996).

The first ILAW PA showed that groundwater transport presents the greatest potential for long-term dose uptake by humans (Mann et al. 1998). Of the numerous radionuclides evaluated in the ILAW PA (including actinium, americium, carbon, cerium, curium, cobalt, cesium, europium, iodine, niobium, nickel, neptunium, protactinium, lead, plutonium, radium, ruthenium, selenium, strontium, tin, technetium, thorium, uranium, and zirconium), the isotopes ¹²⁹I, ²³⁷Np, ⁷⁹Se, ⁹⁹Tc, and ^{234/235/238}U were identified as posing the greatest potential health hazard. Kaplan et al. (1995) described the geochemical factors affecting the transport of these radionuclides in the Hanford Site subsurface environment. It was also determined that the outcome of these simulations was very sensitive to the parameter describing the extent to which radionuclides sorbed to the subsurface sediment, the distribution coefficient, K_d. The distribution coefficient is the ratio of the radionuclide concentration associated with the solid phase to that in the liquid phase (described in more detail in Section 2.0). Near the buried waste, solubility constraints may also control the solution concentrations of contaminants. Thus, this data package contains empirically chosen “solubility concentration limits” for selected contaminants in the regions near the specified wastes.

The purpose of the geochemistry data package is to document the basis for selecting geochemical parameters and input values that will be used in the 2005 version of the IDF PA. This data package includes a discussion of the philosophy and justification for selection and use of the empirical distribution coefficient (K_d) and empirical solubility concentration limits as inputs for contaminant migration analyses. Brief descriptions of the geochemistry of several key contaminants of concern, the spatial zone approach, and the resulting tables of information are also provided. Additional data packages prepared in support of the 2005 IDF include information on the disposal facility (Puigh 2004), inventory (Puigh et al.

2004), waste form release (Pierce et al. 2004), recharge (Fayer and Szecsody 2004), near-field hydrology (Meyer et al. 2004), flow and transport in the natural sediments (Khaleel 2004), and geology (Reidel 2004).

2.0 Philosophy

2.1 Background

The concentrations, mobility, and bioavailability of radionuclides and contaminants in sediment pore water and groundwater are 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; several geochemical processes including oxidation/reduction, aqueous speciation, adsorption/desorption and precipitation/dissolution, diffusion, colloid-facilitated transport, and anion exclusion. Additionally, in the uppermost layer of surface sediment, the mobility of radionuclides also can be increased by biological activity and the drying and subsequent cracking of sediments. Colloid-facilitated transport and anion exclusion have received considerable attention recently in that they can enhance the transport of certain radionuclides. These processes are hard to quantify, and the extent to which they occur is difficult to determine. The importance of colloid-facilitated migration, especially in aquifer systems that do not involve fracture flow of groundwater, is still a subject of debate. The geochemical processes listed above are discussed in detail in sources such as Baes and Mesmer (1976), Garrels and Christ (1965), Langmuir (1997), Lindsay (1979), Morel (1983), Nordstrom and Munoz (1985), Sposito (1989, 1994), Stumm and Morgan (1981), Yariv and Cross (1979), and others, and in the references cited therein. Table 2.1, taken from the U.S. Environmental Protection Agency (EPA) report *Understanding Variation in Partition Coefficient, K_d Values: Volume I. The K_d Model, Methods of Measurement, and Application of Chemical Reaction Codes* (EPA 1999a), summarizes by mechanism, anticipated effects on radionuclide mobility, and key environmental factors associated with each of these geochemical processes. The authors of this report are also principal authors of EPA (1999a) and the other two volumes in this series, *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* (EPA 1999b); and *Volume III. Review of Geochemistry and Available K_d Values for Americium, Arsenic, Curium, Iodine, Neptunium, Radium, and Technetium* (EPA 2004).

To predict contaminant transport through the subsurface accurately, it is essential that the important geochemical processes affecting contaminant transport be identified and described in a scientifically defensible manner. Adsorption/desorption (including ion exchange) and precipitation/dissolution are considered the most important processes affecting radionuclide interactions with sediments. Precipitation/dissolution is more likely to be an important process where elevated concentrations of dissolved radionuclides exist, such as in the near-field environment of radioactive waste disposal facilities, at spill sites of radionuclide-containing wastes, or where steep pH or redox gradients exist. Adsorption/desorption will likely be the key process controlling radionuclide retardation in areas where trace concentrations of dissolved radionuclides exist, such as those associated with far-field environments of disposal facilities or spill sites or in areas where sediments are to be irrigated using radionuclide-contaminated water.

The sorption of radionuclides on sediments is frequently quantified by the partition (or distribution) coefficient, K_d . The K_d parameter is a factor related to the partitioning of a radionuclide between the solid and aqueous phases and 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. The terms “partition coefficient” and “distribution coefficient” are used interchangeably in the literature for the K_d linear isotherm sorption

Table 2.1. Summary of Chemical Processes Affecting the Mobility of Radionuclides and Contaminants (taken from EPA [1999a])

Geochemical Process	Mechanism	Affect on Radionuclide Mobility	Important Factors
Aqueous complexation	Reaction where an aqueous molecular unit (ion) acts as a central group to attract and form a close association with other atoms or molecules	May enhance mobility or retardation, depending on radionuclide and geochemical conditions	<ul style="list-style-type: none"> • Function of pH and redox conditions • Complexation may lower potential for adsorption or increase solubility, which can enhance the potential for mobility • Complexes may more readily bond to sediments and thus retard migration • Organic ligands from humic materials can be present in significant concentrations and dominate radionuclide complexation in some systems
Oxidation/reduction (redox) reactions	Reaction where electrons are transferred completely from one species to another	May enhance mobility or retardation, depending on radionuclide and geochemical conditions	<ul style="list-style-type: none"> • Change in redox status changes aqueous speciation, which may increase or decrease adsorption and solubility • If redox status is low enough to induce precipitation of sulfide minerals, reprecipitation of some radionuclides may be expected • The mobilities of redox-sensitive species are more difficult to predict because many redox reactions are kinetically slow in natural waters, and several elements may never reach equilibrium between their various valence states
Adsorption/desorption and ion exchange	Special case of a complexation reaction where there is a net accumulation of a radionuclide at the interface between solid and aqueous solution phases; does not include development of a three-dimensional molecular structure	Enhances retardation	<ul style="list-style-type: none"> • Occurs primarily in response to electrostatic attraction • Very dependent on pH and mineralogy • Anion adsorption is greatest at low pH and decreases with increasing pH • Cation adsorption is greatest at high pH and decreases with decreasing pH • Some radionuclides may be present as cations or anions depending on pH • Totally to partially reversible; decline in dissolved radionuclide concentration may result in desorption and release of adsorbed radionuclide to water • Likely the key process controlling radionuclide mobility in areas where chemical equilibrium exists

Table 2.1. (contd)

Geochemical Process	Mechanism	Affect on Radionuclide Mobility	Important Factors
Precipitation/ dissolution	Special case of a complexation reaction in which the complex formed by two or more aqueous species is a solid with three-dimensional molecular structure	Enhances retardation	<ul style="list-style-type: none"> • Very dependent on pH and redox conditions • Totally to partially reversible; decline in dissolved radionuclide concentration may result in dissolution of precipitated radionuclide to groundwater • Likely the process where chemical nonequilibrium exists, or areas where high radionuclide concentrations or steep pH and/or redox gradients exist
Diffusion	Molecular process of transport of matter in the absence of advection	Enhances mobility	<ul style="list-style-type: none"> • Flux of matter due to diffusion is proportional to concentration gradient
Colloid-facilitated transport	Radionuclides associated with suspended fine-grained material (smaller than clay size) that may be transported with flowing sediment pore water and groundwater	Enhances mobility	<ul style="list-style-type: none"> • Little information on occurrence, mineralogical and physicochemical properties, or conditions conducive to the generation of mobile colloids • May originate from dispersion of sediments, decementation of secondary mineral phases, and/or precipitation of groundwater constituents • Difficult to collect colloids from sub-surface in a way that minimizes or eliminates sampling artifacts • Difficult to delineate unambiguously between radionuclides in the mobile-aqueous and mobile-solid phases
Anion exclusion	Occurs when the diffuse double layer, an extension of a particle's negative surface charge into the surrounding solution, repulses anions	Enhances mobility to a limited extent	<ul style="list-style-type: none"> • By excluding anions from the diffuse double layer, where water is relatively immobile, anions are restricted to the faster-moving pore water, resulting in an average rate of anion transport greater than the average pore-water velocity defined by Darcy's Law • More pronounced with higher cation exchange capacity, or negative charge, of sediment or rock.

model. Radionuclides that adsorb very strongly to sediment have large K_d values (typically greater than 100 mL/g) compared with radionuclides that are not significantly retarded by adsorption. Radionuclides that do not adsorb to sediment and migrate essentially at the same rate as the water flow have K_d values near 0 mL/g. The K_d model is the simplest yet least robust sorption model available, yet it is the most common measure used in hydrologic transport and biosphere codes to describe the extent to which contaminants are sorbed to sediments. The primary advantage of the K_d model is that it is inserted easily into computer codes to quantify the reduction in the extent of transport of a radionuclide relative to groundwater. The K_d 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 technical issues,

complexities, and shortcomings of the K_d approach to describing radionuclide sorption to sediments are discussed in detail in EPA (1999a) and the references cited therein. Cantrell et al. (2002) discuss the scientific basis for application of the K_d model to the complex wastes of the Hanford Site (Section 2.3).

Throughout this report (especially in Section 3), “sorption” is used as a generic term devoid of mechanism to describe the partitioning of dissolved aqueous-phase constituents to a solid phase. When a radionuclide is associated with a geologic material, it is often not known whether the radionuclide is adsorbed onto the surface of the solid, absorbed into its structure, precipitated as a three-dimensional molecular structure on the surface of the solid, or partitioned into the organic matter (Sposito 1989). The term “sorption” is used to encompass all of these processes when the authors do not have enough information to distinguish the exact mechanism that is controlling the partitioning of the constituent of interest. When discussing the K_d values and empirical solubility concentration limits selected for the 2005 IDF PA, we attempted to be explicit when referring to and differentiating between adsorption- or solubility-controlled processes.

2.2 Relationship Between Distribution Coefficients and Retardation Factors

The distribution coefficient, or K_d value, is the simplest construct describing contaminant sorption to sediments. It is the ratio of the contaminant concentration sorbed to the solid phase divided by the contaminant concentration in the liquid surrounding the solid phase (Equation 2.1):

$$K_d = \frac{C_{solid}}{C_{liquid}} \quad (2.1)$$

where C_{solid} (M/kg) and C_{liquid} (M/L) are the concentration in the solid and liquid phases, respectively. Sorption, as expressed by K_d values, is normalized by weight. Contaminant transport modelers commonly use K_d values to account for chemical interactions between the contaminant and the sediment. The K_d value is used to define the retardation factor, which is the ratio of the average linear velocity of water (m/s) divided by the average linear velocity of the contaminant (m/s). For water-saturated systems, the K_d value is related to the retardation factor (Rf, unitless) by the bulk density (ρ_b , kg/m³) and the porosity (η , m³/m³) (Valocchi 1985; Bouwer 1991) as follows:

$$Rf = \left(1 + \frac{K_d \rho_b}{\eta} \right) \quad (2.2)$$

The bulk density and porosity terms in Equation 2.2 convert the weight-normalized K_d value into a volume-normalized value. For partially saturated sediments, the porosity term is replaced by the volumetric water content of the vadose zone sediments.

2.3 Empirical K_d Construct

The geochemical behavior of radionuclides in the subsurface that are used in the IDF PA are based on two parameters, the distribution coefficient (K_d) value and empirical solubility concentration limit of a specified solid. In its strictest usage, the distribution coefficient is a quasi-thermodynamic construct. It is the ratio of the concentration of a species reversibly adsorbed/exchanged to a geomedium’s surface sites

divided by the concentration of the species in the surrounding solution. Using uranyl as an example, the definition of a species-specific K_d as a quasi-thermodynamic construct is

$$K_{d-thermo} = \frac{X\equiv UO_2^{2+}}{UO_2^{2+}} \quad (2.3)$$

where $X\equiv UO_2^{2+}$ is the activity of the uranyl species reversibly adsorbed to a specific surface site X, and UO_2^{2+} is the activity of dissolved “free” uranyl species at equilibrium with the surface site X. Among the many assumptions underpinning $K_{d-thermo}$ are that adsorption is fully reversible, and the presence of adsorbed uranyl species does not influence subsequent adsorption of other dissolved uranyl or other contaminant species. Thus, a single distribution coefficient is used to represent both sorption and desorption of each contaminant species.

To apply the K_d construct to contaminant transport and performance assessment calculations, the definition of the construct is relaxed for several reasons. In natural systems, many types of sorption sites exist. Also, it is not possible to measure the thermodynamic activity of individual chemical species on the adsorbents’ surfaces. Furthermore, the measurement of thermodynamic activities of dissolved species is rarely performed and, as just mentioned for adsorbates on solids, no techniques exist for measuring their thermodynamic activity. The parameters that can be measured readily are the total contaminant concentration or radionuclide activity (not to be confused with thermodynamic activity) as opposed to the concentration or radioactivity of each individual species. Thus the quasi-thermodynamically based K_d construct, as defined in Equation 2.3, requires differentiating and quantifying each type of surface site and each solution species. Additionally, spatial variability of the surface sites and groundwater chemistry in natural systems cannot be characterized practicably to the degree necessary for the full implementation of species-specific sorption models such as the triple layer surface complexation model (see Kent et al. [1988] for a good overview and Jenne [1998] for a recent compilation of related articles).

The empirical definition of the K_d value becomes the ratio of the concentration of the complete suite of species (the sum of the concentrations of all species that includes the contaminant of interest) sorbed by an assemblage of surface sites divided by the summed concentration of the suite of species (total concentration) in solution. Again, using uranyl as an example, the definition of the quasi-thermodynamic K_d construct would be for a simple system that contained three U(VI) species [UO_2^{2+} , $UO_2(OH)^+$, and $UO_2(OH)_2^0(aq)$]:

$$K_{d-therm} = \frac{\sum \text{Adsorbed U Species}}{\sum \text{Dissolved U Species}} = \frac{X\equiv UO_2^{2+} + X\equiv UO_2(OH)^+ + X\equiv UO_2(OH)_2^0}{UO_2^{2+} + UO_2(OH)^+ + UO_2(OH)_2^0} \quad (2.4a)$$

where $X\equiv$ is an average sorbent site (more than one sorbent site type is expected in nature). The numerator and denominator in Equation 2.4a are summed over contaminant species sorbed as well as sorbent sites. The empirical K_d equation would be

$$K_d = \frac{\text{Total U(VI) on Solid}}{\text{Total U(VI) in Solution}} \quad (2.4b)$$

Among the reasons for selecting the “empirical” K_d construct for the IDF PA, as exemplified by Equation 2.4b, are the following:

1. The bulk of the existing sorption literature on radionuclide sorption, especially at the Hanford Site, can be classified as “empirical” K_d values.
2. Under the expected low concentrations of the contaminants in the far field, sorption can be considered to be independent of contaminant concentration and, therefore, K_d is a constant for a given contaminant/geological material combination under identical (geo)chemical conditions.
3. The K_d can be used directly in codes used for performance assessments, such as PORFLO, VAM3DF, and STOMP used in Hanford Site far-field vadose zone transport calculations (see Khaleel 1999).
4. Perhaps most important, there is no thermodynamically based conceptual model or numerical code that is robust enough to accurately predict the degree of radionuclide adsorption by natural sediments (see below).

The current vision for Hanford Site-wide cumulative risk assessments performed with the System Assessment Capability (SAC) (Kincaid et al. 2000) is to represent contaminant adsorption using the empirical distribution coefficient, K_d , (or linear isotherm) sorption model. Review comments from the Integration Project Expert Panel (IPEP) indicate that work is required to justify the applicability of the empirical K_d sorption model and to identify and defend the range of K_d values that are adopted for assessments. The work plans developed for the DOE Hanford Science and Technology (S&T) Program within the Hanford Site Groundwater/Vadose Zone Integration Project (Integration Project) efforts, SAC, and the core projects of the Integration Project must answer the question, “Is there a scientific basis for the application of the linear sorption isotherm model to the complex wastes of the Hanford Site?” The paper by Cantrell et al. (2002), *Hanford Contaminant Distribution Coefficient Database and Users Guide*, was intended specifically to address this question. The following conclusions and recommendations were taken essentially verbatim from Section 6 of Cantrell et al. (2002). The general thesis of the cited paper is that the empirical K_d construct will continue to be used at Hanford for overall system performance activities and selected key contaminants and geochemical environments will be studied in a more mechanistic way. We concur with the Cantrell et al. (2002) thesis and cited justifications.

- “The linear adsorption model or K_d approach is a useful and practical approach for modeling contaminant adsorption in transport performance assessments. This empirical approach has the advantage of being simple, and a considerable database of Hanford specific K_d values measured under a variety of conditions is available.”
- “An inherent drawback of this approach is its empirical nature. Because the variation in a K_d value cannot be confidently estimated beyond the range of chemical conditions under which it was measured, the utility of any K_d measurement may be good only for that specific set of conditions. This limitation is not a significant problem as long as the site-specific conditions being modeled do not deviate significantly from those for which K_d measurements are available. For situations in which the concentrations of chemical parameters change rapidly within a small spatial zone (e.g., under a leaking high-level waste tank), K_d values generally are not available for all the important contaminants as

a function of all the important parameters in sufficient detail to provide transport modeling results that are sufficiently accurate. In this situation, several approaches could be taken. Each of the possible approaches will require a more detailed knowledge of the geochemical parameters and mechanisms that control adsorption of a particular contaminant under site-specific conditions. The more scientifically rigorous approach would be to conduct detailed mechanistic adsorption studies to determine the influence of all the important geochemical parameters over a broad range of concentrations that could potentially influence adsorption for each contaminant of interest. This approach is likely to be costly and time consuming. A faster and more economical alternative to the more scientifically rigorous approach is to apply available mechanistic information to design an adsorption study in which K_d values are determined over a range of geochemical parameters that have the greatest influence on adsorption. This study would be limited to contaminants that pose the greatest potential risk. It is likely that this approach would only be required for the limited number of waste sites where high concentration wastes were discharged or at leaking high-level waste tank sites. Although this approach is not as ideal as a completely mechanistic approach, it would provide a method to obtain more reliable modeling results in a more economical and timely fashion.” This is the approach that was adopted for the IDF geochemical portion of the IDF PA project. Key contaminants that have been studied in a more mechanistic fashion to date include ^{129}I , ^{99}Tc , ^{79}Se , and U.

- “As a means of increasing the scientific defensibility of using the K_d approach for estimating adsorption in performance assessment modeling, it is recommended that a detailed comparison be made with a transport model in which a more rigorous mechanistic approach to adsorption is used.”

Using site-specific materials in IDF-funded experiments, it is possible to gather relevant data directly and not rely on extrapolation from other sediment and aqueous systems. The problem with the rigorous thermodynamic species approach is that there is no numerical or conceptual model developed that is sufficiently robust to predict accurately the degree of radionuclide adsorption by natural sediment (Sposito 1984; Westall 1986, 1995; Wang et al. 1997; Davis et al. 1998). Mechanistic models, though impractical for PA purposes, provide the necessary paradigms on which technically defensible empirical K_d values must be based. For most of the data used in the IDF PA geochemical data package, sorption experiments have been conducted with site-specific sediment and site-specific groundwater, which resembles natural vadose zone pore waters, and simulated glass leachate. Future work will expand the leachates studied to include grout or cementitious waste fluids, both “fresh” alkaline and “aged” carbonated fluids that represent the evolution of cement in subsurface environments (see Krupka and Serne [1998] for more discussion on cement mineral and pore water evolution.)

Another aspect of the K_d construct that is typically relaxed when used in contaminant transport calculations is the chemical process that it describes. As pointed out earlier, Equation 2.3 implies an adsorption or exchange reaction that is reversible. The laboratory K_d measured with complex natural sediments and perhaps complex natural groundwater solutes often reflect not only adsorption and exchange reactions, but also absorption, specific or somewhat irreversible adsorption, surface complexation, and varying degrees of coprecipitation reactions. Identifying the processes that govern radionuclide chemical behavior is the single most important task needed for estimating K_d values for the IDF PA. Once the dominant geochemical process is identified for a specific geological and chemical environment, the range of empirical K_d values can be narrowed. Radionuclide geochemical processes have been ascertained primarily through experiments in which a key parameter is systematically varied (e.g., suspension pH or ionic strength). The trends displayed during these experiments provide key information

regarding radionuclide behavior and also shed light on which processes may be controlling the radionuclide interaction between the solid and liquid.

The importance of first identifying the dominant geochemical process affecting radionuclide concentrations in the mobile aqueous phase can be illustrated through an experiment conducted for this project (Kaplan et al. 1998a). In this experiment, as the pH of Hanford Site sediment-groundwater slurries was increased from pH 8 to 10, K_d values for U(VI) gradually increased from 1.3 to 3.5 mL/g. Above pH 10.5 the amount of U(VI) removed from the aqueous phase increased more than 500-fold. The initial increase in K_d between pH 8 and 10 was attributed to increased cation exchange capacity of the sediment. That is, the number of pH-dependent adsorption sites in the natural sediment that attract cations increased as pH increased. The latter, more dramatic increase was attributed to coprecipitation of U(VI) with carbonate solid phases that were generated as the pH increased. These conclusions were supported by independent solubility calculations. What we learn from this particular study is much more than that the magnitude of the K_d value should be used as an input parameter to the IDF PA; we also gain a plausible explanation of the processes governing U(VI) removal from solution. As this example illustrates, changes in the dominating chemical processes may account for an appreciable amount of variability in derived K_d values under different geochemical conditions.

2.4 Solubility Constraints

In addition to the K_d construct, solubility products, both thermodynamically and empirically based, are being used to describe radionuclide geochemical behavior in the IDF. Solubility constraints are used for conditions in which the calculated total concentration of the radionuclide and its stable isotopes is believed to exceed the solubility of an assumed controlling phase. The selection of controlling solid phases is based on laboratory experiments and, when experimental data are not available, on literature findings. If the thermodynamic data for the solid phase are not available from laboratory experiments or the literature, they will be calculated using chemical speciation and solubility algorithms. Once the solid phase is selected, the upper limit of the solution concentration of the radionuclide and its stable isotopes will be calculated with the appropriate background electrolyte composition. If the background electrolyte composition remains essentially constant, the solubility product can be assumed to be nearly constant as well. This has led some performance assessment practitioners to refer to solubility constraints as constants, but in reality the solubility constant, K_{sp} , varies with solution chemistry. When radionuclide concentrations exceed the K_{sp} precipitation can be expected, and subsequent radionuclide aqueous concentrations and behavior are controlled by solubility until the solution concentrations drop below the solubility constraining value. At concentrations below this limit, the radionuclide concentration will be controlled by the empirical K_d construct. When the controlling solid cannot be identified but empirical solubility tests clearly indicate that some unidentified phase is controlling solution concentration, an empirical solubility relationship is used. This empirical solubility product includes the key solution parameters as independent variables and the empirical solubility product as the dependent variable. In some cases, the empirical K_{sp} data may be simplified as a constant solubility concentration limit. This is especially true for the 2005 IDF PA because little site/waste form/engineered barrier solubility work has been done to identify the controlling solids. Recently published critical reviews and tabulations of thermodynamic constants completed by the Nuclear Energy Agency (NEA) of the Organisation for Economic Cooperation and Development (OECD) in Palaiseau, France (with multinational funding) are valuable resources for thermodynamic solubility constants. Five compilations are available for the thermodynamic constants for aqueous, solid, and gaseous species containing uranium, americium,

technetium, neptunium, and plutonium (including an update of the earlier published constants) (Grenthe et al. 1992; Silva et al. 1995; Rard et al. 1999; Lemire et al. 2001; Guillaumont et al. 2003).

2.5 Parametric- K_d Model

When using the constant K_d model, the retardation factor is a constant for each layer of geologic media (each layer is assumed to have a constant bulk density and water content or effective porosity). The transport equation based on a constant K_d model does not require knowledge of any other geochemical parameters such as pH or mineralogy, and it is easily solved to determine the solution concentration as a function of time and space. Using the constant K_d model in a retardation factor (Equation 2.2) has caused most of the criticism; few natural groundwater pathways are spatially or geochemically homogeneous to the extent that the retardation factor for a species remains constant for all locations and times.

Clearly, the greatest limitation to the constant K_d approach is that it describes solute partitioning between the aqueous and solid phases for only one set of environmental conditions. Such homogeneity does not exist in nature, and therefore greatly compromises the usefulness of the constant. For instance, when the aqueous phase chemistry was varied, K_d values for americium in a Hanford Site sediment ranged from 0.2 to 53 mL/g, roughly a 200-fold range (Delegard and Barney 1983). Additional variability in the K_d values for americium, though less, was observed when slightly different Hanford Site sediments were used: 4.0 to 28.6 mL/g (Delegard and Barney 1983, Solution 1). Using similar aqueous phases but sediments from around the country, Sheppard et al. (1976) measured K_d values for americium ranging from 125 to 43,500 mL/g. (Interestingly, the lowest K_d in this survey of 12 soils/sediments from U.S. Department of Energy [DOE] national laboratories was found for a Hanford sediment.)

The K_d value in the parametric model varies according to empirically derived relationships with aqueous and solid phase independent parameters. Thus, it has the distinct advantage of being more robust and removes the burden of determining new K_d values for each environmental condition. Because K_d is a function of a large number of variables, it is common to systematically vary several parameters simultaneously in one experiment. Factorial design strategies are most often invoked to determine the systematic change in the dependent variables such as the distribution coefficient resulting from varying the independent variables (Cochran and Cox 1957; Davies 1954; Plackett and Burman 1946; Box and Behnken 1960). Statistical methods commonly used to derive quantitative predictor equations include standard linear or nonlinear regression (Snedecor and Cochran 1967), stepwise regression (Hollander and Wolfe 1973), and adaptive learning networks (Mucciard et al. 1979, 1980). These techniques have been used to develop empirical relationships describing K_d values in terms of other variables for specific Hanford conditions (Routson and Serne 1972; Serne et al. 1973; Routson et al. 1981; Delegard and Barney 1983).

The empirical predictor equations commonly take the form of a nonlinear multinomial expression. For example, after evaluating solutions consisting of several sodium salts, organic chelates, and acids, Delegard and Barney (1983) came up with the following expression for a K_d value for americium on one particular Hanford sediment:

$$\text{Log } [K_d(\text{Am})] = 2.0 + 0.1[\text{NaOH}] - 26.8[\text{HEDTA}] + 153.4[\text{HEDTA}]^2 \quad (2.5)$$

The independent parameters and ranges used to develop Equation 2.5 were selected to simulate a plume of high-level waste that emanates from a steel-lined concrete tank into sediment in the Hanford

Central Plateau. Numerous salts were found to have no significant effect on americium K_d values so were not included in the expression. Delegard and Barney (1983) also evaluated higher exponential and logarithmic terms and determined that these terms did not improve the predictive capabilities of the parametric K_d expression (i.e., the regression coefficients were not significant at $P < 0.05$).

Although the empirical relationships generated from these types of statistical analyses are more powerful than knowledge of individual K_d values, they cannot be used to predict K_d values for conditions beyond the range studied. For example, the parametric K_d values generated by Delegard and Barney (1983) for the Central Plateau are likely inappropriate for the ILAW plume because the chemistry of the aqueous phase leaving the IDF will be appreciably different than fluids leaked from single-shell tanks.

These types of statistical relationships are devoid of causality and therefore provide no certain information on the mechanism by which the radionuclide partitioned to the solid phase, whether by adsorption, absorption, precipitation, or coprecipitation. That is, the statistical analyses may suggest a very strong relationship between one variable, for instance, pH, and the distribution coefficient, when the actual sorption process may be controlled by iron oxide adsorption. Because pH and iron oxide surface charge are covariant, a statistical relationship could be calculated suggesting that sorption is solely caused by pH.

The parametric K_d model can be used in the retardation factor term (Equation 2.2). When used in a transport equation, the transport code must also track the value of the independent variables such as NaOH and HEDTA for the example described in Equation 2.5 at each point in space and time. Tracking other variables is necessary to continually update the concentration of these independent variables that change 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 needed to solve for the contaminant's concentration. 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 Rf when called by the main transport code. The added complexity in solving the transport equation with parametric K_d sorption models and its empirical nature may be the reasons this technique has been used sparingly for waste disposal safety assessment exercises (e.g., see application of parametric K_d model by Routson and Serne [1972]).

2.6 Overview of Mechanistic Adsorption Models

Mechanistic models explicitly accommodate the dependency of adsorption values on contaminant concentration, competing ion concentrations, variable surface charge on the adsorbent, and solute species distribution. Incorporating mechanistic or semimechanistic concepts into adsorption models is attempted because such models become more robust and, perhaps more importantly from the standpoint of the IDF PA, more scientifically defensible. There are several mechanistic models describing solute adsorption; some are accurate only under limited environmental conditions (Sposito 1984). For instance, the Stern model is better for describing adsorption of inner sphere complexes, whereas the Gouy-Chapman model is better for describing outer sphere or diffuse swarm adsorption (Sposito 1984; Westall 1986). The complexity of installing these adsorption models into existing transport codes that are favored for disposal system performance assessment and the diversity of Hanford Site waste leachate/sediment/contaminant combinations of interest would require a data collection effort more intense and costly than is likely to

occur. A brief description of the state of the science is presented below. References to excellent review articles have been included in the discussion to provide the interested reader with additional information.

Several mechanistic models have been proposed, but their application to complex natural sediments has not been resolved (Westall and Hohl 1980; Sposito 1984; Westall 1986; Schindler and Sposito 1991). Any complete mechanistic description of chemical reactions at the mineral-electrolyte interface must include a description of the electrical double layer. While this fact has been recognized for years, a satisfactory description of the double layer at the mineral-electrolyte interface still does not exist.

Part of the difficulty of characterizing this interface stems from the fact that natural mineral surfaces are very irregular. They 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 average characteristics of the surface and the interface. Parson (1982) discussed the surface chemistry of single crystals of pure metals and showed that the potential of zero charge of different crystal faces on the same pure metal can differ by over 400 mV. For an oxide surface, this difference was calculated by Westall (1986) to be energetically equivalent to a variation in the zero-point-of-charge of more than 6 pH units. This example indicated that an observable microscopic property of a polycrystalline surface might result from a combination of widely different microscopic properties and that characterization of these surfaces will remain somewhat operational in nature.

Another fundamental problem encountered in characterizing reactions at the mineral-electrolyte interface is the coupling between electrostatic and chemical interactions, which makes it difficult to distinguish which interaction causes what effects. Westall and Hohl (1980) have shown that many models for reactions at the mineral-electrolyte interface are indeterminate in this regard.

Many of the studies from which our understanding of reactions at the mineral-electrolyte interface has developed were based on titration of suspensions of minerals. Resolving questions left open by such research requires that the mineral surfaces be defined better (by many different spectroscopic and experimental methods) and that mathematical methods be developed for interpreting the data.

Experimental data on interactions at the mineral-electrolyte interface can be represented mathematically through empirical models and mechanistic models. An empirical model can be defined as a mathematical description of the experimental data without any particular theoretical basis. For example, the K_d , Freundlich isotherm, Langmuir isotherm, Langmuir Two-Surface Isotherm, and Competitive Langmuir are considered empirical models by this definition (Sposito 1984). Mechanistic models are based on thermodynamic concepts such as reactions described by mass action laws and material balance equations. Four of the most commonly used mechanistic models include the Helmholtz, Gouy-Chapman, Stern, and Triple Layer models (Sposito 1984). Empirical models are often mathematically simpler than mechanistic models and are suitable for characterizing sets of experimental data with a few adjustable parameters or for interpolating between data points. On the other hand, mechanistic models contribute to an understanding of the chemistry at the interface and are often used for describing data from complex multicomponent systems for which the mathematical formulation (i.e., functional relations) for an empirical model might not be obvious. Mechanistic models can also be used for interpolation and characterization of data sets in terms of a few adjustable parameters. However, mechanistic models are often mathematically more complicated than empirical relationships. Adjustable parameters are required for both mechanistic and empirical models but not for the K_d model.

Application of mechanistic adsorption models for studying the retardation of contaminants in Hanford sediments has been limited but some studies are in progress. Barnett et al. (2002) used an extension of the diffuse double-layer surface complexation model developed for the U(VI) adsorption onto ferrihydrite by Waite et al. (1994) to predict U(VI) adsorption as a function of pH on sediment samples from the Upper Ringold Formation. J. A. Davis^(a) and coworkers at the U.S. Geological Survey are using a generalized surface complexation model based on the approach described in Davis and Curtis (2003) and Curtis et al. (2004) to model and study the retardation of uranium in the Hanford 300 Area plume in 300-FF-5. The studies by Barnett et al. (2002) and Davis are discussed Section 3.7.3.

2.7 Gravel- K_d Issue

Essentially all K_d values in the literature and most that have been measured at the Hanford Site were generated from sediments that do not contain any gravel, i.e., particles greater than 2 mm. Some subsurface regions of the IDF site are composed primarily of gravel-sized particles; in fact, the gravel-dominated strata below the IDF site contain at least 90% by mass particles larger than 2 mm (see Reidel 2004). At issue is that K_d values for some contaminants may be lower in sediments containing gravel because of the reduced surface area in the field compared to the lab-tested solids with which the radionuclides interact. This is referred to as the gravel K_d issue. Experiments were conducted with Hanford sediments to evaluate methods to address the gravel K_d issue (Kaplan et al. 1999; Appendix A of this document). Three gravel-corrected K_d conceptual models, K_{dgc} , were evaluated in Kaplan et al. (1999): 1) a correction based on surface area ($K_{dgc,surf}$), 2) a correction based on the assumption that the gravel simply diluted the $K_{d<2mm}$ and had no sorption capacity ($K_{dgc,g=0}$), and 3) a correction based on the assumption that the K_d of the entire sediment (K_{dtot}) was a composite of the $K_{d<2mm}$ and the $K_{d>2mm}$ values ($K_{dgc,g=x}$). Based on data for the adsorption of trace concentrations of strontium, on average, $K_{d<2mm}$ tended to overestimate K_{dtot} by 28%; $K_{dgc,g=x}$ overestimated K_{dtot} by only 5%; $K_{dgc,g=0}$ and $K_{dgc,surf}$ underestimated K_{dtot} by 10 and 13%, respectively. Although, $K_{dgc,g=x}$ provided the best estimate of actual values (K_{dtot}), the input values for $K_{dgc,g=0}$ are appreciably easier to acquire. See Appendix A for additional data on the gravel correction.

The $K_{dgc,g=0}$ was used to correct for the conservative case “empirical” K_d values in the gravel-dominated sequence in the IDF stratigraphy (described in more detail below) and is defined as

$$K_{dgc,g=0} = (1 - g)K_{d<2mm} \quad (2.6)$$

where g is the gravel weight fraction of sediment in the field and $K_{d<2mm}$ is the traditional K_d value measured using the less than 2-mm fraction. Equation 2.6 greatly improves the accuracy of the empirical K_d construct for Hanford sediments for contaminants that sorb to Hanford sediments mainly by surface area-dominated and cation exchange-dominated reactions. Some contaminants that belong in these two categories are cesium, strontium, radium, and many lanthanides and transition metal fission products. It is not clear that the adsorption of actinides and oxyanion metals such as pertechnetate [Tc(VII)], chromate [Cr(VI)], uranyl [U(VI)], and selenate [Se(VI)] is realistically predicted using Equation 2.6 and its underlying construct. From the standpoint of the IDF PA, Equation 2.6 provides a more conservative K_d value than the traditional $K_{d<2mm}$ commonly used in performance assessment calculations for most soils and sediments. Because the stratigraphic profile below the IDF site (see Section 4.0) does contain zones of

(a) U.S. Geological Survey, Menlo Park, California.

gravel-containing sands, the gravel correction construct, which lowers laboratory-measured K_d values as a function of gravel content, has a significant effect on the migration velocity of most sorbing contaminants.

2.8 Moisture Dependency of K_d Values

The moisture dependency of K_d values has been evaluated (Lindenmeier et al. 1995; Kaplan et al. 1996; Gamedainger et al. 1998, 2001). Based on our findings to date, as well as on the literature, our belief on this subject is that there is a slight decrease in K_d values for U(VI) and other likely contaminants as the moisture content in a system decreases. Supporting this contention is that four of the five sediments tested to date showed this trend. The sediment that did not show this trend had only two K_d data points, one from a saturated system and the other from an unsaturated system (Kaplan et al. 1996). This decrease in K_d for U(VI) as percent saturation decreased may be attributed to the fact that, as the degree of saturation decreases, solutes come into contact with fewer exchange sites. But with more contact time between the vadose zone sediments and the pore water, diffusion processes may allow the contaminants to interact with sediment adsorption sites that are hidden in dead-end pore spaces. The dead-end pore spaces may be created during the laboratory flow-through column experiments performed at unsaturated moisture contents, although they also occur in nature as determined in some field studies. That is, the slight dependency [decrease in K_d for U(VI)] of K_d as percent saturation decreased may be caused by a physical process that will be less important in the field than a chemical process. An alternative explanation is that higher ionic-strength fluid exists in the double layer of partially saturated sediments, leading to weaker sorption. This latter explanation is less likely because the double layer around particle surfaces reaches only nanometers into the water, whereas the uniform film thickness of pore fluid around unsaturated Hanford Site sediments is estimated to be several micrometers (see Appendix B for a brief discussion). For the 2005 IDF PA, we will ignore the K_d dependency on moisture content and use the K_d values measured in traditional saturated tests. If the flow models used in future performance assessment calculations (beyond the 2005 IDF PA) are capable of modeling the mobile-immobile water concepts presented in van Genuchten (1981), the effect of moisture content on the retardation factor can be accommodated without altering the K_d value. Consequently, all K_d estimates used in future calculations for the vadose zone may be slightly lower than those derived from traditional tests conducted in saturated systems.

2.9 Colloid-Facilitated Transport of Contaminants

Contaminant transport is traditionally modeled as a two-phase system: a mobile aqueous phase and an immobile solid phase. Over the last 15 years, we have become increasingly aware of a third phase, a mobile solid phase. This mobile solid phase, mobile colloids, consists of organic and/or inorganic sub-micron particles that move with groundwater flow. When radionuclides are associated with colloids, the net effect is that radionuclides can move faster through the system than would be predicted on the basis of reversible sorption. It is not known whether colloids in the subsurface environment of the Hanford Site enhance contaminant transport. Furthermore, it is not known whether mobile colloids in a plume emanating from the IDF will have significant effects on contaminant transport rates.

