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**Geochemical Data Package for the
Hanford Immobilized Low-Activity Tank
Waste Performance Assessment (ILAW-PA)**

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Abstract

Lockheed Martin Hanford Company (LMHC) is designing and assessing the performance of disposal facilities to receive radioactive wastes that are currently stored in single- and double-shell tanks at the Hanford Site. The preferred method of disposing of the portion that is classified as low-activity waste (ILAW) is to vitrify the liquid/slurry and place the solid product in near-surface, shallow-land burial facilities. The LMHC project to assess the performance of these disposal facilities is the Hanford ILAW Performance Assessment (PA) Activity. The goal of this project 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 prediction of contaminant migration from the facilities. This migration is expected to occur primarily via the movement of water through the facilities and the consequent transport of dissolved contaminants in the pore water of the vadose zone.

Pacific Northwest National Laboratory (PNNL) assists LMHC in their performance assessment activities. One of the PNNL tasks is to provide estimates of the geochemical properties of the materials comprising the disposal facility, 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 constraints. 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 solution concentration limit, a constant value. In future Geochemical Data Packages we will determine whether a more rigorous measure of solubility is necessary or warranted based on the dose predictions emanating from the ILAW 2001 PA and reviewers' comments.

The K_d 's and solution concentration limits for each contaminant are direct inputs to subsurface flow and transport codes used to predict the performance of the ILAW system. In addition to the best-estimate K_d 's, a reasonable conservative value and a range are provided. We assume that K_d values are log normally distributed over the cited ranges. Presently we do not give estimates for the range in solubility limits or their uncertainty. However we supply different values for both the K_d 's and solution concentration limits for different spatial zones in the ILAW system and supply time-varying K_d 's for the concrete zone, should the final repository design include concrete vaults or cement amendments to buffer the system pH.

If warranted, more technically rigorous information on uncertainty in the geochemical parameter values and estimates of the changes in parameter values over time will be supplied in future data packages.

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1.0 Introduction

The Hanford Immobilized Low-Activity Tank Waste Performance Assessment (ILAW-PA) examines the long-term environmental and human health effects associated with the planned disposal of the vitrified low-activity fraction of waste presently contained in Hanford Site tanks. Greater than 200,000 m³ of tank waste has been created as the result of separating nuclear materials from irradiated nuclear fuels. This waste has been stored in 18 underground tank farms. 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 contain most of the radionuclides, will be stored at Hanford until a national repository is approved. The low-activity fraction will be disposed as vitrified waste in the Hanford Site 200 East Area.

The design of the ILAW disposal facilities is evolving. Although there are four existing concrete vaults with a total useable volume of about 15,000 m³ that could be used current design staff are contemplating trench disposal in the 200-E Area of the Hanford Reservation.

The first ILAW performance assessment of the 200 East Area was completed in 1998 and it 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 this PA, (included Ac, Am, C, Ce, Cm, Co, Cs, Eu, I, Nb, Ni, Np, Pa, Pb, Pu, Ra, Ru, Se, Sn, Sr, Tc, Th, U, and Zr), the following isotopes were identified as posing the greatest potential health hazard: ¹²⁹I, ²³⁷Np, ⁷⁹Se, ⁹⁹Tc, and ^{234/235/238}U. 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 below). Near the buried vitrified waste, solubility constraints may also control the solution concentrations of contaminants. Thus, this data package contains empirically chosen “solubility limits” for selected contaminants in the regions close to the vitrified waste (see discussions below).

The purpose of this data package is to document the basis for selecting geochemical parameters and input values that will be used in the 2001 version of the ILAW-PA. In addition to the database, the philosophy, approach, and review process are presented.