Mobile colloid formation is commonly described as a three-step process: genesis, stabilization, and transport. Colloid genesis describes how the submicron particles are formed in groundwater. Stabilization describes how the colloids are brought into suspension, which is a function of the colloid and

groundwater composition and water flow forces. Transport describes how the suspended colloids move through the porous media or are retained by physical forces such as diffusion, straining, gravitational settling, or physicochemical attraction to the matrix.

Regarding the first step, colloid genesis, there is little doubt that radionuclide-bearing colloids will be generated at the IDF site. Ramsay (1988) presented strong evidence for the existence of colloid particles in glass and cement leachates and provided an in-depth review of the various types of colloids that may exist (e.g., glass fragments, precipitation products, geological materials, secondary phases formed from glass leachate). Based on experiments using Hanford Site groundwater and colloids, it is less likely that colloids would remain suspended in glass leachate, cement leachate, or Hanford groundwater (McGraw and Kaplan 1997). The ionic strengths of these solutions greatly exceed the critical flocculation concentration (the minimum electrolyte concentration to induce colloid flocculation) of most particles. Even in uncontaminated Hanford groundwater, where the ionic strength would be at its lowest, the critical flocculation concentration is likely exceeded by 300 to 600% depending on the type of colloid in suspension. Hence, at this time we assume that colloid-facilitated transport of contaminants below the IDF facility is not a significant risk-driving process because the Hanford vadose zone sediment-pore water environment is not conducive to stabilizing colloids in the transporting fluid. Based on this logic, we will not consider colloid-facilitated transport an important process in the IDF PA until there is compelling evidence that our assessment is flawed. A recent Hanford tank leak-relevant colloid study also shows that ¹³⁷Cs transport through Hanford sediments via colloids is not likely to be significant from a long-term risk perspective (Zhuang et al. 2003).

3.0 Geochemistry of Contaminants of Concern

This chapter provides a brief description of the geochemistry of several key contaminants of concern that have been identified by subsurface transport simulations as presenting the greatest health risks for the groundwater pathway. In the 2001 version of the ILAW PA, Mann et al. (2001) discuss the predicted radionuclide fluxes for the groundwater pathway, and identified ^{99}Tc , ^{129}I , ^{237}Np , and uranium isotopes as key radionuclides of concern for this pathway. The expected radionuclide inventories to be used for 2005 IDF PA are discussed in Puigh (2004). The review of ^{79}Se was retained from the previous version of this document (Kaplan and Serne 2000) because it had been identified as a possible radionuclide of concern in an earlier ILAW PA (Mann et al. 1998). Sections on the geochemistry of chromium and nitrate have been added because of their importance as possible contaminants of concern for the Hanford Site in general. Emphasis is placed on describing the chemical processes relevant to the behavior of these contaminants in the IDF's unsaturated zone, which is coarse sand-textured alkaline sediment with low natural organic matter concentrations. Geochemical information relevant to other environments, such as reducing environments, is also provided to address possible near-field systems and/or possible localized stagnant silt/mud regions in the upper unconfined aquifer.

To describe these processes, computer modeling methods were used to calculate equilibrium thermodynamic principles, the distributions of predominant aqueous species, and potential solubility controls for the environmentally important oxidation states of each of the contaminants of concern. The results of these speciation and solubility calculations are presented as a series of Eh-pH (or Pourbaix) diagrams. The diagrams are presented to highlight important general aspects of the aqueous speciation, redox, and solubility behavior of chromium, iodine, nitrogen (as nitrate/nitrite/ammonia), neptunium, selenium, technetium, and uranium. The Eh-pH diagrams were calculated using *The Geochemist's Workbench*[®] (Version 4.0) software and the expanded thermodynamic database file thermo.com.V8.R6+.dat provided with it. The theory behind the calculation of Eh-pH diagrams is discussed by Garrels and Christ (1965), Langmuir (1997), Nordstrom and Munoz (1985), and others. Lawrence Livermore National Laboratory (LLNL) developed the thermodynamic database file to use with the EQ3/6 geochemical model. This file does include the thermodynamic values for the uranium species listed in the critical review by Grenthe et al. (1992) but predates publication of the critical reviews of thermodynamic values for technetium and neptunium species by Rard et al. (1999) and Lemire et al. (2001), respectively, and the update to these earlier critical reviews by Guillaumont et al. (2003). Unless otherwise noted, the Eh-pH diagrams were calculated at 25°C for a contaminant concentration of 1×10^{-8} mol/L and total carbonate concentrations of 1×10^{-3} mol/L, which were arbitrarily selected to help demonstrate the importance of aqueous complexation, redox, and possible solubility reactions for each contaminant.

Two Eh-pH diagrams were calculated for each element. The first diagram for each set shows only the dominant aqueous species and was calculated suppressing precipitation of any solids that may have been thermodynamically oversaturated for the specified conditions. The second Eh-pH diagram was calculated without this constraint and shows Eh-pH regions where the solubility of the indicated solid(s) is exceeded and thus could precipitate. Each diagram contains two dashed black lines at (Eh 1.2 V–pH 0 to Eh 0.4 V–pH 14) and (Eh 0.0 V–pH 0 to Eh -0.8 V–pH 14) that represent the Eh-pH boundaries for the breakdown of water to its gaseous components at equilibrium at 25°C and 1 atm pressure. The redox conditions for essentially all environmental systems occur in the region between these water stability limits.

The Eh-pH conditions of primary interest to the 2005 IDF PA are oxidizing conditions at pH values greater than approximately 7. A pH in the range from 7.5 to 8.5 is expected for vadose zone pore fluid and groundwater that are not chemically affected by leachates from the IDF disposal cells. Higher pH values of approximately 9.5 and as high as 12.5 are expected for fluids that are chemically influenced by glass and cement leachates, respectively (see Section 4).

3.1 Chromium

The geochemical behavior of chromium has been reviewed by Rai et al. (1988), Palmer and Wittbrodt (1991), Richard and Bourg (1991), and Palmer and Puls (1994). Ball and Nordstrom (1998) present a critical review of the thermodynamic properties for chromium metal and its aqueous ions, hydrolysis species, oxides, and hydroxides.

3.1.1 Oxidation States and 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 natural environments. Chromium(VI) exists only under oxidizing conditions, whereas Cr(III) exists over a wide range of pH and Eh conditions. Chromium(VI) tends to be soluble, forms anionic or neutral dissolved species, and can be very mobile (Nriagu and Nieboer 1988). In contrast, Cr(III) tends to precipitate, form cationic dissolved species, and become immobile in saturated sediments under moderately alkaline to slightly acidic conditions.

The reduction of Cr(VI) to Cr(III) by abiotic and biotic processes has been the subject of extensive studies recently because of its significant effect on the mobility of chromium in waste streams, vadose zones, sediments, and groundwaters. These reaction processes are the basis for certain remediation technologies such as permeable barriers composed of zero-valent iron particles (i.e., as metallic iron) (e.g., Cantrell et al. 1995) or sodium-dithionite reduced soils (e.g., Fruchter et al. 2000), which are being tested for immobilization of groundwater contaminants. Microbial reduction of Cr(VI) also has been suggested as a potential mechanism for removal of chromium from contaminated groundwaters and waste streams.

Chromium(VI) is a strong oxidant and is rapidly reduced in the presence of such common electron donors as aqueous Fe(II), ferrous [Fe(II)] 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 Fe(II) derived from magnetite (Fe₃O₄) and ilmenite (FeTiO₃) (White and Hochella 1989), hematite (Fe₂O₃) (Eary and Rai 1989), and pyrite (FeS₂) (Blowes and Ptacek 1992). Eary and Rai (1989) attributed the reduction of Cr(VI) to Cr(III) by hematite (Fe₂O₃) to hematite containing trace quantities of Fe(II).

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). Eary and Rai (1989) determined that this reaction does not appear to be slowed by the presence of dissolved oxygen. Dissolved oxygen and manganese-dioxide minerals (e.g., pyrolusite [β -MnO₂]) are the only two constituents in the environment known to oxidize Cr(III). 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.

The oxidation of Cr(III) by dissolved O₂ and manganese oxides has been verified in laboratory experiments. The rate of oxidation of Cr(III) by O₂ is very slow (Van der Weijden and Reith 1982; Eary and Rai 1987), whereas oxidation by manganese oxides, such as manganite (γ -MnOOH), has been determined experimentally to be fast (Johnson and Xyla 1991). Studies by Johnson and Xyla (1991) indicated that the Cr(III) oxidation by manganite consisted of an adsorption step, three separate electron transfer steps, and a desorption step. Because the reaction was found to be independent of pH and ionic strength, Johnson and Xyla (1991) suggested that a reaction at the manganite surface is the rate limiting step for Cr(III) oxidation via this reaction process.

Figure 3.1 is an Eh-pH diagram that shows the dominant aqueous species of chromium predicted to be present at 25°C and a total concentration of 1×10^{-8} mol/L dissolved chromium. Chromium(VI) has relatively simple hydrolysis behavior, forming primarily anionic species including HCrO₄⁻ (bichromate) and CrO₄²⁻ (chromate) at pH values less and greater than 6.5, respectively, and Cr₂O₇²⁻ (dichromate) at higher concentrations of dissolved chromium (Baes and Mesmer 1976; Palmer and Wittbrodt 1991; Richard and Bourg 1991). Chromium(VI) as chromate (CrO₄²⁻) is likely to be the dominant chromium species in the Hanford vadose zone and upper unconfined aquifer because its domain of predominance extends over a wide range of pH and Eh conditions that are appropriate for the vadose zone and upper unconfined aquifer (Figure 3.1). Chromium(III) exists predominantly as Cr³⁺ below pH 4 in the Cr(III)-H₂O system. With increasing pH, hydrolysis of Cr³⁺ yields CrOH²⁺, Cr(OH)₂⁺, Cr(OH)₃⁰(aq), and Cr(OH)₄⁻. At higher chromium concentrations, polynuclear species such as Cr₂(OH)₂⁴⁺ and Cr₃(OH)₄⁵⁺ can form slowly at 25°C (Baes and Mesmer 1976). Chromium(III) complexes with dissolved ligands such as fluoride, ammonia, and cyanide (Baes and Mesmer 1976). Figure 3.1 is similar to one in Ball

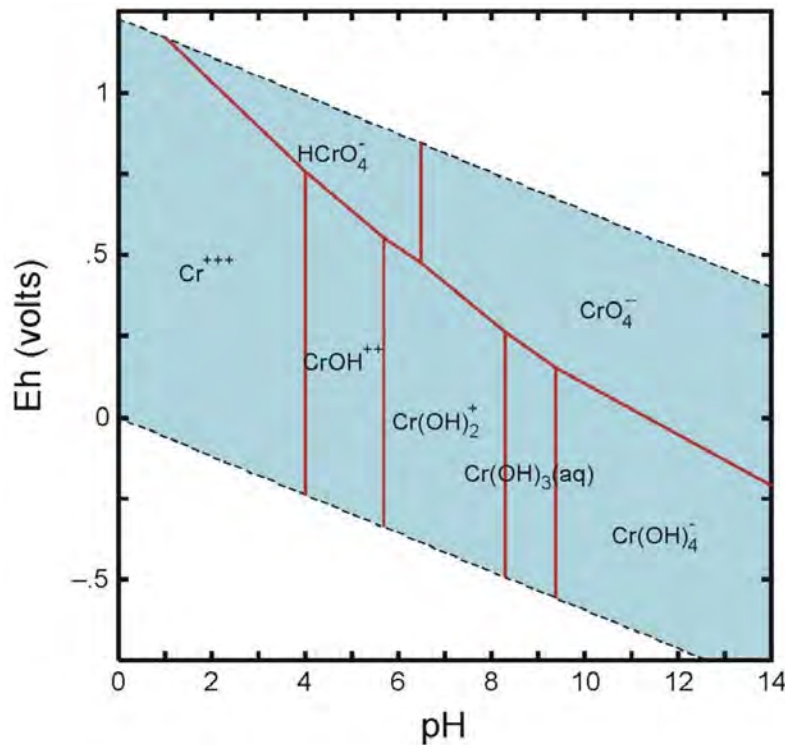


Figure 3.1. Eh-pH Diagram Showing Dominant Aqueous Species of Chromium. (Diagram was calculated at a total concentration of 1×10^{-8} mol/L dissolved chromium at 25°C.)

and Nordstrom (1998), but Ball and Nordstrom's figure shows pH stability ranges for the aqueous species $\text{Cr}(\text{OH})_2^+$ and $\text{Cr}(\text{OH})_3^0(\text{aq})$ that are smaller and larger, respectively, than those in Figure 3.1.

3.1.2 Precipitation and Coprecipitation

The concentrations of dissolved Cr(VI) in the vadose zone and unconfined aquifer under the IDF are not expected to be affected by the precipitation of Cr(VI)-containing mineral phases. Though several Cr(VI)-containing minerals are known, they only occur at sites highly contaminated with chromium; e.g., Palmer and Wittbrodt (1991) identified PbCrO_4 (crocoite), $\text{PbCrO}_4 \cdot \text{H}_2\text{O}$ (iranite), and K_2CrO_4 (tarapacite) in chromium sludge from a plating facility. Palmer and Wittbrodt (1990) 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 successful remediation of chromium-contaminated sites by pump-and-treat technologies.

Baron et al. (1996) have identified two iron-chromate precipitates, $\text{KFe}_3(\text{CrO}_4)_2(\text{OH})_6$ and $\text{KFe}(\text{CrO}_4)_2 \cdot 2\text{H}_2\text{O}$, in a soil contaminated by chrome plating solutions. Powder X-ray diffraction analyses by Baron et al. (1996) showed that most of the Cr(VI) in the contaminated soil is present at $\text{KFe}_3(\text{CrO}_4)_2(\text{OH})_6$, which is a chromate analog of the sulfate mineral jarosite. The transformation reaction between these two precipitates shows that $\text{KFe}(\text{CrO}_4)_2 \cdot 2\text{H}_2\text{O}$ will form in more acidic, potassium-, and chromate-rich conditions relative to $\text{KFe}_3(\text{CrO}_4)_2(\text{OH})_6$ (Baron et al. 1996). Solubility and dissolution rate experiments by Baron and Palmer (1996) indicate that $\text{KFe}_3(\text{CrO}_4)_2(\text{OH})_6$ is stable over a wide range of conditions and could form in a Cr(VI)-contaminated aquifer.

In some sediment systems under moderately and highly reducing conditions, the concentration of dissolved chromium may be controlled by the precipitation of Cr(III) solids. Because Cr(III) tends to precipitate, it is considered relatively immobile under moderately alkaline to slightly acidic conditions. Figure 3.2 shows the Eh-pH region (tan area) that calculates as oversaturated with respect to the minerals eskolaite (Cr_2O_3) and breznaitite (Cr_3S_4) for an aqueous solution containing a total concentration of dissolved chromium of 10^{-8} mol/L. Several investigators have presented evidence suggesting the formation of solubility-controlling solids of Cr(III) in sediments. Hem (1977), for example, reported that the total chromium concentration in groundwater beneath Paradise Valley, Arizona, was close to the solubility of Cr_2O_3 . Rai et al. (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 three 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). Sass and Rai (1987) determined that Cr(III) can precipitate with Fe(III) to form a solid solution with the general composition $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3$ when the pH is greater than 4. The solubility of chromium in this solid solution decreases as the mole fraction of Fe(III) increases (Sass and Rai 1987).

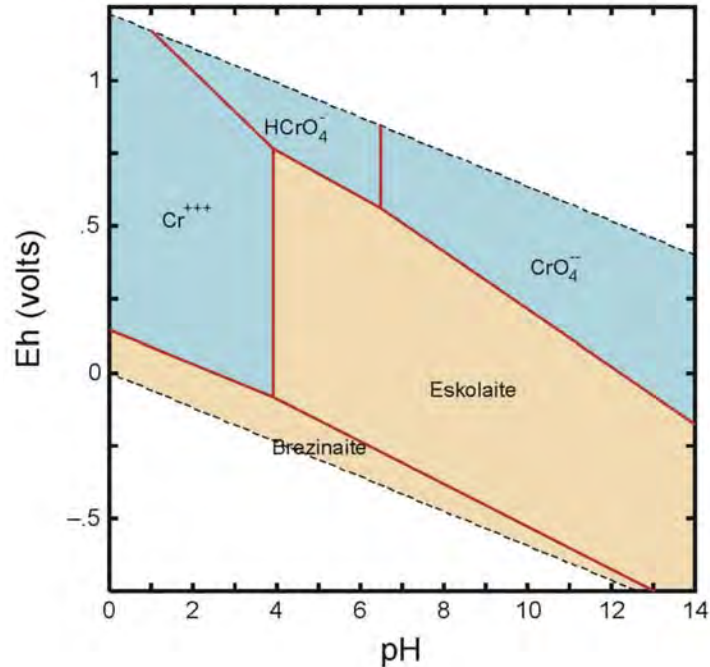


Figure 3.2. Stability Diagram Showing Eh-pH Region (tan) that Calculates as Oversaturated with Respect to the Solubility of Cr(III) Solids. (Diagram was calculated at total concentration of 1×10^{-8} mol/L dissolved neptunium at 25°C.)

3.1.3 Sorption

EPA (1999b) provides a detailed review of the available adsorption information for Cr(VI). Because Cr(VI) exists primarily as the anion CrO_4^{2-} in most oxic sediment systems, the extent to which Cr(VI) sorbs to sediments is appreciably less than that of Cr(III). As an anion, Cr(VI) does not readily adsorb in sediments to any significant extent under most geochemical conditions, and therefore is considered very mobile in aqueous systems.

Most information on Cr(VI) adsorption comes from studies with pure mineral phases (Leckie et al. 1980; Davis and Leckie 1980; Griffin et al. 1977). These studies suggest that Cr(VI) adsorbs strongly to gibbsite ($\alpha\text{-Al}_2\text{O}_3$) and amorphous iron oxide [$\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (am)] at low to medium pH values (i.e., pH 2 to 7) and adsorbs weakly to silica (SiO_2) at all but very low pH. These results can be explained by considering the isoelectric points 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 below the isoelectric point, the mineral has a net positive charge. Hence, anion adsorption, such as that for chromate, iodide, nitrate, selenate, and pertechnetate, generally increases as the pH becomes progressively lower than the isoelectric point.

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 CrO_4^{2-} , sulfate may compete for adsorption sites when present in higher concentrations (Leckie et al. 1980). Phosphate exhibits a greater competitive effect on CrO_4^{2-} adsorption (MacNaughton 1977), reducing sorption by around 50% 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 one 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, possibly because sorption of Cr(III) by sediment is commonly attributed to precipitation processes for Cr(III)-containing solids. Chromium(III) rapidly hydrolyzes and precipitates as the hydroxide $\text{Cr}(\text{OH})_3$ and/or coprecipitates with $\text{Fe}(\text{OH})_3$ (Hem 1977; Artiola and Fuller 1979). Limited studies infer that Cr(III), like other +3 cationic metals, is strongly and specifically absorbed by soil iron and manganese oxides (Korte et al. 1976).

Cantrell et al. (2003) compiled in a single source K_d values measured with Hanford sediment for radionuclides and contaminants of concern that have potential environmental effects in the vadose zone and groundwater at the Hanford Site. Cantrell et al. (2003, Table 10) list the K_d values determined for Cr(VI) with Hanford sediment; they found only a limited number of studies of Cr(VI) adsorption on Hanford sediment. The measured K_d values for Cr(VI) on Hanford sediment range from 0 to 1, with typical values being zero or close to zero, and based on these results concluded that adsorption of Cr(VI) is very low to nonexistent under normal Hanford groundwater conditions unless conditions are acidic. The adsorption of Cr(VI) is expected to increase with decreasing pH because dissolved Cr(VI) exists as an anionic species. Cantrell et al. noted that the available data indicate the K_d values for Cr(VI) adsorption to Hanford sediment under acidic conditions increase significantly with increasing equilibration time. It is speculated that this may be caused by the reduction of dissolved Cr(VI) to Cr(III) by the slow release of Fe(II) from basaltic minerals in the Hanford sediment (Cantrell et al. 2003). This reduction in turn results in the precipitation of solid $\text{Cr}(\text{OH})_3$ and the apparently high K_d values.

3.2 Iodine

There are 24 known isotopes of iodine, and 18 of them have half-lives of less than 1 day. The only stable isotope is ^{127}I . Its average natural abundance in geologic materials is 5 mg/kg (Gu and Schulz 1991) and its concentration in uncontaminated surface waters is typically less than 1 mg/L (Stumm and Morgan 1981). The isotope of concern for long-term disposal at the Hanford Site is ^{129}I , which has a half-life of 1.57×10^7 years (Tuli 2004). The environmental behavior of iodine has been reviewed by Lieser and Steinkopff (1989), Whitehead (1984), Coughtrey et al. (1983), and Ames and Rai (1978).

3.2.1 Oxidation States and Aqueous Speciation

Although the environmental chemistry of iodine is normally assumed to be simple and well known, recent studies suggest that the fate and mobility of iodine in environmental systems may be more complex than expected due to the multiple redox states that may exist under oxidizing conditions. The -1, +5, and molecular I_2 [$\text{I}_2^0(\text{aq})$] oxidation states are those most relevant for iodine in environmental systems. Iodine usually exists in fresh water in the -1 oxidation state as iodide (I^-) (Whitehead 1984). In alkaline and marine environments, iodine usually exists in the +5 oxidation state as iodate (IO_3^-) (Whitehead 1984). Iodide (I^-) and IO_3^- were the most commonly detected species in rainwater collected after the Chernobyl accident (Muramatsu et al. 1990). The other oxidation states of iodine, such as +1 and +7, are known but are unstable in natural systems (Lieser and Steinkopff 1989). Figure 3.3 is an Eh-pH diagram that shows the dominant aqueous species of iodine predicted to be present at 25°C and a total concentration of 1×10^{-8} mol/L dissolved iodine. Iodide is likely to be the dominant iodine species in the Hanford Site's

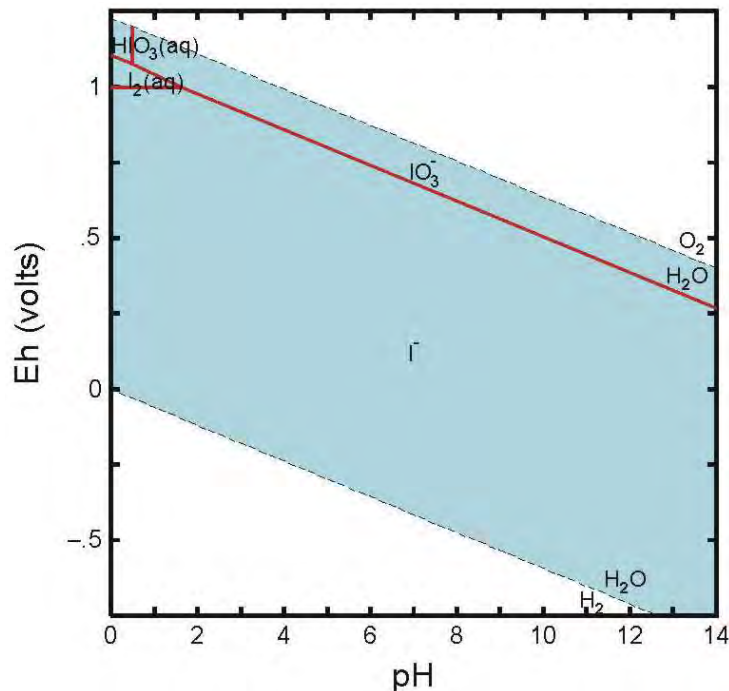
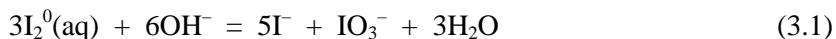


Figure 3.3. Eh-pH Diagram Showing Dominant Aqueous Species of Iodine. (Diagram calculated at a total concentration of 1×10^{-8} mol/L dissolved iodine at 25°C .)

upper unconfined aquifer because its domain of predominance extends almost over the entire pH and Eh range for the stability of water (Figure 3.3). Under oxidizing acidic conditions, molecular $\text{I}_2^0(\text{aq})$ may form from the reduction of IO_3^- or the oxidation of I^- . Oxidation of $\text{I}_2^0(\text{aq})$ to produce IO_3^- , the second most abundant form of iodine in aqueous systems, is easily accomplished in basic solution by the reaction (Cotton and Wilkinson 1972):



Thus, the IO_3^- form of iodine is likely dominant in the well-oxidized, high-pH systems that may exist in the near field of the IDF site. Iodide and IO_3^- tend to exist as free ions, but the complexes they form are generally the most soluble of all halide complexes.

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

3.2.2 Precipitation and Coprecipitation

Precipitation of I compounds is not likely to be a dominant reaction path for I in the glass leachate. Iodide, in comparison with the other halides, forms especially weak complexes with metal ions as a result of its large size (0.22-nm ionic radius) (Langmuir 1979). The metals with which I^- and IO_3^- form sparingly soluble compounds, such as silver, barium, mercury, lead, and palladium (Pourbaix 1966), exist in

nature at very low concentrations. The low concentrations of iodine in the contaminant plume likely will exist either as free species or as highly soluble complex species.

Results recently published by Mattigod et al.^(a) (2002, 2003) from waste glass weathering studies conducted in support of the ILAW/IDF PA suggest that under oxic conditions, secondary products that form from the weathering of ILAW waste glasses may incorporate small masses of anionic contaminants such as iodide (I^-), selenate (SeO_4^{2-}), and pertechnetate (TcO_4^{2-}) that may be resistant to remobilization. Mattigod et al. (2002, 2003) have conducted tests to identify the type of secondary minerals that form from the accelerated weathering of vitrified waste glasses and to evaluate potential incorporation of ^{125}I (as I^-), ^{75}Se (as SeO_4^{2-}), and ^{99}Tc (as TcO_4^{2-}) from groundwater spiked with these radionuclides into the secondary mineral weathering products. Mattigod et al. identified the formation of zeolite minerals such as zeolite P, analcime, and cancrinite as weathering products in static tests conducted at 160°C with two waste glasses (LAWBP1 and LAWA44) leached with uncontaminated Hanford groundwater. These glasses were selected because their compositions are expected to be similar to the actual glasses resulting from the vitrification of Hanford tank wastes. Mattigod et al. present details on the procedures and rationale and the compositions of materials and leachates used in their experiments. Mattigod also completed experiments with radionuclide-spiked groundwater and determined that ~9 to 18% of ^{125}I , ~6 to 15% of ^{75}Se , and ~<1 to 12% of ^{99}Tc were sorbed in reaction products (i.e., secondary crystalline phases and hydrated gel layer) that formed from the leaching of waste glasses. Mattigod et al. (2003)^(a) found a similar amount of ^{75}Se sorption (~8 to 14%) but a slightly lower degree of ^{125}I sorption (~12 to 13%) when 1 M NaOH was used as the spiked leachate. Mattigod et al. (2003, 2004) then conducted a series of desorption tests to determine the extent of remobilization of the radionuclides that had been sorbed in the glass weathering products. Their results indicate that ~55 to 80% and ~30 to 90% of the sorbed ^{125}I , ~60 to 70% and 30 to 90% of the sorbed ^{75}Se , and ~40 to 58% and up to 67% of the sorbed ^{99}Tc , respectively, in the weathered LAWBP1 and LAWA44 glasses did not easily desorb from the weathering glasses when contacted with groundwater-like solutions.

Until this apparent coprecipitation (or specific adsorption) of I^- , SeO_4^{2-} , and TcO_4^{2-} in waste glass weathering products is further quantified, this process is not included in transport calculations or the geochemical data package for the 2005 IDF PA. This will build a degree of conservatism into the calculations that could be removed if quantitative data for the extent of weathering product formation per unit mass of waste glass and the mass of coprecipitated contaminants of interest in these weathering products become available at a later date.

The precipitation of iodine-containing solids is not likely to be an important process in the far field due to the low concentrations of iodine in environmental systems and the high solubility of iodine-containing minerals. Iodine can be found as a primary component in some rare, naturally occurring minerals that are associated with evaporite and brine deposits (Johnson 1994; Doner and Lynn 1977). Iodide is commonly present in substitution for other halogen elements, such as chloride and bromide, whereas IO_3^- typically is associated with sulfate- or nitrate-type minerals. Such minerals are expected to be highly soluble in sediments.

(a) Mattigod SV, RJ Serne, BP McGrail, VL LeGore, and KE Parker. 2004. "Sequestration of radionuclides (^{125}I , ^{54}Se , ^{99}Tc) in secondary crystalline minerals resulting from chemical weathering of selected waste glasses." To be submitted to *Radiochimica Acta*.

3.2.3 Sorption

Two types of reactions between anions and inorganic solids are recognized: specific and nonspecific adsorption. Specific adsorption refers to incorporation of anions as a ligand in the coordination shell of an adsorbent; nonspecific adsorption refers to adsorption of anions by simple coulombic (electrostatic) interactions with positive charges. Iodine anions are believed to sorb primarily through nonspecific anion-exchange reactions on mineral surfaces (Gu and Schulz 1991) and specific adsorption on organic substances (Walters and Winchester 1971). Nonspecific sorption may occur at the localized positive charges that occur on 1) iron and aluminum oxide surfaces, 2) edges of aluminosilicate clay surfaces where the oxygen atoms are not fully coordinated by aluminum or silicon atoms, and 3) amine and amino groups of organic substances. These positive charges, which increase with decreasing pH, attract anions electrostatically. Whitehead (1973), for example, reported that sorption of I⁻ by soils was associated with both soil organic matter and iron and aluminum oxides, with the oxides increasingly important under more acidic conditions. The maximum amounts sorbed by two surfaces occurred at pH 6.6. At this pH, the amounts of I⁻ sorbed were found to be closely related to the contents of organic matter but not to iron or aluminum oxides or clay. At pH values less than 5, the removal of iron and aluminum resulted in a marked reduction in I⁻ sorption. Whitehead (1974) further observed that freshly precipitated ferric and aluminum oxides sorbed substantial amounts of I⁻ from solutions of pH less than 5.5, but the amount decreased to zero as the pH approached 7. Presumably, this trend reflects the presence of an increasing amount of positive charge (anion-exchange capacity) on the amphoteric oxide surfaces at lower pH levels.

An extensive review of iodine adsorption studies on sediments, soils, pure minerals, oxide phases, and crushed rock materials is presented in EPA (2004). Ticknor and Cho (1990) studied the interaction of I⁻ and IO₃⁻ over a pH range of 7.5 to 8.0 with a number of minerals including calcite, chlorite, epidote, goethite, gypsum, hematite, kaolinite, bentonite, muscovite, and quartz. No I⁻ sorption was detected from any of the solutions on any of the minerals. Iodate was removed from solution to a somewhat greater extent than I⁻. Bentonite, calcite, gypsum, and muscovite adsorbed no IO₃⁻. Muramatsu et al. (1990) reported that neither I⁻ nor IO₃⁻ sorbed to quartz sand. Based on these studies, it was concluded that the low I⁻ and IO₃⁻ sorption was the result of the low anion-exchange capacities of the minerals at the high pH of the systems investigated. Recently, Kaplan et al. (1999, 2000a) showed that some naturally occurring 2:1 phyllosilicate minerals have the ability to sorb large amounts of I⁻. K_d values of greater than 60 mL/g were measured for illites. Illite generally accounts for approximately 20% of the clay fraction of Hanford Site sediments. Even at pH greater than 9, K_d values for I⁻ for these illites were greater than 20 mL/g. Subsurface Hanford sediment with a pH of 8 had K_d values that average 3 mL/g and ranged from 0.1 to 10 mL/g.

Um et al. (2004) completed a series of experiments to determine the linearity and reversibility of I⁻ adsorption onto Hanford formation sediment from an ILAW borehole (well name 299-E24-21; borehole number C3177) at the 200 East Area of the Hanford Site. The adsorption experiments were conducted using uncontaminated Hanford groundwater spiked with dissolved ¹²⁵I (as an analog tracer for ¹²⁹I). Um et al. (2004) determined that I⁻ adsorption was low (K_d = 0.2 mL/g) at pH 7.5 and could be represented by a linear isotherm up to a total concentration of 100 mg/L dissolved I⁻. The results of their desorption experiments indicate that up to 60% of adsorbed I⁻ was readily desorbed after 14 days by I⁻ free groundwater. Because I⁻ adsorption was determined to be at least partially reversible, Um et al. (2004) proposed that the weak adsorption affinity would result in release of I⁻ when uncontaminated waters contact ¹²⁹I-contaminated sediments in the vadose zone and aquifer systems.

Um and Serne^(a) completed a series of batch and column adsorption studies of ⁹⁹Tc, ¹²⁹I, ⁷⁹Se, and ⁹⁰Sr on Hanford sediments collected from ILAW borehole #2 (borehole number C3177) at the Hanford 200 East Area. The batch sorption experiments were conducted on this Hanford sediment using both uncontaminated Hanford groundwater and simulated glass leachates spiked with individual radionuclides. Um and Serne reported K_d values for the adsorption of ¹²⁵I, which was used as a surrogate for ¹²⁹I, in Hanford groundwater on C3177 sediment from 45-, 110-, and 215-ft depths below ground surface of 0.41 ± 0.01 (pH 7.8), 0.17 ± 0.04 (pH 7.8), and 0.25 ± 0.02 mL/g (pH 7.7), respectively. The K_d values for ¹²⁵I measured in simulated glass leachates for the equivalent sediment samples were 0.08 ± 0.01 (pH 9.1), 0.16 ± 0.08 (pH 9), and 0.04 ± 0.01 mL/g (pH 9), respectively. These measurements indicate low adsorption affinity for iodide on these sediments in both Hanford groundwater and simulated glass leachates. Um and Serne^(a) concluded that these adsorption data, especially the tests using simulated glass leachate, corroborate values obtained for sediments collected in the past from nearby locations and for generic aqueous solutions such as regional groundwater. Um and Serne also noted that the new results provide more technical defensibility for past performance assessment predictions that did not use site-specific sediments and/or leachates.

Kaplan et al. (2003) studied the influence of glass leachate on the hydraulic, physical, mineralogical, and sorptive properties of Hanford sediment. The ILAW generated from the Hanford Site will be disposed as a vitrified waste, and the leachate from this waste will have a high pH and high ionic strength. Kaplan et al. (2003) reacted NaOH solutions, a simplified surrogate for glass leachate, with quartz sand, a simplified surrogate for the Hanford subsurface sediment, and Warden soil, an actual Hanford sediment. Following contact with three concentrations of NaOH solutions, Kaplan determined the changes in hydraulic conductivity, porosity, moisture retention, mineralogy, aqueous chemistry, and soil radionuclide distribution coefficients for the contacted solids. Kaplan et al. (2003) observed significant changes in mineralogy under chemical conditions approaching the most caustic glass leachate conditions predicted in the near field of the ILAW/IDF site, as approximated by 0.3 M NaOH. The clay minerals in the Hanford sediment underwent the greatest dissolution, thereby increasing the relative proportions of the more resistant minerals, e.g., quartz, feldspar, and calcite, in the remaining sediment. Kaplan et al. (2003) detected some reprecipitation of solids (mostly amorphous gels) after caustic contact with both solids. These precipitates increased the moisture retention in both sediments, likely because of water retained within the gel coatings. The hydraulic conductivities were slightly lower, but because of experimental artifacts, Kaplan et al. (2003) did not consider these reductions significant. Kaplan et al. (2003) concluded that there were no large differences in the hydraulic properties of the quartz sand or Warden silt loam soil after 192 days of contact with caustic fluids similar to glass leachate.

Kaplan et al. (2003) also completed batch sorption tests with Warden soil to measure the K_d values for cesium, strontium, iodide, selenate, and pertechnetate in soils treated with caustic solutions for up to 360 days. Although some clay minerals, such as smectites and kaolinite, almost totally dissolved within a year of contact with 3 M NaOH (and, by inference, after longer time frames for 0.3 M NaOH, a more realistic surrogate for ILAW glass leachate), other sorbing minerals such as illite and chlorite did not react appreciably. Kaplan et al. (2003) concluded that the net effect of glass leachate on the sorptive properties of Hanford sediments for the cited radionuclides of concern to the IDF is not expected to be significant. Specifically, little change was determined for the K_d values for cesium, and the strontium K_d values

(a) Um W and RJ Serne. 2004. "Sorption and Transport Behavior of Radionuclides in the Proposed Low-Level Radioactive Waste Disposal Facility at the Hanford Site, Washington." Submitted to *Radiochimica Acta*.

increased significantly in the simulated glass leachates versus natural groundwater. Kaplan et al. proposed that increased strontium sorption and resulting high K_d values were likely due to precipitation with CaCO_3 at these high pH conditions. They did not detect any appreciable adsorption for iodide, selenate, or pertechnetate (i.e., $K_d \sim 0$) on Hanford sediment contacted with NaOH solutions. Some adsorption of selenate was measured in control tests using sodium perchlorate solutions at neutral pH, but after caustic treatment and in high pH solutions, selenate sorption was determined to be nil. No iodide or pertechnetate technetium sorption was observed for the neutral-pH perchlorate or the high-pH NaOH solutions as a function of time or ionic strength. Kaplan et al. (2003) concluded that adsorption reactions likely would not retard the migration of selenate, iodide, or pertechnetate from high pH and saline glass leachate percolating through the near-field ILAW/IDF vadose zone sediments. Kaplan et al. noted that in the “far field” vadose zone in past performance assessment calculations, some sorption was allowed for selenate. Even if the caustic glass leachate completely dominates the entire vadose zone beneath the IDF, and there is no sorption of selenate under these geochemical conditions, Kaplan et al. (2003) proposed that the dilution and pH neutralization of the glass leachate-modified pore water that would occur in the upper unconfined aquifer would result in some selenate adsorption onto these aquifer sediments.

Cantrell et al. (2003) compiled in a single source the K_d values measured with Hanford sediment for radionuclides and contaminants of concern that have potential environmental impacts in the vadose zone and groundwater at the Hanford Site. Cantrell et al. concluded that I^- is expected to be the dominant species of dissolved iodine in Hanford groundwater based on the study of Kaplan and Serne (2000). Table 11 in Cantrell et al. (2003) lists the K_d values measured for iodide (I^-) adsorption onto Hanford sediment. Based on their review, they concluded that I^- adsorption is relatively low, and under typical Hanford Site groundwater conditions, K_d values for I^- range from approximately 0 to 2 mL/g, with a range of 0 to 0.2 mL/g being most typical. Cantrell et al. (2003) indicated that the available data suggest that I^- adsorption is consistent with anionic adsorption in general, in that it appears to increase under acidic conditions. However, the available data may not be sufficient to confirm this conclusion. Cantrell et al. noted that pH is usually 7 or greater in most Hanford geochemical environments due to the ubiquitous occurrence of carbonates in Hanford sediments. Alkaline conditions are also expected for local vadose zone areas contaminated by discharges of highly caustic wastes from disposal trenches and leaking underground storage tanks at the Hanford Site. Some studies compiled by Cantrell et al. (2003) also show that long equilibration periods (>100 days) result in a nonlinear increase in K_d values for I^- with time. Cantrell et al. (2003) could not identify an obvious reason for this increase in I^- adsorption with time. They note that others have speculated that this phenomenon may have been affected by the formation of microbial colonies as some have observed in similar long-term adsorption experiments. Because such conditions are not expected to be typical of Hanford Site groundwater, Cantrell et al. (2003) recommended that these high K_d values be ignored for typical transport modeling exercises.