2.0 Philosophy

2.1. Relation Between Distribution Coefficients and Retardation Factors

The distribution coefficient, or Kd 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 1):

$$Kd = \frac{C_{solid}}{C_{liquid}} \quad (1)$$

where C_{solid} ($M\ kg^{-1}$) and C_{liquid} ($M\ L^{-1}$) are the concentration in the solid and liquid phases, respectively. It is important to note that sorption, as expressed by Kd values, is normalized by weight. Contaminant transport modelers commonly use Kd values to account for chemical interactions between the contaminant and the sediment. The Kd value is used to define the retardation factor, which is the ratio of the average linear velocity of water ($m\ s^{-1}$) divided by the average linear velocity of the contaminant ($m\ s^{-1}$). For water saturated systems, the Kd value is related to the retardation factor (Rf, unitless) by the bulk density (ρ_b , $kg\ m^{-3}$) and the porosity (η , $m^3\ m^{-3}$) as follows (Valocchi 1984, Bouwer 1991):

$$Rf = \left(1 + \frac{Kd\rho_b}{\eta} \right) \quad (2)$$

The bulk density and porosity terms in Equation 2 convert the weight-normalized Kd value into a volume-normalized value. Note that for partially saturated sediments, the porosity term is replaced by the volumetric water content of the vadose zone sediments.

2.2. “Empirical” Kd Construct

The geochemical behavior of radionuclides in the subsurface will be described for the ILAW-PA using two parameters, the distribution coefficient (Kd value) and the solubility product (K_{sp}) of a specified solid. The distribution coefficient is a thermodynamic construct. It is the ratio of the concentration of a species reversibly adsorbed/exchanged to a geomeia’s surface sites divided by the concentration of the species in the surrounding solution. Using uranyl as an example, the definition of a specie-specific Kd as a thermodynamic construct is:

$$K_{d-thermo} = \frac{X \equiv UO_2^{2+}}{UO_2^{2+}} \quad (3)$$

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 $K_{d-thermo}$ is 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.

However, in order to apply the K_d construct to contaminant transport and performance assessment calculations, the definition of the construct is relaxed. The definition needs to be relaxed for several reasons. In natural systems, a multitude of different types of sorption sites exists. Also, it is very difficult 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 the measurement of their thermodynamic activity. The parameters that can be readily measured are the total contaminant concentration or radionuclide activity (not to be confused with thermodynamic activity) as opposed to the concentration/radioactivity of each individual species. Thus, the K_d construct, as defined in Equation 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 can not practicably be characterized 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 total concentration of all species that include 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 thermodynamic K_d construct would be for a simple system that contained three U(VI) species [UO_2^{2+} , $UO_2(OH)^+$, and $UO_2(OH)_2^0$]:

$$K_{d-therm} = \frac{\sum \text{Adsorbed U Species}}{\sum \text{Dissolved U Species}} = \frac{X \equiv UO_2^{2+} + X \equiv UO_2(OH)^+ + X \equiv UO_2(OH)_2^0}{UO_2^{2+} + UO_2(OH)^+ + UO_2(OH)_2^0} \quad (4a)$$

where $X \equiv$ is an average sorbent site (more than one sorbent site-type is expected in nature). The numerator and denominator in Equation 4a are summed over contaminant species sorbed as well as sorbent sites. The empirical K_d equation would be

$$K_d = \frac{\text{total U(VI) on solid}}{\text{total U(VI) in solution}} \quad (4b)$$

Among the reasons for selecting the "empirical" K_d construct for the 2001 ILAW-PA, as exemplified by Equation 4b, is

- 1) the bulk of the existing sorption literature on radionuclide sorption, especially at Hanford 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) K_d can be used directly in codes used for performance assessments such as the code PORFLO used in past ILAW predictions and the code VAM3DF to be used in future far-field vadose zone transport calculations (see Khaleel 1999), and
- 4) perhaps most importantly, there is presently 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).

By using site-specific materials in ILAW-funded experiments, it is possible to gather relevant data directly and not to rely on extrapolation from other sediment and aqueous systems. The problem with the rigorous thermodynamic species approach is that, there is presently no numerical or conceptual model developed that is sufficiently robust to predict accurately the degree of radionuclide adsorption by natural sediment (Sposito 1984, Westall 1994, Westall 1986, Wang et al. 1997, Davis et al. 1998). However, mechanistic models provide the necessary paradigms upon which technically defensible “empirical” K_d values must be based. For most of the data used in the ILAW PA geochemical data package, sorption experiments have been conducted with site-specific sediment and site-specific groundwater, which resembles natural vadose-zone porewaters.

Mechanistic models, although impractical for PA purposes, provide the necessary paradigms upon which “empirical” K_d values must be based.

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 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 (co)precipitation reactions. Identifying the processes that govern radionuclide chemical behavior is the single most important task necessary for estimating K_d values for the ILAW 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.

Identifying the processes that govern radionuclide chemical behavior is the single most important task necessary for estimating K_d values. Once the dominant geochemical process is identified for a specific set of environmental conditions, the range of reasonable values for the “empirical” K_d parameter can be narrowed.

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 sediment-groundwater slurries was increased from pH 8 to 10, U(VI)- K_d values 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 by >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, which attract cations, increased as the pH increased. The latter more dramatic increase was attributed to (co)precipitation of U(VI) with carbonate phases. These conclusions were supported by independent solubility calculations. What we learn from this particular study is much more than simply the magnitude of the K_d value that should be used as an input parameter to the ILAW PA; we 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.

2.3. 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 ILAW disposal site. The solubility constraints used for conditions where the calculated concentrations of the radionuclides are believed to exceed the solubility of an assumed controlling phase. The selection of controlling solid phases will be based on laboratory experiments and when experimental data are not available, on literature results. If the thermodynamic data for the solid phase is not available from laboratory experiments or the literature, then it will be calculated using chemical speciation and solubility algorithms. Once the solid phase is selected, the upper limit of radionuclide concentration will be calculated with the appropriate background electrolyte composition. If the background electrolyte composition remains essentially constant then the solubility product can be assumed to also be nearly constant. This has lead some PA 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 is controlled by solubility. At concentrations below this limit, the radionuclide concentration will be controlled by the “empirical” K_d construct. When the controlling solid can not be identified but empirical solubility tests clearly indicate that some unidentified phase is controlling solution concentration, then an empirical solubility relationship will be used. This empirical solubility product will include 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 concentration limit. This is especially true for the 2001 ILAW PA because little site/waste form/engineered barrier solubility work has been performed that identifies the controlling solids. Recent thermodynamic tabulations by the Nuclear Energy Agency in France may prove to be valuable references. Three books are currently available with data on U, Am, and Tc [see Grenthe et al. 1992, Silva et al.

When the controlling solid could not be identified but empirical solubility tests clearly indicate that some phase is controlling solution concentration, then an empirical solubility relationship will be constructed.

1995, and Amaia Sandino and Osthols 1999, respectively]. Other solubility data for other radionuclides can be found at the NEA web page <http://www.nea.fr/html/dbtdb>.

2.4. 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 saturated 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. It is the use of the constant- K_d model in retardation factor (Equation 2) that has caused most of the criticism; few natural groundwater pathways are spatially or geochemically homogeneous to the extent that the retardation factor for a species remains constant.

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, Am- K_d values in a Hanford sediment ranged from 0.2 to 53 mL/g, roughly a 200-fold range (Delegard and Barney 1983). Additional variability in the Am- K_d values, albeit less, was observed when slightly different Hanford 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 Am- K_d values ranging from 125 to 43,500 mL/g. (Interestingly, the lowest K_d in this survey of 12 soils/sediments from DOE-national laboratories was in 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 the K_d is a function of a large number of variables, it is common to vary systematically several parameters simultaneously in one experimental study. Factorial design strategies are most often invoked to determine the systematic change resulting from varying the independent variables on the dependent variables, typically the distribution coefficient (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). All these techniques have been used to develop empirical relationships describing K_d values in terms of other variables (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 americium's K_d value on one particular Hanford sediment:

$$\text{Log } [K_d(\text{Am})] = 2.0 + 0.1[\text{NaOH}] - 26.8[\text{HEDTA}] + 153.4[\text{HEDTA}]^2 \quad (5)$$

The independent parameters and their ranges used to develop Equation 5 were selected to simulate the plume of a HLW emanating from a steel-lined concrete tank into a sediment in the Hanford Site 200 Area Plateau. Numerous salts were found to have no significant effect on americium K_d values and therefore 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 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 200 Area Plateau are likely inappropriate for the vitrified LLW plume because the chemistry of the aqueous phase will be appreciably different.