3.3 Neptunium

There are 16 known isotopes of neptunium from ^{228}Np to ^{241}Np (Keller 1971). Only ^{237}Np , a neutron reactor product of ^{238}Np ($n, 2n$) and ^{235}Np (n, γ), with a half-life of 2.144×10^6 years (Tuli 2004) is of interest to the IDF PA. The environmental chemistry and mobility of neptunium in surface water, groundwater, and geologic environments has been reviewed by others, such as Silva and Nitsche (1995), Tanaka et al. (1992), Lieser and Mühlenweg (1988), Coughtrey et al. (1984), Thompson (1982), Onishi et al. (1981), and Ames and Rai (1978).

3.3.1 Oxidation States and Aqueous Speciation

Neptunium may exist in the +3, +4, +5, +6, and +7 valence states, but only the +4, +5, and possibly +6 states are relevant to natural environments. Neptunium(VI) is stable only in highly oxidizing solutions and is therefore not important under most environmental conditions. Neptunium(V) exists in oxidizing environmental systems and is considered relatively mobile because Np(V) aqueous species do not readily adsorb to sediment, and Np(V) solids are quite soluble. Neptunium(IV) occurs under reducing conditions and is less mobile than Np(V). Like U(IV) and Pu(IV), Np(IV) may form sparingly soluble oxide and hydroxide solids that limit the mobility of Np(IV) under reducing conditions.

The reduction of redox-sensitive elements such as neptunium by abiotic and biotic processes has been the subject of considerable interest because these reactions have a significant effect on the environmental mobility of redox-sensitive elements. For example, redox-sensitive elements can be immobilized by surface-mediated, heterogeneous reduction/sorption reactions on Fe(II)-containing oxide and silicate minerals that exist as coatings on sediment particles and/or primary constituents of sediments (see review in White [1990]). The heterogeneous electrochemical reactions occur by electron transfer reactions in which the Fe(II) is oxidized to Fe(III), and the redox-sensitive contaminant is reduced to a lower valence state, such as reduction of Np(V) to Np(IV). Surface-mediated, heterogeneous reduction/sorption of Np(V) has been studied by Hakanen and Lindberg (1991), Susak et al. (1983), Meyer et al. (1984), and Bondietti and Francis (1979).

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

The thermodynamic data for neptunium aqueous species and solids are limited and not well known relative to other radionuclides. Lemire et al. (2001) have published an extensive, detailed critical review of the chemical thermodynamics of neptunium. As noted at the beginning of Section 3.0, the thermodynamic values compiled in Lemire et al. (2001) are not in the thermodynamic database used to calculate the Eh-pH diagrams discussed in this report. Figure 3.4 is an Eh-pH diagram showing the dominant aqueous species for dissolved neptunium calculated at 25°C and concentrations of 1×10^{-8} mol/L total dissolved neptunium, 1×10^{-3} mol/L total dissolved carbonate, and 5×10^{-6} mol/L total dissolved fluoride. Under oxidizing conditions, the neptunyl ion, NpO_2^+ , calculates to be the dominant Np(V) aqueous species at pH values less than 8.5. At higher pH values, anionic Np(V) carbonate complexes, such as $\text{NpO}_2\text{CO}_3^-$ and $\text{NpO}_2(\text{CO}_3)_3^{5-}$, are predicted to be the aqueous complexes under oxidizing conditions. Under reducing conditions, the hydroxyl complex $\text{Np}(\text{OH})_4^0(\text{aq})$ is the dominant Np(IV) aqueous complex at pH values greater than 4 (Figure 3.4). Based the available thermodynamic data, the species NpF_2^{2+} may be the important Np(IV) aqueous complex at very acidic pH values under moderately oxidizing to reducing conditions.

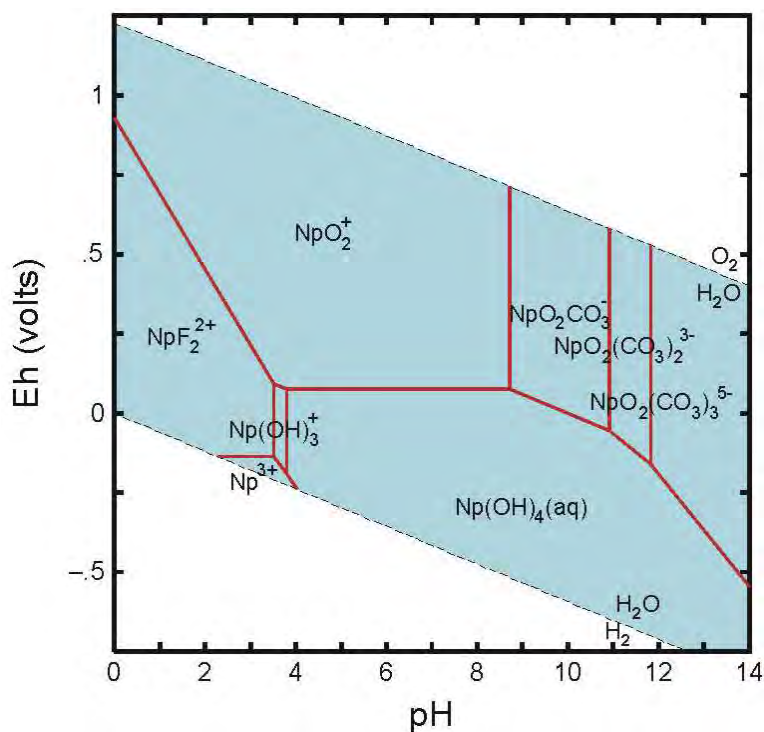


Figure 3.4. Eh-pH Diagram Showing Dominant Aqueous Species of Neptunium. (Diagram was calculated at a total concentration of 1×10^{-8} mol/L dissolved neptunium at 25°C.)

3.3.2 Precipitation and Coprecipitation

The solubility of Np(V) has been studied extensively for estimating the maximum solubility concentrations of dissolved neptunium that might be released under oxidizing conditions from a geologic repository for high-level radioactive waste with subsequent migration in groundwater systems (e.g., Novak and Roberts 1995, Neck et al. 1994, Lemire 1984). If the concentrations of dissolved Np(V) are sufficiently high, the solubility of Np(V) may be controlled by hydroxide or carbonate solids. In carbonate-free aqueous solutions with OH^- as the only complexing ligand, the maximum concentration of dissolved Np(V) is likely determined by the solubility product of solids, such as $\text{Np}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ (Efurd et al. 1998) or solid NpO_2OH (Al Mahamid et al. 1998; Roberts et al. 1996). In carbonate-rich solutions, a variety of solids, such as hydrated $\text{NaNpO}_2\text{CO}_3$ (Neck et al. 1994; Lemire et al. 1993), $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2$ (Al Mahamid et al. 1998; Neck et al. 1994; Lemire et al. 1993), and KNpO_2CO_3 (Al Mahamid et al. 1998; Lemire et al. 1993), have been studied as possible solubility controls for the maximum concentrations of dissolved Np(V) under oxidizing conditions.

Under reducing conditions, Np(IV) is not considered very mobile because it forms sparingly soluble oxide and hydroxide solids. Solids such as Np(IV) hydrous oxide (Nakayama et al. 1996; Rai and Ryan 1985), amorphous $\text{NpO}_2 \cdot x\text{H}_2\text{O}$ (Rai et al. 1987b), and amorphous NpO_2 (Rai et al. 1999) have been studied as possible solubility controls for Np(IV). In the study by Itagaki et al. (1991), the precipitation of amorphous $\text{NpO}_2 \cdot x\text{H}_2\text{O}$ and its colloids were found to be important to the mobility of neptunium in environmental systems. Figure 3.5 shows that solid NpO_2 is oversaturated over a large range of Eh-pH conditions for a system containing 1×10^{-8} mol/L total dissolved neptunium, 1×10^{-3} mol/L total dissolved

carbonate, and 5×10^{-6} mol/L total dissolved fluoride. In the Eh-pH region defined by the tan-colored area in Figure 3.5, NpO_2 calculates to be oversaturated based on the available thermodynamic data and may precipitate at these Eh-pH conditions to limit the maximum concentration of dissolved technetium in sediment.

3.3.3 Sorption

An extensive review of neptunium adsorption studies on sediments, soils, pure minerals, oxide phases, and crushed rock materials is presented in EPA (2004). Neptunium(V) species adsorb to some extent to iron oxide and clay minerals, but not to a major degree on most common minerals. Therefore, dissolved Np(V) is considered to be relatively mobile in soil systems. The singly charged neptunyl ion, NpO_2^+ , is likely the dominant species of neptunium in the oxidizing environment of the Hanford Site vadose zone (Ames and Rai 1978). NpO_2^+ does not compete favorably with Ca^{2+} and other common divalent ions for adsorption sites on sediments. Consequently, K_d values for neptunium are usually relatively low (Routson et al. 1976; Sheppard et al. 1976).

The results of experimental studies indicate that the adsorption of Np(V) has a strong dependence on pH, especially for iron oxides (Kohler et al. 1999; Girvin et al. 1991; Allard 1984). Typically, the sorption of Np(V) on minerals is negligible at pH values less than 5, and increases rapidly at pH values between 5 and 7. This pH-dependency is expected for ions that are present in solution primarily as cations, such as NpO_2^+ (EPA 1999a). In carbonate-containing solutions, the adsorption of Np(V) on iron

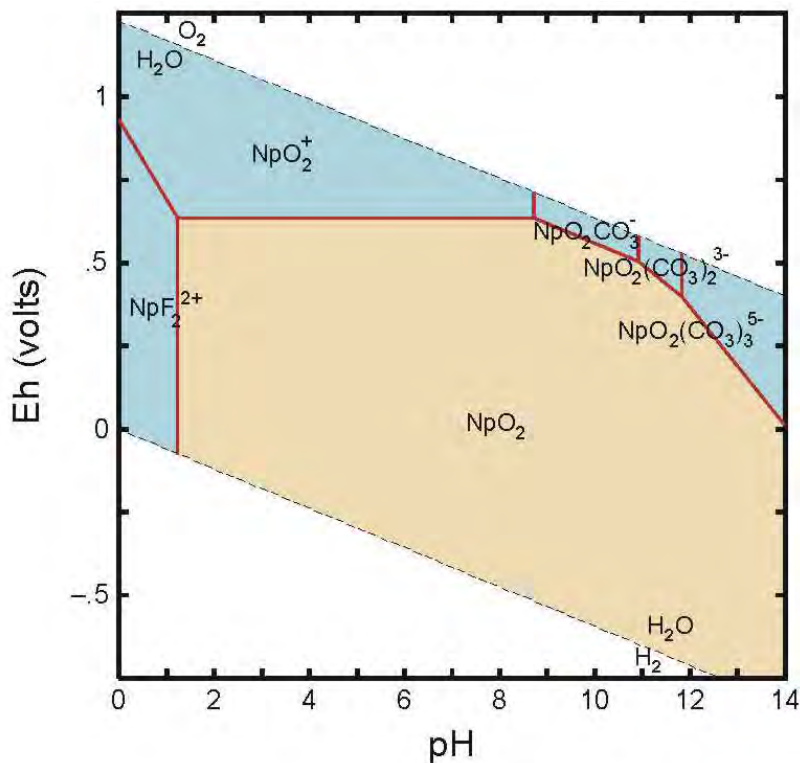


Figure 3.5. Stability Diagram Showing Eh-pH Region (tan colored) that Calculates as Oversaturated with Respect to the Solubility of Neptunium Solids. (Diagram was calculated at a total concentration of 1×10^{-8} mol/L dissolved neptunium at 25°C.)

oxides has been observed to decrease at pH values greater than 7 to 9 in response to the formation of aqueous Np(VI) carbonate complexes (Kohler et al. 1999). This latter behavior is analogous to that observed for the adsorption of U(VI) in carbonate-solutions at alkaline pH values (see Section 3.7.3).

Benson (1961) examined Np sorption to 25 common sulfide, silicate, and carbonate minerals using trace amounts of neptunium in Columbia River water at 80°C. Neptunium was adsorbed poorly or not at all by the minerals tested. Robertson (1974) determined the speciation of neptunium in the cooling water effluent from N Reactor. Through the use of ultrafiltration and cation- and anion-exchange resins, the following distribution was observed: 25% particulate, 70% cationic, <3% anionic, and <1% nonionic. The fact that neptunium may become associated with a particulate phase may have implications regarding the potential role of subsurface mobile colloids in enhancing contaminant transport.

A few studies have been conducted to evaluate the propensity of neptunium to adsorb to Hanford sediments (Routson et al. 1976; Serne et al. 1993). Their results suggest low-to-moderate adsorption and are included in this data package.

Cantrell et al. (2003) compiled in a single source the K_d values measured with Hanford sediment for radionuclides and contaminants of environmental concern to the vadose zone and groundwater at the Hanford Site. Table 13 in Cantrell et al. (2003) lists the compiled K_d values determined for Np(V) using Hanford sediment. The compiled K_d values generally range from 2 to 30 mL/g, suggesting to them that Np(V) adsorption is generally moderate under these geochemical conditions. Cantrell et al. noted that lower K_d values could result at contact times of one day or less and high concentrations of dissolved calcium or ethylenediaminetetraacetic acid, whereas higher K_d values could result at higher solution pH values. They concluded that moderate migration of Np(V) could occur in the vadose zone and groundwater under natural Hanford conditions.

3.4 Nitrate

The behavior of nitrogen species, such as nitrate, in aqueous, soil, and geochemical systems has been discussed by Lindsay (1979), Lindsay et al. (1981), Stumm and Morgan (1981), Rai et al. (1987c), Hem (1986), and others. A large number of studies have been completed related to the chemical and biological processes that transfer nitrogen between the atmosphere, lithosphere, hydrosphere, and biosphere. Many of these nitrogen transformations in the lithosphere are controlled in large part by microorganisms. The significance and rates of these reactions are in general difficult to quantify because of the many variables that influence the rates of reactions. Nitrate is highly mobile and does not sorb or precipitate in sediment systems.

3.4.1 Oxidation States and Aqueous Speciation

Nitrogen can exist in several oxidation states from +6 to -3 in natural environments. In natural waters, nitrogen exists primarily in the +5 (nitrate, NO_3^-), +3 (nitrite, NO_2^-), 0 [$\text{N}_2(\text{gas})$], and -3 (ammonium, NH_4^+) oxidation states. Nitrogen can occur in other forms, such as cyanide (CN^-), in aqueous systems affected by industrial waste disposal. The rate at which equilibrium is reached among the different redox states of nitrogen is very slow in abiotic systems because of the high activation energies associated with nitrogen redox reactions (Lindsay et al. 1981).

Figure 3.6 is an Eh-pH diagram that shows the dominant aqueous species of nitrogen predicted to be present at 25°C and a total concentration of 1×10^{-8} mol/L dissolved nitrogen. The stability diagram was calculated assuming that $N_2(\text{gas})$ is unreactive and the aqueous system represented in Figure 3.6 is not in equilibrium with $N_2(\text{gas})$. Figure 3.6 shows that NO_3^- (nitrate) is the dominant nitrogen species over the entire pH range for oxic systems. Under mildly reducing conditions and lower redox conditions, nitrogen as the cationic NH_4^+ and neutral $\text{NH}_3^0(\text{aq})$ species are the dominant aqueous species at pH values less and greater than approximately 9.2, respectively. Under mildly reducing conditions, there are also two narrow Eh-pH regions where N(III) as $\text{HNO}_2^0(\text{aq})$ (very acidic conditions) and NO_2^- (near-neutral to very basic pH conditions) are predicted to be stable.

Nitrate under reducing conditions such as those that may occur from the presence of organic carbon cocontaminants can be reduced by certain strains of bacteria to form $N_2(\text{gas})$. This process is referred to as denitrification, and it acts only on nitrate ions. Besides the need for nitrate, reducing conditions, and energy source for the bacteria, temperature and pH also affect the rate of denitrification. Rates of denitrification approach zero at 2°C and pH values less than 5 (de Haan and Zwerman 1978).

Relative to the vadose zone under the IDF, nitrogen will be present as the highly mobile NO_3^- (nitrate) species based on thermodynamic considerations and characterization data for Hanford vadose zone sediments. For example, characterization of vadose zone sediments taken under Hanford tanks that have leaked liquid wastes containing dissolved nitrate and nitrite solutions indicate that the nitrogen is present in these impacted sediments as nitrate (for example, see Serne et al. 2002a, through d, 2004a, b).

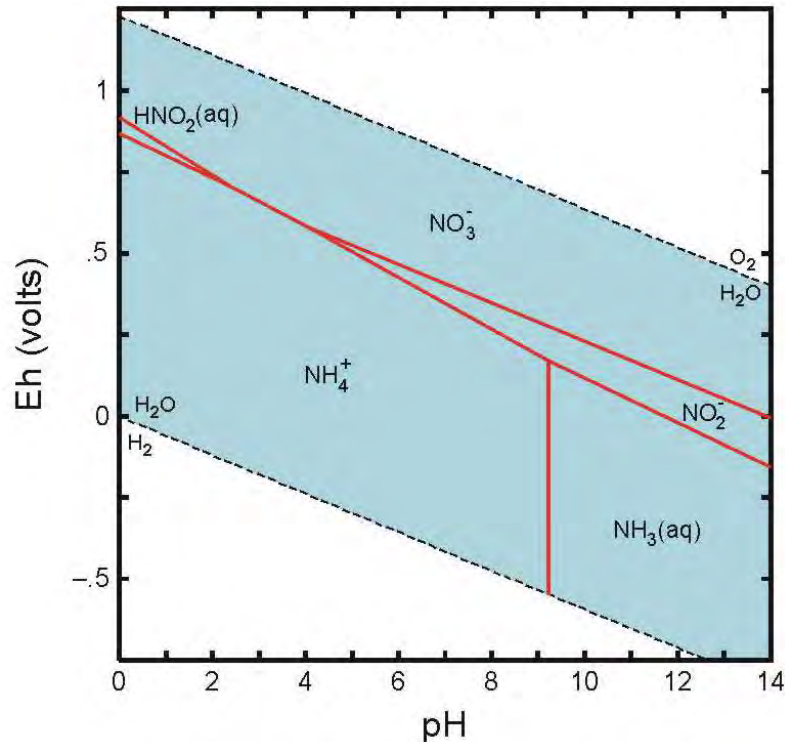


Figure 3.6. Eh-pH Diagram Showing Dominant Aqueous Species of Nitrogen. (Diagram was calculated at a total concentration of 1×10^{-8} mol/L dissolved nitrogen at 25°C.)

3.4.2 Precipitation and Coprecipitation

Nitrate-containing minerals such as nitratine (soda niter, NaNO_3) and niter (KNO_3) do occur in some natural systems. These minerals are highly soluble and restricted in occurrence to highly concentrated nitrate systems, such as evaporite deposits. Although nitratine has been identified in waste sludges in Hanford tank wastes, such phases are not expected to exist, especially from leachates from the IDF, in the vadose zone or unconfined aquifer.

Bickmore et al. (2001) recently reported the formation of a nitrate form of cancrinite. $\{(\text{Na,Ca,K})_{6-9}(\text{Si,Al})_{12}\text{O}_{24}[(\text{CO}_3),(\text{SO}_4),\text{Cl}_2,(\text{NO}_3)_2,(\text{OH})_2]_{2-4}\cdot n\}$. In studies of mineral precipitation on quartz sand reacted with simulated Hanford tank solutions. Bickmore et al. (2001) conducted a set of batch experiments with low solid-to-solution ratios in which high pH, high NaNO_3 solutions with dissolved aluminum were reacted with quartz sand at 89°C . Because cancrinite exhibits cation-exchange properties, investigators have speculated on the potential effect that precipitated cancrinite might have on sequestration (i.e., sorption) of contaminants of concern. Research related to solubility, kinetics of precipitation, and sorption properties of cancrinite relative to the interaction of simulated Hanford tank wastes and vadose zone sediments continues, and it is too early to judge the extent to which cancrinite precipitation might affect the mobility of contaminants in such environments. Given the thermal regime associated with Hanford storage tanks and composition (and rate of release) of the waste solutions that have leaked into the vadose zone, these conditions are far more extreme than those expected for leachates from IDF waste, and precipitation of a nitrate-form of cancrinite is not likely to occur or affect contaminant migration in the vadose zone under the IDF.

3.4.3 Sorption

Nitrate is one of the most widespread contaminants associated with past Hanford operations. The most prominent portions of this contamination originated at waste sites in the 200 Areas and spread toward the southeast (Hartman et al. 2004). Elevated nitrate concentrations in some areas of the Hanford Site are likely related to offsite activities. For example, elevated nitrate levels measured in groundwater from the 200-ZP-1 Operable Unit in the western part of the Hanford Site are believed to be due to offsite agriculture, the application of fertilizers, and irrigation (Hartman et al. 2004). Nitrate contamination in the 1100-EM-1 groundwater interest likely results from industrial and agricultural uses of the Hanford Site (Hartman et al. 2004).

Nitrate does not readily adsorb on minerals under near-neutral and slightly alkaline pH conditions common in sediment systems and is typically not included in most databases of K_d values such as Thibault et al. (1990). Nitrate (NO_3^-) and nitrite (NO_2^-) are typically assigned K_d values of 0 mL/g. As anions, their adsorption is expected to be high under acidic conditions, decrease with increasing pH values, and be essentially nil at slightly to highly basic pH conditions. Ammonium (NH_4^+) cations are highly adsorbed to mineral surfaces, but no attempt was made in this review to identify K_d values for this nitrogen species because it not expected to be present in Hanford vadose zone sediments.

Cantrell et al. (2003) identified only one study in which nitrate (NO_3^-) adsorption was measured using Hanford sediment. The limited number of K_d values determined for NO_3^- from this study are listed in Table 12 in Cantrell et al. (2003). Based on these measurements, they concluded that within experimental error, that NO_3^- adsorption under Hanford relevant conditions is essentially zero (i.e., $K_d = 0$).

3.5 Selenium

Selenium-79 is a long-lived fission product whose half-life is 2.95×10^5 years (Tuli 2004). The stable, nonradioactive form of selenium is ubiquitous, especially in sediments in the western United States. After nonradioactive selenium was found to be the cause of reduced fecundity of migrating birds in the mid-1980s (Ohlendorf et al. 1988), much research was directed at understanding the environmental fate of selenium.

The geochemistry and environmental behavior of selenium in sediment, soil, groundwater, and geological systems is reviewed by the National Academy of Sciences (NAS 1976), Rai et al. (1984), Elrashidi et al. (1989), Mayland et al. (1989), McNeal and Balistreri (1989), and others. The aqueous speciation and possible solubility controls for selenium in soil systems are discussed by Rai et al. (1984) and Elrashidi et al. (1989).

3.5.1 Oxidation States and Aqueous Speciation

Selenium can be found in the -2, 0, +4, and +6 oxidation states (Baes and Mesmer 1976). The Eh-pH diagram in Figure 3.7 shows the dominant aqueous species for dissolved selenium. The diagram was calculated at 25°C using a concentration of 1×10^{-8} mol/L total dissolved selenium and is consistent with the Eh-pH diagram given for selenium inorganic aqueous species in Rai et al. (1984). As indicated in Figure 3.7, dissolved selenium will be present in the +6 oxidation state (selenate) under oxidizing

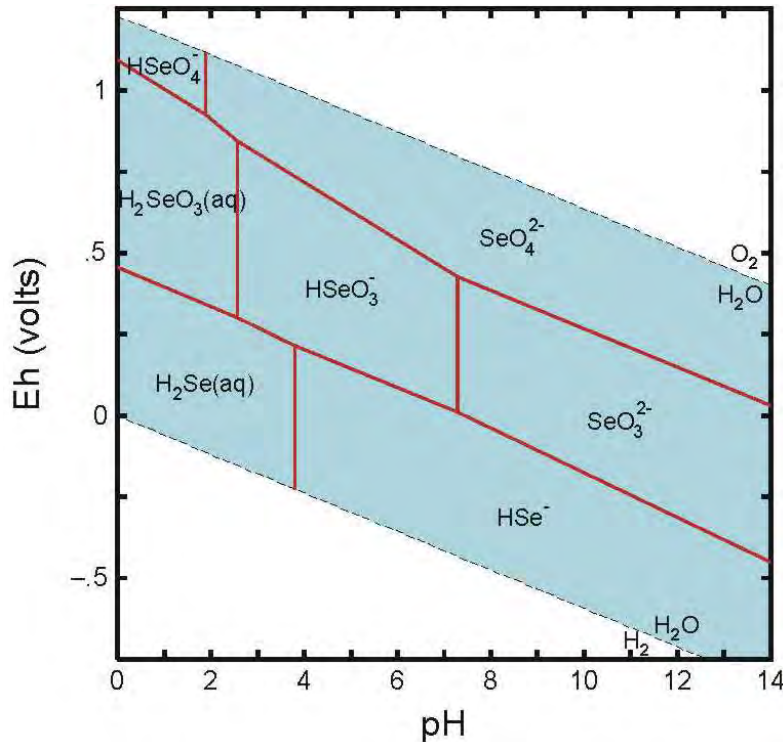


Figure 3.7. Eh-pH Diagram Showing Dominant Aqueous Species of Selenium. (Diagram was calculated at a total concentration of 1×10^{-8} mol/L dissolved selenium at 25°C.)

conditions as the dominant species HSeO_4^- and SeO_4^{2-} at pH values less than and greater than 2, respectively. Under moderately oxidizing to reducing conditions, the Se(IV) (selenite) species $\text{H}_2\text{SeO}_3^0(\text{aq})$, HSeO_3^- , and SeO_3^{2-} calculate to be dominant at pH values less than approximately 2.5, from 2.5 to 7, and greater than 7, respectively. Selenate and selenite may form ion-pair species with Ca^{2+} . The Se(-II) species $\text{H}_2\text{Se}^0(\text{aq})$ and HSe^- are the dominant aqueous species of selenium, at pH values less than and greater than about 4, respectively, under highly reducing conditions. The Eh-pH diagram (Figure 3.7) also indicates that dissolved selenium in the -2, +4, and +6 oxidation states will be present as anionic species at pH values greater than 4 under all redox conditions within the stability range of water.

The formation of methylated forms of selenium, such as dimethyl selenide (CH_3SeCH_3) and dimethyl diselenide ($\text{CH}_3\text{SeSeCH}_3$), has been detected and studied in laboratory experiments and environmental systems (e.g., Chasteen 1998; Guo et al. 1999; Zhang et al. 1999; Zhang and Frankenberger 2000). Chasteen (1998) gives a detailed review of the volatile chemical species of selenium. Due to the relatively high vapor pressure of these compounds, the formation of methylated forms of selenium can be significant contributors to the mobility of selenium in environmental systems.

3.5.2 Precipitation and Coprecipitation

In some sediment systems under moderately and highly reducing conditions, the concentration of dissolved selenium may be controlled by precipitation of selenium solids such as elemental selenium (Se^0). Figure 3.8 shows the Eh-pH region (tan area) that calculates as oversaturated with respect to solid Se^0 for an aqueous solution containing a total concentration of dissolved selenium of 10^{-8} mol/L.

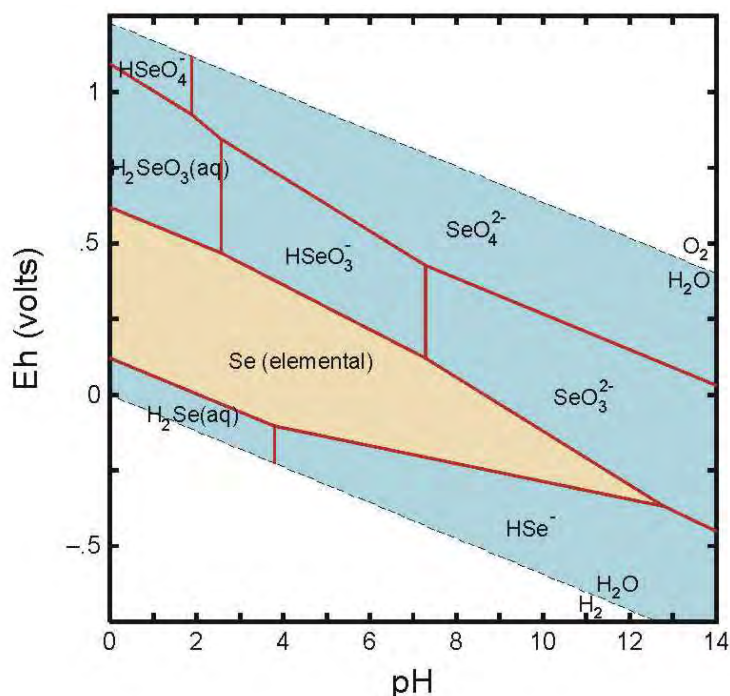


Figure 3.8. Stability Showing Region (tan colored) that Calculates to be Oversaturated with Respect to the Solubility of Elemental Selenium. (Diagram was calculated at a total concentration of 1×10^{-8} mol/L dissolved selenium at 25°C.)

Figure 3.8 is essentially identical to the Eh-pH solubility diagram in McNeal and Balistrieri (1989). These calculations indicate that elemental selenium is relatively insoluble in sediments over a wide range of pH and moderately reducing conditions and would limit the mobility of selenium in such environmental systems. In highly reducing and organic-rich systems containing dissolved sulfide or bisulfide, selenium-sulfide solids and metal selenides such as ferroselite (FeSe_2) are insoluble and would limit the concentration of dissolved selenium and its mobility in soil systems. Though several solid phases such as FeSe_2 are predicted to be stable under relatively reducing conditions, and some studies indicate that precipitation may be occurring, no definitive information on selenium solubility-controlling solids is available. The solubility products, K_{sp} , for FeSe_2 or the other selenium compounds, moreover, are not well defined.

Geering et al. (1968) has proposed that formation of the solid $\text{Fe}(\text{OH})_4\text{SeO}_3$ may help explain the insolubility of selenium in sediments as well as the strong association of selenium with iron in precipitates. Benjamin and Bloom (1981) observed that metal ion adsorption onto amorphous iron oxyhydroxides was enhanced in the presence of an iron-selenium solid phase adsorbed on the oxyhydroxide surface. They observed that selenite was irreversibly adsorbed on crystalline iron oxide surfaces (goethite, hematite).

Selenium can be reduced to its lower oxidation states by abiotic and biotic processes. Studies by Losi and Frankenberger (1998), Nelson et al. (1996), Poole and Porter (1999), and others show that dissolved selenium can be reduced by bacteria. These reactions can result in the bioreduction of selenium to insoluble forms, such as solid elemental selenium (Se^0) or $\text{S}_{1-x}\text{Se}_x$, which will limit the mobility and bioavailability of selenium in sediment systems.

As discussed previously, results by Mattigod et al. (2002, 2003)^(a) from waste glass weathering studies conducted in support of the ILAW/IDF PA suggest that under oxic conditions, secondary products that form from the weathering of ILAW waste glasses may incorporate small masses of anionic contaminants, such as selenate, that may be resistant to remobilization. The reader is referred to Section 3.2.2 for a description of the studies by Mattigod et al. (2002, 2003).^(a) With respect to the uptake of selenate, Mattigod et al. (2003, 2004) determined in experiments completed with radionuclide-spiked groundwater that ~6 to 15% of ^{75}Se was sorbed in the secondary crystalline phases and hydrated gel layer that formed from the leaching of waste glasses. Mattigod et al. (2003)^(a) found a similar amount of ^{75}Se sorption (~8 to 14%) when 1 M NaOH was used as the spiked leachate. In desorption experiments, Mattigod et al. determined that ~60 to 70% and 30 to 90% of the sorbed ^{75}Se , respectively, in the weathered LAWBP1 and LAW44 glasses did not easily desorb from the weathering glasses when contacted with groundwater-like solutions. Until this apparent coprecipitation (or specific adsorption) of Se(VI) in waste glass weathering products is further quantified, this process is not included in transport calculations or the geochemical data package for the 2005 IDF ILAW PA. This will build a degree of conservatism into the PA calculations that could be dealt with (removed) if quantitative data for the extent of weathering product formation per unit mass of waste glass and the mass of coprecipitated contaminants of interest in these weathering products become available at a later date.

(a) Mattigod SV, RJ Serne, BP McGrail, VL LeGore, and KE Parker. 2004 (in review). "Sequestration of radionuclides (^{125}I , ^{54}Se , ^{99}Tc) in secondary crystalline minerals resulting from chemical weathering of selected waste glasses." To be submitted to *Radiochimica Acta*.

3.5.3 Sorption

The concentration of selenium in most soil systems under oxidizing conditions is likely controlled by adsorption processes. Because the dominant aqueous species of Se(IV) and Se(VI) are anionic over the pH range of most soils (see Figure 3.7), the adsorption of selenium to mineral surfaces would be expected to be minimal to zero in most soil systems under oxidizing and moderately reducing conditions. Laboratory studies indicate that, in spite of their anionic nature, Se(IV) (selenite) and Se(VI) (selenate) may be adsorbed significantly by some soils. The experimental evidence suggests that crypto-crystalline and amorphous forms of SiO₂, Al₂O₃, and Fe₂O₃ control selenium adsorption (John et al. 1976; Singh et al. 1981). Studies with pure mineral phases demonstrate that hydrous oxides of iron and aluminum and amorphous aluminosilicates have a high affinity for Se(IV, VI) (Leckie et al. 1980; Hingston et al. 1968), which significantly exceeds that of layer lattice silicates (Frost and Griffin 1977; Hamby and Gissel-Nelson 1977; Singh et al. 1981). Selenium(VI) may be adsorbed more strongly by clay minerals than selenite (Frost and Griffin 1977), while the inverse applies to iron hydrous oxides (Leckie et al. 1980; Benjamin and Bloom 1981).

The adsorption of Se(IV) and Se(VI) on goethite, amorphous iron oxyhydroxide, and gibbsite is strongly pH dependent (Hingston et al. 1968, 1972; Leckie et al. 1980). The anions are strongly sorbed under acidic conditions, but sorption decreases with increasing pH. Limited experimental evidence suggests that, at a given pH, selenium adsorbs to neutral and positively charged amphoteric oxide surfaces displacing water, hydroxyls, and other adsorbed ligands (e.g., sulfate, silicate) until the surface is neutral in charge (Rajan 1979).

The presence of competing anions may reduce Se(IV) and Se(VI) adsorption by using limited ligand-exchange sites and reducing surface net positive charge. Phosphate reduces selenium adsorption on goethite, though some sites are specific to selenium (Hingston et al. 1971). Sulfate reduces Se(VI) adsorption on amorphous iron oxyhydroxides in a manner consistent with the competitive Langmuir equation (Leckie et al. 1980).

Um and Serne^(a) completed a series of batch and column adsorption studies of ⁹⁹Tc, ¹²⁹I, ⁷⁵Se (a surrogate for ⁷⁹Se), and ⁹⁰Sr on Hanford sediments collected from an ILAW borehole (C3177) at the 200 East Area. The batch sorption experiments were conducted using both uncontaminated Hanford groundwater and simulated glass leachates spiked with individual radionuclides. Um and Serne reported K_d values for the adsorption of ⁷⁵Se (as selenate) in Hanford groundwater on C3177 sediment from the 45-, 110-, and 215-ft below ground surface of 7.14±0.18 (pH 7.7), 7.17±0.20 (pH 7.6), and 8.65±0.34 mL/g (pH 7.6), respectively. The K_d values for ⁷⁵Se measured in simulated glass leachate for the equivalent sediment samples were 1.35±0.10 (pH 9.0), 2.68±0.12 (pH 8.9), and 1.08±0.09 mL/g (pH 8.9), respectively. These measurements indicate intermediate adsorption affinity for selenium on these sediments in both Hanford groundwater and simulated glass leachates. Um and Serne concluded that these adsorption data corroborate values obtained for sediments collected in the past from nearby locations and for generic aqueous solutions such as regional groundwater. They also noted that the new results provide more technical defensibility for past ILAW/IDF performance assessment predictions that did not use site-specific sediments and/or leachates.

(a) Um W and RJ Serne. 2004. "Sorption and Transport Behavior of Radionuclides in the Proposed Low-Level Radioactive Waste Disposal Facility at the Hanford Site, Washington." Submitted to *Radiochimica Acta*.

As described in Section 3.2.3, Kaplan et al. (2003) studied the influence of NaOH solutions, a simplified surrogate for glass leachate, on the hydraulic, physical, mineralogical, and sorptive properties of Hanford sediment. This study also included a series of batch sorption tests with Warden soil that Kaplan et al. used to measure the K_d values for cesium, strontium, iodide, selenate, and pertechnetate in soils treated with caustic solutions for up to 360 days. Kaplan et al. did not detect any appreciable adsorption for iodide, selenate, or pertechnetate (i.e., $K_d = 0$) on Hanford sediment contacted with NaOH solutions. Some adsorption of selenate was measured in control tests using sodium perchlorate solutions at neutral pH, but after caustic treatment and in high pH solutions, selenate sorption was determined to be nil. Section 3.2.3 contains a more complete summary of the results from Kaplan et al. (2003).

Table 14 in Cantrell et al. (2003) lists the compiled K_d values determined for Se(VI) using Hanford sediment. Based on their review, Cantrell et al. (2002) concluded that at trace concentrations, adsorption of Se(VI) to Hanford sediment is low to moderate, with K_d values typically ranging from 3 to 10 mL/g. At higher Se(VI) concentrations they found that the published selenium K_d values were lower, (0 to 3 mL/g). Consistent with the anionic character of Se(VI), the data compiled by Cantrell et al. indicate that Se(VI) adsorption increases under acidic conditions and decreases under basic conditions.

3.6 Technetium

All isotopes of technetium are radioactive. Several technetium isotopes are obtained by the fissioning of nuclear fuels in the reactor. The technetium isotopes and their yields resulting from uranium fission include ^{99}Tc , 6.06%; ^{101}Tc , 5.6%; ^{102}Tc , 4.3%; ^{103}Tc , 3.0%; ^{104}Tc , 1.8%; ^{105}Tc , 0.9%; and ^{106}Tc , 0.19%. Of these, only ^{99}Tc is a potential hazard from long-term burial of ILAW and other DOE defense wastes because this isotope has a long half-life (2.11×10^5 years) (Tuli 2004).