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 it be 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). When used in a transport equation, the transport code must also keep track of the current value of the independent variables (such as [NaOH] and [HEDTA] for the examples described above; Equation 5) at each point in space and time. Keeping track of 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 necessary 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 R_F , 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.

2.5. Overview of Mechanistic Adsorption Models

Mechanistic models explicitly accommodate the dependency of K_d values on contaminant concentration, competing ion concentrations, variable surface charge on the adsorbent, and solute species distribution. Incorporating mechanistic, or semi-mechanistic, concepts into models is attempted because the models become more robust and, perhaps more importantly, for the standpoint of the ILAW PA, 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 a better model for describing adsorption of inner-sphere complexes, whereas the Gouy-Chapman model is a better model for describing outer-sphere or diffuse swarm adsorption (Sposito 1984, Westall 1986). The complexity of installing these models into existing transport codes that are favored for complete disposal system performance assessment and the diversity of Hanford waste leachate/sediment/contaminant combinations of interest would require a data collection effort more intense and costly than is likely to be available. A brief description of the state of the science is present 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; however, their application to complex natural sediments is not 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 micro-crystalline structures that exhibit quite different chemical properties when exposed to solutions. Thus, examination of the surface by virtually any experimental method yields only averaged characteristics of the surface and the interface. Parson (1982) discussed the surface chemistry of single crystals of pure metals and showed that the potential of zero charge of different crystal faces of 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 six pH units. This example indicated that an observable microscopic property of a polycrystalline surface might be the result of a combination of widely different microscopic properties and that characterizations 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 make it difficult to distinguish their effects between each other. 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 current understanding of reactions at the mineral-electrolyte interface have developed were based on titration of colloidal suspensions of minerals. Resolving questions left open by such research requires that the mineral surfaces be better defined (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 two different approaches: 1) empirical models and 2) 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 refer to models 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). The 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 understand of the chemistry at the interface and are often used for describing data from complex multi-component 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.

2.6. Gravel- K_d Issue

Essentially all K_d values in the literature and that have been measured at the Hanford site were generated from sediments that do not contain any gravel, particles >2-mm. However, there are regions in the subsurface of the ILAW site that are composed primarily of gravel-sized particles. At issue is that K_d values will likely be lower in sediments containing gravel because of the reduced surface area in the field as compared to the lab tested solids for the radionuclides to interact with. This is referred to as the gravel- K_d issue. Experiments were conducted with Hanford sediments to evaluate a number of methods to address the gravel- K_d issue (Kaplan et al. 1999 and see Appendix A). Three gravel-corrected K_d conceptual models, $K_{d_{gc}}$, were evaluated in this study: a correction based on surface area ($K_{d_{gc,surf}}$), a correction based on the assumption that the gravel simply diluted the $K_{d_{<2mm}}$ and had no sorption capacity ($K_{d_{gc,g=0}}$), and a correction based on the assumption that the K_d of the entire sediment ($K_{d_{tot}}$) was a composite of the $K_{d_{<2mm}}$ and the $K_{d_{>2mm}}$ values ($K_{d_{gc,g=x}}$). Based on data for the adsorption of trace concentrations of Sr, on average, $K_{d_{<2mm}}$ tended to overestimate $K_{d_{tot}}$ by 28%; $K_{d_{gc,g=x}}$ overestimated $K_{d_{tot}}$ by only 5%; $K_{d_{gc,g=0}}$ and $K_{d_{gc,surf}}$ underestimated $K_{d_{tot}}$ by 10 and 13%, respectively. Although, $K_{d_{gc,g=x}}$ provided the best estimate of actual values ($K_{d_{tot}}$), the input values for $K_{d_{gc,g=0}}$ are appreciably easier to acquire. Additional data regarding the gravel-correction can be found in Appendix A.

To account for the presence of gravel in the study area, K_d values will be lowered in a conservative method, whereby the gravel will be assumed to have no sorptive capacity for the radionuclides.

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

$$K_{d_{gc,g=0}} = (1 - g)K_{d_{<2mm}}, \quad (6)$$

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 <2-mm fraction. Equation 6 greatly improves the accuracy of the “empirical” K_d construct for Hanford sediments and perhaps more importantly from the stand

point of the ILAW PA, it provides in all cases a more conservative K_d value than the traditional $K_{d<2mm}$ commonly used in such calculations.

2.7. Moisture Dependency of K_d Values

The moisture dependency of K_d values has been and continues to be evaluated by our group (Lindenmeier et al. 1995, Kaplan et al. 1996, and Gamerainger et al. 1998). Based on our findings to date, as well as the literature, our present belief on this subject is that there is a slight decrease in U(VI)- K_d values as the moisture content in a system decreases. In support of 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 porewater, 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, which will become 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 since the double-layer around particle surfaces reach only nanometers into the water, whereas the uniform film thickness of pore fluid around unsaturated Hanford sediments is estimated to be several micrometers (see Appendix C for a short discussion). For the 2001 ILAW 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 the future PA’s (beyond the 2001 ILAW PA) are capable of modeling the mobile-immobile water concepts presented in van Genuchten (1981), then 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 the future PA’s for the vadose zone would be slightly lower than values derived from traditional tests conducted in saturated systems. We will also continue studies on the effects of partial saturation on the K_d of U(VI) for one more year in hopes of resolving the issue.

To account for a possible moisture dependency of K_d values, all K_d estimates assigned to the vadose zone will be slightly lower than values derived from traditional tests conducted in saturated systems.

2.8. 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, there has been an increasing awareness of a third, mobile solid phase. This mobile solid phase, mobile colloids, consists of organic and/or inorganic submicron-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 if mobile colloids in a plume emanating from the ILAW waste site 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, or 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 ILAW disposal site. Ramsay (1988) presented strong evidence for the existence of colloid particles in glass and cement leachate and provided an in-depth review of the various types of colloids that can/may exist (e.g., glass fragments, precipitation products, geological materials, secondary phases formed from glass leachate). However, based on experiments using Hanford groundwater and colloids, there is little likelihood that colloids would remain suspended in glass leachate, cement leachate, or Hanford groundwater (McGraw and Kaplan 1997). The ionic strength 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. This would minimize colloid-facilitated transport of radionuclides from the disposal site. Hence, colloid-facilitated transport of contaminants will not be considered as an important transport process in the ILAW PA until there is compelling evidence that our assessment is flawed.

There is little doubt that colloids with radionuclides associated with them will be generated at the disposal site. However, there is little likelihood that colloids would remain in suspension in glass leachate, cement leachate, or even uncontaminated Hanford groundwater because of the high ionic strength of these waters. This would minimize colloid-facilitated transport of radionuclides from the disposal site.

3.0 Geochemistry of Key Radionuclides

This section provides a brief description of the geochemistry of radionuclides identified by preliminary subsurface transport simulations as presenting the greatest health risks. Emphasis is placed on describing the chemical processes relevant to the Hanford unsaturated zone, which is a 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 a possible localized stagnant silt/mud region in the upper unconfined aquifer.

3.1. Iodine

There are 24 known isotopes of I, 18 of these isotopes 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 <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 1.7×10^7 years.

3.1.1. Aqueous Speciation

Iodine usually exists in fresh water in the minus one oxidation state as iodide (I^-) (Whitehead 1984). In alkaline and marine environments, iodine usually exists in the VII oxidation state as iodate (IO_3^-) (Whitehead 1984). Iodide 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, III and V, are much less frequently found in nature. Iodide is likely to be the dominant iodine species in the Hanford upper unconfined aquifer because its domain of predominance extends throughout the pH scale, completely covering a large part of the stability domain of water (Figure 1; Ticknor and Cho 1990). Oxidation of I_2 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 well-oxidized, high-pH systems as may exist in the near field of the ILAW disposal site. Iodide and IO_3^- tend to exist as free ions, but the complexes they do form are generally the most soluble of all halide complexes.