The behavior of technetium in environmental systems, especially under oxidizing conditions, has been reviewed extensively by Lieser (1993), Gu and Schulz (1991), Sparks and Long (1987), Meyer et al. (1985), Beasley and Lorz (1984), Coughtrey et al. (1983), Onishi et al. (1981), Wildung et al. (1979), Ames and Rai (1978), and others. Hughes and Rossotti (1987) reviewed in detail the solution chemistry of technetium. Studies of technetium under reducing conditions are much fewer than studies conducted under oxic conditions.

3.6.1 Oxidation States and Aqueous Speciation

Technetium exists in oxidation states from +7 to -1. In natural environments, the most stable oxidation states of technetium are +7 and +4 under oxidizing and reducing conditions, respectively. The most stable and characteristic oxidation state of technetium in slightly acid, neutral, or basic aqueous solutions in equilibrium with the atmosphere is pertechnetate ion (TcO_4^-) in which technetium is in the +7 oxidation state (Coughtrey et al. 1983; Hanke et al. 1986). Various Tc(V), Tc(IV), or Tc(III) species may be formed under reducing conditions (Pilkington 1990); the most stable of these reduced oxidation states is generally Tc(IV) (Bondietti and Francis 1979). Other reduced oxidation states are encountered chiefly in complex compounds (Mazzi 1989). Reduced technetium aqueous species are rapidly oxidized to Tc(VII) by atmospheric oxygen (Coughtrey et al. 1983). Regardless of the oxidation state emanating from the near field, technetium is likely to be in the +7 oxidation state once it reaches the far field.

The reduction of Tc(VII) to Tc(IV) by abiotic and biotic processes has recently been the subject of extensive studies because it has a significant effect on the mobility of technetium in waste streams, vadose zones, sediments, and groundwater. These reaction processes are the basis for certain remediation technologies such as permeable barriers composed of zero-valent iron particles (i.e., as metallic iron) or sodium-dithionite reduced soils, which are being tested for immobilization of groundwater contaminants. Microbial reduction of Tc(VII) has also been suggested as a potential mechanism for removing technetium from contaminated groundwaters and waste streams (e.g., Lovley 1993, 1995). Certain dissimilatory metal reducing bacteria and sulfate reducing bacteria have been determined to be capable of coupling the oxidation of organic carbon or hydrogen to the reduction of Tc(VII) to Tc(IV) (Lloyd and Macaskie 1996; Lloyd et al. 1997, 1998, 1999, 2000a,b; Wildung et al. 2000; Fredrickson et al. 2000).

Figure 3.9 is an Eh-pH diagram showing the dominant aqueous hydrolytic species of technetium in the absence of dissolved ligands other than hydroxide. The diagram was calculated at 25°C using a concentration of 1×10^{-8} mol/L total dissolved technetium. Dissolved technetium is present in oxic environmental systems as the aqueous Tc(VII) oxyanion species TcO_4^- over the complete pH range of natural waters and is not known to form any strong aqueous complexes. The TcO_4^- anion is essentially nonadsorptive, i.e., K_d values are ≈ 0 mL/g at near-neutral and basic pH values (EPA 2004) and also highly soluble (Baes and Mesmer 1976; Pilkington 1990). The concentration of Tc(VII) in sediments and groundwater will therefore not be limited by adsorption or solubility processes and thus will be highly mobile in oxic environments.

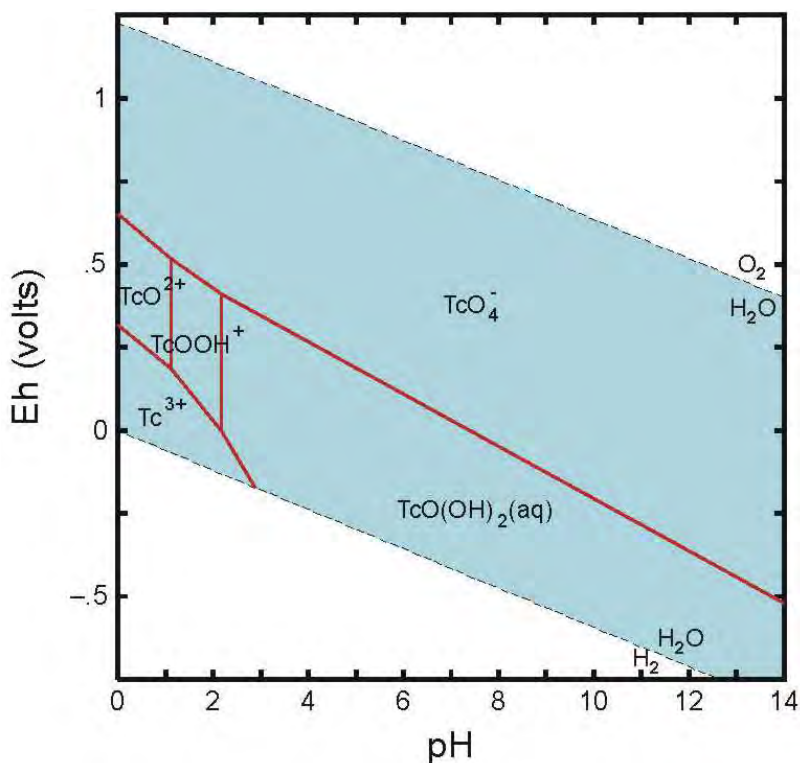


Figure 3.9. Eh-pH Diagram Showing Dominant Aqueous Species of Technetium. (Diagram was calculated at a total concentration of 1×10^{-8} mol/L dissolved technetium at 25°C.)

In alkaline solutions and low redox potentials, technetium aqueous speciation is dominated at pH values greater than 2 by the neutral Tc(IV) species $\text{TcO}(\text{OH})_2^0(\text{aq})$ in the absence of dissolved carbonate (Figure 3.9). In carbonate-containing waters, Tc(IV) carbonate complexes such as $\text{TcCO}_3(\text{OH})_2^0(\text{aq})$ and $\text{TcCO}_3(\text{OH})_3^-$ may become important aqueous complexes of technetium (Eriksen et al. 1992; Paquette and Lawrence 1985). Thermodynamic calculations suggest the possible formation of Tc^{3+} at pH values less than 2 under extremely reducing conditions. Technetium(IV) is sparingly soluble and highly sorbed and is therefore considered to be essentially immobile in reducing environments.

Rard et al. (1999) published an extensive, detailed review of the chemical thermodynamics of technetium aqueous species and solids. As previously noted, the thermodynamic database used to calculate the Eh-pH diagram herein predates the data tabulated by Rard et al. Although the thermodynamic stability of TcO_4^- is well established, thermodynamic data for other aqueous complexes and solids containing technetium in its various valence states are extremely limited. The absence of such data precludes the use of thermodynamic calculations to evaluate the environmental behavior of reduced species of dissolved technetium with respect to pH, Eh, and the presence of important dissolved complexing ligands such as dissolved phosphate, sulfate, chloride, and others. The Tc(IV) carbonate complexes $\text{TcCO}_3(\text{OH})_2^0(\text{aq})$ and $\text{TcCO}_3(\text{OH})_3^-$ are the only non-hydrolytic aqueous complexes of technetium for which Rard et al. (1999) list Gibbs free energy of formation ($\Delta G_{f,298}$) values. The thermodynamic constants listed for $\text{TcCO}_3(\text{OH})_2^0(\text{aq})$ and $\text{TcCO}_3(\text{OH})_3^-$ are based on the solubility study of solid $\text{TcO}_2 \cdot x\text{H}_2\text{O}$ completed in presence and absence of CO_2 gas by Eriksen et al. (1992). No independent measurements exist to verify the composition and thermodynamic properties of the Tc(IV) aqueous carbonate complexes.

Technetium(IV) carbonate complexes likely affect the aqueous speciation and solubility of Tc(IV) at near-neutral and/or basic pH conditions. The results of other studies suggest the formation of Tc(IV) aqueous carbonate complexes. For example, Paquette and Lawrence (1985) reported spectroelectrochemical evidence for the formation of aqueous carbonate complexes with both Tc(III) and Tc(IV). Wildung et al. (2000) studied the effects of electron donor and the presence of dissolved bicarbonate on enzymatic reduction of Tc(VII) by the metal-reducing bacterium *Shewanella putrefaciens* CN32. Based on the results of experiments conducted in bicarbonate solutions, Wildung et al. proposed the formation of a soluble, negatively charged Tc(IV) carbonate complex that exceeds Tc(VII) in electrophoretic mobility and possibly dominates the speciation of dissolved Tc(IV) over neutral and basic pH values. Given that anionic aqueous complexes do not readily adsorb to geologic materials under near-neutral and basic pH conditions, Wildung et al. (2000) suggested that the formation of anionic Tc(IV) carbonate complex(es) may represent an important mechanism for technetium migration in reducing geochemical environments. Generally, it has been assumed that technetium mobility in reducing environments is limited by the low solubility of Tc(IV) hydrous oxide (see Section 3.6.2) and adsorption of aqueous Tc(IV) hydrolytic complexes. Given that dissolved carbonate is ubiquitous in surface and subsurface environments, further research is needed to determine the composition and thermodynamic properties of Tc(IV) carbonate complexes.

Many species distribution calculations and Eh-pH diagrams presented in literature published before the critical review by Rard et al. (1999) include the aqueous neutral dimer species $[\text{TcO}(\text{OH})_2]_2^0(\text{aq})$. For many calculations, $[\text{TcO}(\text{OH})_2]_2^0(\text{aq})$ was predicted to be the dominant Tc(IV) species at neutral and basic pH values instead of the monomer $\text{TcO}(\text{OH})_2^0(\text{aq})$. Moreover, the calculated Eh-pH stability field for the dimer $[\text{TcO}(\text{OH})_2]_2^0(\text{aq})$ expanded in Eh-pH space with increasing concentrations of dissolved Tc(IV) due

to its stoichiometric factor. Rard et al. (1999) found it difficult to evaluate the results of the study on which the dimer species and associated thermodynamic constant were based and thus did not accept those results and the species $[\text{TcO}(\text{OH})_2]_2^0(\text{aq})$ for their thermodynamic database for technetium compounds.

3.6.2 Precipitation and Coprecipitation

Precipitation of “pure” Tc(VII)-containing solids is not likely to be an important geochemical process affecting ^{99}Tc transport through the Hanford Site vadose zone. Technetium(VII) forms very soluble oxides and halide complexes (Baes and Mesmer 1976) and does not form solubility-controlling phases in geochemical systems. On the other hand, recent unpublished work on sludge from Hanford single-shell tanks before and after sluicing retrieval shows that technetium can be incorporated into (coprecipitate) other sparingly soluble compounds that form within the Hanford tank environments. It is not clear yet whether the technetium remains Tc(VII) or gets reduced to Tc(IV)—or whether the technetium that is actually incorporated into the solid crystal structure is just physically trapped.

If Tc(VII) is reduced to Tc(IV) in the near field, it may form a number of sparingly insoluble compounds such as $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ or technetium sulfide solids. Numerous investigations have been conducted to determine the properties and hydration number of solid $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ (see review of studies in Rard et al. 1999). Characterization data for this solid are limited, and a range of compositions, such as TcO_2 (cr), $\text{TcO}_2 \cdot n\text{H}_2\text{O}$, $\text{TcO}(\text{OH})_2$, and $\text{Tc}(\text{OH})_4$, have been proposed by various investigators. This solid is considered to be essentially amorphous (Rard et al. 1999). The authors of this report know of no studies that have compared the X-ray diffraction characteristics of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ samples formed by different abiotic and biotic processes. Meyer et al. (1991) studied the solubility of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ over the pH range 1 to 10. The hydration numbers determined by Meyer et al. (1991) for their technetium solids ranged from 0.44 to 4.22 and from 1.38 to 1.81 for solids precipitated from acid and basic solutions, respectively. For the formula used for $\text{TcO}_2 \cdot n\text{H}_2\text{O}$, Rard et al. (1999) selected 1.6, which corresponds to the value suggested by Meyer et al. (1991). As Rard et al. (1999) noted, the exact value for the hydration number has no effect on the solution chemistry and predicted environmental mobility of dissolved technetium.

Figure 3.10 shows the Eh-pH conditions under which an aqueous solution containing 1×10^{-7} mol/L total dissolved technetium calculates to be oversaturated with technetium solids. In the Eh-pH region defined by the tan area in Figure 3.10, the solid $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ calculates as oversaturated based on the available thermodynamic data and may precipitate at these Eh-pH conditions to limit the maximum concentration of dissolved technetium in sediments under these redox potentials. Concentrations less than about $1 \times 10^{-7.5}$ mol/L total dissolved technetium are below the predicted solubility of $\text{TcO}_2 \cdot 2\text{H}_2\text{O}(\text{am})$. Thus, the Eh-pH figure was generated using the higher concentration of ^{99}Tc [1×10^{-7} mol/L] so that a stability field for the solid would be shown.

The solubility of technetium in contact with hydrated TcO_2 was investigated by Pilkington (1990), who found that pH had little effect on measured solubility of technetium over the pH range of 1 to 12.5. The presence of organic materials increased the measured solubility of technetium by a factor of 10, indicating that complexation between dissolved organic materials and technetium is important. Wildung et al. (1986) suggested that low molecular-weight organic ligands may increase the solubility of reduced forms of technetium, whereas complexation with the high molecular-weight organic ligands, particularly insoluble organic ligands, may lead to precipitation. Schulte and Scoppa (1987) showed that Tc(IV) had a strong tendency to coordinate with ligands containing highly polar groups and negatively charged ligands.

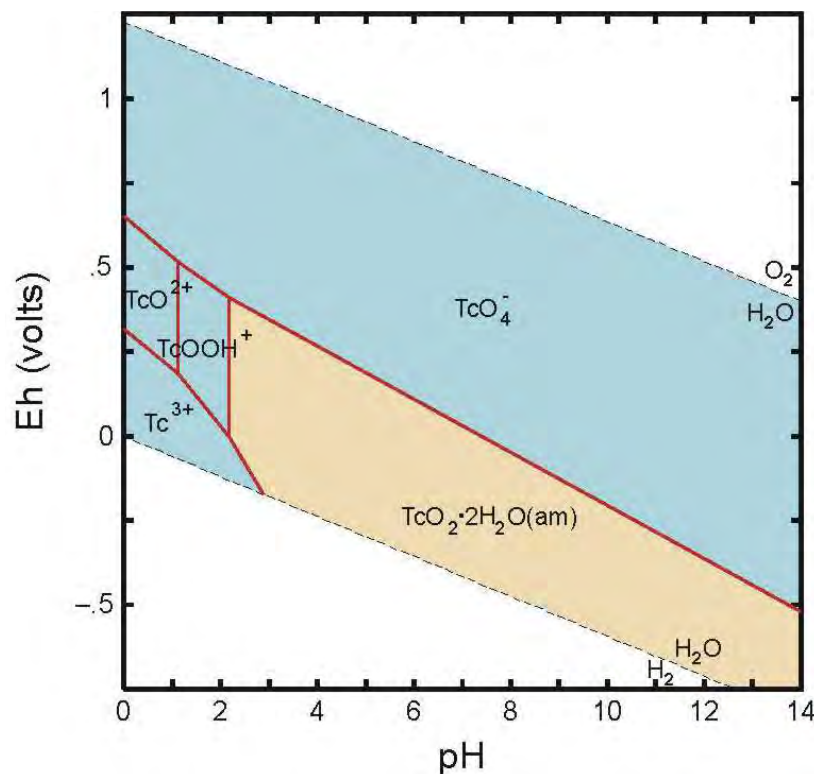


Figure 3.10. Stability Diagram Showing Eh-pH Region (tan colored) that Calculates to be Oversaturated with Respect to the Solubility of Technetium Solids. (Diagram was calculated at a total concentration of 1×10^{-7} mol/L dissolved technetium at 25°C.)

In reduced iron-sulfide systems, Tc(VII) can be reduced to Tc(IV) with coprecipitation with FeS solid (mackinawite) (Wharton et al. 2000; Livens et al. 2004). Due to the poorly ordered structures of the precipitates, Wharton et al. (2000) were not able to confirm whether Tc(IV) was incorporated in the structure of the FeS solid or precipitated as a distinct technetium solid phase. Their X-ray absorption spectroscopy (XAS) results suggest that the reduction of technetium at these conditions may have precipitated a TcS_2 -like phase (Wharton et al. 2000). The more recent results of Livens et al. (2004) show that the reaction product of Tc(VII) on the surface of mackinawite is reduced to oxidation state +4 and forms a TcS_2 -like species. Upon oxidation in air, the mackinawite forms goethite (FeOOH), and the technetium remains in the reduced +4 oxidation state but in an oxide rather than sulfide form.

Results recently published by Mattigod et al. (2002, 2003)^(a) from waste glass weathering studies conducted in support of the ILAW/IDF PA suggest that under oxic conditions, secondary products that form from the weathering of ILAW waste glasses may incorporate small masses of anionic contaminants, such as iodide (I^-), selenate (SeO_4^{2-}), and pertechnetate (TcO_4^{2-}), making them resistant to remobilization. The studies of Mattigod et al. are discussed in more detail in Section 3.2.2. Mattigod et al. (2003)^(a) completed experiments with radionuclide-spiked groundwater and determined that $\sim <1$ to 12% of ^{99}Tc was sorbed with reaction products that formed from the leaching of waste glasses. In desorption tests,

(a) Mattigod SV, RJ Serne, BP McGrail, VL LeGore, and KE Parker. 2004. "Sequestration of radionuclides (^{125}I , ^{54}Se , ^{99}Tc) in secondary crystalline minerals resulting from chemical weathering of selected waste glasses." To be submitted to *Radiochimica Acta*.

Mattigod et al. determined that up to 67% of the sorbed ^{99}Tc in the weathered LAWBP1 and LAWA44 glasses did not easily desorb from the weathering glasses when contacted with groundwater-like solutions. Until this apparent coprecipitation (or specific adsorption) of I^- , SeO_4^{2-} , and TcO_4^{2-} in waste glass weathering products is further quantified, this process is not included in transport calculations or the geochemical data package for the 2005 IDF ILAW PA. This will build a degree of conservatism into the performance assessment calculations that could be dealt with (removed) if quantitative data for the extent of weathering product formation per unit mass of waste glass and the mass of coprecipitated contaminants of interest in these weathering products become available at a later date.

3.6.3 Sorption

Numerous studies on the sorption of technetium on sediments, soils, pure minerals, oxide phases, and crushed rock materials have been conducted. An extensive review of these studies is presented in EPA (2004). These studies consist primarily of measurements of K_d values for Tc(VII). The adsorption of Tc(VII) oxyanion TcO_4^- is expected to be very low to zero, i.e., K_d values of ≈ 0 mL/g at near-neutral and basic pH conditions and to increase when pH values decrease to less than 5.

Several studies have shown that retention of technetium by solid phases is related to the physico-chemical properties of the solid phase (reviewed by Ames and Rai [1978], Gu and Schulz [1991]). These studies indicate that systems containing low amounts of clay, organic carbon, and aluminum/iron oxides show very little adsorption. Bowen (1966) reported that, in oxic conditions, 90% of added TcO_4^- was readily extractable from soils and assumed to remain in solution either as the free ion or weakly adsorbed to ion-exchange sites. Similarly, Wildung et al. (1977) reported that under oxic conditions, 78 to 88% of the TcO_4^- added to soil could be extracted easily 30 days after application. Under anaerobic conditions, Cataldo et al. (1978) reported that technetium removal from solution by soils could exceed 97% in two to five weeks.

The K_d values for Tc(VII) sorbed on sediments high in organic matter can be large. In a study of seven mineral soils and 27 organic soils, Sheppard et al. (1990) reported that, in addition to the redox status, the organic matter content of soils plays an important role in technetium sorption. Evidence of the complexation between organic materials and technetium has also been presented by Van Loon et al. (1986), who indicate that such complexes can be readily synthesized by chemical reduction of pertechnetate in the presence of organic matter. Wildung et al. (1974) determined that the sorption of TcO_4^- is positively correlated to the organic carbon content of soils, but studies of the effect that organic material has on the sorption of Tc(VII) in soils are limited.

Reduced technetium precipitates or organic matter-technetium complexes are not resolubilized by the chelating agents, EDTA and DTPA, which are known to form stable technetium complexes (Stalmans et al. 1986). This would indicate that EDTA and DTPA complexes are not as strong as the technetium organic matter complexes, suggesting that naturally occurring organic matter may play a significant role in technetium transport by forming relatively stable technetium complexes. Whether these complexes are soluble or insoluble depends on the size of the organic ligand. It is not known whether the organic matter-Tc(IV) complexation reaction can favorably compete with Tc(IV) hydrolysis reactions.

Um and Serne^(a) completed a series of batch and column adsorption studies of ⁹⁹Tc, ¹²⁹I, ⁷⁹Se, and ⁹⁰Sr on Hanford sediments collected from an ILAW borehole (C3177) at the 200 East Area on the Hanford Site. The batch sorption experiments were conducted using both uncontaminated Hanford groundwater and simulated glass leachates spiked with individual radionuclides. Um and Serne reported K_d values for the adsorption of ⁹⁹Tc on C3177 sediment from 110 ft below ground surface of 0.00 ± 0.00 (pH 7.6) and 0.00 ± 0.00 (pH 9.0), respectively, for Hanford groundwater and the simulated glass leachate. These results indicate no adsorption affinity for ⁹⁹Tc on these sediments at these geochemical conditions. Um and Serne conclude that these adsorption data corroborate values obtained for sediments collected in the past from nearby locations and for generic aqueous solutions such as regional groundwater. They also noted that the new results provide more technical defensibility for past ILAW/IDF performance assessment predictions that did not use site-specific sediments and/or leachates.

As described previously (Section 3.2.3), Kaplan et al. (2003) studied the influence of NaOH solutions, a simplified surrogate for glass leachate on the hydraulic, physical, mineralogical, and sorptive properties of Hanford sediment. The study also included a series of batch sorption tests with Warden soil that Kaplan et al. (2003) used to measure the K_d values for cesium, strontium, iodide, selenate, and pertechnetate in soils treated with caustic solutions for up to 360 days. Kaplan et al. did not detect any appreciable adsorption for iodide, selenate, or pertechnetate (i.e., $K_d = 0$) on sediment contacted with NaOH solutions. Section 3.2.3 has a more complete summary of results from Kaplan et al. (2003).

Cantrell et al. (2003) compiled the K_d values measured with Hanford sediment for radionuclides and contaminants of environmental concern to the vadose zone and groundwater at Hanford. Table 15 in Cantrell et al. (2003) lists the K_d values determined for Tc(VII) using Hanford sediment. The data compiled by Cantrell et al. indicate that Tc(VII) adsorption is low under nearly all conditions relevant to the Hanford vadose zone and upper unconfined aquifer with K_d values ranging from zero to a high of approximately 1 mL/g. They note that the Tc(VII) K_d values at the upper end of this range also have large standard deviations. K_d values approaching 1 mL/g appeared to be most representative in one study, but this was not substantiated by K_d values determined in other studies. Cantrell et al. (2003) concluded that, under normal Hanford conditions, zero is the most appropriate K_d value for Tc(VII), and 0.0 to 0.1 mL/g is the best estimate for the range for Tc(VI) K_d values. At the higher pH generated by glass leaching, the K_d for pertechnetate is even lower than for circumneutral pH groundwaters. Thus the K_d for Tc(VII) in the ILAW glass-dominated IDF near-field vadose zone is best fixed as 0 mL/g.

3.7 Uranium

The geochemical behavior of uranium has received extensive study due to the importance of uranium as an energy source and geochronology indicator. The uranium isotopes of interest in waste disposal and their respective half-lives include ²³³U, 1.592×10^5 years; ²³⁴U, 2.455×10^5 years; ²³⁵U, 7.04×10^8 years; ²³⁶U, 2.342×10^7 years; and ²³⁸U, 4.468×10^9 years (Tuli 2004). There have been several published reviews of the geochemical behavior of uranium. Langmuir (1978) and an updated discussion in Langmuir (1997) are particularly noteworthy. In 1999, an extensive compilation of detailed reviews on the mineralogical, geochemical, and environmental behavior of uranium was published in Burns and Finch (1999). This compilation is especially valuable because of the detail and recentness of the included papers, the

(a) Um W and RJ Serne. 2004. "Sorption and Transport Behavior of Radionuclides in the Proposed Low-Level Radioactive Waste Disposal Facility at the Hanford Site, Washington." Submitted to *Radiochimica Acta*.

extensive list of references, and the wide range of topics covered. Topics covered in this compilation of papers include the reviews of the mineralogy and paragenesis of uranium minerals; the genesis of uranium ore deposits; the geochemical behavior of uranium in natural fluids; environmental aspects of uranium geochemistry such as microbial effects, groundwater contamination, and nuclear waste disposal; and analytical techniques for characterization of uranium-bearing phases (Burns and Finch 1999).

3.7.1 Oxidation States and Aqueous Speciation

Uranium can exist in the +3, +4, +5, and +6 oxidation states in aqueous environments. Uranium(VI), i.e., uranyl, UO_2^{2+} , and U(IV) are the most common oxidation states of uranium in natural environments. Uranium exists in the +6 oxidation state under oxidizing to mildly reducing environments. Uranium(IV) is stable under reducing conditions and considered relatively immobile because U(IV) forms sparingly soluble minerals such as uraninite (UO_2). 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) such that it is a transient species in nature.

As with the redox of technetium, the reduction of U(VI) to U(IV) by abiotic and biotic processes has received considerable attention recently because the oxidation state of uranium has a significant effect on its mobility in waste streams and the natural environment. These reaction processes are the basis for certain remediation technologies such as permeable barriers composed of zero-valent iron particles, i.e., metallic iron or sodium-dithionite-reduced soils. Microbial reduction of U(VI) has also been suggested as a potential mechanism for removal of uranium from contaminated waters and soils, (e.g., Lovley 1993, 1995). Suzuki and Banfield (1999) provide a detailed review and extensive reference list on the interactions between uranium and microorganisms.

Grenthe et al. (1992) and Guillaumont et al. (2003) have published an extensive series of critical reviews of the thermodynamics of uranium. These references are the most detailed review completed to date of the available thermodynamic data for inorganic uranium compounds.

Dissolved U(VI) tends to form strong complexes with inorganic oxygen-containing ligands such as hydroxide, carbonate, and phosphate. Aqueous UO_2^{2+} hydrolyzes to form a number of aqueous hydroxo complexes, including UO_2OH^+ , $(\text{UO}_2)_2(\text{OH})_2^{2+}$, $(\text{UO}_2)_3(\text{OH})_5^+$, and $\text{UO}_2(\text{OH})_3^-$. In aqueous systems equilibrated with air or higher pCO_2 and at near-neutral to high pH, carbonate complexes [$\text{UO}_2\text{CO}_3^0(\text{aq})$, $\text{UO}_2(\text{CO}_3)_2^{2-}$, $\text{UO}_2(\text{CO}_3)_3^{4-}$] will dominate, but at lower pH the hydrolysis species will dominate as CO_2 solubility decreases. The Eh-pH diagram in Figure 3.11 shows the dominant aqueous species calculated for dissolved uranium at 25°C using concentrations of 1×10^{-8} mol/L total dissolved uranium, 1×10^{-3} mol/L total dissolved carbonate, and 5×10^{-6} mol/L total dissolved fluoride. The aqueous speciation of U(VI) in carbonate-containing water at near-neutral and basic higher pH values is dominated by a series of strong anionic aqueous carbonate complexes [e.g., $\text{UO}_2\text{CO}_3^0(\text{aq})$, $\text{UO}_2(\text{CO}_3)_2^{2-}$, and $\text{UO}_2(\text{CO}_3)_3^{4-}$]. Because anions do not readily adsorb to mineral surfaces at basic pH conditions, formation of anionic U(VI) carbonate complexes at pH values greater than 6 results in increased U(VI) solubility, decreased U(VI) adsorption, and increased mobility of uranium. Because of the high hydroxide, high carbonate, and low organic concentrations expected in both the near and far fields of the Hanford IDF site, dissolved U(VI) is likely to exist as a complexed carbonate and/or, to a lesser extent, as a hydroxide-complexed species. The Hanford vadose zone and upper unconfined aquifer environments contain adequate carbonate

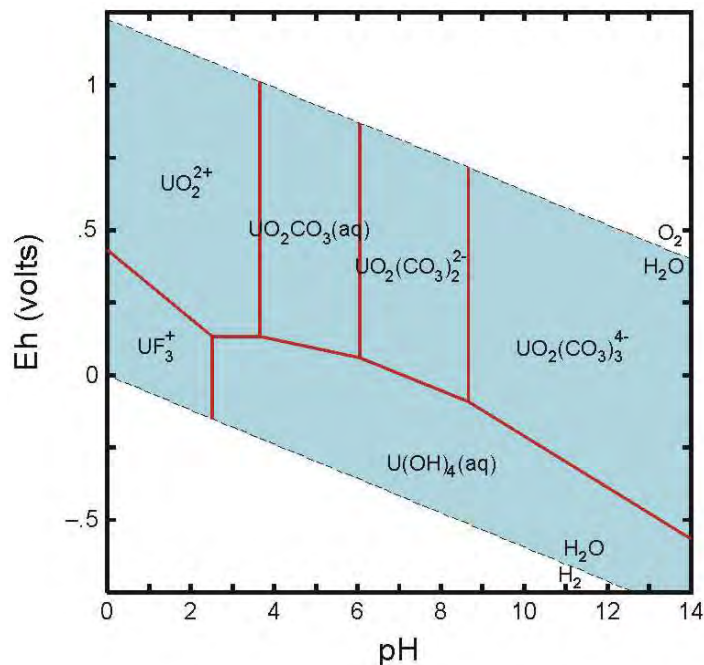


Figure 3.11. Eh-pH Diagram Showing Dominant Aqueous Species of Uranium. (Diagram calculated at a total concentration of 1×10^{-8} mol/L dissolved uranium at 25°C diagram.)

concentrations for these uranyl carbonate complexes to dominate the aqueous speciation of uranium. In fact, direct verification of the uranyl carbonate dominance in vadose zone pore waters from borehole 299-E33-45 is presented in Knepp (2002, Appendix D).

Recent studies indicate that a dissolved calcium uranyl carbonate complex may also have an important effect on the geochemical behavior of U(VI) in calcium-rich aqueous systems at near-neutral to basic pH conditions. Bernhard et al. (1996, 2001) used spectroscopic techniques to investigate aqueous complexation in the system Ca^{2+} -U(VI)- CO_3^{2-} - H_2O . The results of their series of studies provide evidence for the formation of a strong, uncharged aqueous complex, $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0(\text{aq})$. Aqueous speciation calculations based on stability constants published by Kalmykov and Choppin (2000) and Bernhard et al. (2001) for the formation of $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0(\text{aq})$ indicate that this species would be a predominant species under oxidizing conditions from pH 6 to 10 in calcium-rich waters containing dissolved U(VI). Because studies by Kalmykov and Choppin (2000) and Bernhard et al. (2001) are so recent, inclusion of the complex $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0(\text{aq})$ is only recently showing up in published aqueous speciation calculations for U(VI) (e.g., Brooks et al. 2003). Caution should be exercised when including $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0(\text{aq})$ and its stability constant in aqueous U(VI) speciation and solubility calculations. In the detailed critical review of thermodynamic constants for key radionuclides, Guillaumont et al. (2003) did not accept the formation constants published for the aqueous complex $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0(\text{aq})$. Guillaumont et al. (2003) believed that the published studies provided excellent evidence for complex formation between cations (such as Ca^{2+}) and $\text{UO}_2(\text{CO}_3)_3^{4-}$, but indicated that the constants listed in the literature had a large uncertainty and likely overpredicted the strength and stability of $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0(\text{aq})$. A detailed discussion of the reasons for their decision is given in Guillaumont et al. (2003).

Phosphate- UO_2^{2+} complexes such as $\text{UO}_2\text{HPO}_4^0(\text{aq})$ and UO_2PO_4^- could be important in aqueous systems with a pH between 6 and 9 when the total concentration ratio $(\text{PO}_4^{3-} / \text{CO}_3^{2-})_{\text{total}}$ is $\geq 10^{-1}$ (Sandino and Bruno 1992; Langmuir 1978). Complexes with SO_4^{2-} , F^- and possibly Cl^- are potentially important U(VI) species where concentrations of these anions are high, but their stability is considerably less than that of the carbonate and phosphate complexes (Grenthe et al. 1992).

Under reducing conditions, the speciation of U(IV) is dominated by the neutral aqueous species $\text{U}(\text{OH})_4^0(\text{aq})$ at pH values greater than 2. Complexation of U(IV) with natural organic humic and fulvic acids has been suggested as an important process ($\log K = 12$ to 16 ; Birch and Bachofen 1990). Hence, U(IV) could form stable organic complexes, increasing the solubility of the U(IV). In general, U(IV) species form stronger organic complexes than do the U(VI) species (Birch and Bachofen 1990).

3.7.2 Precipitation and Coprecipitation

Given the omnipresence of carbonate in Hanford vadose zone and unconfined aquifer system and the formation of strong aqueous U(VI) carbonate complexes, precipitation or coprecipitation of a solid phase likely will not control the mobility of U(VI) under oxidizing conditions in the vadose zone areas unaffected by waste discharges and the unconfined aquifer at the Hanford Site. If the near-field conditions become sufficiently reducing to maintain dissolved uranium in the +4 oxidation state, U(IV) readily precipitates as sparingly soluble minerals such as uraninite (UO_2). Under such conditions, uranium is therefore considered relatively immobile. Figure 3.12 shows the Eh-pH region (tan area) in which

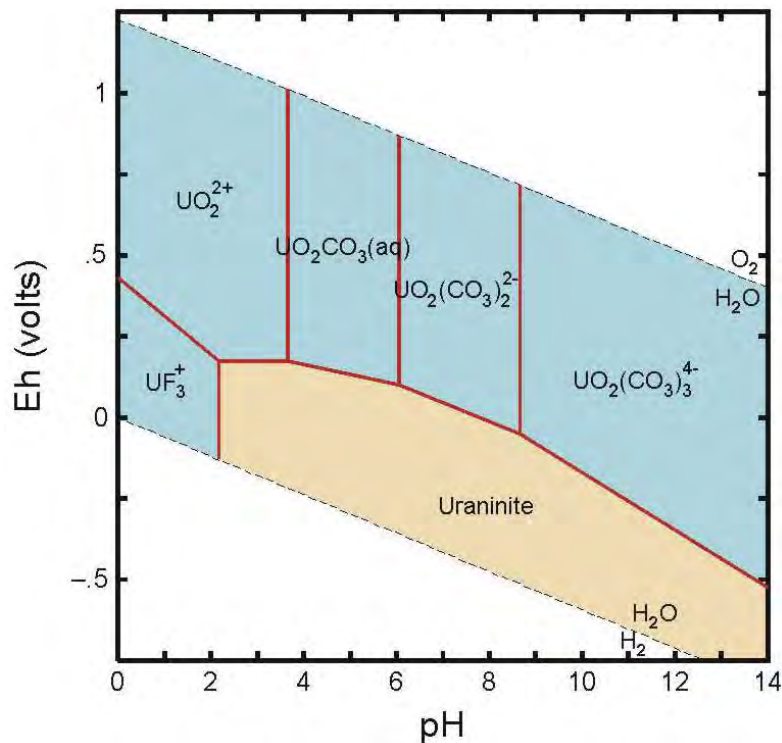


Figure 3.12. Stability Diagram Showing Eh-pH Region (tan colored) that Calculates as Oversaturated with Respect to the Solubility of Uraninite (UO_2). (Diagram was calculated at a total concentration of 1×10^{-8} mol/L dissolved uranium at 25°C .)

uraninite (UO₂) calculates to be oversaturated for a total concentration of 1×10⁻⁸ mol/L dissolved uranium based on the available thermodynamic data. In geologic systems represented by these Eh-pH conditions (tan area in Figure 3.12), uraninite may precipitate and limit the maximum concentration of dissolved uranium to 1×10⁻⁸ mol/L or less in those sediments.

Precipitation and coprecipitation processes may also be important for U(VI) for some oxidizing environmental conditions. Depending on the geochemical conditions, several different uranium coprecipitates may form depending on the pore fluid chemistry (Finch and Murakami 1999; Falck 1991; Frondel 1958). For example, solubility processes may be particularly important for U(VI) under oxidizing conditions in some uranium-contaminated sediments that are partially saturated (or dry) between periods of recharge or the pore fluids become isolated in micropores in the minerals. Under these conditions, the concentration of uranium in the residue pore fluids may exceed the solubility limits for U(VI)-containing minerals and/or coprecipitate with other minerals such as iron oxides, or undergo coupled sorption-reduction of aqueous U(VI) by Fe(II)-containing minerals. Potentially important mineral solubility controls for U(VI) include compreignacite (K₂U₆O₁₉·11H₂O), uranophane [Ca(UO₂)₂(SiO₃)₂(OH)₂·5H₂O], boltwoodite [K(H₃O)UO₂(SiO₄)·1.5H₂O], sklodowskite [Mg(UO₂)₂(SiO₃)₂(OH)₂·5H₂O], becquerelite (CaU₆O₁₉·10H₂O), carnotite [(K₂(UO₂)₂(VO₄)₂·3H₂O), schoepite (UO₃·2H₂O), rutherfordine (UO₂CO₃), tyuyamunite [Ca(UO₂)₂(VO₄)₂·5–8H₂O], autunite^(a) [Ca(UO₂)₂(PO₄)₂·10–12H₂O], and potassium autunite [K₂(UO₂)₂(PO₄)₂·10–12H₂O] (Langmuir 1997).

Uranium is also sequestered in the glass weathering products formed in short-term laboratory experiments such that coprecipitation reactions in the glass vault should be considered in the 2005 IDF PA if quantitative data are available. Besides determining the loading capacity of the weathering products for uranium and other contaminants, the long-term stability of weathering products needs to be established.

Several characterization studies at DOE sites such as Hanford, Fernald, Oak Ridge, and Savannah River suggest that sediments and soils contaminated from disposal or spills of uranium-containing liquid wastes at these sites have uranium-containing minerals or coprecipitates present (e.g., Delegard et al. 1986 ; Serne et al. 2002a ; Zachara et al. 2002a; Catalano et al. 2004 ; Buck et al. 1994, 1996 ; Morris et al. 1996; Roh et al. 2000; Bertsch et al. 1994; Hunter and Bertsch 1998). The studies related to Hanford, some of which are ongoing, are described below. Other studies pertaining to the characterization of uranium contamination in soils at other DOE sites that may be of interest to the reader include those pertaining to Fernald (Buck 1994, 1996; Morris et al. 1996), Oak Ridge (Roh et al. 2000), and Savannah River Sites (Bertsch et al. 1994; Hunter and Bertsch 1998).