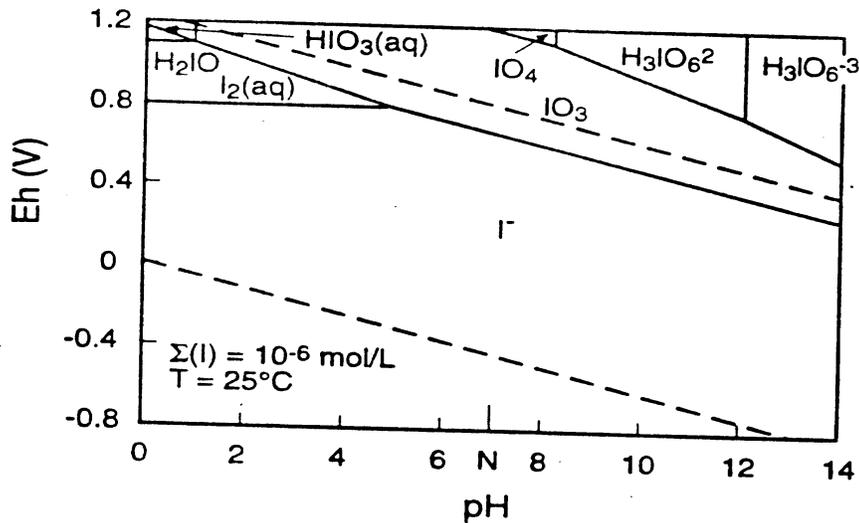


Figure 1. Eh and pH Diagram for Iodine/Water System (Ticknor and Cho 1990)

3.1.2. Precipitation and Coprecipitation

Precipitation of iodide compounds is not likely to be a dominant reaction path for iodide 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, Ag, Ba, Hg, Pb, and Pd (Pourbaix 1966) exist in nature at very low concentrations. The low concentrations of iodine in the contaminant plume will likely exist as either free species or as highly soluble complex species. However we are finding that the weathering products of glass, zeolites and clays, do seem to incorporate several anionic contaminants, including pertechnetate, Se, and I (it is not clear whether the species is I^- or IO_3^- at this time). Results will be published in a PNNL progress report in early FY00 and past progress that describes preliminary tests are found in Mattigod et al. 1998. At the present time we will not include this apparent co-precipitation or specific adsorption (see below) of iodine leached from the glass into or onto the zeolites and clays that form in transport calculations or the geochemical data package for the 2001 ILAW PA. This will build in a degree of conservatism that will be dealt with (removed) when quantitative data on co-precipitation is available certainly by the time that the 2003 ILAW PA is scheduled.

3.1.3. Sorption

Two types of reactions between anions and inorganic solids are recognized: specific adsorption and nonspecific adsorption. Specific adsorption refers to incorporation of anions as a ligand in the coordination shell of an adsorbent, while 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 through specific adsorption on organic substances (Walters and Winchester 1971). Nonspecific sorption may occur at the localized positive charges that occur on 1) Fe- and Al- oxide surfaces, 2) edges of aluminosilicate clay surfaces where the oxygen

atoms are not fully coordinated by Al or Si atoms, and 3) on 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 Fe and Al 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 Fe- or Al- oxides or clay. At pH<5, the removal of Fe- and Al-oxides resulted in a marked reduction in I⁻ sorption. Whitehead (1974) further observed that freshly precipitated ferric- and Al-oxides sorbed substantial amounts of I⁻ from solutions of pH <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.

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. The authors 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) showed that some naturally occurring 2:1 phyllosilicate minerals have the ability to sorb large amounts of iodide. K_d values >60 mL/g were measured for illites. Illite generally accounts for about 20% of the clay fraction of Hanford sediments. Even at pH >9, iodide K_d values for these illites were >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.

3.2. Neptunium

There are 16 known isotopes of Np from ²²⁸Np to ²⁴¹Np (Keller, 1971). Only ²³⁷Np, a neutron reactor product of ²³⁸Np (n, 2n), and ²³⁵Np (n, γ), with a half-life of 2.14 x 10⁶ years, are of interest to the ILAW PA.

3.2.1. Aqueous Speciation

Neptunium exists in aqueous solutions in five oxidation states, Np(III), Np(IV), Np(V), Np(VI), and Np(VII). In the absence of complexing agents, the first four oxidation states exist as hydrated ions Np⁺³-H₂O, Np⁺⁴-H₂O, NpO₂⁺-H₂O, NpO₂⁺²-H₂O (Ames and Rai 1978). Np(VII) is a strong oxidizing agent that is stable in strong alkaline solution as NpO₅⁻³. Between pH 0 to 9, NpO₂⁺ is the common Np species formed in aqueous environments (Ames and Rai 1978). Above pH 9 (and >100 mg/L carbonate) an uncharged bicarbonate complex is formed. According to Keller (1971), Np(V) does not form hydroxide complexes below pH of 7. Np(V) exists as the singly-charged neptunyl ion, NpO₂⁺, with symmetrical linear bonding (O-Np-O)⁺. It hydrolyses only at a pH of greater than 7, disproportionates only at high-acid concentrations, and

forms no poly-nuclear complexes (Keller 1971). NpO_2^+ ion complexes only weakly with inorganic ligands.

3.2.2. Precipitation and Coprecipitation

In an oxidizing environment, Np solids in an increasing order of stability are Np(OH)_4 , NpO_2 , $\text{NpO}_2(\text{OH})_2$. Because NpO_2 can maintain a very high concentration of Np in solution, it is unlikely that NpO_2 would be found as a discrete solid in terrestrial environments. It may exist in very reducing conditions as a solid.

3.2.3. Sorption

A singly charged neptunyl ion, NpO_2^+ , is likely the dominant species of Np in the oxidizing environment of the Hanford 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, Np-K_d values are usually relatively low (Routson et al. 1976, Sheppard et al. 1976). Benson (1961) examined Np sorption to 25 common sulfide, silicate, and carbonate minerals using trace amounts of Np 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 Np in the cooling water effluent from the Hanford 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% non-ionic. The fact that Np may become associated with a particulate phase may have significant ramifications regarding the potential role of subsurface mobile colloids in enhancing contaminant transport. A few studies have been conducted to evaluate the propensity of Np to adsorb to Hanford sediments (Rouston et al. 1976, Serne et al. 1993). Their results suggest low-to-moderate adsorption and are included in this data package.

A singly charged neptunyl ion, NpO_2^+ , is likely the dominant species in the oxidizing environment of the Hanford vadose zone. Neptunyl sorbs poorly to most minerals.

3.3. Selenium

^{79}Se is a long-lived fission product whose half-life is not well established. One estimate is 6.5×10^4 years but the value may be as much as ten times larger. ILAW is monitoring current efforts to resolve the half-life issue. ^{79}Se is commonly found as a fission product in spent fuel elements. The stable, nonradioactive form of Se is ubiquitous, especially in the western U.S. sediments. After nonradioactive Se was found to be the cause of reduced fecundity of migrating birds in the mid-1980s, much research was directed at understanding the environmental fate of Se.

3.3.1. Aqueous Speciation

Selenium exists in natural aqueous environments in -2, +4, and +6 valence states. Most of the Se species in natural waters exist as anions: selenate [Se(VI)] or selenite [Se(IV)]. Under reducing conditions, H_2Se^0 would dominate below pH 3.8 and HSe^- would dominate above pH 3.8 (Rai and Zachara 1984). The selenite species would predominate under intermediate to slightly oxidizing conditions. Highly oxidizing conditions ($\text{pe} + \text{pH} > 15$) are necessary for SeO_4^{2-} to form to a significant extent. Selenate and selenite may form ion-pair species with Ca^{2+} . Solid phases in order of increasing solubility are FeSe_2 , FeSe , and CuSe (Rai and Zachara 1984). However, the solubility product K_{sp} , for FeSe_2 or the other compounds are not well-defined.