Delegard et al. (1986) investigated the use of an ion exchange-based technique for removing dissolved uranium from contaminated groundwater underlying the then newly activated 216-U-16 and the retired 216-U-1 and 216-U-2 liquid waste disposal cribs in the 200W Separations Areas on the Hanford Site. Analysis of groundwater samples from area wells near these cribs indicated that the dissolved uranium was present as poorly adsorbing, aqueous anionic U(VI) carbonate complexes such as UO₂(CO₃)₂²⁻ (see speciation in Figure 3.11). X-ray diffraction (XRD) analysis of sediment samples from well 299-W19-11 indicated that the mineralogy of the sediments consisted primarily of quartz, illite, and feldspar. Sediment taken at a depth of 10.8 m from well 299-W19-11 was also found to contain uranium

(a) Autunite often refers to an entire group of secondary U(VI) minerals of the general formula R²⁺(UO₂)₂(XO₄)₂·nH₂O, where R = Ca, Cu, Mg, Ba, Na₂, and other metals, and XO₄ = PO₄ or AsO₄.

precipitates in the form of meta-autunite. At the time of the studies by Delegard et al. (1986), the uranium in these sediments had been remobilized by water flow resulting from nearby disposal of cooling water.

Serne et al. (2002a) recently conducted characterization, leaching, and adsorption/desorption studies of uranium-contaminated sediments collected at near-surface waste sites in the 300 Area at the Hanford Site. Scanning electron microscopy and molecular probe analyses indicate that uranium in the soil samples is likely present as coprecipitate and/or discrete uranium particles. The detailed analyses completed by Serne and coworkers to date have not determined the exact identification of the uranium phases. Their analyses indicate that uranium is present in the +6 valence state. The molecular probe data suggest that the crystalline uranium phases are likely clarkeite $[(\text{Na,Ca,Pb})_2(\text{UO}_2)\text{O}(\text{OH}) \cdot 0\text{-}1\text{H}_2\text{O}]$ or uranophane. Extended X-ray absorption fine structure (EXAFS) analyses suggest that the U(VI)-containing phases are likely uranyl phosphates and/or silicates based on the interatomic distance considerations. Laser fluorescence spectroscopy measurements indicate that the uranium-contaminated sediments do not contain uranyl phosphates. The investigators are continuing these analyses and their interpretation of the data to resolve the differences in the results from EXAFS and laser fluorescence spectroscopy.

A series of characterization studies by Zachara et al. (2002a) (and references cited in this paragraph) was conducted to identify the form and oxidation state of uranium in samples of waste-contaminated sediment from borehole 299-E33-45, which was drilled through the waste plume east of Hanford Tank 241-BX-102. These studies by Zachara et al. are being published in technical journals. The results of the studies indicate that uranium precipitated in the +6 valence state and formed discrete particles or particle aggregates in the contaminated vadose zone sediments. McKinley et al. (2002)^(a) analyzed thin sections of the contaminated sediments from BX-102 core using X-ray microprobe (XMP), X-ray absorption fine structure (XAFS), X-ray absorption near-edge structure (XANES), electron microprobe (EMP), and SEM. Their results showed that the uranium particles were typically 1 to 3 μm in diameter and occasionally formed radiating clusters of acicular crystals. McKinley et al. (2002)^(a) found that the uranium particles occurred in microfractures in the sediment particles and did not exhibit any association with any specific sediment mineral phase(s) that could have been a surface catalyst for their precipitation. Their chemical analyses indicated that the uranium particles were composed of uranium, silicon, oxygen, sodium, and potassium. McKinley et al. suggest boltwoodite, sodium boltwoodite $[(\text{Na,K})(\text{UO}_2)(\text{SiO}_3\text{OH}) \cdot 1.5\text{H}_2\text{O}]$, or weeksite $[\text{K}_{1-x}\text{Na}_x(\text{UO}_2)_2(\text{Si}_5\text{O}_{13}) \cdot 4\text{H}_2\text{O}]$ as possible identities for the uranium phases in the sediment samples. McKinley et al. propose that uranium precipitation in the microfractures was constrained by diffusion mass transfer and the kinetics for the reactions within this environment were driven by the large reactive surface area relative the enclosed volume of pore fluid.

Catalano et al. (2002, 2004) used XAFS spectroscopy, X-ray microdiffraction (μXRD), and micro-scanning X-ray fluorescence (μSXRF) techniques to investigate the speciation and spatial distribution of uranium in samples collected from the BX-102 borehole. Their study did not reveal any evidence for immobilization of uranium by in situ reduction in the sediments. The analyses by Catalano et al. (2004) indicated that the uranium particles were composed of sodium boltwoodite $[\text{Na}(\text{UO}_2)(\text{SiO}_3\text{OH}) \cdot 1.5\text{H}_2\text{O}]$. Catalano et al. (2004) found no evidence for the presence of any other uranophane group minerals.

(a) McKinley JP, JM Zachara, C Liu, and SC Heald. 2004. "Precipitation of waste uranium as a uranyl silicate in microfractures." Submitted for publication in *Science*.

Zachara et al. (2002a) and Wang and coworkers^(a) used time-resolved U(VI) laser fluorescence spectroscopy (TRLFS) to characterize the uranium phases present in sediment samples from the BX-102 core. Although an exact match was not found, the results of their TRLFS study indicated that the uranium particles in the microfractures of the sediment particles were a uranyl silicate mineral, such as uranophane, boltwoodite, or soddyite [(UO₂)₂SiO₄·2H₂O].

Liu et al.^(b) conducted dissolution studies of the uranium mineralization identified in the microfractures of mineral particles from the uranium-contaminated sediment collected from the BX-102 borehole. The experiments were completed using sodium, sodium-calcium, and ammonia electrolytes over the pH range from 7.0 to 9.5 under ambient CO₂ pressure. The results of Liu et al. show that the rate and extent of uranium dissolution was affected by mineral solubility, the concentration of dissolved carbonate, and the mass transfer rate within intraparticle regions. Although the concentrations of uranium dissolved by electrolytes below pH 8.2 reached steady state conditions within a month, Liu et al. found that uranium concentrations continued to increase for more than 200 days at pH values of 9.0 and higher. The results of geochemical modeling calculations by Liu et al. show that the measured steady-state concentrations of dissolved uranium in the dissolution experiments were consistent with the solubility of sodium boltwoodite and/or uranophane. Liu et al. determined that a pseudo-first-order rate constant could be used to predict the dissolution kinetics of the uranyl-silicate mineralization in the three sediments over a range of pH, electrolyte compositions, and bicarbonate/carbonate concentrations used in these experiments. Liu et al. cautioned that except for the case of bounding calculations, use of a single-value K_d model would be inadequate to predict the sorption and release of uranium from the BX-102 borehole sediments. Liu et al. suggest that geochemical models that incorporate solubility, dissolution kinetics, and mass transfer rates would be required to accurately predict uranium mobility for these environmental conditions.

Investigations funded by the DOE Hanford Science and Technology Program within the Groundwater/Vadose Zone Integration Protection Project are underway to study uranium-contaminated sediments from the 300 Area uranium plume in 300-FF-5 and develop reactive transport modeling approaches to assist with evaluation of alternative remediation approaches. On May 10-11, 2004, a topical workshop was conducted to provide an update of the results from the laboratory investigations of the sediment samples from the 300 Area uranium plume and reactive transport modeling studies. The meeting included participation from the DOE, Environmental Protection Agency, Washington State Department of Ecology, DOE National Laboratories, U.S. Geological Survey, and Hanford stakeholders. The Web site, <http://www.hanford.gov/cp/gpp/public/workshops.cfm> includes presentations from this workshop. Presentations on the characterization of 300 Area process pond and vadose-zone sediments from the 300 Area uranium plume and the development of a generalized surface complexation model (discussed in Section 3.7.3) to predict the sorption of uranium in these sediments are briefly discussed here. As these studies are ongoing, the presenters cautioned that the results presented at the workshop presentations are preliminary, continue to be refined and are open to re-interpretation. J. P. McKinley and coworkers at PNNL are using SEM, electron microprobe, and X-ray microprobe (with EXAFS capabilities) analyses to

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- (a) Wang Z, JM Zachara, PL Gassman, C Liu, O Qafoku, and JG Catalano. 2004. "Fluorescence spectroscopy of U(VI)-silicates and U(VI)-contaminated Hanford sediment." Submitted to *Geochimica et Cosmochimica Acta*.
- (b) Liu C, JM Zachara, O Qafoku, JP McKinley, SM Heald, and Z Wang. 2004. "Dissolution of uranyl microprecipitates from subsurface sediments at the Hanford Site, USA." Submitted to *Geochimica et Cosmochimica Acta*.

characterize the nature of uranium contamination in the process pond and vadose sediments from the 300 Area uranium plume. There results to date (taken essentially verbatim from the presentation) are the following:

- For process pond sediments, most of the uranium contamination is associated with a calcium carbonate phase and alumino-silicate mineralization at very low concentration, and particles of discrete reduced phase (UO₂) were observed imbedded in precipitates.
- In upper vadose sediments, the characterization results were similar to those for the North Pond sediments, with a low-level uranium contamination associated with a calcium carbonate phase and discrete U(VI) oxides segregated in alumino-silicate rind.
- In intermediate vadose sediments, secondary mineral clasts were rare. Low-level uranium contamination is associated with a calcium carbonate phase and discrete U(VI) oxides segregated in alumino-silicate rind.
- In the deep vadose sediment, surface secondary mineralization extended the level of groundwater

J. G. Catalano (Stanford University) presented the results of X-ray absorption spectroscopy (XAS) analyses of the uranium contamination in the 300 Area samples. The EXAFS spectra for the North Pond samples indicated that the uranium was at least partially coordinated by carbonate. Some of the spectra also suggested that a separate uranium precipitate, possibly a hydroxide phase, was also present.

3.7.3 Sorption

The dissolved concentrations of U(VI) beyond the very near field of the IDF likely will be controlled by adsorption processes in Hanford vadose zone and unconfined aquifer system. Because U(VI) exists primarily as strong aqueous anionic U(VI) carbonate complexes, which do not readily adsorb to the naturally negatively charged Hanford Site sediments at neutral-to-alkaline pH conditions, U(VI) is considered moderately to highly mobile in Hanford aqueous systems away from local sources of uranium contamination. An extensive review of published uranium adsorption studies is given in EPA (1999b). Uranium(VI) adsorbs onto a variety of minerals and related phases, including clays (Ames et al. 1982; Chisholm-Brause et al. 1994), oxides and silicates (Hsi and Langmuir 1985; Waite et al. 1994), and natural organic material (Borovec et al. 1979; Shanbhag and Choppin 1981; Read et al. 1993). Important environmental parameters affecting uranium adsorption include redox conditions, pH, and concentrations of complexing ligands such as dissolved carbonate, ionic strength, and mineralogy.

As with the adsorption of most dissolved metals, pH has a significant effect on U(VI) adsorption because pH strongly influences U(VI) aqueous speciation and the number of exchange sites on variable-charged surfaces of solids such as iron oxides, aluminum oxides, and natural organic matter. Uranium sorption to iron oxides and smectite clay has been shown to be extensive in the absence of CO₃²⁻ (Kent et al. 1988; Hsi and Langmuir 1985; Ames et al. 1982). In the presence of CO₃²⁻ and organic complexants, U(VI) sorption was shown to be substantially reduced or severely inhibited (Hsi and Langmuir 1985; Kent et al. 1988; Ames et al. 1982). Depending on the adsorbent, the measured adsorption of U(VI) 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 3 to 5, reaches a maximum in adsorption in the pH range

from 5 to 7 to 8, and then decreases with increasing pH at values greater than 7 to 8, depending on adsorbent (see Figure J.4 in EPA [1999b] and references cited therein). The observed increase in U(VI) adsorption onto sediments from acidic to near-neutral pH values is due to the dominant U(VI) aqueous species being cationic and neutral over this pH range. The subsequent decrease in U(VI) adsorption with increasing pH values results from the dominant U(VI) aqueous species being anionic U(VI) carbonate complexes. In the absence of dissolved carbonate, uranium sorption to iron oxide and clay minerals has been shown to be extensive and remains at a maximum at pH values near and above neutral (Kent et al. 1988; Hsi and Langmuir 1985; Ames et al. 1982). In the presence of carbonate and organic complexants, U(VI) adsorption has been shown to be substantially reduced or inhibited at neutral to basic pH values. Even differences in partial pressures of CO₂ have a major effect on uranium adsorption at neutral pH conditions. Waite et al. (1994), for example, showed that the percent of U(VI) adsorbed onto ferrihydrite decreases from approximately 97 to 38% when CO₂ is increased from ambient (0.03%) to elevated (1%) partial pressures.

Other secondary factors may affect the mobility of uranium as well. For example, in low ionic-strength solutions, the uranyl ion concentrations probably will be affected, in part, by cation-exchange adsorption process. Uranium(VI) will adsorb onto clays, organics, and oxides, and this will limit its mobility. As the ionic strength of an oxidized solution increases, other ions, notably Ca²⁺, Mg²⁺, and K⁺, will displace the uranyl ion, forcing it into solution. Not only will other cations out-compete the U(VI) for exchange sites, but carbonate ions will form strong soluble complexes with the uranyl ion, further lowering its affinity for positively charged solids while increasing the total amount of uranium in solution (Yeh and Tripathi 1991).

Some of the sorption processes in which U(VI) participates are not completely reversible. Sorption onto iron and manganese oxides can be a major process for extraction of uranium from solution. These oxide phases act as a short-term, 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 mediating the transfer of the metal between the two phases is slow.

Solid-phase organics are another possible sink for uranyl ions in soils and to smaller extents in sediments. The mechanisms for uranium sequestration onto organic-rich sediments are numerous and complex. One mechanism may involve sorption of the uranyl cation onto exchange sites such as carboxylic acid groups. These groups can coordinate with the uranyl ion, displacing water of hydration and forming stable complexes. A process like this probably accounts for a significant fraction of the organically bound uranium in soils and, perhaps, in sediments. Alternatively, sedimentary organics may reduce dissolved U(VI) species to U(IV) species. These reduced species are generally low in solubility and may remain associated with the organic phase after precipitation as a reduced oxide. Little seems to be known about the nature of organic uranium associations in soils or sediments on a molecular level, although several different types of interactions may be taking place. The amount of naturally occurring organic substances such as fulvic and humic acids is quite low in the subsurface of the Hanford Site. There is a possibility that the contaminant plume leaving the near field may contain some organic substances (sulfur polymer cement contains 5% organic binder, and asphalt also may be used in covers). Both of these engineered materials possess some of chemical properties of the organic substances found in natural systems.

Rancon (1973) studied the adsorption of uranium using four soils and three pure-phase minerals. Quartz was characterized as inert ($K_d = 0$ mL/g), calcite was a poor uranium adsorber ($K_d = 7$ mL/g), and illite and other 2:1 clays ($K_d = 139$ to 270 mL/g) were the best adsorbers of uranium from solution. Acidic, organic-rich soils showed higher uranium sorption ($K_d = 33$ mL/g) than soils containing carbonate minerals ($K_d = 16$ mL/g). The importance of U(VI) sorption to inorganic solid phases such as clays and iron oxides may be minor in many natural environments because of the limited quantity of these materials, the presence of particulate or dissolved organic matter, and/or dissolved carbonate.

Formation of complexes between U(VI) and organic ligands such as humic and fulvic particulates has been studied frequently because of interest in ore-forming environments. At ambient temperatures ($\sim 25^\circ\text{C}$), uranium is adsorbed to humic substances through rapid ion-exchange and complexation processes with carboxylic and other acidic functional groups (Idiz et al. 1986; Boggs et al. 1985; Shanbhag and Choppin 1981; Nash et al. 1981; Borovec et al. 1979). The adsorption often is followed by reduction to the U(IV) species followed by precipitation of UO_2 (Andreyev and Chumachenko 1964). In studies with lignite, the uranyl species formed a stable complex with the lignite without subsequent reduction; reduction only occurred at elevated temperatures (Nakashima et al. 1984). Organic matter does have the capacity to act as a reductant, most notably because of the presence of quinone, sulfone, and reduced metal porphyrin (tetrapyrroles) moieties (Macalady et al. 1986).

Gamerding et al. (1998) conducted a series of experiments using an unsaturated flow apparatus (UFATM) to measure the adsorption and mobility of U(VI) under partial moisture saturation conditions that are relevant to waste burial sites and vadose-zone far-field conditions at the Hanford Site. The sediments used for these measurements included a medium-coarse sand, Touchet bed fine sand, and Warden silt loam. The experiments were conducted with uncontaminated groundwater with pH 8.4 from the Hanford Site. For the conditions considered for their experiments, Gamerding et al. (1998) determined that U(VI) K_d values decreased with decreasing moisture saturation irrespective of sediment texture. The K_d values determined by Gamerding et al. (1998) for the medium-coarse sand decreased from 0.48 to 0.16 mL/g at moisture saturations from 30 to 12%, respectively. For the fine sand, the U(VI) K_d values were 1.42 and 0.39 mL/g at moisture saturations of 66 and 22%, respectively. For the silt loam, the U(VI) K_d values were 4.05 and 1.81 mL/g at moisture saturations of 83 and 41%, respectively. There is a concern that the reduction in K_d values may partly be an artifact of the short residence times in the UFA as opposed to a physicochemical process, such as sorption sites that are not exposed to water, and thus adsorbates, such as U(VI), in the unsaturated sediments. Until we are fully convinced that K_d values are, in fact, lower for unsaturated moisture conditions based on more fully understood physicochemical mechanisms, we will continue to use K_d values based on traditional batch and column tests performed under saturated conditions.

The 300 Area study by Serne et al. (2002a) (see Section 3.7.2) also included laboratory experiments to measure the adsorption characteristics of uranium in near-surface sediment samples collected from the 300 Area. Serne et al. (2002a) completed adsorption experiments to investigate the effects of dissolved uranium concentrations, pH, and dissolved inorganic carbon (as carbonate/bicarbonate) concentrations on uranium adsorption onto uncontaminated sediment. Uranium adsorption K_d values ranged from 0 mL/g to more than 100 mL/g depending on which solution parameter was being adjusted. Results of the experiments showed that total concentration of dissolved inorganic carbon had the largest affect on uranium adsorption onto uncontaminated 300 Area sediment. Solution pH also was shown to be important in laboratory tests. The mineral content of the natural sediment buffers pH to a nearly constant value, which

therefore minimizes the overall effect of pH changes in the 300 Area sediments. Results from the batch adsorption tests by Serne et al. (2002a) also indicate that uranium sorption onto the background sediment is linear up to uranium concentrations of 3 mg/L (holding all other parameters constant), which is well above the values found in the upper unconfined aquifer. Thus, the linear isotherm assumption holds for uranium in the 300 Area sediment-pore water environment.

Barnett et al. (2002) recently used batch adsorption experiments and a surface complexation model to study the pH-dependent adsorption of U(VI) on sediment and soil samples from Hanford, Oak Ridge, and Savannah River. The sediment sample from the Hanford Site was from the Upper Ringold Formation, obtained from the White Bluffs area above the Columbia River. Barnett et al. (2002) used the surface complexation model developed for U(VI) adsorption onto ferrihydrite by Waite et al. (1994) to predict U(VI) adsorption on these sediments as a function of pH. Application of this model necessitated that Barnett et al. (2002) assume that all of the dithionite-citrate-bicarbonate extractable iron oxides in these sediment samples was present as ferrihydrite. The modeling results of Barnett et al. (2002) qualitatively predicted the main characteristics of the pH-dependent adsorption of U(VI) on these sediments in carbonate-containing systems. Barnett et al. (2002) suggested that this modeling approach could be used to assess the relative mobility of U(VI) in geochemical systems by indicating whether U(VI) was weakly or strongly adsorbed onto the geologic materials. Surface complexation models likely will receive increased use in the future in developing a better understanding of surface reactions and site conceptual models and in estimating limiting K_d values for the adsorption of metals, especially for uranium, in the vadose zone and other geochemical environments.

As discussed in Section 3.7.2, investigations are currently underway to study uranium-contaminated sediments from the 300 Area uranium plume in 300-FF-5 and develop reactive transport modeling approaches to assist with evaluation of alternate remediation approaches. J. A. Davis and coworkers from the U.S. Geological Survey presented the results of laboratory studies and progress toward developing a generalized surface complexation model (SCM) based on the approach described in Davis and Curtis (2003) and Curtis et al. (2004) to model uranium sorption in sediment samples from the 300 Area uranium plume. Based on the studies completed to date, Davis and coworkers concluded (taken essentially verbatim from their presentation):

- U(VI) desorption is very sensitive to alkalinity changes.
- Contaminated sediment samples contain significant fractions of both adsorbed (labile) and “co-precipitated” U(VI).
- Coprecipitated U(VI) can be dissolved by hydroxylamine hydrochloride extractions.
- Semi-empirical generalized SCM describes the partitioning of the labile U(VI) fraction reasonably well, but likely needs further testing with other samples.

Cantrell et al. (2003) compiled the K_d values measured with Hanford sediment for radionuclides and contaminants of environmental concern to the vadose zone and groundwater at Hanford. Table 16 in Cantrell et al. (2003) lists the compiled K_d values determined for U(VI) using Hanford sediment. The compiled data indicate that U(VI) adsorption is low to moderate with K_d values ranging from approximately 0.2 to 4 for natural Hanford groundwater conditions. Serne et al. (1993) reported

K_d values that were much higher, but Cantrell et al. considered some of these values suspect and noted that adsorption should be lower for U(VI) adsorption measured in acid process waste by Serne et al. (1993) due to the lower equilibrium pH values reached in these experiments. The K_d value for U(VI) from the acid process waste was much higher than observed in any other studies (Serne et al. 1993). As indicated by Cantrell et al. (2003), the maximum in the adsorption of U(VI) on natural sediment in groundwater systems occurs in the pH range from approximately 6 to 8, with adsorption decreasing at lower pH values due to protonation of the adsorption sites and the dominance of cationic aqueous U(VI) species at lower pH conditions (Payne and Waite 1991; Davis 2001). As discussed previously, the adsorption of U(VI) on sediment also decreases with increasing pH values at pH values greater than about 7 due to the formation of anionic aqueous U(VI) carbonate species and the deprotonation of the surface sites. Cantrell et al. (2003) noted that the high K_d values reported for U(VI) by Serne et al. (1993) were used in the geochemistry data package report for the 2001 ILAW PA, where Kaplan and Serne (2000) recommended a K_d range for $^{234/235/238}\text{U}$ of 0.1 to 80 mL/g. Based on their more recent analysis, Cantrell et al. (2003) now conclude that a K_d range of 0.2 to 4 mL/g is more likely representative for U(VI) for geochemical conditions associated with the vadose zone and unconfined aquifer systems at the Hanford Site. The K_d range listed for $^{234/235/238}\text{U}$ by Cantrell et al. will be used in the data package for the 2005 IDF PA. Of note is the fact that K_d values for U(VI) in vadose zone sediments affected by waste leachate may be lower than the range 0.2 to 4 mL/g that Cantrell et al. (2003) recommended for background Hanford geochemical conditions. More discussion is found in Section 6.0.

3.8 Other Studies of Potential Interest

The DOE and its contractors at the Hanford Site have funded numerous studies pertaining to the geochemical processes affecting the sorption and migration of contaminants in the sediments and groundwater at Hanford. Many of these studies are cited in the geochemistry summaries provided above, which focus on geochemical processes and studies pertaining primarily to conditions and contaminants of interest with respect to the IDF.

During the past few years, the results of several contaminant geochemistry studies unrelated to the IDF also have been published. These studies were typically supported by DOE through its Environmental Management Science Program (EMSP), Hanford Science and Technology (S&T) Program within the Groundwater/ Vadose Zone Integration Protection Project, and Hanford Site contractors, such as CH2M HILL. These studies may be of interest to the reader and may have potential relevance to the performance assessment calculations in ways unforeseen at this time. The majority of these studies focus on understanding the geochemical interactions when highly caustic and highly saline Hanford tank waste solutions contact vadose sediments and the impact of these reactions on contaminant mobility. These studies are simply listed below without summary or critique, and include the following experimental and modeling studies:

- Identifying sources of subsurface contamination from isotopic measurements – Christensen et al. (2004) and Maher et al. (2003)
- Biochemical processes at groundwater-surface water boundaries – Moser et al. (2003)
- Geomicrobiology of waste-contaminated vadose sediments – Fredrickson et al. (2004)

- Reactions of simulated Hanford tank solutions (i.e., highly alkaline NaNO₃ solutions) with vadose zone sediments – Bickmore et al. (2001), Flury et al. (2004), Nyman et al. (2000), Qafoku et al. (2003a, c, 2004), Um et al.,^(a) Wan et al. (2004a, b), Zhao et al. (2004)
- Radionuclide sorption behavior and sediment reactions associated with interaction of simulated Hanford tank solutions with vadose zone sediments
 - Cesium – Chorover et al. (2003), Flury et al. (2002, 2004), Liu et al. (2003a, b, 2004), McKinley et al. (2001, 2004), Steefel et al. (2003), Zachara et al. (2002b), Zhuang et al. (2003)
 - Chromium(VI) – Qafoku et al. (2003b), Zachara et al. (2004)
 - Iodine(-I) – Um et al.^(a)
 - Selenium(VI) – Um et al.^(a)
 - Strontium – Chorover et al. (2003), Um et al.^(a)
 - Technetium(VII) – Um et al.^(a)

(a) Um W, SD Samson, RJ Serne, SB Yabusaki, and KL Nagy. “The effects of secondary mineral precipitates on radionuclide transport and sequestration at the Hanford Site.” Submitted to *Environmental Science and Technology*.

4.0 Approach

The geochemical data for both the near and far fields are organized into nine lookup tables, one for each environmental zone that was chosen to represent the pathway for contaminant release from the IDF to the Columbia River. It is important to understand that the current disposal baseline for the IDF is two large football field-sized disposal cells into which various solid wastes (ILAW glass, various solid and solidified low-level radioactive wastes, various solid mixed wastes, and spent glass melters) will be placed. The following is a brief description of the IDF facility taken from Puigh (2004). The interested reader is referred to Puigh (2004) for more information.

The proposed IDF will be located on the ILAW site southwest of the 200 East Area's PUREX facility on the Hanford Site. The facility's trench design is an expandable lined landfill approximately 410 m wide and up to 13.2 m deep. The length of the trench, oriented in the north-south direction, will be divided into two distinct cells, each of which can be expanded to accommodate waste receipts during its operational life. The design includes sloped (3:1) side walls for the trench. The landfill will be divided lengthwise (north-south orientation) into two distinct cells. The easternmost, Cell 2, will contain the low-level radioactive waste (ILAW glass from the WTP). Cell 1 will contain a mixture of waste types (ILAW glass, supplemental technology vitrified wastes [bulk vitrified wastes], "traditional" solid wastes [low-level and mixed low-level], secondary wastes from vitrification off-gas scrubbing systems and spent melters). Each cell is designed to meet the Resource Conservation and Recovery Act (RCRA) liner requirements with leachate collection and leak detection systems. The leachate collection system includes two RCRA compliant liners [including high-density polyethylene (HDPE) geomembrane and admix drainage layers], each associated with sumps, pumps, and leak-detection equipment. The IDF trench design includes backfilled native sandy soil around and on top of the waste containers in the facility. The closure plan is to cover the landfill with a modified RCRA Subtitle C barrier. The barrier is designed to prevent intrusion and to provide hydrologic protection and containment for a performance period of 500 years. The barrier overhang will extend beyond the edge of the IDF trench. The surface barrier has not yet been designed for the IDF but is expected to include various layers of coarse and fine sediments, asphalt, asphaltic concrete, and a surface topsoil in which mixed perennial grasses, shrubs, and sagebrush will be planted. Beneath the surface barrier, a sand-gravel capillary break is assumed that will divert away from the trench any moisture that may come through the surface barrier. The various barriers are intended to minimize the amount of water that enters the trench.

The physical, chemical, and radiological properties of the waste at the time of disposal have not been completely determined. The WTP ILAW glass waste form is expected to be contained in right circular, steel cylindrical containers (1.22 m diameter by 2.29 m tall). The spent melters will be overpacked, likely with carbon steel that provides the necessary shielding, contamination control, and structural rigidity to allow direct burial of the spent melters as MLLW. For this risk assessment, it is assumed that a 1-inch-thick steel rectangular overpack is used for the LAW melters, and both the LAW and HLW melters are assumed to be grouted into their respective overpacks. The waste package designs that will be used to dispose of LLW and MLLW solid wastes in the IDF are not known, but likely will include 55 gallon drums and steel waste burial boxes. For the 2005 IDF performance assessment, we have assumed that all the WTP supplemental technology waste is processed by the bulk vitrification (BV) process. The BV waste package geometry has not been finalized. The preliminary waste package design assumes a rectangular box having dimensions of 2.4 m (H) x 7.5 m (L) x 3.0 m (W) (8' x 24' x 10'). The loading of

waste into each IDF cell is assumed to be in “close pack array” layers called lifts. The planning lift thickness corresponds to the waste stack height (typically 2.3 m) and cover soil layer (typically 1 m). The current planning is to locate spent melters on the bottom lift (Lift 1).

Our assumption is that Cell 2, containing ILAW glass waste, will generate a leachate whose chemistry is dominated by the ILAW waste glass. The chemical composition of the ILAW glass leachate was determined for the 2001 ILAW PA and is described in more detail in Section 6. The other cell, Cell 1, with all the waste types, could generate several types of leachates that at this time have not been investigated or measured. For the 2005 IDF PA, we assume three scenarios are possible. The first is that leachate from Cell 1 is also dominated by ILAW glass dissolution and that subsequent interactions with the vadose zone are the same as described for Cell 2. The second scenario is that the leachate from Cell 1 is dominated by cement dissolution in the near-field vadose zone sediments below the IDF facility. The third scenario is that Cell 1, and for that matter Cell 2 also, contains no significant quantities of dissolved species, and thus its major constituent chemistry is assumed to be that of native vadose zone pore water, which is similar to natural Hanford groundwater. The features of all the conceptual geochemical zones are presented in Tables 4.1 through 4.3. The tables assume that the entire vadose zone is either completely impacted by waste leachate or is not impacted at all. Should the vadose zone pore waters outside of the IDF facility itself be partially waste-leachate impacted, then the appropriate Zones 2a, 2b, and 3a can be added as appropriate to cover specific depth ranges. The appropriate K_d and empirical solubility concentration values for each zone are found in Section 5 and designated in Tables 4.1 through 4.3.

Table 4.1. Conceptual Features of the Geochemical Zones for the IDF Cell 1 that Contains all Types of IDF Wastes and Has Leachate Dominated by Cement

Zone (Data Table)	Solid Phases	Aqueous Phase	Geochemical Parameters Used in Zone
Zone 1b – Cementitious Secondary Wastes and Near Field (Tables 5.3 and 5.4)	Three assemblages of cementitious minerals will exist, based on cement age; fresh cement with pH = 12.5, moderately aged cement with pH ~10.5, and completely aged cement with pH ~ 8.5	Three types of concrete leachate chemistries controlled by different aged solid phases: young concrete leachate pH 12.5, then pH 10.5, final pH 8.5; generally high in ionic strength and high radionuclide concentration	K_d , empirical solubility concentration limits
Zone 2a – Chemically Impacted Far Field in Sand Sequence (Table 5.5)	Sand-dominated sequence, slightly altered because of contact with moderately caustic aqueous phase	pH 8 (background) to 11, ionic strength 0.01 (background) to 0.1, low radionuclide concentration	K_d
Zone 3a – Chemically Impacted Far Field in Gravel Sequence (Table 5.7)	Same as zone 2a, except in gravel-dominated sequence	Same as zone 2a, except in gravel-dominated sequence	K_{dgc}
Zone 4 – Far Field in Gravel Sequence (Table 5.8)	Unaltered Hanford Site gravel sequence (90% gravel, 10% <2mm)	Unaltered Hanford Site groundwater, except for trace levels of radionuclides	K_{dgc}
Zone 5 – Unconfined Far Field Aquifer Conditions (Table 5.9)	Sand-dominated sequence, not altered by composition of leachate from wastes	pH ~8 (background), ionic strength 0.01 (background) to 0.1, except for possible trace levels of radionuclide concentrations	K_d

Table 4.2. Conceptual Features of the Geochemical Zones for the IDF Cell 1 that Contains all Types of IDF Wastes and Has Leachate Outside IDF Dominated by Natural Recharge Water. (Leachate from waste does not contain significant concentrations of macro constituents. If there is some impact from the leachate, Zones 2a, 2b, and 3a should be added as appropriate.)

Zone (Data Table)	Solid Phases	Aqueous Phase	Geochemical Parameters Used in Zone
Zone 1a – Vitrified Wastes and Near Field (Tables 5.1 and 5.2)	Glass, secondary phases formed from glass degradation, and backfill and engineered barrier materials	Glass leachate: high pH, high ionic strength, high radionuclide concentrations	K_d , empirical solubility concentration limits
Zone 1b – Cementitious Secondary Wastes and Near Field (Tables 5.3 and 5.4)	Three assemblages of cementitious minerals will exist, based on cement age; fresh cement with pH = 12.5, moderately aged cement with pH ~10.5, and completely aged cement with pH ~ 8.5	Three types of concrete leachate chemistries controlled by different aged solid phases: young concrete leachate pH 12.5, then pH 10.5, final pH 8.5; generally high in ionic strength and high radionuclide concentration	K_d , empirical solubility concentration limits
Zone 2b – Far Field in Sand Sequence with Natural Recharge (no impact from wastes) (Table 5.6)	Sand-dominated sequence, not altered because leachate from solid wastes contains insignificant concentrations of leached material	pH ~8 (background), ionic strength 0.01 (background) to 0.1, low radionuclide concentration	K_d
Zone 3b –Far Field in Gravel Sequence (Table 5.8)	Same as zone 2b, except in gravel-dominated sequence	Same as zone 2b, except in gravel-dominated sequence	K_{dgc}
Zone 4 – Far Field in Gravel Sequence (Table 5.8)	Unaltered Hanford Site gravel sequence (90% gravel, 10% <2mm)	Unaltered Hanford Site groundwater, except for trace levels of radionuclides	K_{dgc}
Zone 5 – Unconfined Far Field Aquifer Conditions (Table 5.9)	Sand-dominated sequence, not altered by composition of leachate from wastes	pH ~8 (background), ionic strength 0.01 (background) to 0.1, except for possible trace levels of radionuclide concentrations	K_d

Schematic representations of the various zones for disposal Cell 1, which contains all the waste forms, are presented in Figures 4.1 and 4.2 for various scenarios. Figure 4.3 is a third schematic representation for zones associated with the disposal cell that contains only ILAW glass or for the cell with mixed waste types that has leachate dominated by glass.

Each look-up table contains “empirical” K_d and/or solubility concentration limit values. For each contaminant in each environmental zone, a most-probable estimate, a reasonable lower-bounding estimate, and a likely range of estimates are provided for the K_d values. The distribution for all contaminant-specific K_d parameters and empirical solubility concentration limits is assumed to be normally distributed about the most probable value for stochastic modeling. For each data entry, comments and references are provided to support the values.

One class of reactions that is not accounted for in the look-up tables is complexation of metal-like radionuclides with organic ligands that are formed when cellulosic (e.g., wood, paper, and cardboard) and other organic wastes (e.g., clothing, plastics, and rubber) degrade. These types of materials were not present in the past ILAW disposal facility. It is also not clear at this point whether large enough masses

Table 4.3. Conceptual Features of the Geochemical Zones for Cell 2 that Contains ILAW Glass Only or Cell 1 that has Leachate Dominated by Glass Throughout Vadose Zone. (If the vadose zone is not impacted by glass leachate, Zones 2a and 3a are replaced by Zones 2b and 3b.)

Zone (Data Table)	Solid Phases	Aqueous Phase	Geochemical Parameters Used in Zone
Zone 1a – Vitrified Wastes and Near Field (Tables 5.1 and 5.2)	Glass, secondary phases formed from glass degradation, and backfill and engineered barrier materials	Glass leachate: high pH, high ionic strength, high radionuclide concentrations	K_d , empirical solubility concentration limits
Zone 2a – Chemically Impacted Far Field in Sand Sequence (Table 5.5)	Sand-dominated sequence, slightly altered because of contact with moderately caustic aqueous phase	pH 8 (background) to 11, ionic strength 0.01 (background) to 0.1, low radionuclide concentration	K_d
Zone 2b – Far Field in Sand Sequence with Natural Recharge (no impact from wastes) (Table 5.6)	Sand-dominated sequence, not altered because leachate from solid wastes contains insignificant concentrations of leached material	pH ~8 (background), ionic strength 0.01 (background) to 0.1, low radionuclide concentration	K_d
Zone 3a – Chemically Impacted Far Field in Gravel Sequence (Table 5.7)	Same as Zone 2a, except in gravel-dominated sequence	Same as zone 2a, except in gravel-dominated sequence	K_{dgc}
Zone 3b – Far Field in Gravel Sequence (Table 5.8)	Same as zone 2b, except in gravel-dominated sequence	Same as zone 2b, except in gravel-dominated sequence	K_{dgc}
Zone 4 – Far Field in Gravel Sequence (Table 5.8)	Unaltered Hanford Site gravel sequence (90% gravel, 10% <2mm)	Unaltered Hanford Site groundwater, except for trace levels of radionuclides	K_{dgc}
Zone 5 – Unconfined Far Field Aquifer Conditions (Table 5.9)	Sand-dominated sequence, not altered by composition of leachate from wastes	pH ~8 (background), ionic strength 0.01 (background) to 0.1, except for possible trace levels of radionuclide concentrations	K_d

of such materials will be present in the LLW and MLLW solid wastes to be disposed in Cell 1 of the IDF facility to significantly affect the fate of contaminants that leach and interact with the subsurface at Hanford. Discussions with informed staff working on the IDF PA led to a fairly strong consensus that this potential “enhanced migration” issue has a very low probability of impacting IDF. However, for completeness, the available literature on the impacts of organic degradation products on nuclear waste constituents leached from buried wastes will be reviewed, critically analyzed, and discussed in the next geochemical data package cycle. For the 2005 IDF PA, no consideration of this organic ligand enhanced mobility issue has been taken.

Whenever possible, the estimates provided in these tables were based on Hanford Site-specific experiments. Values are included for measurements actually completed using sediment samples from IDF boreholes. For example, Kaplan et al. (1998c) measured radionuclide K_d values using sediment from 299-E17-21. More recently, Um et al. (2004) completed a series of experiments to determine the linearity and reversibility of Γ adsorption onto Hanford formation sediment from the ILAW borehole #2 (well 299-

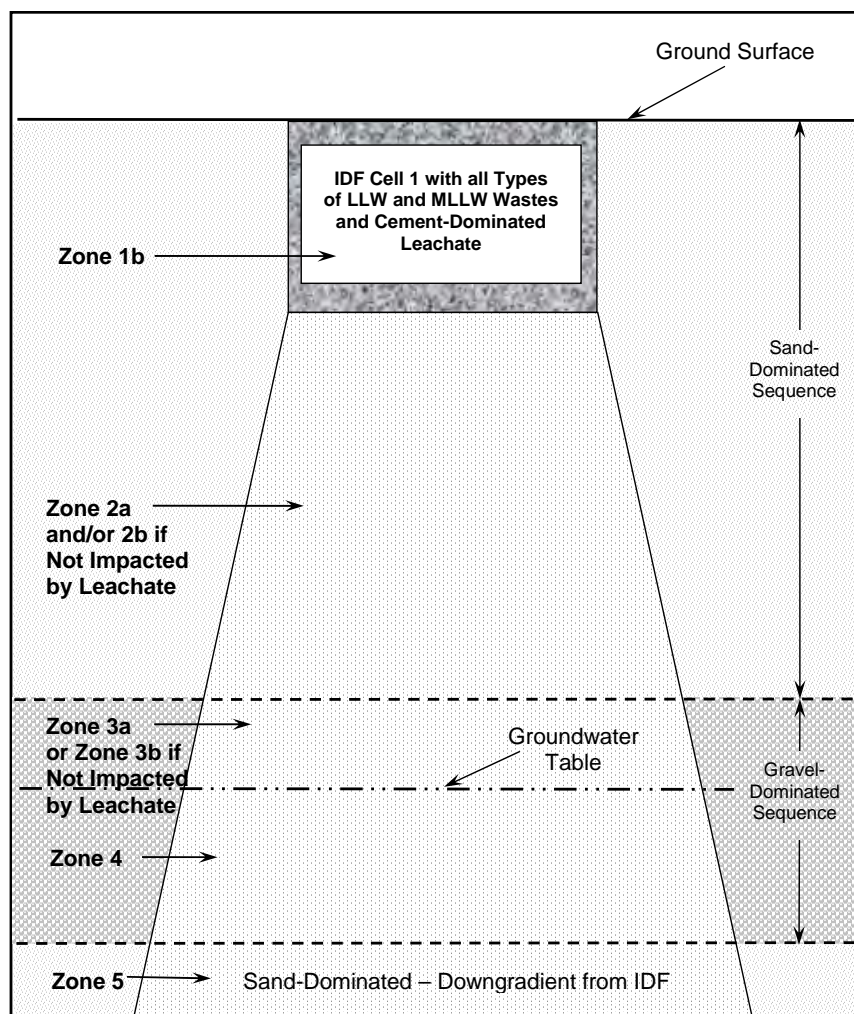


Figure 4.1. Schematic Representation (not to scale) of the Geochemical Zones for an IDF Cell (Cell 1) that Contains all Types of Wastes and Has a Pore Fluid Dominated by Cement Leachate in Portions of Vadose Zone

E24-21, borehole C3177). Um and Serne^(a) also completed a series of batch and column adsorption studies for ⁹⁹Tc, ¹²⁹I, ⁷⁵Se (as a surrogate for ⁷⁹Se), and ⁹⁰Sr on sediments from ILAW borehole #2 (C3177). Serne et al. (2002a) presents data on U(VI) K_d values for a Hanford formation coarse-grained sediment from the 300 Area that is similar in texture, mineralogy, and other geochemical parameters to Hanford formation sediments obtained at the IDF site. Of particular note is the fact that the study by Serne et al. (2002a) used coarse-grained sediments that included the natural gravel content (1.80 wt%) and thus no gravel correction factors would be necessary excepting for zones within the IDF sediments that contain substantially larger percentages of gravel.

Generic literature or offsite data were used when site-specific data were not available. Careful selection of generic literature K_d values was required to ensure that the experimental conditions used to

(a) Um W and RJ Serne. 2004. "Sorption and Transport Behavior of Radionuclides in the Proposed Low-Level Radioactive Waste Disposal Facility at the Hanford Site, Washington." Submitted to *Radiochimica Acta*.

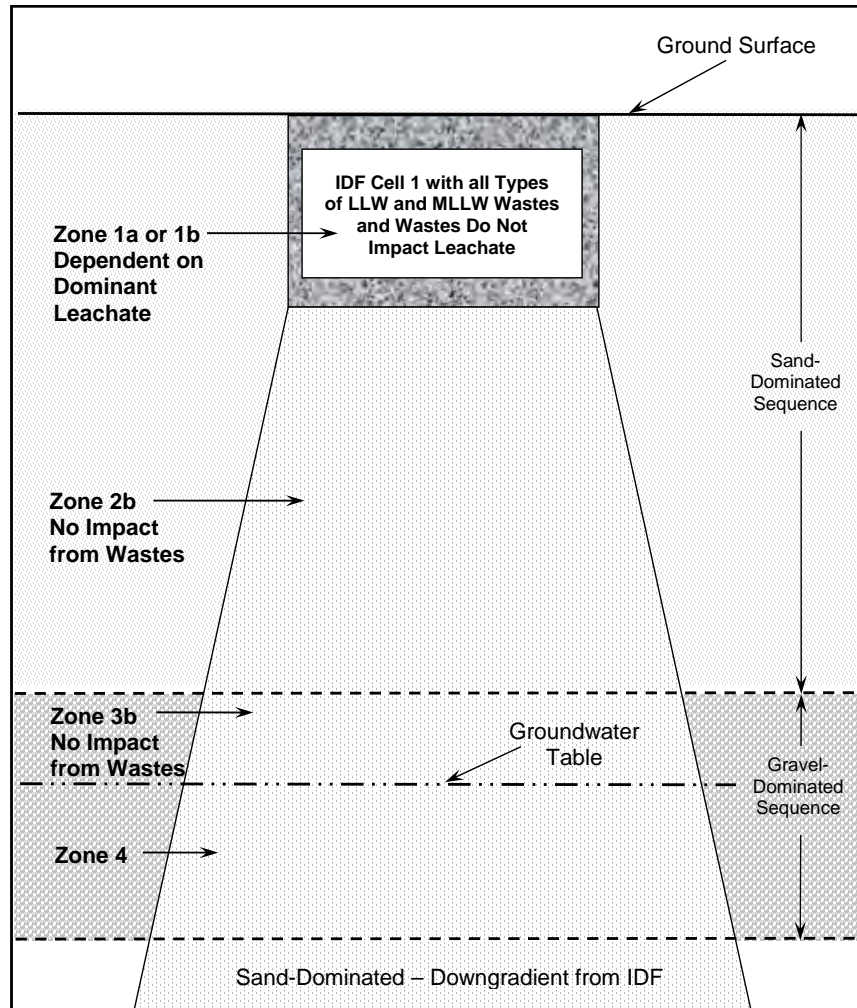


Figure 4.2. Schematic Representation (not to scale) of the Geochemical Zones for an IDF Cell (Cell 1) that Contains all Types of Wastes and Has Pore Fluid Dominated by Natural Recharge and Wastes that Do Not Leach to any Significant Extent

generate the K_d values were appropriate for the IDF-specific zones. Consequently, expert opinion and geochemistry experience were used where non-site-specific data were used; rationale and experimental evidence to support the expert opinion are provided. In some cases, there were no generic data available and we were forced to use “expert judgment” to estimate values. The estimated values that have no actual measurements to defend the choices are identified.

Based on boreholes 299-E17-21 and 299-E24-21 and the geology data package (see Reidel 2004), the stratigraphy below the IDF site has two general sequences, a sand-dominated sequence that is divided into three layers (from shallow to deep L3, L2, L1) that exists from ~0 to 75 m below the surface, and a gravel-dominated sequence that exists from ~75 to ~145 m below the surface (Reidel et al. 1998). The sand-dominated sequence (with the three designated layers L3, L2, and L1) has essentially no gravel, except for a few thin gravel lenses (Reidel et al. 1998). The deeper gravel-dominated sequence consists of ~90% gravel. Gravel-corrected K_d values (g in Equation 2.6 = 0.9) were used for radionuclides in the gravel-dominated sequence (Zones 3a, 3b, and 4 in Tables 4.1 and 4.2). Little information is available

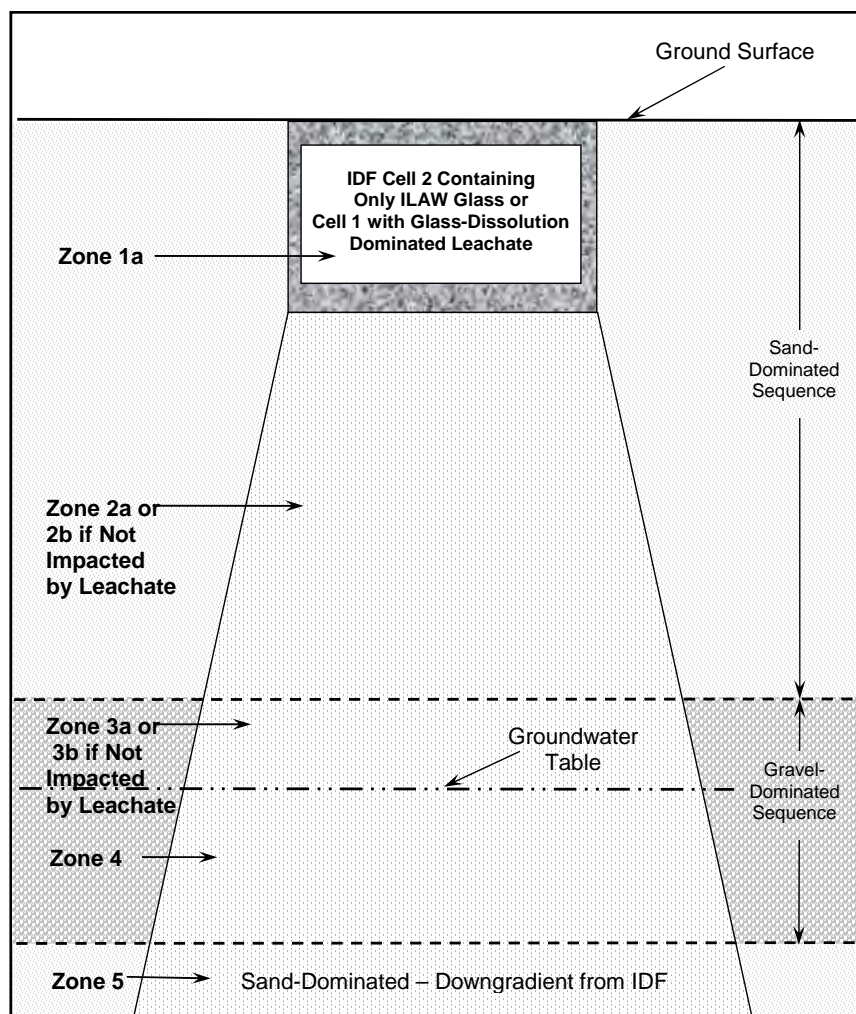


Figure 4.3. Schematic Representation (not to scale) of the Geochemical Zones for an IDF Cell (Cell 2) that Contains Only ILAW Glass or Glass-Dominated Cell 1 and Has Pore Fluid in Portions of Vadose Zone Dominated by Leachate from Glass Dissolution. (If impact from leachate does not affect entire vadose zone, Zones 2b and 3b are inserted as appropriate.)

about the properties and distribution of a mud layer that may exist within the gravel-dominated sequence at ~110 to 135 m below the ground surface. Unique K_d values will not be assigned to this potential layer. This is a conservative simplification because reducing (sulfide odor is associated with some core samples) clays in this zone likely have a large sorption capacity as a result of a large cation-exchange capacity and surface area and a large potential for reductive precipitation. If this reducing mud layer were found to be present in a large area underneath the IDF site, it would warrant more attention, especially for the fate of the high-dose redox-sensitive contaminants, such as neptunium, selenium, technetium, and uranium, discussed in Section 3.0.

The conceptual details of each of the geochemical zones shown in Figures 4.1 through 4.3 are described below.

Zone 1a – Near-Field/Vitrified Waste: The chemistry in this zone is dominated by the presence of glass leachate until all the glass has dissolved, which, based on the 2001 ILAW PA, is well beyond 10,000 years. Glass leachate has high pH (~9.5), ionic strength (especially dissolved sodium and borate and dissolved carbonate/bicarbonate from equilibrating with atmospheric carbon dioxide), and radionuclide activity.

Radionuclide behavior in this zone is affected by unique solid phases dominated by glass, its weathering products, and backfill/engineered barrier materials. No contaminant adsorption will be considered on the glass. As reaction time increases, radionuclides will be incorporated and coprecipitated into secondary phases formed from glass dissolution. Accounting for these processes will be closely linked with the glass waste-form leaching data package (McGrail et al. 1999; Pierce et al. 2004). For the 2001 ILAW PA, no credit was taken for the coprecipitation of contaminants into the weathered glass secondary phases because adequate quantitative data for secondary minerals formed on the new British Nuclear Fuels Limited (BNFL) glass formulations had not been obtained. The long-term stability of the weathering products found in the short-term hydrothermal (90°C) tests had also not been determined at that time. Recent studies by Mattigod et al. (1998, 2002, 2003) on secondary phases formed from weathering other glass recipes indicate that the coprecipitation process for trace contaminants into the zeolites and clays that may occur. However, our understanding of the long-term fate of contaminants sequestered in newly formed secondary minerals from glass weathering is still incomplete, such that we will continue to recommend in the 2005 IDF PA that no credit be taken for sequestration via coprecipitation of contaminants in secondary minerals. The Subsurface Transport Over Reactive Multiphases (STORM) simulator (McGrail and Bacon 1998; Bacon et al. 2004) is being used to simulate contaminant release rates from the near field of the disposal facility for input to the ILAW and IDF performance assessments. If STORM calculations for the 2005 IDF PA suggest that discrete “pure” phase contaminant minerals form, for example U(VI) silicates, then credit should be taken because the stability of such minerals is better understood than mixed solid phase coprecipitates consisting of common major constituents and trace contents of contaminants of concern. The K_d values and empirical solubility concentration limits in Zone 1a are found, respectively, in Tables 5.1 and 5.2.

Zone 1b – Near Field/Cementitious Secondary Waste: The chemistry in this zone is dominated by the presence of cement leachate and weathered cement minerals/compounds, which have high pH, moderate ionic strength, and high-to-moderate radionuclide activity. The cement leachate chemistry will change with time as the cement degrades and weathers. The assemblage of secondary minerals that form is different from that formed from glass degradation; thus, the radionuclide behavior is expected to differ from Zone 1a. Zone 1b also will contain backfill materials. The K_d values and empirical solubility concentration limits in Zone 1b are found, respectively, in Tables 5.3 and 5.4

The cement weathering times discussed in Krupka and Serne (1998) and Bradbury and Sarott (1995) were used to develop look-up tables for both K_d values (onto degraded concrete/aggregate) and solubilities (in cement pore waters and leachates) as a function of time. Three temporal environments are considered: fresh cement with pH 12.5, moderately aged cement with pH ~10.5, and completely aged cement with pH ~8.5. It is possible that the glass leachate will maintain a basic pH condition for tens of thousands of years such that only the first two time-dependent chemistries will be experienced in the IDF PA system conceptual model.

The convention of Bradbury and Sarott (1995) for the three types of physicochemical environments through which all cements and concretes progress was used for the development of a preferred database of K_d values and empirical solubility concentration limits. The following text describing the three temporal environments was taken from Krupka and Serne (1998).

Temporal Environment I: This environment occurs immediately after the cement hardens and is wetted by infiltrating water. The cement pore water is characterized as having a high pH (>12.5), high ionic strength, and high concentrations of potassium and sodium resulting from the dissolution of alkali impurities in the clinker phases. The high concentration of sodium is sometimes augmented by the dissolution of inorganic salts that have been solidified and buried in the disposal facility. Hydration is still continuing during Temporal Environment I with the formation of C-S-H gel (i.e., the CaO-SiO₂-H₂O amorphous material that hardens and constitutes “cement”) and portlandite [Ca(OH)₂]. The composition of the cement pore fluid is at equilibrium with portlandite during this time. The duration of Temporal Environment I is relatively short when compared to the later “environments.” Based on the modeling estimates discussed in Berner (1992), this environment may last for the first 100 to 10,000 years dependent on the rate of water influx. We proffer that for the IDF, Temporal Environment I will last for 5,000 to greater than 10,000 years in the very near field around cement-solidified wastes because recharge water rates will be quite low as controlled by the IDF surface cover.

Temporal Environment II: During this period, the soluble salts of the alkali metals are all dissolved. The pH of the cement pore water is initially controlled at a value of 12.5 by the solubility of portlandite, but decreases to 10.5 after portlandite is consumed. The C-S-H and portlandite are the major solid phases present. Temporal Environment II may last for a long time, and its duration depends on how much water percolates through the system and the mass of cement present in the disposal facility. The flux of water must dissolve all the slightly soluble portlandite before this environment changes. Using the estimates from Berner (1992), this environment may last from 100 to 10,000 years to 1,000 to 100,000 years. We proffer that for the IDF, Temporal Environment II will last for greater than 10,000 to 50,000 years in the very near field around cement-solidified wastes because recharge water rates will be quite low as controlled by the IDF surface cover.

Temporal Environment III: The concentration of portlandite has been reduced to such an extent by this period that the solubility of C-S-H now controls the pH of the cement pore fluid. The C-S-H starts to dissolve incongruently with a continual decrease in pH. At the end of this evolution, Temporal Environment III can be conceptualized as leaving only silica (SiO₂) as the solubility control for the pore fluid pH. The ionic strength of the cement pore fluid during this period is low and its initial pH is ~10.5 or less. For simplicity, the final end point of Temporal Environment III can be considered somewhat analogous to the geochemical conditions of the “normal” ambient soil environment. Of the three “environment” types, the duration of Temporal Environment II is thus the longest in which the pore fluid composition is influenced by the hydration and dissolution reactions of the cement components. We proffer that, for the IDF, Temporal Environment III will not occur until at least 10,000 years has elapsed in the very near field around cement-solidified wastes because recharge water rates will be quite low, controlled by the IDF surface cover. The end state of Temporal Environment III (essentially ambient sediment conditions) may never be reached in the near field of the IDF or even the entire vadose zone because of the impacts of slow dissolution of the ILAW glass. That is, the entire vadose zone under the IDF may always be slightly alkaline (pH ~9), dominated by sodium, soluble boron, and bicarbonate as opposed to normal ambient

vadose zone pore waters that are dominated by calcium, magnesium, bicarbonate and sulfate. (See Serne et al. [2002a, 2004b] for background chemical compositions of Hanford sediment vadose zone pore waters.)

Zone 2a – Chemically Impacted Far Field in Sand Sequence: The chemistry in this zone has been impacted primarily by the ILAW glass leachate, such that the pore water has a moderate pH between 8 (background) and 9.5, a moderate ionic strength between 0.01 (background) to 0.1, and low radionuclide activity (below empirical solubility concentration limits). This zone contains moderately altered Hanford formation sediment. This zone starts at the outside edge of the near-field IDF-impacted Zones 1a and 1b and ends at the start of the gravel-dominated sequence (Zone 3a) (e.g., see Figure 4.1). Contaminants will be controlled primarily by adsorption and not solubility constraints. Empirical solubility concentration limits in this zone should be considered if additional information becomes available that supports doing so. If the glass leachate and cement waste from leachates do evolve to less basic and lower ionic-strength chemical solutions at long times, then the K_d values in Zone 2a will approach those for Zone 2b. The K_d values in Zone 2a are found in Table 5.5, which shows K_d values for less than 2-mm sized sediments.

Zone 2b – Far Field in Sand Sequence with Natural Recharge: The chemistry in this zone is assumed to not be affected by the leachates from solid waste or solidified concrete waste packages. The recharge water percolating around and through the IDF cell containing solid and cement-solidified wastes (Figure 4.2) resembles background vadose zone pore water laden with small concentrations of contaminants. The pore water has a moderate pH ~8 (background), a moderate ionic strength between 0.01 (background) to 0.03, and low radionuclide activity (below empirical solubility concentration limits). This zone starts at the outside edge of the near-field IDF-impacted Zones 1a and 1b and ends at the start of the gravel-dominated sequence (Zone 3a [Figures 4.1 and 4.3] or Zone 3b/4 [Figure 4.2] dependent upon which IDF cell is being described). Contaminants will be controlled primarily by adsorption and not solubility constraints. The K_d values in Zone 2b are found in Table 5.6, which shows K_d values for less than 2-mm sized sediments for natural Hanford Site groundwater.

Zone 3a – Chemically Impacted Far Field in Gravel Sequence: The chemistry in this zone has been affected by leachates from the glass wastes and perhaps cement waste forms (if large quantities are emplaced in IDF), such that its pore water has a moderate pH between 8 (background) and 10, a moderate ionic strength between 0.01 (background) to 0.1, and low radionuclide activity (below empirical solubility concentration limits). This zone exists in the gravel-dominated sequence. The K_d values in this zone will be identical to those for Zone 2a, except that the K_d values are gravel-corrected. If the glass leachate and cement waste form leachates do evolve to less basic and lower ionic-strength chemical solutions at long time frames, then the K_d values in Zone 3a will approach those for Zone 4 at some future time. If the surface covers work as expected even during alteration back to natural sediment conditions, then infiltration rates are likely to be too low to completely leach and weather the glass and cementitious waste forms to their final aged state where they would meld mineralogically and chemically to ambient sediments. The gravel-corrected K_{dgc} values in Zone 3a are found in Table 5.7.

Zone 3b and 4 – Far Field in Gravel Sequence: Zone 3b (Figure 4.2) is located above the water table and Zone 4 (all figures in Section 4) is located below the water table. Both zones are in the 90% gravel-dominated sequence found below the IDF reserved portion of the Hanford Site (see Reidel 2004 for more discussion). The groundwater and non-impacted vadose zone pore water are assumed not to be impacted significantly by major constituents that leach from the waste forms, and thus the concentrations of major

solutes are present at natural background levels. The water in this zone is assumed to be “significantly tainted” only by contaminants and not by major common constituents from leachates of the glass and/or cement waste forms. Hanford Site groundwater is dominated by calcium and bicarbonate and has a pH of 8 and an ionic strength of 0.005 to 0.01 M. The K_d values in the look-up table for this zone will remain constant with time. This is equivalent to assuming that the salts emanating from Zones 1a and 1b have been completely removed by the geomedia or diluted to insignificant levels when compared to natural groundwater by the time the solution reaches Zones 3b and 4. This is equivalent to assuming that the groundwater flow is sufficiently large that it will dilute IDF leachates to the point that no competitive effects exist from the waste form leachates. The K_{dgc} values in Zones 3b and 4 can be considered to be time invariant in our conceptual model and are listed in Table 5.8.

Zone 5 – Unconfined Far-Field Aquifer: This environment is found deep in the unconfined aquifer under the IDF facility and farther downgradient toward the Columbia River in the upper unconfined aquifer. We assume that the groundwater flow is sufficiently large that it will dilute IDF leachates to the point that no competitive effects exist from the waste form leachates. The K_d values in the unconfined aquifer can be considered to be time invariant in our conceptual model. The K_d values for the ambient unconfined aquifer in sand dominated (or at least gravel with less than 90% greater than 2-mm sized particles) sediments are found in Table 5.9.

5.0 Summary Tables

Geochemical input values for the geochemical zones described in Tables 4.1 through 4.3 and illustrated schematically in Figures 4.1 through 4.3 are presented in Tables 5.1 through 5.9, respectively. For Zones 1a and 1b, empirical solubility concentration limits are provided for some contaminants where appropriate. If the near-field solution concentration of a contaminant is above the “solubility limit,” the empirical solubility concentration limit will be used to control the solution concentration; if the solution concentration is below this value, then the K_d values will be used in the retardation factor equation to calculate solution concentrations. Four K_d values are provided in each table cell: a reasonable conservative K_d , a “best” estimate (or most probable) K_d , and upper and lower K_d limits. The reasonable conservative K_d is a reasonable lower-bounding value that takes into consideration potential conditions that may enhance radionuclide migration. This estimate was usually identical to the lower value of the range. For a few situations, the lower limit was not selected as the reasonable conservative K_d value because the lower limit value originated from a questionable experiment or the experimental conditions used to generate the value would yield a lower value than the conditions of the zone of interest merit. The “best” estimates are presented to provide guidance on what the most likely K_d value is for a given condition. This was based primarily on some central value of the literature or laboratory K_d values and on expert judgment. The concept of using a central value, the statistics, and some of the raw data involved in identifying this central value was presented by Kaplan and Serne (1995) for iodine, neptunium, selenium, technetium, and uranium. Newer Hanford- and IDF-specific K_d data have been factored into the choice of the “best” estimate for all contaminants using the same concepts presented in Kaplan and Serne (1995). The range is provided to help in uncertainty estimates and sensitivity analyses. The distribution of K_d values within this range is assumed to be a normal distribution.

For the empirical solubility concentration limits, only reasonable conservative and “best” estimate (or most probable) values are given. No ranges or solubility concentration distributions are given at this time. If the 2005 IDF PA shows that solubility constraints are important, then some effort will be undertaken to improve the uncertainty/sensitivity of future performance assessment calculations. Finally, supporting references for the selection of the various K_d and empirical solubility concentration limits or estimates are provided in the tables.

Table 5.1. K_d Values for Zone 1a - Near Field/Vitrified Waste^(a)

Radio-nuclide	Reasonable Conservative K_d (mL/g)	"Best" K_d (mL/g)	K_d Range (mL/g)	Justification/References ^(b)
³ H, Cl, Tc, Ru, C, N as nitrate, Cr(VI), Nb	0	0	0 to 1	C, Cl, N as nitrate, Cr(VI) as chromate and Tc are anionic. ³ H will move with H ₂ O. Ru has often been suggested as being water coincident in tank leak scenarios based on gamma borehole logging. C as carbonate in high pH tank environments is insoluble and combines with alkaline earths. To account for insolubility a K_d value > 0 is appropriate but to keep C from getting stuck permanently in this source (high impact) zone the value was set at 0 (1, 2, 3, 9, 10). A recent Tc K_d measurement for a synthetic ILAW glass leachate and IDF sand sediment from 299-E24-21 showed 0 mL/g with high reproducibility for triplicate tests (10). Limited information available for geochemical behavior of Nb. Nb expected to be anionic at pH >7; see discussion in Robertson et al. (13).
I	0.04	0.1	0.04 to 0.16	Non-zero K_d values exist for this condition, 1.04 ± 0.02 and 1.07 ± 0.03 mL/g, were measured in Hanford sediments in high pH, high ionic-strength conditions (8). But more recent sorption tests using IDF borehole sediment from 299-E24-21 and a synthetic glass leachate showed K_d values ranged from 0.04 to 0.16. These new values are chosen as most realistic for Zone 1a (10).
Se	0	1	0 to 3	(10) measured the K_d for selenate in synthetic glass leachate onto IDF borehole sediments and found non-zero values consistently for 6 tests. Values ranged from 1 to 3 mL/g with good precision.
Ac, Am, Ce, Cm, Eu	2	5	2 to 10	Estimated (2, 4)
Cs	1	1.5	1 to 25	Based on observations at T-106, ¹³⁷ Cs seemed to peak at ~10 ft below the base (elevation) of the tank and nitrate at ~80 ft. This implies an in situ Rf of ~8 or a K_d value of ~1 or 2 mL/g during the initial tank leak. The lack of cesium in groundwater beneath tanks suggests it has not broken through. (7) measured a K_d of 26 mL/g for simulated REDOX tank liquor. But the results are not consistent with inferred Cs migration using gamma borehole logging at SX tank farm (6).
Co, Ni, Np, Pa, Sn	0.1	0.2	0.1 to 4	Estimated (4).
Sr, Ra	4	15	4 to 70	Here it is assumed that caustic tank liquors are a surrogate for glass and cement leachate. Sr is known to be rather insoluble in tank liquors and does not migrate through soils in tank liquor as rapidly as other cations (4). Using IDF borehole specific sediment and synthetic glass leachate a value of 70 ± 1 mL/g was obtained (10).
Th, Zr, Pb, Pu	5	10	5 to 100	Estimated (2, 4).

Table 5.1. (contd)

Radio-nuclide	Reasonable Conservative K_d (mL/g)	"Best" K_d (mL/g)	K_d Range (mL/g)	Justification/References ^(b)
U	0.05	0.2	0 to 800	See Section 6.2 for details that are based on the study of (11). Earlier data in (5) reported U(VI) K_d values increased from ~2 to >500 mL/g when the pH of a Hanford sediment/groundwater slurry increased from 8.3 to greater than 10.5. The extremely high K_d was attributed to U coprecipitation either as uranium phases or as calcite phases. These results however are not relevant for glass leachates that do not contain adequate Ca to allow calcite precipitation. Calcite precipitation decreases the concentration of dissolved carbonate/bicarbonate that forms strong anionic U(VI) carbonate complexes that are highly soluble and resistant to adsorption at slightly alkaline pH values. Glass leachates are projected to be pH ~9 to 9.5 with ~0.034 M inorganic carbon mostly as bicarbonate (12) that will complex dissolved U(VI) lowering the K_d to values well below those reported in (5). For now assume that glass leachate is dominated by sodium bicarbonate/carbonate solution that allows anionic U(VI) carbonate species to predominate and sorption to be very low.
<p>(a) The aqueous phase has a high pH, high radionuclide concentrations, and high ionic strength; the solid phase is dominated by backfill, glass, and glass secondary phases (Figure 4.1). No gravel correction to K_d values.</p> <p>(b) References; 1 = Ames and Rai (1978); 2 = Thibault et al. (1990); 3 = Martin (1996); 4 = Ames and Serne (1991); 5 = Kaplan et al. (1998a); 6 = Hartman and Dresel (1997); 7 = Serne et al. (1998); 8 = Kaplan et al. (1998b); 9 = Um et al. (2004); 10 = Um and Serne (2004, in review); 11 = Serne et al. (2002a); 12 = STORM code predictions of the long-term steady state glass leachate composition. See Section 6.2 for more discussion; 13 = Robertson et al. (2003)..</p>				

Table 5.2. Empirical Solubility Concentration Limits for Designated Solids in Zone 1a - Near Field/Vitrified Wastes^(a)

Radio-nuclide	Reasonable Conservative Empirical Solubility Concentration Limit (M)	“Best” Empirical Solubility Concentration Limit (M)	Justification/References ^(b)
³ H, Cl, Tc, I, Se, Ru, C, N as nitrate and Cr as chromate	---	----	At present, none of these contaminants have solubility constraints in glass leachate. Tc, C, Se, Cl, and I are anionic. ³ H is considered to be present as water. Ru may be present as the RuO ₄ ⁻ .
Ac, Am, Ce, Cm, Eu,	1×10 ⁻⁷	1×10 ⁻⁹	Assume that glass leachate has high pH and is similar to concrete leachates. Concrete leachate solubility values can be realistically applied for hydrous oxide/metal hydroxides being the controlling solid. Solubility of these types solids are dependent almost solely on pH and nothing else in the pore fluids (1, 2, 3)
Cs	----	----	No solubility constraint is expected. But Cs could be incorporated into the glass weathering products. Ignoring this should be conservative but not overly so, seeing as adsorption will prevent Cs from reaching the water table.
Co, Ni	5×10 ⁻⁴	5×10 ⁻⁷	Assume that metal hydroxide is controlling solid and thus pH is the only sensitive variable. There is data for alkaline cement conditions and we will assume they hold for alkaline glass leachates (1, 2, and 3).
Nb, Np, Pa, Sn	5×10 ⁻⁴	5×10 ⁻⁶	Assume that metal hydroxide is the controlling solid. There is empirical data in Ewart et al. (3) that predicts much lower than thermodynamic predictions (1, 2, 3).
Ra	1×10 ⁻⁵	3×10 ⁻⁶	Ra sulfate is the controlling solid. Bayliss et al. (4) found no precipitation for Ra at 10 ⁻⁷ M in concrete leachate.
Sr	2×10 ⁻⁵	1×10 ⁻⁷	Sr carbonate forms in cements (1, 2, 3) but for glass leachates we are not sure. These values may need to be revised or not used in order to be conservative.
Th, Zr, Pb, Pu	5×10 ⁻⁷	1×10 ⁻⁸	Assume solubility controlling phase of hydroxide/hydrous oxides for Th, Zr, Pu and hydroxycarbonates for Pb. There is data for Th and Pu in cement leachates under oxidizing and reducing conditions. We chose the oxidizing conditions (3). Other assessments of these values are presented in (1, 2).
U	1×10 ⁻⁶	----	For the 2005 performance assessment, no empirical solubility concentration limit on glass leachate will be used unless STORM calculations predict a known pure U phase is forming. In the 2001 performance assessment, the STORM calculations did not identify any pure U solid phase for which its solubility was exceeded in the leachates.
(a) The aqueous phase has a high pH, high radionuclide concentrations, and high ionic strength; the solid phase is dominated by backfill, glass, and glass secondary phases (Table 4.3 and Figure 4.3). No gravel correction to K _d values.			
(b) References: 1 = Krupka and Serne (1998); 2 = Brady and Kozak (1995); 3 = Ewart et al. (1992); 4 = Bayliss et al. (1989); 5 = Kaplan et al. (1998a)			

Table 5.3. K_d Values for Zone 1b – Near Field/Cementitious Secondary Wastes^(a)

Radio-nuclide	Young Concrete (pH ~ 12.5)			Moderately Aged Concrete (pH ~ 10.5)			Aged Concrete (pH ~ 8.5)			Justification/References ^(b)
	Conservative K_d (mL/g)	“Best” K_d (mL/g)	K_d Range (mL/g)	Conser-vative K_d (mL/g)	“Best” K_d (mL/g)	K_d Range (mL/g)	Conser-vative K_d (mL/g)	“Best” K_d (mL/g)	K_d Range (mL/g)	
³ H, Tc, N as nitrate and Cr as chromate	0	0	0 to 2	0	0	0 to 2	0	0	0 to 1	Tc and chromate may be slightly sorbed to concrete, albeit, very little (1, 2, 3, 4, 5, 6).
Cl	0.8	8	0.8 to 25	1	2	1 to 5	0	0	0 to 1	Estimated. French sulfate-resistant cement had a Cl K_d of 25 mL/g (7). Cl diffused through cement disks slower than ³ H (8). Cl K_d to cement powder after 24-hr contact time = 0.8 mL/g (9)
I	10	20	10 to 150	5	8	5 to 15	1	2	1 to 5	Iodide K_d values of seven types of concrete samples increased gradually over three months, then leveled off to between 25 and 130 mL/g (10, 11). After 300 days contact with various cements, 77 to 98% iodide and even more iodate sorbed. I sorption to cement is very concentration dependent: at 10^{-8} M I K_d = 1,000 mL/g at 10^{-2} M I K_d = 1.4 mL/g (12). I sorption to cement is highly reversible (12). Iodine K_d in 7 day contact = 2.5 mL/g; after 30 days 7.7 mL/g (13).
C	10	20	10 to 1,000	5	10	5 to 1,000	0	0	0	Carbon-14 chemistry is complicated in cement; C coprecipitation more important process in concrete than adsorption. See solubility discussion in Table 5.4 and (18).
Ac, Am, Ce, Cm, Eu	2,000	5,000	2,000 to 40,000	1,000	5,000	1,000 to 30,000	400	500	400 to 1,000	Trivalent metal K_d values to concrete exceed those to sediments (1). Am K_d >10,000 mL/g (14). Am K_d ~12,000 mL/g based on diffusion tests of cement (15). Am K_d values ranged from 2,500 to 35,000 mL/g for seven fresh (unaged)-concrete blends (10, 11). Am K_d for 65-yr old concrete sample = 10,000 (10, 11). Fresh cement Am- K_d = 2000 for 24-hr contact time (9). Eu- K_d = 2,400 mL/g for 24 hr contact time (9). Very large K_d values may reflect precipitation reactions that occurred during the adsorption measurements (24).
Co, Ni, Ra, Sn	70	100	70 to 250	70	100	70 to 250	7	10	7 to 25	Co- K_d = 4,300 mL/g (9). Ni- K_d for 3 cement types: 500 to 3000 mL/g (16), 1500 mL/g (9), and 500 to 3,000 mL/g (17).

Table 5.3. (contd)

Radio-nuclide	Young Concrete (pH ~ 12.5)			Moderately Aged Concrete (pH ~ 10.5)			Aged Concrete (pH ~ 8.5)			Justification/References ^(b)
	Conservative K_d (mL/g)	“Best” K_d (mL/g)	K_d Range (mL/g)	Conser-vative K_d (mL/g)	“Best” K_d (mL/g)	K_d Range (mL/g)	Conser-vative K_d (mL/g)	“Best” K_d (mL/g)	K_d Range (mL/g)	
Cs	2	3	2 to 5	20	30	20 to 50	20	30	20 to 50	Cs K_d values in hardened HTS cement discs, pH ~13.3, were 3 mL/g (7). Cs K_d values of 0.2 mL/g were measured in hardened sulfate resisting cement (12). Many authors have reported increase sorption at pH ~12.5 (13, reviewed by 23).
Nb	0	40	0 to 6,000	0	40	0 to 3,500	0	4	0 to 600	Nb sorption data limited but suggests high sorption in fresh cement (22, 23).
Np, Pa	1,400	2,000	1,400 to 10,000	1,400	2,000	1,400 to 10,000	140	200	140 to 500	The dominant protactinium species is assumed to be Pa O ₂ ⁺ . NpO ₂ ⁺ is assumed to be a reasonable analog (19). Np sorption test to seven different 65-yr old cements using cement pore water reached steady state after 30 days, K_d values ranged from 1,500 to 9,500 mL/g (10, 11). User is cautioned that very large K_d values may reflect precipitation reactions that occurred during the adsorption measurements (24).
Ru, Se	1	2	1 to 800	1	2	1 to 100	0	1	0 to 300	Estimated. Dominant species for Se and Ru were assumed to SeO ₄ ²⁻ and RuO ₄ ²⁻ respectively (19). Ru K_d values in Hanford sediment (not concrete) did not change systematically with pH; at pH 8.5 the K_d value was 274 mL/g; at pH 10.4, 44 mL/g; and at pH 14, 752 mL/g (21). Using a pH 12 simulated tank waste solution and Hanford sediment, K_d values for Ru ranged from 2.14 to 0 mL/g, averaging ~0.8 mL/g (20). Sulfate may be used as an analog for selenate chemical behavior in concrete. Sulfate (or sulfite) is often included in concrete mixes, and therefore it would be expected to be retained strongly by concrete, primarily by coprecipitation constraints. Selenate adsorption, independent of precipitation processes, would be expected to be rather large.

Table 5.3. (contd)

Radio-nuclide	Young Concrete (pH ~ 12.5)			Moderately Aged Concrete (pH ~ 10.5)			Aged Concrete (pH ~ 8.5)			Justification/References ^(b)
	Conservative K _d (mL/g)	“Best” K _d (mL/g)	K _d Range (mL/g)	Conser-vative K _d (mL/g)	“Best” K _d (mL/g)	K _d Range (mL/g)	Conser-vative K _d (mL/g)	“Best” K _d (mL/g)	K _d Range (mL/g)	
Pb, Pu, Th	1,000	5,000	1,000 to 10,000	1,000	5,000	1,000 to 10,000	100	500	100 to 1,000	Estimated. Using three 65-yr-old crushed concrete samples and seven fresh concrete samples, Th-K _d values were 2,500 to 5,500 mL/g (10, 11). Th-K _d values were: consistently less than Am-K _d values, greater than U-K _d values, and very similar to Np Pu K _d values (10, 11). Pu-K _d values ranged from 1,000 to 12,000 mL/g (10, 11). Concrete containing reducing agents (BFS) did not have greater Pu K _d values than those that did not contain reducing agents. High K _d values are attributed to high solubility of Pu in high pH solutions, not to adsorption/ absorption processes (22).
U	700	1,000	700 to 2,500	700	1,000	700 to 2,500	70	100	70 to 250	U(VI)-K _d values for seven types of cement = 350 to 13,000, average = ~1000 and median = 1,400 mL/g (10, 11).

(a) The aqueous and solid phases in this zone are greatly influenced by the presence of concrete. The concrete is assumed to age and form three distinct environments (Krupka and Serne 1998).

(b) References: 1 = Angus and Glasser (1985); 2 = Gilliam et al. (1989); 3 = Tallent et al. (1988); 4 = Brodda (1988); 5 = Serne (1990); 6 = Serne et al. (1992); 7 = Sarott et al. (1992); 8 = Johnston and Wilmot (1992); 9 = Kato and Yanase (1993); 10 = Allard et al (1984); 11 = Høglund et al. (1985); 12 = Atkinson and Nickerson (1988); 13 = Hietanen et al. (1985); 14 = Ewart et al. (1988); 15 = Bayliss et al. (1991); 16 = Hietanen et al. (1984); 17 = Pilkington and Stone (1990); 18 = Allard et al. (1981); 19 = Pourbaix (1966); 20 = Ames and Rai (1978); 21 = Rhodes (1957a,b); 22 = Krupka and Serne (1998); 23 = Bradbury and Sarott (1995); 24 = EPA (1999a).

Table 5.4. Empirical Solubility Concentration Limits for Designated Solids for Zone 1b - Near Field/Cementitious Secondary Wastes^(a)

Radio-nuclide	Young Concrete (pH ~ 12.5)		Moderately Aged Concrete (pH ~ 10.5)		Aged Concrete (pH ~ 8.5)		Justification/References ^(b)
	Conservative (M)	“Best” Solubility Concentration Limit (M)	Conser-vative (M)	“Best” Solubility Concentration Limit (M)	Conser-vative (M)	“Best” Solubility Concentration Limit (M)	
³ H, ³⁶ Cl, Tc, I, N, Ru, Se	---	---	---	---	---	---	It was assumed that no solubility constraints exist for these species, although there could be some isotope exchange into cement and secondary minerals.
C	10 ⁻⁵	10 ⁻⁶	10 ⁻³	10 ⁻⁴	10 ⁻²	10 ⁻³	Estimated. ¹⁴ C chemistry is complicated in cement; C coprecipitation more important process in concrete than adsorption. Calcite will be a good controlling solid and the ¹⁴ C will be isotopically exchanged with stable C For young concrete assume that portlandite controls Ca to 6 x 10 ⁻³ M. For moderately aged cement and aged cement that the Ca is controlled at 10 ⁻² M by some undefined reactions.
Ac, Am, Ce, Cm, Eu	1x10 ⁻⁷	1x10 ⁻⁹	3x10 ⁻⁷	3x10 ⁻⁸	1x10 ⁻⁵	1x10 ⁻⁷	Known cement values can be realistically applied for hydrous oxide/metal hydroxides being the controlling solid. These solids are dependent almost solely on pH, and nothing else in the pore fluids (1, 2, 3).
Cr	---	---	---	---	---	---	It was assumed that no solubility constraints exist for this species. Though solubility data are not available, a recent characterization study (7) indicated the presence chromate-enriched ettringite (Ca ₆ Al ₂ ((S,Cr)O ₄) ₂ (OH) ₁₂ ·26H ₂ O) and hydrocalumite (3CaO·Al ₂ O ₃ ·CaCrO ₄ ·nH ₂ O) in Cr(VI)-contaminated concrete from a former hard-chrome plating facility.
Co, Ni	5x10 ⁻⁴	5 x 10 ⁻⁷	5x10 ⁻⁴	1x10 ⁻⁶	1x10 ⁻³	2x10 ⁻⁵	Assume that metal hydroxide is controlling solid and thus pH is the only sensitive variable. There is data for alkaline cement conditions and predictions for groundwater (aged cement end member) (1, 2, 3).
Nb, Np, Pa, Sn	5x10 ⁻⁴	5x10 ⁻⁶	1x10 ⁻³	5x10 ⁻⁴	1x10 ⁻³	5x10 ⁻⁴	Assume that metal hydroxide is the controlling solid. There is empirical data in Ewart et al. (3) that predicts much lower than thermodynamic predictions (1, 2, 3).

Table 5.4. (contd)

Radio-nuclide	Young Concrete (pH ~ 12.5)		Moderately Aged Concrete (pH ~ 10.5)		Aged Concrete (pH ~ 8.5)		Justification/References ^(b)
	Conservative (M)	“Best” Solubility Concentration Limit (M)	Conser-vative (M)	“Best” Solubility Concentration Limit (M)	Conser-vative (M)	“Best” Solubility Concentration Limit (M)	
Cs	---	---	---	---	---	---	No solubility constraint is expected.
Ra	1×10^{-5}	3×10^{-6}	1×10^{-5}	3×10^{-6}	1×10^{-5}	3×10^{-6}	Ra sulfate is the controlling solid. Bayliss et al. (4) found no precipitation for Ra at 10^{-7} M in concrete leachate.
Sr	2×10^{-5}	1×10^{-7}	2×10^{-4}	1×10^{-6}	5×10^{-3}	1×10^{-3}	Sr carbonate forms in cements (1, 2, 3) and could be a plausible control in sediments also.
Pb, Pu, Th, Zr	5×10^{-7}	1×10^{-8}	5×10^{-7}	1×10^{-8}	5×10^{-6}	1×10^{-7}	Assume hydroxide/hydrous oxides for Th, Zr, Pu and hydroxycarbonates for Pb. There is data for Th and Pu in cement leachates under oxidizing and reducing conditions. We chose the oxidizing conditions (3). Other assessments of Pb, Pu, Th, and/or Zr solubility under these conditions have been conducted (1, 2).
U	1×10^{-6}	1×10^{-7}	1×10^{-6}	1×10^{-7}	1×10^{-5}	1×10^{-6}	Two reports (1, 2) discuss solubility in cements using U(VI) hydrous oxide [schoepite] and uranophane [calcium U(VI) silicate] as solubility control. Ewart et al. (3) show some empirical data for solubility in cement waters. Kaplan et al. (5) reported U- K_d values increased from ~2 to >500 mL/g when the pH of a Hanford sediment/groundwater slurry increased from 8.3 to > 10.5. The extremely high K_d was attributed to U coprecipitation either as uranium phases or as calcite phases. Serne et al. (6) discusses solubility of U in presence of groundwater.
<p>(a) The aqueous and solid phases in this zone are greatly influenced by the presence of concrete. The concrete is assumed to age and form three distinct environment (Krupka and Serne 1998).</p> <p>(b) References: 1 = Krupka and Serne (1998); 2 = Brady and Kozak (1995); 3 = Ewart et al. (1992); 4 = Bayliss et al. (1989); 5 = Kaplan et al. (1998a); 6 = Serne et al. (1999); 7 = Palmer (2000).</p>							

Table 5.5. K_d Values for Zone 2a - Chemically Impacted Far Field in Sand Sequence^(a)

Radionuclide	Reasonable Conservative K_d (mL/g)	"Best" K_d (mL/g)	K_d Range (mL/g)	Justification/References ^(b)
³ H, Cl, N as nitrate, Cr as chromate, Tc, Nb	0	0	0 to 0.1	Tc, chromate, nitrate and Cl are anionic and under slightly alkaline conditions formed by glass or cement leachates Hanford sediments show very little tendency to adsorb anions. ³ H will move with H ₂ O. Limited information available for geochemical behavior of Nb. Nb expected to be anionic at pH >7; see discussion in Robertson et al. (19).
Ac, Am, Ce, Cm, Eu	100	350	100 to 1,500	Am- K_d values: In low-ionic-strength Ca system, >1200 mL/g; in low-ionic-strength Na system, 280 mL/g (1)
C	5	20	5 to 50	Estimated. ¹⁴ C geochemistry complex and poorly described by K_d construct. ¹⁴ C is expected to enter liquid, solid and gas phase through volatilization (CO ₂ -gas), precipitation with calcite, isotopic exchange, and adsorption. Based on Martin (9), who measured ¹⁴ C- K_d values in Hanford sediments using uncontaminated Hanford groundwater (relatively low ionic strength). ¹⁴ C as H ¹⁴ CO ₃ K_d values increased during a 70 day contact time from 0 (1-hr contact time) to 400 mL/g in sediment and 20 (1-hr contact time) to 360 mL/g in calcite. ¹⁴ C removed by solid phases never stabilized during 70 days, suggesting coprecipitation reaction.
Co	150	300	150 to 2,000	In 0.01 to 1 M Na system, K_d is 1060 to 4760 mL/g (2) In 0.01 to 1 M Ca system, K_d is 222 to 640 mL/g (2) Forms complexes, especially with organics.
Cs	40	80	40 to 2,000	Estimated. In low-ionic-strength Na system, K_d is 64 to 1,170 mL/g (2). No complexes. In low-ionic-strength Ca system, K_d is 790 to 1360 mL/g (2). Unpublished recent results from Zachara (PNNL, EMSP project) using Hanford sediments and simulated tank waste indicate that Cs sorption decreases markedly compared to when ionic strength is appreciably lower.
I	0	0.1	0 to 0.2	Anion. Um and Serne (15) show low but non-zero K_d values that range between 0.04 and 0.16 for synthetic glass leachate contacting a typical IDF borehole sand. Even with additional dilution with native pore waters the pH will be higher than ambient in Zone 2 so the glass leachate values will be used for Zone 2 also.
Ni, Sn	40	80	40 to 400	Ni is similar to Co but adsorbs slightly less possibly because of moderate complexing. Estimated (3, 4)
Np, Pa	0.2	0.8	0.2 to 5	Np K_d values in low-ionic-strength solutions = 0.4 to 4 mL/g (1). The dominant protactinium species is assumed to be PaO ₂ ⁺ . NpO ₂ ⁺ is assumed to be a reasonable analog (10). Based on studies conducted at the Whiteshell Laboratories (personal communications with T. T. (Chuck) Vandergraaf, Atomic Energy of Canada Limited, Pinawa, Manitoba, Canada), Pa sorbs appreciably more than Np. Thus, Pa- K_d estimates based on measured Np- K_d values will be conservative.
Pb	20	100	20 to 1,000	Good absorber, insoluble. Estimated (4).
Pu	80	200	80 to 1,000	K_d is >98 mL/g (5)

Table 5.5 (contd)

Radionuclide	Reasonable Conservative K_d (mL/g)	“Best” K_d (mL/g)	K_d Range (mL/g)	Justification/References ^(b)
Ra, Sr	0.2	10	0.2 to 50	Na system, 1.7 to 42 mL/g for Sr- K_d (2). Ca system, 0.3 to 1.6 mL/g for Sr- K_d (2). In 4 M NaNO ₃ , Sr- K_d in Hanford sediment was 5 mL/g (pH 8), and 10 mL/g (pH 10) (12). Near identical K_d values using Savannah River Site Sediments and 30% NaNO ₃ (13). Based on periodicity considerations, Ra would be expected to sorb more strongly to sediments than Sr, but no Hanford Ra- K_d values are available. Thus, basing Ra- K_d estimates on measured Sr- K_d values will likely provide a conservative Ra- K_d estimate.
Ru	0	1	0 to 500	May form RuO ₄ ²⁻ and/or anionic complexes with nitrates and nitrites. Estimate (3, 6, 7).
Se	1	2	0 to 10	Anionic. Se K_d measured at the ILAW/IDF site had K_d values of 6.7 ± 0.4 mL/g (14). Results of a Se sorption experiment to Hanford sediments in high ionic strength (NaOH and NaOCl ₄) indicate Se K_d values range from 0 to 18 mL/g; but values for 0.03 NaOH are 0 mL/g and are beyond the causticity of probable glass leachates (16). K_d values will be chosen from recent tests on IDF borehole sediments with synthetic glass leachate that yielded K_d values which ranged from 1 to 3 mL/g (15).
Th, Zr	40	300	40 to 500	Sandy soil data, K_d is 40 to 470 mL/g for Th (8).
U	0.05	0.2	0 to 500	See section 6 for details that rely on Serne et al. 2002a (17). Earlier data by Kaplan et al. (11) reported U(VI) K_d values increased from ~2 to >500 mL/g when the pH of a Hanford sediment/groundwater slurry increased from 8.3 to > 10.5. The extremely high K_d was attributed to U coprecipitation either as uranium phases or as calcite phases. But these data are not relevant for glass leachates that do not contain adequate Ca to allow calcite precipitation that removes carbonate/bicarbonate anions that keep U(VI) highly soluble and resistant to adsorption at slightly alkaline pH values. Glass leachates are projected to be pH ~9 to 9.5 with ~0.034 M inorganic carbon mostly as bicarbonate (18) that will complex dissolved U(VI) lowering the K_d to values well below those reported in (11). For now assume that glass leachate is dominated by sodium bicarbonate/carbonate solution that allows anionic U(VI) carbonate species to predominate and sorption to be very low.

(a) The aqueous phase is moderately altered from the cement and glass leachate emanating from zones 1 and 2; pH is between 8 (background) and 11, and the ionic strength is between 0.01 (background) and 0.1. The solid phase is in the sand-dominated sequence and is slightly altered due to contact with the moderately caustic aqueous phase (Table 4.3 and Figure 4.3).

(b) References: 1 = Routson et al. (1976); 2 = Routson et al. (1978); 3 = Ames and Serne (1991); 4 = Kaplan et al. (1995); 5 = Rhodes (1957a,b); 6 = Ames and Rai (1978); 7 = Barney (1978); 8 = Sheppard et al. (1976); 9 = Martin (1996); 10 = Pourbaix (1966); 11 = Kaplan et al. (1998a); 12 = Rhodes and Nelson (1957); 13 = Prout (1959); 14 = Kaplan et al. (1998c); 15 = Um and Serne (2004, in review); 16 = Kaplan et al. (2003); 17 = Serne et al. (2002a); 18 = STORM code predictions of the long-term steady state glass leachate composition—see Section 6.0 for more discussion; 19 = Robertson et al. (2003).

Table 5.6. K_d Values for Zone 2b - Far Field in Sand Sequence with Natural Recharge (no impact from wastes)^(a)

Radionuclide	Reasonably Conservative K_d (mL/g)	"Best" K_d (mL/g)	K_d Range (mL/g)	Justification/References ^(b)
³ H, Cl, Tc, N as nitrate, Cr(VI) as chromate, Nb	0	0	0 to 0.6	Tc exists predominantly as TcO ₄ ⁻ . A review of Hanford sediment Tc- K_d values showed a range of -2.8 to 0.6 mL/g for 15 observations; median was 0.1 mL/g (1). Later studies did not change this range but did decrease the median slightly to -0.1 mL/g (2). Negative K_d values are physically possible and may not be an experimental artifact (2). ³ H is expected to move along with water. Cl and nitrate are expected to behave as a dissolved anionic species. Most recent results using ILAW specific borehole sediments [299-E17-21 and 299-E21-24] yielded Tc- K_d of 0 mL/g. See (18) and (19) for details. (21) lists K_d values for Cr(VI), nitrate, and Tc in Tables 10, 12, and 15, respectively that give ranges of 0 to 1, 0 (all ground-water values), and 0 to 0.1 mL/g, respectively. These ranges are used in SAC to perform stochastic predictions for contaminant transport in natural Hanford groundwater/aquifer predictions. Limited information available for geochemical behavior of Nb. Nb expected to be anionic at pH >7; see discussion in Robertson et al. (22).
Ac, Am, Ce, Cm, Eu	60	300	60 to 1,300	Am- K_d : 67 to >1,200 mL/g (3). Am- K_d : 125 to 833 mL/g (4)
C	0.5	5	0.5 to 1,000	Assumed dominant species: HCO ₃ ⁻ . Three processes will be acting on the ¹⁴ C to take it out of solution: adsorption onto the calcite surface, volatilization as CO ₂ gas, and precipitation into the calcite structure. The latter process is largely irreversible; therefore, it is not well represented by the K_d construct (K_d assumes that adsorption occurs as readily as desorption). Volatilization is entirely removed from the definition of the K_d construct. In systems that contain higher concentrations of carbonate minerals, such as the calccrete layer in the 200 West Area, an appreciably higher K_d should be used to account for the isotopic dilution/precipitation reaction that may occur. A K_d of 100 mL/g would be appropriate for such a system. Since most of the 100 and 200 plateau areas contain <1% carbonate, lower K_d values are warranted for these areas, such as 0.5 mL/g. K_d values of ¹⁴ C of >250 mL/g have been measured in calcite (5). At 100K, the C-14 is widely distributed down gradient from a major source (crib) associated with reactor operations. (Additional references: 6, 7, 8, 9, 10). Estimated range.
Co	1,000	2,000	1,000 to 12,500	Na system, 1,290 to 2,120 mL/g (11) Ca system, 2,000 to 3,870 mL/g (11) Hanford sediment/groundwater system 11,600 to 12,500 mL/g (12)
Cs	500	2,000	500 to 4,000	Na system, 1,410 to 1,590 mL/g (11) Hanford sediment/groundwater system, 540 to 3,180 mL/g (12). Most recent results using ILAW specific borehole sediments (299-E17-21) yielded K_d of 2,030 597. See Kaplan et al. (18) for details.

Table 5.6. (contd)

Radionuclide	Reasonably Conservative K_d (mL/g)	“Best” K_d (mL/g)	K_d Range (mL/g)	Justification/References ^(b)
I	0	0.25	0.0 to 15	A review of Hanford sediment I- K_d values showed a range of 0.7 to 15 mL/g for 9 observations; median was 0.7 mL/g (1). Later studies increased this range to 0.2 to 15 mL/g; the median was decreased to 0.3 mL/g (2). Results using ILAW specific borehole sediments (299-E17-21) yielded K_d of 0 mL/g (18), but more recent results by Um et al. (19) for ILAW borehole 299-E24-21 show non-zero K_d with an average value of 0.2 to 0.3 mL/g for far-field. (21) recommends a range of 0 to 2 mL/g for general Hanford transport conditions performed by SAC.
Ni, Sn	50	300	50 to 2,500	Ni: Hanford sediment/groundwater system, 440 to 2,350 mL/g (12). A study of a broad range of sediments, including those from Hanford, had Ni- K_d values of 50–340 mL/g (13).
Np	2	15	2 to 25	A review of Hanford sediment Np- K_d values showed range of 2.4 to 21.7 mL/g for four observations; median was 17.8 mL/g (1). Later studies increased the slightly to 2.2 to 21.7 mL/g; the median was slightly lowered, 15 mL/g (2). (21) recommends a range of 2 to 30 mL/g for SAC stochastic transport predictions. This range is nearly identical to our chosen range for deterministic IDF predictions.
Pb	8,000	10,000	8,000 to 80,000	pH 6 and no competing ions: 13,000 to 79,000 mL/g (14)
Pu	50	150	50 to 2,000	Pu(V, VI): pH 4 to 12: 80 to >1,980 mL/g (15)
Ra, Sr	5	14	5 to 200	Sr K_d values: Na system, 173 mL/g, 49 to 50 mL/g (11) Ca system, 8 to 13 mL/g, 5 to 19 mL/g (11) 5 to 120 mL/g (15) 19.1 to 21.5 mL/g (12) Na system, pH 7 to 11, 14.9 to 25.1 mL/g (16) Data using ILAW borehole sediment [299-E17-21] yielded 14.3±1.6. See (18). Most recent data using ILAW borehole sediment from 299-E24-21 showed Sr K_d was 14.6±1.1 mL/g in excellent agreement with (18).
Ru	10	20	10 to 1,000	Estimated (17 as cited in 11)
Se	3	7	3 to 15	Hanford groundwater/sediment system: -3.44 to 0.78 mL/g (12). Most recent data using ILAW borehole sediment [299-E17-21] yielded K_d values ranging from 3.75 to 10.85 mL/g and had an average of 6.7±1.9 mL/g (18). More recent data for ILAW borehole 299-E24-21 yielded a K_d range from 7.1 to 8.65 for 6 measurements in Hanford groundwater. [19]. The latter two studies are in excellent agreement. Cantrell et al. 2003 [21] recommends a range of 0 to 3 and 3 to 10 mL/g for Se for “higher” and “low/trace” concentrations of Se for SAC stochastic predictions. Our range is slightly larger but the best and reasonable conservative values we recommend for the IDF deterministic PA activities fit within the range chosen for trace concentrations of Se.
Th, Zr	40	1,000	40 to 2,500	Estimated. Zr: pH 6 to 12 : 90 to >2,000 mL/g (15)

Table 5.6. (contd)

Radionuclide	Reasonably Conservative K_d (mL/g)	"Best" K_d (mL/g)	K_d Range (mL/g)	Justification/References ^(b)
U	0.2	1	0.1 to 4	A review of Hanford sediment U- K_d values showed range of 0.1 to 79.3 mL/g for 13 observations; median was 0.6 mL/g (1). Results from later studies support the range (2). In all reported data, some U was adsorbed by Hanford sediments and >90% of the values were between 0.6 and 4 mL/g. Most recent work with the ILAW Borehole sediment [299-E17-21] yielded K_d of 0.6 ± 0.1 . See (18). An extensive new data set for sediments from the 300 Area that studied the K_d for U(VI) as a function of pH and carbonate concentration found values that ranged from ~0 to 7 mL/g (20); but for typical groundwater conditions the range narrows to 0.2 to 4 mL/g as reviewed and critically evaluated by Cantrell et al. (21). The "reasonable conservative" and "best" K_d values chosen for the IDF activities fall within Cantrell et al.'s narrow range of recommended U values.
<p>(a) K_d values in this table describe sorption of radionuclides to Hanford sediment-dominated sequence under far field conditions. The aqueous phase is assumed to be untainted Hanford vadose zone pore water (similar to Hanford groundwater) except for trace levels of radionuclide and the solid phase is assumed to be natural Hanford sand-dominated sequence sediment. The literature values upon which the values were based upon had an aqueous phase near-neutral pH, ionic strength between ~0 to 0.01, trace radionuclide concentrations.</p> <p>(b) References: 1 = Kaplan and Serne (1995); 2 = Kaplan et al. (1996); 3 = Routson et al. (1976); 4 = Sheppard et al. (1976); 5 = Martin (1996); 6 = Striegl and Armstrong (1990); 7 = Garnier (1985); 8 = Allard et al. (1981); 9 = Mozeto et al. (1983); 10 = Zhang et al. (1995); 11 = Routson et al. (1978); 12 = Serne et al. (1993); 13 = Serne and Relyea (1983); 14 = Rhoades et al. (1994); 15 = Rhodes (1957a); 16 = Nelson (1959); 17 = Rhodes (1957a,b); 18 = Kaplan et al. (1998a); 19 = Um et al. (2004) and Um and Serne (2004, in review); 20 = Serne et al. (2002a); 21 = Cantrell et al. (2003); 22 = Robertson et al. (2003).</p>				

Table 5.7. Gravel-Corrected K_d Values (K_{dgc}) for Zone 3a - Chemically Impacted Far Field in Gravel Sequence^(a)

Radionuclide	Reasonable Conservative K_{dgc} (mL/g)	“Best” K_{dgc} (mL/g)	K_{dgc} Range (mL/g)	Justification/References ^(b)
³ H, Cl, N as nitrate, Cr as chromate, Tc, Nb	0	0	0 to 0.01	No gravel-corrected K_d data available. Tc, nitrate, chromate and Cl are anionic. ³ H will move with H ₂ O. Limited information available for geochemical behavior of Nb. Nb expected to be anionic at pH >7; see discussion in Robertson et al. (18).
Ac, Am, Ce, Cm, Eu	10	35	10 to 150	No gravel-corrected K_d data available. Am- K_d values: In low-ionic-strength Ca system, >1,200 mL/g; in low-ionic-strength Na system, 280 mL/g (1)
C	0.5	2	0.5 to 5	Estimated. No gravel-corrected K_d data available. ¹⁴ C geochemistry complex and poorly described by K_d construct. ¹⁴ C is expected to enter liquid, solid and gas phase through volatilization (CO ₂ -gas), precipitation with calcite, isotopic exchange, and adsorption. Based on Martin (9), who measured ¹⁴ C- K_d values in Hanford sediments using uncontaminated Hanford groundwater (relatively low ionic strength). K_d values increased during a 70 day contact time from 0 (1-hr contact time) to 400 mL/g in sediment and 20 (1-hr contact time) to 360 mL/g in calcrete. ¹⁴ C removed by solid phases never stabilized during 70 days, suggesting coprecipitation reaction.
Co	15	30	15 to 200	No gravel-corrected K_d data available. In low-ionic-strength Na system, 1060 to 4760 mL/g (2) In low-ionic-strength Ca system, 222 to 640 mL/g (2) Forms complexes, especially with organics.
Cs	4	8	4 to 200	No gravel-corrected K_d data available. No complexes. Estimated. In 0.01 to 0.1 M Na system, 64 to 1170 mL/g (2). In 0.01 to 0.1 M Ca system, 790 to 1,360 mL/g (2). Unpublished recent results from Zachara (PNNL, EMSP project) using Hanford sediments and simulated tank waste indicate that Cs sorption decreases markedly compared to when ionic strength is appreciably lower.
I	0	0	0 to 0.02	No gravel-corrected K_d data available. Anion. Estimated.
Ni, Sn	4	8	4 to 40	Ni is similar to Co but adsorbs slightly less possibly because of moderate complexing. Estimated (3, 4)
Np, Pa	0.02	0.08	0.04 to 0.5	No gravel-corrected K_d data available. Np K_d values in low-ionic-strength solutions = 0.4 to 4 mL/g (1). The dominant protactinium species is assumed to be PaO ₂ ⁺ . NpO ₂ ⁺ is assumed to be a reasonable analog (10). Based on studies conducted at the Whiteshell Laboratories (personal communication with T. T. (Chuck) Vandergraaf, Atomic Energy of Canada Limited, Pinawa, Manitoba, Canada), Pa sorbs appreciably more than Np. Thus, Pa- K_d estimates based on measured Np- K_d values will be conservative.
Pb	2	10	2 to 100	No gravel-corrected K_d data available. Good absorber, insoluble. Estimated (4).
Pu	8	20	8 to 100	No gravel-corrected K_d data available. >98 mL/g (5)

Table 5.7. (contd)

Radionuclide	Reasonable Conservative $K_{d\text{gc}}$ (mL/g)	"Best" $K_{d\text{gc}}$ (mL/g)	$K_{d\text{gc}}$ Range (mL/g)	Justification/References ^(b)
Ra, Sr	0.02	1	0.02 to 5	Na system, 1.7 to 42 mL/g for Sr- K_d (2). Ca system, 0.3 to 1.6 mL/g for Sr- K_d (2). In 4 M NaNO ₃ , Sr- K_d in Hanford sediment was 5 mL/g (pH 8), and 10 mL/g (pH 10) (12). Near identical K_d values using Savannah River Site Sediments and 30% NaNO ₃ (13). Sr- K_d values measured in low-ionic-strength conditions and with Hanford sediments containing gravel are presented in Kaplan et al. (17). Based on periodicity considerations, Ra would be expected to sorb more strongly to sediments than Sr, but no Hanford Ra- K_d values are available. Thus, basing Ra- K_d estimates on measured Sr- K_d values will likely provide a conservative Ra- K_d estimate.
Ru	0	0.1	0 to 50	No gravel-corrected K_d data available. May form RuO ₄ ²⁻ and/or anionic complexes with nitrates and nitrites. Estimate (3, 6, 7).
Se	0.02	0.04	0.02 to 1	No gravel-corrected K_d data available. Anionic. Se K_d measured at the ILAW/IDF site had K_d values of 6.7 ± 0.4 mL/g (14). Results of a Se sorption experiment to Hanford sediments in high ionic strength (NaOH and NaOCl ₄) indicate Se K_d values of ~0 to 18 mL/g. (15) but pH and ionic strength are likely too extreme for zone 3.
Th, Zr	4	30	4 to 50	No gravel-corrected K_d data available. Sandy soil data, 40 to 470 mL/g for Th (8).
U	0.02	0.2	0.02 to 5	Serne et al. (16) batch K_d data used sediments with some gravel included. To account for having 90% gravel in this zone, lower the K_d value for the reasonable conservative case even lower (0.02 from 0.05 mL/g) than used for sand sediments.
<p>(a) The aqueous phase is moderately altered from the cement and glass leachate emanating from zones 1 and 2; pH is between 8 (background) and 11, and the ionic strength is between 0.01 (background) and 0.1. The solid phase is in the sand-dominated sequence and is slightly altered due to contact with the moderately caustic aqueous phase (Figure 4.1).</p> <p>(b) References: 1 = Routson et al. (1976); 2 = Routson et al. (1978); 3 = Ames and Serne (1991); 4 = Kaplan et al. (1995); 5 = Rhodes (1957a,b); 6 = Ames and Rai (1978); 7 = Barney (1978); 8 = Sheppard et al. (1976); 9 = Martin (1996); 10 = Pourbaix (1966); 11 = Kaplan et al. (1998a); 12 = Rhodes and Nelson (1957); 13 = Prout (1959); 14 = Kaplan et al. (1998c); 15 = Kaplan et al. (2003); 16 = Serne et al. (2002a); 17 = Kaplan et al. (2000b); 18 = Robertson et al. (2003).</p>				

Table 5.8. Gravel-Corrected K_d Values (K_{dgc}) for Zones 3a and 4–Far Field in Gravel Sequence^(a)

Radionuclide	Reasonable Conservative K_{dgc} (mL/g)	“Probable” K_{dgc} (mL/g)	K_{dgc} Range (mL/g)	Justification/References ^(b)
³ H, Cl, N as nitrate, Cr as chromate, Tc, Nb	0	0	0 to 0.06	No laboratory results of gravel- K_d values available. N, Cr(VI) and Tc exist predominantly as NO_3^- , CrO_4^{2-} , and TcO_4^- , respectively. A review of Hanford sediment Tc- K_d values showed a range of -2.8 to 0.6 mL/g for 15 observations; median was 0.1-mL/g (1). Later studies did not change this range but did decrease the median slightly to -0.1 mL/g (2). Negative K_d values are possible and may not be an experimental artifact (2). ³ H is expected to move along with water. Cl is expected to behave as a dissolved anionic species. Most recent results using ILAW specific borehole sediments [299-E17-21] yielded Tc- K_d of 0 mL/g (18). Gravel correction of negative K_d values in Estimated K_d Range was assumed to make K_d less negative by a factor of 0.9 because of reduced surface area that would create the anion exclusion. Limited information available for geochemical behavior of Nb. Nb expected to be anionic at pH >7; see discussion in Robertson et al. (21).
Ac, Am, Ce, Cm, Eu	6	30	6 to 130	No laboratory results of gravel- K_d values available. Am- K_d : 67 to >1,200 mL/g (3). Am- K_d : 125 to 833 mL/g (4)
C	0.05	0.5	0.05 to 100	No laboratory results of gravel- K_d values available. Assumed dominant species: HCO_3^- . Three processes will be acting on the ¹⁴ C to take it out of solution: adsorption onto the calcite surface, volatilization as CO ₂ gas, and precipitation into the calcite structure. The latter process is largely irreversible; therefore, it is not well represented by the K_d construct (K_d assumes that adsorption occurs as readily as desorption). Volatilization is entirely removed from the definition of the K_d construct. In systems that contain higher concentrations of carbonate minerals, such as the calcrete layer in the 200 West Area, an appreciably higher K_d should be used to account for the isotopic dilution/precipitation reaction that may occur, a K_d of 100 mL/g would be appropriate for such a system. Since most of the 100 and 200 plateau areas contain <1% carbonate, lower K_d values are warranted for these areas, such as 0.5 mL/g. K_d values of ¹⁴ C of >250 mL/g have been measured in calcite (5). At 100K Area, the C-14 is widely distributed down gradient from a major source (crib). Additional references: 6, 7, 8, 9, and 10. Estimated range.
Co	100	200	100 to 1,250	No laboratory results of gravel- K_d values available. Na system, 1,290 to 2,120 mL/g (11); Ca system, 2,000 to 3,870 mL/g (11); Hanford sediment/groundwater system 11,600 to 12,500 mL/g (12)
Cs	50	200	50 to 400	No laboratory results of gravel- K_d values available. Na system, 1,410 to 1,590 mL/g (11) Hanford sediment/groundwater system, 540 to 3,180 mL/g (12). Most recent results using ILAW specific borehole sediments [299-E17-21] yielded K_d of 2,030±597(18).
I	0	0.02	0 to 1.5	No laboratory results of gravel- K_d values available. A review of Hanford sediment I- K_d values showed a range of 0.7 to 15 mL/g for 9 observations; median was 0.7-mL/g (1). Later studies increased this range to 0.2 to 15 mL/g; the median was decreased to 0.3 mL/g (2). Recent results using ILAW specific borehole sediments [299-E17-21] yielded K_d of 0 mL/g. See Kaplan et al. (18) for details.
Ni, Sn	5	30	5 to 250	No laboratory results of gravel- K_d values available. Ni: Hanford sediment/groundwater system, 440 to 2,350 mL/g (12). A study of a broad range of sediments, including those from Hanford, had Ni- K_d values of 50 to 340 mL/g (13).

Table 5.8. (contd)

Radionuclide	Reasonable Conservative K_{dgc} (mL/g)	“Probable” K_{dgc} (mL/g)	K_{dgc} Range (mL/g)	Justification/References ^(b)
Np, Pa	0.2	1.5	0.2 to 2.5	No laboratory results of gravel- K_d values available. A review of Hanford sediment Np- K_d values showed range of 2.4 to 21.7 mL/g for four observations; median was 17.8 mL/g (1). Later studies increased K_d values to 2.2 to 21.7 mL/g; the median of these later studies was 15 mL/g (2). The dominant protactinium species is assumed to be PaO_2^+ and NpO_2^+ is assumed to be a reasonable analog (19). Based on studies conducted at the Whiteshell Laboratories (personal communications with TT (Chuck) Vandergraaf, Atomic Energy of Canada Limited, Pinawa, Manitoba, Canada), Pa sorbs appreciably more than Np. Thus, Pa- K_d estimates based on measured Np- K_d values will be conservative.
Pb	800	1,000	800 to 8,000	No laboratory results of gravel- K_d values available. pH 6 and no competing ions: 13,000 to 79,000 mL/g (14)
Pu	5	15	5 to 200	No laboratory results of gravel- K_d values available. Pu(V, VI): pH 4 to 12: 80 to >1,980 mL/g (17)
Ra, Sr	0.5	1.4	0.5 to 20	Sr K_d values: Na system, 173 mL/g, 49 to 50 mL/g (11), Ca system, 8 to 13 mL/g, 5 to 19 mL/g (11), 5 to 120 mL/g (15), 19.1 to 21.5 mL/g (12), Na system, pH 7 to 11, 14.9 to 25.1 mL/g (16). Recent data using ILAW borehole sediment [299-E17-21] yielded Sr K_d values of 14.3 ± 1.6 mL/g (18). See Appendix A in [18] for Sr K_d values with sediments containing gravel. Based on periodicity considerations, Ra expected to sorb more strongly to sediments than Sr but no Hanford Ra K_d values are available. Thus, basing Ra K_d estimates on measured Sr K_d values likely provides conservative Ra K_d estimate.
Ru	1	2	1 to 100	No laboratory results of gravel K_d values available. Estimated (17 as cited in 11)
Se	0.3	0.7	0.3 to 1.5	No lab results of gravel K_d values available. Hanford groundwater/sediment system: -3.44 to 0.78 mL/g (12). Most recent data using ILAW borehole sediment [299-E17-21], which did not contain measurable amounts of gravel, yielded K_d values ranging from 3.75 to 10.85 mL/g and had an average of 6.7 ± 1.9 mL/g (18).
Th, Zr	4	100	4 to 250	Estimated. No laboratory results of gravel- K_d values available. Zr: pH 6 to 12: 90 to >2,000 mL/g (15)
U	0.1	1.0	0.01 to 7	Serne et al. (20) used 300 Area Hanford formation sediments with some gravel and got a range of K_d values from ~0 to 7 mL/g. U K_d values were highly influenced by bicarbonate/carbonate concentration and pH. pH of nonimpacted gravel sediments at Hanford is ~8 and bicarbonate/carbonate concentrations are <5 meq/L. For sediments with 90% gravel but normal solution chemistry, assume a very conservative K_d value would be 10% of the most probable case or 0.1 mL/g. A review of Hanford sediment U- K_d values showed range of 0.1 to 79.3 mL/g for 13 observations; median was 0.6-mL/g (1). Results from later studies support the range (2). In all reported data, some U was adsorbed by Hanford sediments and >90% of the values were between 0.6 and 4 mL/g. Most recent work with the ILAW Borehole sediment [299-E17-21] yielded K_d of 0.6 ± 0.1 for a sand sediment but no gravel correction information was available from this data set. See (18).
<p>(a) Aqueous phase is untainted Hanford groundwater except for trace levels of radionuclides; solid phase is composed of the unaltered gravel-dominated sequence material (Table 4.3 and Figure 4.3). K_{dgc} is the gravel-corrected K_d value as defined in Equation 2.6. K_d values for the far field, without a gravel correction, are presented in Appendix C of this document.</p> <p>(b) References: 1 = Kaplan and Serne (1995); 2 = Kaplan et al. (1998b); 3 = Routson et al. (1976); 4 = Sheppard et al. (1976); 5 = Martin (1996); 6 = Striegl and Armstrong (1990); 7 = Garnier (1985); 8 = Allard et al. (1981); 9 = Mozeto et al. (1983); 10 = Zhang et al. (1995); 11 = Routson et al. (1978); 12 = Serne et al. (1993); 13 = Serne and Relyea (1983); 14 = Rhoads et al. (1994); 15 = Rhodes (1957a); 16 = Nelson (1959); 17 = Rhodes (1957a,b); 18 = Kaplan et al. (1998c); 19 = Pourbaix (1966); 20 = Serne et al. (2002a); 21 = Robertson et al. (2003).</p>				

Table 5.9. K_d Values for Zone 5—Unconfined Far-Field Aquifer Conditions^(a)

Radionuclide	Reasonably Conservative K_d (mL/g)	“Best” K_d (mL/g)	K_d Range (mL/g)	Justification/References ^(b)
³ H, Cl, Tc, N as nitrate, Cr(VI) as chromate, Nb	0	0	0 to 0.6	Tc exists predominantly as TcO_4^- . A review of Hanford sediment Tc- K_d values showed a range of -2.8 to 0.6 mL/g for 15 observations; median was 0.1 mL/g (1). Later studies did not change this range but did decrease the median slightly to -0.1 mL/g (2). Negative K_d values are physically possible and may not be an experimental artifact (2). ³ H is expected to move along with water. Cl and nitrate are expected to behave as a dissolved anionic species. Most recent results using ILAW specific borehole sediments [299-E17-21 and 299-E21-24] yielded Tc- K_d of 0 mL/g. See Kaplan et al. (18) and Um and Serne (19) for details. Cantrell et al. (21) lists K_d values for Cr(VI), nitrate, and Tc in Tables 10, 12, and 15, respectively that give ranges of 0 to 1, 0 (all groundwater values), and 0 to 0.1 mL/g, respectively. These ranges are used in SAC to perform stochastic predictions for contaminant transport in natural Hanford groundwater/aquifer predictions. Limited information available for geochemical behavior of Nb. Nb expected to be anionic at pH >7; see discussion in Robertson et al. (22).
Ac, Am, Ce, Cm, Eu	60	300	60 to 1,300	Am- K_d : 67 to greater than 1,200 mL/g (3). Am- K_d : 125 to 833 mL/g (4)
C	0.5	5	0.5 to 1,000	Assumed dominant species: HCO_3^- . Three processes will be acting on the ¹⁴ C to take it out of solution: adsorption onto the calcite surface, volatilization as CO ₂ gas, and precipitation into the calcite structure. The latter process is largely irreversible; therefore, it is not well represented by the K_d construct (K_d assumes that adsorption occurs as readily as desorption). Volatilization is entirely removed from the definition of the K_d construct. In systems that contain higher concentrations of carbonate minerals, such as the calcrete layer in the 200 West Area, an appreciably higher K_d should be used to account for the isotopic dilution/precipitation reaction that may occur. A K_d of 100 mL/g would be appropriate for such a system. Since most of the 100 and 200 plateau areas contain <1% carbonate, lower K_d values are warranted for these areas, such as 0.5 mL/g. K_d values of ¹⁴ C of >250 mL/g have been measured in calcite (5). At 100K, the C-14 is widely distributed down gradient from a major source (crib) associated with reactor operations. (Additional references: 6, 7, 8, 9, 10). Estimated range.
Co	1000	2000	1,000 to 12,500	Na system, 1,290 to 2,120 mL/g (11) Ca system, 2,000 to 3,870 mL/g (11) Hanford sediment/groundwater system 11,600 to 12,500 mL/g (12)
Cs	500	2000	500 to 4,000	Na system, 1,410 to 1,590 mL/g (11) Hanford sediment/groundwater system, 540 to 3,180 mL/g (12). Most recent results using ILAW specific borehole sediments [299-E17-21] yielded K_d of 2,030 ± 597. See Kaplan et al. (18) for details.
I	0	0.25	0.0 to 15	A review of Hanford sediment I- K_d values showed a range of 0.7 to 15 mL/g for 9 observations; median was 0.7 mL/g (1). Later studies increased this range to 0.2 to 15 mL/g; the median was decreased to 0.3 mL/g (2). Results using ILAW specific borehole sediments [299-E17-21] yielded K_d of 0 mL/g (18), but more recent results by Um et al. [19] for ILAW borehole 299-E24-21 show non zero K_d with an average value of 0.2 to 0.3 mL/g for far-field. Cantrell et al. 2003 [21] recommends a range of 0 to 2 mL/g for general Hanford transport conditions performed by SAC.
Ni, Sn	50	300	50 to 2,500	Ni: Hanford sediment/groundwater system, 440 to 2,350 mL/g (12). A study of a broad range of sediments, including those from Hanford, had Ni- K_d values of 50 to 340 mL/g (13).

Table 5.9. (contd)

Radionuclide	Reasonably Conservative K_d (mL/g)	“Best” K_d (mL/g)	K_d Range (mL/g)	Justification/References ^(b)
Np	2	15	2 to 25	A review of Hanford sediment Np- K_d values showed range of 2.4 to 21.7 mL/g for 4 observations; median was 17.8 mL/g (1). Later studies increased the slightly to 2.2 to 21.7 mL/g; the median was slightly lowered, 15 mL/g (2). Cantrell et al. 2003[21] recommends a range of 2 to 30 mL/g for SAC stochastic transport predictions. This range is nearly identical to our chosen range for deterministic IDF predictions.
Pb	8000	10,000	8,000 to 80,000	pH 6 and no competing ions: 13,000 to 79,000 mL/g (14)
Pu	50	150	50 to 2,000	Pu(V, VI): pH 4 to 12: 80 to greater than 1,980 mL/g (15)
Ra, Sr	5	14	5 to 200	Sr K_d values: Na system, 173 mL/g, 49 to 50 mL/g (11); Ca system, 8 to 13 mL/g, 5 to 19 mL/g (11); 5 to 120 mL/g (15); 19.1 to 21.5 mL/g (12) Na system, pH 7 to 11, 14.9 to 25.1 mL/g (16); Data using ILAW borehole sediment [299-E17-21] yielded 14.3±1.6. See (18). Most recent data using ILAW borehole sediment from 299-E24-21 showed Sr K_d was 14.6±1.1 mL/g in excellent agreement with (18).
Ru	10	20	10 to 1,000	Estimated (17 as cited in 11)
Se	3	7	3 to 15	Hanford groundwater/sediment system: -3.44 to 0.78 mL/g (12). Most recent data using ILAW borehole sediment [299-E17-21] yielded K_d values ranging from 3.75 to 10.85 mL/g and had an average of 6.7±1.9 mL/g (18). More recent data for ILAW borehole 299-E24-21 yielded a K_d range from 7.1 to 8.65 for 6 measurements in Hanford groundwater. [19]. The latter two studies are in excellent agreement. Cantrell et al. 2003 [21] recommends a range of 0 to 3 and 3 to 10 mL/g for Se for “higher” and “low/trace” concentrations of Se for SAC stochastic predictions. Our range is slightly larger but the best and reasonable conservative values we recommend for the IDF deterministic PA activities fit within the range chosen for trace concentrations of Se.
Th, Zr	40	1000	40 to 2,500	Estimated. Zr: pH 6 to 12 : 90 to >2,000 mL/g (15)
U	0.2	1	0.1 to 80	A review of Hanford sediment U(VI) K_d values showed range of 0.1 to 79.3 mL/g for 13 observations; median was 0.6 mL/g (1). Results from later studies support the range (2). In all reported data, some U(VI) was adsorbed by Hanford sediments and >90% of the values were between 0.6 and 4 mL/g. Most recent work with the ILAW Borehole sediment (299-E17-21) yielded K_d of 0.6 ± 0.1. See (18). An extensive new data set for sediments from the 300 area that studied the K_d for U(VI) as a function of pH and carbonate concentration found values that ranged from ~0 to 7 mL/g [Serne et al. (20)], but for typical groundwater conditions the range narrows to 0.2 to 4 mL/g as reviewed and critically evaluated by Cantrell et al. (21). The “reasonable conservative” and “best” K_d values chosen for the IDF activities fall within the narrow range of recommended U(VI) values given by Cantrell et al.(21).
<p>(a) K_d values in this table describe sorption of radionuclides to Hanford sediment-dominated sequence under far field conditions. The aqueous phase is assumed to be untainted Hanford groundwater except for trace levels of radionuclide and the solid phase is assumed to be natural Hanford sand-dominated sequence sediment. The literature values upon which the values were based upon had an aqueous phase near-neutral pH, ionic strength between ~0 to 0.01, trace radionuclide concentrations.</p> <p>(b) References: 1 = Kaplan and Serne (1995); 2 = Kaplan et al. (1996); 3 = Routson et al. (1976); 4 = Sheppard et al. (1976); 5 = Martin (1996); 6 = Striegl and Armstrong (1990); 7 = Garnier (1985); 8 = Allard et al. (1981); 9 = Mozeto et al. (1983); 10 = Zhang et al. (1995); 11 = Routson et al. (1978); 12 = Serne et al. (1993); 13 = Serne and Relyea (1983); 14 = Rhoades et al. (1994); 15 = Rhodes (1957a); 16 = Nelson (1959); 17 = Rhodes (1957a,b); 18 = Kaplan et al. (1998a); 19 = Um et al. (2004) and Um and Serne (2004, in review); 20 = Serne et al. (2002a) 21 = Cantrell et al. (2003); 22 = Robertson et al. (2003).</p>				

6.0 History of K_d Values Selected for Key Contaminants of Concern

This data package is the third compilation of K_d values prepared for use in an ILAW/IDF PA. Over time, three sets of calculations have been performed to predict the consequences of burying vitrified wastes in the south-central portion of the 200 East Area at Hanford Site. The three efforts to evaluate future risks associated with onsite burial are known as the 1998 ILAW PA (Mann et al. 1998), the 2001 ILAW PA (Mann et al. 2001) and the supplemental ILAW waste form initial selection risk assessment (Mann et al. 2003b). The fourth effort to predict future impacts and risks associated with the burial of wastes in the IDF is the 2005 IDF PA, to be completed next year.

Selection and documentation of K_d values and empirical solubility concentration limits are the subject of this report. The K_d values recommended for some of the potentially mobile contaminants of concern for the three sets of PA calculations already completed and the soon-to-start 2005 IDF PA have evolved as the Hanford-specific sorption database has increased and knowledge of the fate and transport properties of these key contaminants has improved. Table 6.1 lists the K_d values that were recommended for the key mobile contaminants (and major dose/chemical risk drivers) for each of the three activities and the upcoming 2005 IDF PA. Not all contaminants were assessed in each PA, but K_d values were recommended for a large suite of contaminants for each assessment. This section describes the reason for changes in K_d values selected over time for the listed key contaminants. As shown in Table 6.1, there is essentially no change in the recommended K_d values for nitrate, Cr(VI), and ^{99}Tc . Thus these three mobile contaminants will not be discussed further.

6.1 K_d Values for ^{129}I

The K_d values for ^{129}I have evolved with time as more Hanford-specific conditions were measured. The K_d values recommended for the 1998 ILAW PA were influenced by the general literature, which suggests moderate adsorption. Thus a K_d value of 3 mL/g for ^{129}I was chosen at that time. Between 1998 and 2001, several Hanford-specific iodide adsorption studies yielded inconsistent results (Kaplan et al. 1998b; 2003) especially when using solutions with pH values greater than natural (ambient) pH 8 conditions. Because of the uncertainty and lack of a clear understanding of the controlling mechanisms in these empirical tests, we made a conservative recommendation and selected a K_d of 0 mL/g for ^{129}I for the 2001 ILAW PA calculations. After the 2001 PA, we focused new IDF-funded testing on iodide adsorption using Hanford sediments. We are now confident that there is, in fact, low adsorption of iodide.

The STORM code was used in the 2001 ILAW PA to predict the chemical evolution of the pore water in the vadose zone below the ILAW IDF. Table 6.2 lists the long-term, steady-state chemical composition of glass leachate and vadose zone pore water predicted by the STORM code for the 2001 ILAW PA. The 2001 STORM code calculations indicated that the pore water for the entire vadose zone below the IDF would be similar to this composition in the long term. Recent iodide adsorption measurements by Um and Serne^(a) using a simulated glass leachate based on the composition in Table 6.2 shows a decreased adsorption at a pH value of 9.5, but the K_d is consistently greater than zero (Section 3.2.3). We

(a) Um W and RJ Serne. 2004. "Sorption and Transport Behavior of Radionuclides in the Proposed Low-Level Radioactive Waste Disposal Facility at the Hanford Site, Washington." Submitted to *Radiochimica Acta*.

Table 6.1. Evolution of Recommended K_d Values (mL/g) for Selected Key Contaminants

Contaminant	1998 ILAW PA			2001 ILAW PA and 2003 Supplemental PA			Recommended for 2005 IDF PA		
	Zone	Conservative K_d	Most Probable K_d	Zone	Conservative K_d	Most Probable K_d	Zone	Conservative K_d	Most Probable K_d
		----- mL/g -----			----- mL/g -----			----- mL/g -----	
Nitrate	all zones	0	0	all zones	0	0	all zones	0	0
Cr(VI)	all zones	0	0	all zones	0	0	all zones	0	0
^{99}Tc	all zones	0	0	near field-glass	0.1 (0) ^(a)	1 (0) ^(b)	all zones	0	0
				chemically-impacted sand	0	0			
				all other zones	0	0			
^{129}I	all zones	0	3	near field-glass	0	0	near field-glass	0.04	0.1
				near field-concrete	0	2 (0) ^(a)	near field-concrete	1	2
				chemically impacted sand	0	0	chemically impacted sand	0	0.1
				non-impacted sand	0	0.1	non-impacted sand	0	0.25
				chemically impacted gravel	0	0	chemically impacted gravel	0	0
				non-impacted gravel	0	0.01	non-impacted gravel	0	0.02
U(VI)	all zones	0	0.6	near field-glass	5 (0) ^(b)	20 (0.6) ^(a)	near field-glass	0.05	0.2
				near field-concrete	70 (0) ^(b)	100 (0.6) ^(a)	near field-concrete	70	100
				chemically impacted sand	2 (0) ^(b)	10 (0.6) ^(a)	chemically impacted sand	0.05	0.2
				non-impacted sand	0.5 (0) ^(b)	0.6	non-impacted sand	0.2	1
				chemically impacted gravel	0.2 (0) ^(b)	1	chemically impacted gravel	0.02	0.2
				non-impacted gravel	0.05 (0) ^(b)	0.06	non-impacted gravel	0.1	1

Table 6.1. (contd)

Contaminant	1998 ILAW PA			2001 ILAW PA and 2003 Supplemental PA			Recommended for 2005 IDF PA		
	Zone	Conservative K _d	Most Probable K _d	Zone	Conservative K _d	Most Probable K _d	Zone	Conservative K _d	Most Probable K _d
		----- mL/g -----			----- mL/g -----			----- mL/g -----	
⁷⁹ Se	all zones	0	0	near field-glass	0	0	near field-glass	0	1
				near field-concrete	0	1	near field-concrete	0	1
				chemically impacted sand	2	4	chemically impacted sand	1	2
				non-impacted sand	3	7	non-impacted sand	3	7
				chemically impacted gravel	0.2	0.4	chemically impacted gravel	0.02	0.04
				non-impacted gravel	0.3	0.7	non-impacted gravel	0.3	0.7
<p>(a) In the 2001 ILAW PA calculations, some of the recommended K_d values were not used and more conservative numbers were selected. The more conservative numbers used in those PA code calculations are shown in parentheses</p> <p>(b) In the 2001 ILAW PA calculations, a sensitivity calculation was completed using K_d values of 0 mL/g for the conservative K_d values for U(VI) in the vadose zone regions indicated.</p>									

Table 6.2. Predicted Composition of Glass Leachate and Long-Term Vadose Zone Pore Water Based on the 2001 STORM Code Calculations

Constituent	Concentration	
pH	=	9.5
Ionic Strength	=	0.03 M
	----- mM -----	-- meq/L --
Al	0.2	0.60
B	7.23	21.69
Ca	0.0001	0.00
CO ₃ ²⁻	7.54	15.08
HCO ₃ ⁻	26.8	26.80
Cr	0.00716	0.01
Fe	1.00×10 ⁻⁷	0.00
K	0.112	0.11
Mg	0.675	1.35
Na	38.5	38.50
Si	1.95	
Ti	0.000226	0.00
Zn	0.870	1.74
Zr	5.51×10 ⁻⁷	0.00

have not studied the adsorption of iodide onto gravel-dominated sediments to determine whether the gravel-correction construct described in this report is viable. Thus for conservatism, we have decreased the K_d values measured for ¹²⁹I on sands by a factor of 10 to estimate K_d values for the gravel-dominated zones. Table 6.1 lists ¹²⁹I K_d values recommended for the 2005 IDF PA for a conservative sensitivity calculation and for the most probable or base case. The most probable K_d values are low for ¹²⁹I, but greater than zero.

6.2 K_d Values for U(VI)

The selection of recommended K_d values for U(VI) has been difficult over time because of the great sensitivity of U(VI) adsorption to the pH and concentration of dissolved carbonate/bicarbonate in fluids used in adsorption tests [see general discussion of U(VI) aqueous speciation in Section 3.7.1 and adsorption in Section 3.7.3]. In 1998, the value of 0.6 mL/g was recommended based on some Hanford-specific work and much general literature that indicated some adsorption for U(VI) on coarse-grained sediments with low organic matter content and slightly alkaline pH in bicarbonate-dominated waters. For chemically impacted zones, K_d values for U(VI) much greater than 0.6 mL/g were recommended for the 2001 ILAW PA. Recommendation of these values was based on information from the studies by Kaplan et al. (1998a), literature reviews on radionuclide sorption in cement (Krupka and Serne 1998), and analyses of contaminated sediment columns that showed relative mobility of uranium was significantly less than those of nitrate and ⁹⁹Tc in vadose zone sediments under Hanford Site tanks that had leaked in the past. Our selection was influenced by the fact that uranium appeared to adsorb or precipitate readily from liquids contacting Hanford sediments when the pH was raised from ambient to more alkaline values. There were numerous empirical observations to support this conclusion. As shown in Table 6.1, our

recommended K_d values for U(VI) in impacted zones were 10 mL/g or greater. The 2001 ILAW PA calculations binned various contaminants to reduce computation run costs such that many contaminants with recommended K_d values greater than 0.6 mL/g were binned and assumed to have a K_d equal to 0.6 mL/g. As long as the travel times were greater than 10,000 years at the chosen receptor location or if the consequences (dose or concentration) were significantly below levels of concern, no calculations were performed using the recommended larger K_d values. Such was the case in the 2001 ILAW PA.

Since 2001, several additional studies have been completed at Hanford, where uranium adsorption has been studied and the chemical composition of the glass leachate has become available. The STORM code also predicted that the entire vadose zone below the ILAW glass disposal cell would be affected by the slow leaching of the waste glass such that the pore fluids would have the composition listed in Table 6.2. This fluid is dominated by dissolved sodium and borate from the glass and by dissolved bicarbonate/carbonate from the assumed equilibration with atmospheric carbon dioxide. The predicted pH of 9.5 is another key factor to consider because the solubility of dissolved inorganic carbon (bicarbonate/carbonate) increases in aqueous solutions at equilibrium with the atmosphere as pH increases and inorganic carbon forms strong anionic aqueous complexes with U(VI) [e.g., $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$] that exhibit minimal adsorption and are highly soluble reactions (see discussion in Section 3.7.1).

Detailed U(VI) sorption studies using fluids with varying chemical composition (pH, bicarbonate/carbonate, and ionic strength) and a coarse Hanford formation sand (included ~2% gravel) sediment from the 300 Area of Hanford were reported by Serne et al. (2002a). The U(VI) K_d values they measured in a high ionic-strength-simulated pore water solution whose composition is listed in Table 6.3 are listed in Tables 6.4 through 6.6. The chemical composition of the “high ionic-strength water” in Serne et al. (2002a) is similar in composition (dominated by dissolved sodium and inorganic carbon), but slightly more dilute, than that predicted glass leachate as given in Table 6.2. Uranium K_d values obtained upon contact of the high ionic strength solution at pH 7.5 ± 0.3 with the 300 Area Hanford sediment are shown in Table 6.4 as a function of the starting concentrations of dissolved U(VI). The K_d values vary from 0.28 to 0.56 mL/g. Additional results from Serne et al. (2002a) with the high ionic-strength solution as a function of pH show that when the pH is increased slightly above 7.5, the K_d values decrease significantly, as shown in Table 6.5. Serne et al. (2002a) also conducted experiments using a simpler sodium bicarbonate-sulfate solution to evaluate the impact of total dissolved inorganic carbon bicarbonate/

Table 6.3. Composition of the High Ionic-Strength-Simulated Pore Water Solution Used for U(VI) K_d Measurements by Serne et al. (2002a)

Constituent	Concentration	
	----- mM -----	---- meq/L ----
Cations		20
Anions		20
Ca	2	4
Na	16	16
HCO_3^-	10	10
NO_3^-	4	4
SO_4^{2-}	3	6

Table 6.4. K_d Values (mL/g) Measured for U(VI) by Serne et al. (2002a) at Different Initial Concentrations of Dissolved U(VI) Using Hanford Formation Coarse Sand and High Ionic-Strength Solution (pH = 7.5±0.3) with the Composition Listed in Table 6.3

Initial Conc. Dissolved U(VI) (ppb)	Sample Number	K_d	Average K_d
		----- (mL/g) -----	
50	B11493-1	0.36	0.28
	B11493-2	0.20	
250	B11493-3	0.54	0.43
	B11493-4	0.32	
500	B11493-5	0.58	0.56
	B11493-6	0.55	
750	B11493-7	0.49	0.45
	B11493-8	0.40	
1,500	B11493-9	0.55	0.53
	B11493-10	0.51	
3,000	B11493-11	0.45	0.44
	B11493-13	0.43	
5,000	B11493-12	0.35	0.35
	B11493-14	0.36	

Table 6.5. K_d Values (mL/g) Measured for U(VI) by Serne et al. (2002a) as a Function of pH Using Hanford Formation Coarse Sand and High Ionic-Strength Solution with the Composition Listed in Table 6.3

Initial Conc. Dissolved U(VI) (ppb)	Sample Number	pH	K_d (mL/g)
500	High I.S.-1	6.26	137.8
	High I.S.-2	6.77	8.63
	High I.S.-3	7.49	0.31
	High I.S.-4	7.36	0.36
	High I.S.-5	7.93	-0.09 ^a
	High I.S.-6	7.97	-0.07 ^(a)
3,000	High I.S.-7	6.53	6.09
	High I.S.-8	6.68	3.93
	High I.S.-9	7.26	0.16
	High I.S.-10	7.11	0.20
	High I.S.-11	7.90	0.02
	High I.S.-12	7.89	0.03

(a) The concentration of adsorbed U(VI) used to calculate the K_d was determined by subtracting the total amount of dissolved U(VI) from the initial concentrations of dissolved U(VI). For conditions of very low adsorption of U(VI), negative K_d values are therefore possible, and should be considered to equal 0 mL/g.

carbonate on U(VI) adsorption at fixed pH (pH 7.5±0.3). These U(VI) K_d values approach values as low as zero at total bicarbonate concentrations of equal to or greater than 12 meq/L as shown in Table 6.6. This concentration of total dissolved bicarbonate is less than the ~40 meq/L inorganic carbon recommendation of very low K_d values presented in Table 6.1 for the regions of the vadose zone affected by the composition of the glass leachate in the IDF PA.

The chemical composition predicted from the STORM code calculations for leachates that percolate out of the IDF are based on a detailed data set for glass leaching and a well-accepted kinetic dissolution model (see Pierce et al. 2004), but the subsequent interactions with the vadose zone sediments have not been characterized to the same extent. Up until this time, it was not realized that a more accurate assessment of the pore water composition would be important in selecting K_d values for key contaminants such as U(VI). During the 2005 IDF PA activities, a more robust and accurate conceptual model will be developed to better address the chemical evolution of the glass leachate as it migrates through the sediments under the IDF.

One key reaction that will need to be added to the modeling calculations is the ion exchange of sodium that leaches from the glass with calcium and magnesium that naturally exist on the sediment exchange sites. The sediment contains a large source of calcium and magnesium (~40 to 70 meq/kg of sediment) that can react with the carbon dioxide equilibrated glass leachate and perhaps decrease the concentrations of dissolved inorganic carbon in response to calcite precipitation. Other calcium- and sodium-bearing secondary minerals may also form, such as those identified in laboratory experiments completed to investigate the pore fluid and mineral reactions resulting from contact of simulated tank leak fluids with Hanford sediments (see references noted in Section 3.8). Wan et al. (2004a, b) and references

Table 6.6. K_d Values (mL/g) Measured for U(VI) by Serne et al. (2002a) as a Function of Dissolved Inorganic Carbon (Bicarbonate) Using Hanford Formation Coarse Sand and High Ionic-Strength Sodium-Bicarbonate-Sulfate Solution (constant ionic strength and pH = 7.5±0.3)

Initial Conc. Dissolved U(VI) (ppb)	Sample Number	Total Dissolved HCO ₃ ⁻ (mM)	K_d	Average
			----- (mL/g) -----	
500	High I.S.-1	2.57	0.38	0.35
	High I.S.-2	2.47	0.32	
	High I.S.-3	6.46	0.08	0.06
	High I.S.-4	6.18	0.05	
	High I.S.-5	14.8	-0.47 ^a	
	High I.S.-6	12.3	-0.51 ^a	
3,000	High I.S.-7	2.66	0.22	0.20
	High I.S.-8	2.63	0.17	
	High I.S.-9	6.49	0.16	0.15
	High I.S.-10	5.83	0.14	
	High I.S.-11	12.42	0.03	0.05
	High I.S.-12	12.02	0.07	

(a) The concentration of adsorbed U(VI) used to calculate the K_d was determined by subtracting the total amount of dissolved U(VI) from the initial concentrations of dissolved U(VI). For conditions of very low adsorption of U(VI), negative K_d values are therefore possible, and should be considered to equal 0 mL/g.

cited therein showed that these ion exchange and precipitation reactions consume hydroxyl and thus decrease the solution pH. The lowering of the pH and presence of more calcium and magnesium should, in turn, decrease the predicted concentration of total dissolved inorganic carbon in the pore fluids. Lower pH and lower concentrations of dissolved inorganic carbon in the pore fluids should result in U(VI) K_d values that are larger than the values found in the studies by Serne et al. (2002a). Whether the K_d values for U(VI) would increase to greater than 4 mL/g (or even 1 mL/g) as found for ambient groundwater conditions (see tabulation of Hanford-specific K_d values in Cantrell et al. [2003]) and under several of the leaking single-shell tanks (see discussion and references cited in Section 3.8) remains to be seen.

In Table 6.1 for uranium, we deviate from using the gravel correction convention of reducing the K_d value measured for sand by 90% as we have done for all other contaminants. We justify this change based on the fact that dissolved inorganic carbon (carbonate and bicarbonate) and pH are the two dominant variables that have the greatest effect on U(VI) adsorption. Our laboratory testing with 300 Area sediment (see Serne et al. 2002) that contain some gravel shows that U(VI) sorption is not significantly reduced by the presence of gravel. We thus chose uranium K_d values (see Table 6.1) for gravel zones the same as for sand zones. We feel this is a defensible position for dealing with this key risk-driving contaminant.

Additional laboratory experiments may be necessary to validate the lower K_d values recommended for U(VI) (see Table 6.1) in the 2005 IDF PA calculations for the vadose zone regions impacted by the composition of the glass leachate and to better determine the effects of having 90% gravel present. Specific laboratory experiments would need to be conducted to determine 1) the composition of the glass leachate, especially its pH and concentration of total dissolved inorganic carbon; 2) the volume of vadose-zone sediment that will be affected by the composition of the glass leachate; 3) the U(VI) K_d value determined using IDF-specific vadose-zone sediments and the best estimate of the compositions of the glass leachate; and 4) the effects of having predominantly gravel-sized particles present in specific strata.

6.3 K_d Values for ^{79}Se

In 1998, little Hanford-specific data existed for the adsorption properties of selenium (as selenate or selenite). For the 1998 ILAW PA, it was, therefore, recommended that the K_d values for ^{79}Se be set at 0 mL/g. Between 1998 and 2001, batch K_d studies (Kaplan et al. 1998c) were completed using several Hanford sediments, including IDF borehole 299-E17-21. The solution used in these measurements was uncontaminated groundwater, and the sediments were dominated by sand-sized particles. Kaplan et al. (1998b) also studied the adsorption of ^{75}Se , as a surrogate for ^{79}Se , from Hanford groundwaters with pH values that had been adjusted to higher than normal values. The measurements suggest that some significant adsorption of selenate would be expected for both groundwater and higher pH solutions. Thus for the 2001 ILAW PA, the “most probable” K_d value for selenium was chosen as 4 mL/g.

More recent work by Kaplan et al. (2003) indicates that selenate adsorption to Hanford sediments is nil for highly alkaline solutions. This is consistent with geochemical principles (see discussion in EPA 1999a and references therein) that suggest that anionic species, such as selenite and selenate, should show reduced sorption at greater-than-neutral pH conditions onto any sediment containing minerals with variably charged adsorption surface sites, such as iron and aluminum hydrous oxide minerals and particle coatings.

Um and Serne^(a) used an uncontaminated groundwater and a simulated glass leachate based on the composition for the long-term, steady-state chemical composition of glass leachate and vadose zone pore water predicted by the STORM code for the 2001 ILAW PA (See Table 6.2) to study selenate adsorption onto three samples of Hanford formation sediments from another IDF borehole (299-E24-21 [ILAW borehole #2 – C3177]). The K_d values measured by Um and Serne for selenate are described in Section 3.5.3. These tests also contained a trace amount of stable selenate (few parts per billion) that was not present in the earlier studies by Kaplan et al. (1998b, c). Because these earlier studies used only the carrier-free ⁷⁵Se isotope (which essentially means the mass of selenium present was infinitesimal), we later became concerned that the K_d results might be biased high by not having some selenium mass present. The most recent results by Um and Serne^(a) corroborate the selenium K_d values obtained by Kaplan et al. (1998c) for natural groundwater and Hanford sediments, but do indicate that selenium K_d values for more alkaline solutions, including simulated glass leachate, are considerably smaller than 4 mL/g, the value recommended in 2001. Thus, for the 2005 IDF PA, we changed (decreased) the K_d value for ⁷⁹Se for the chemically impacted zones, where the glass leachate forces the pore fluid pH to be elevated above background. No changes were made to the K_d values for selenium for the near-field concrete-impacted zone. During preparation of this data package, we determined that for the 2001 data package, the recommended K_d values for the chemically impacted gravel zone had inadvertently not been reduced by the factor of 10 to account for the assumed 90% gravel content. Thus there is a change (correction) to the recommended 2005 K_d values for this zone.

Um and Serne^(a) measured the K_d for selenate in simulated glass leachate onto IDF borehole sediments (see Section 3.5.3) and consistently found non-zero K_d values for selenium for six tests. Their values for the simulated glass leachate ranged from 1 to 3 mL/g with good precision. At long time periods, we assume that glass weathering products will adsorb some selenium. Therefore we recommend that a non-zero K_d is appropriate and chose a K_d value of 1 mL/g for selenate for the long-term near-field zone. Based on the results of Um and Serne, we also are more confident that the “most probable” K_d for ⁷⁹Se for the chemically unaltered pore water/groundwater fluid can be increased from 4 to 7 mL/g (see Table 6.1). We have not tested selenium adsorption on Hanford sediments that contain significant quantities of gravel-sized material. We therefore rely on the conservative gravel-correction factor (see Equation 2.6) and assume that the gravel-dominated sequence at the bottom of the vadose zone and at the upper unconfined aquifer has 90% gravel. This effectively reduces the recommended K_d values in gravel zones by a factor of 10 as listed in Table 6.1. To build in further conservatism, the chemically impacted gravel values were reduced further. It is likely that the chemically impacted sand zone controls the travel time of selenium in the PA calculations.

(a) Um W and RJ Serne. 2004. “Sorption and Transport Behavior of Radionuclides in the Proposed Low-Level Radioactive Waste Disposal Facility at the Hanford Site, Washington.” Submitted to *Radiochimica Acta*.

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Appendix A

A Less Conservative Approach to Correcting K_d Values for the Presence of Gravel

Appendix A

A Less Conservative Approach to Correcting K_d Values for the Presence of Gravel

An alternative approach to correcting K_d values, which is less conservative than the approach used in the data package, is provided. This approach was developed from a project conducted in conjunction with the ILAW PA, and is described in Kaplan et al. (2000).

The equation used for gravel-corrected K_d values was:

$$Kd_{gc,g=0} = (1 - f)Kd_{<2mm} \quad (\text{A.1})$$

where f equaled 0.9. Thus, all the K_d values in the gravel-dominated sequence were reduced by an order of magnitude ($1 - f = 1 - 0.9 = 0.1$). An alternative correction would be:

$$Kd_{gc,g=x} = (1 - f)Kd_{<2mm} + (f)Kd_{>2mm} \cdot \quad (\text{A.2})$$

Equation A.1 underestimated actual K_{dtotal} by 28% to 47%, whereas Equation A.2 slightly overestimated K_{dtotal} by 3% to 5% (Kaplan et al. 2000). Equation A.1 is conservative and Equation 2.2 is not, although the difference between K_{dtotal} and $K_{dgc,g=x}$ is not significant ($P < 0.05$). Equation A.1 becomes less and less accurate, i.e., the degree to which it underestimates K_{dtotal} increases, as the percent of gravel (f) increases. At $f = 0.9$, $K_{dgc,g=0}$ will greatly underestimate the actual K_{dtotal} .

An attempt was made to apply Equation A.2 to the gravel corrections. We have laboratory data on strontium and cesium for $K_{d>2mm}$, i.e., 2 of the 26 radionuclides for which K_d data are needed for the data package. The ratio of $K_{d>2mm}/K_{d<2mm}$ for strontium and cesium were 0.23 and 0.42, respectively.

Assuming all radionuclides have a $K_{d>2mm}/K_{d<2mm}$ of 0.23, we can rewrite Equation A.2 as:

$$Kd_{gc,g=x} = (1 - f)Kd_{<2mm} + (f)0.23Kd_{<2mm} \cdot \quad (\text{A.3})$$

and then by setting $f = 0.9$, this simplifies to:

$$Kd_{gc,g=x} = 0.31Kd_{<2mm} \cdot \quad (\text{A.4})$$

Thus, gravel-corrected K_d values based on Equation A.4 will be 210% greater than those based on Equation A.1. Equation A.4 is likely to provide a more accurate estimate than Equation A.1, especially at the high-gravel concentrations needed for the PA. Perhaps more importantly, more uncertainty is associated with the approach presented in A.4 due to the lack of $K_{d<2mm}$ for each radionuclide (Kaplan et al. 2000).

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Appendix B

Discussion on Double Layer and Film Thickness

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Discussion on Double Layer and Film Thickness

The double layer thickness was estimated from the Debye-Huckel Parameter (K) (Hiemenz and Rajagopalan 1997):

$$K = \left[\left(\frac{1000e^2 N_A}{\epsilon k_B T} \right) \sum_i z_i^2 M_i \right]^{1/2} \quad (\text{B.1})$$

where K^{-1} (m) is sometimes used to estimate the double layer thickness, e is the electric charge (or charge of an electron, units = C), N_A is Avogadro's number, ϵ is fluid permittivity ($\text{C V}^{-1} \text{m}^{-1}$), k_B is Boltzmann's constant (J K^{-1}), z is the valence of the electrolyte, and M is the electrolyte concentration (M).

Assuming Ca^{2+} and SO_4^{2-} are the dominant ions at an ionic strength of 10 mM, the double layer thickness based on Equation B.1 is 1.5×10^{-9} m.

The film thickness was calculated with the following equation taken from Hillel (1980):

$$\lambda = \frac{\theta}{\rho_b A_{ss}} \quad (\text{B.2})$$

where λ is the film thickness (cm), θ is the volumetric water content, A_{ss} is the specific surface area (cm^2/g), and ρ_b is the bulk density (g/cm^3). Using $\theta = 0.6$, $\rho_b = 1.25 \text{ g}/\text{cm}^3$, and A_{ss} of $2000 \text{ cm}^2/\text{g}$ in Equation B.2, the film thickness (λ) = $2.4 \text{ }\mu\text{m}$.

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Appendix C

Information Requested for Near-Field Geochemical Transport Modeling

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Information Requested for Near-Field Geochemical Transport Modeling

Reactive transport modeling of the vitrified waste leaching and the near field is being performed using the computer code STORM that is described in the Waste Form Leaching Data Package (McGrail et al. 1999). The STORM code requires that the user provide the chemical formulas for the reactions needed to form the solid minerals that constitute the sediments and engineered barriers surrounding the glass waste forms and any secondary precipitates that form during the weathering process as water percolates into the IDF and interacts with the glass forms. Our Geochemical Data Package document will provide guidance and input to the STORM code. The mineralogy of the Hanford sand sediments that might be used for backfill and the native Hanford formation sands and gravels have been partially characterized at the IDF site (see Horton et al. [2003]). Further, some quantitative mineralogy of Hanford formation sediments taken from outcrops and from the sides of other solid waste disposal facilities in the 200 East and 200 West Areas has been reported. The data on pages 5 through 28 in Serne et al. (1993) list detailed mineralogical, geochemical, hydrologic, and physical characterization information for four sediments. Other quantitative mineralogy characterization of sediments underlying single-shell tank farms is found in Serne et al. (2002) and Lindenmeier et al. (2003). All this mineralogical information can be used as input to STORM.

In fiscal year (FY) 2000, about 10 of the 21 samples from the ILAW borehole (299-E17-21) drilled in FY 1998 were characterized for quantitative mineralogy using the same techniques discussed in Serne et al. (1993). The 21 samples were used to obtain site-specific K_d values, cation exchange capacities, particle sizes, and hydrologic parameters in FY 1998-1999. These data have been documented in topical reports (Kaplan et al. 1998; Reidel et al. 1998) and companion 2001 data packages (Khaleel 1999; Reidel and Horton 1999).

Mineralogy data needed for the STORM code reactive transport calculations for cement and concrete are available in Criscenti and Serne (1990), Criscenti et al. (1996), and Krupka and Serne (1996) and references cited therein. Hydrologic and physical properties of cement and concrete are discussed in Meyer and Serne (1999) and references cited therein. No actual data are available for cement solidified secondary waste forms, which will be co-disposed in the IDF, at this time.

It is unlikely that the 2005 IDF PA predictions will attempt to model all chemical dissolution/precipitation reactions for the backfill sediments, natural sediments, or solidified secondary waste forms that will constitute the IDF at closure. One practical reason for this omission is that the 2001 ILAW PA predicted wide margins of safety even using simple (and conservative) conceptual models for the very near-field interactions of the ILAW waste form with surrounding backfill and natural vadose-zone sediments. We expect the reaction products that precipitate from weathering of the various waste forms to be placed in the IDF and the surrounding backfill and natural vadose-zone sediments will sequester contaminants to a greater extent than the currently used simplified conceptual models allow.

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