3.3.2. Precipitation and Coprecipitation

Although several solid phases (such as FeSe_2) are predicted to be stable under relatively reducing conditions, and some studies indicate precipitation may be occurring, no definitive information on solubility-controlling solids is available. $\text{Fe}(\text{OH})_4\text{SeO}_3$ was proposed (Geering et al. 1968) to help explain the insolubility of Se in soils as well as the strong association of Se with Fe in precipitates. Benjamin and Bloom (1981) observed that metal ion adsorption onto amorphous iron oxyhydroxides was enhanced in the presence of an Fe-Se solid phase adsorbed on the oxyhydroxide surface. Benjamin and Bloom (1981) observed that selenite was irreversibly adsorbed on crystalline iron oxide surfaces (goethite, hematite). As mentioned in the Iodide section, recent laboratory tests where glass doped with anionic forms of Se, I, and Tc were weathered in water show that significant masses of these elements are incorporated into secondary minerals (clays and zeolites) that form. Thus ignoring co-precipitation and/or specific adsorption of these elements in the vault region may significantly over-estimate the transport and dose calculations in the 2001 ILAW PA. However, until we gain a better understanding of the glass weathering products, their long-term stability, and the incorporation process(es), we will not take credit for these retention processes until the 2003 ILAW PA.

3.3.3. Sorption

Laboratory studies indicate that, in spite of their anionic nature, selenite and selenate may be adsorbed significantly by some soils. The experimental evidence suggests that crypto-crystalline and amorphous forms of SiO_2 , Al_2O_3 , and Fe_2O_3 control Se adsorption (John et al. 1976, Singh et al. 1981). Studies with pure mineral phases demonstrate that hydrous oxides of Fe and Al 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, Hamdy and Gissel-Nelson 1977). (Singh et al. 1981). Selenate may be adsorbed more strongly by clay minerals than selenite (Frost and Griffin 1977), while the inverse applies to hydrous oxides of Fe (Leckie et al. 1980, Benjamin and Bloom 1981).

Though selenite ($\text{pK}_2:7.9$) and selenate ($\text{pK}_2:1.7$) differ appreciably in their acidity, little difference is seen in their adsorption by soil.

The adsorption of Se(IV) and Se(VI) on goethite, amorphous iron oxyhydroxide, and gibbsite is strongly pH dependent (Hingston et al. 1968, Leckie et al. 1980, Hingston et al. 1972). The anions are strongly sorbed under acidic conditions, but sorption decreases with increasing pH. Limited experimental evidence suggests that, at a given pH, Se 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 Se adsorption on goethite, though some sites are specific to Se (Hingston et al. 1971). Sulfate reduces SeO_4^{2-} adsorption on amorphous iron oxyhydroxides in a manner consistent with the competitive Langmuir equation (Leckie et al. 1980). The Se adsorption tests using Hanford-specific sediments and groundwater/alkaline leachates are described in this data package.

3.4. Technetium

All isotopes of Tc are radioactive. Several Tc isotopes are obtained by the fissioning of nuclear fuels of U in the reactor. The Tc isotopes and their yields resulting from U 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 fission products, only ^{99}Tc is a potential hazard from long-term burial of ILAW, because this isotope has a long half-life (2.12×10^5 years).

3.4.1. Aqueous Speciation

Technetium exists in valence states from (VII) to (-I). The most stable and characteristic oxidation state of Tc in slightly acid, neutral, or basic aqueous solutions in equilibrium with the atmosphere is pertechnetate ion (TcO_4^-) in which Tc is in the heptavalent state (Coughtrey et al. 1983, Hanke et al. 1986). Various Tc(V), Tc(IV), or Tc(III) species may be formed under reduced conditions (Pilkington 1990). However, the most stable of these reduced oxidation states is generally Tc(IV) (Bondietti and Francis 1979). The nature of the Tc(IV) species is uncertain: the most common species is $\text{TcO}_2(\text{s})$ (Bondietti and Francis 1979, Gu and Schulz 1991). The reduced Tc species are rapidly oxidized to Tc(VII) by atmospheric oxygen (Coughtrey et al. 1983), and therefore, regardless of the oxidation state of the Tc emanating from the near field, it is likely to be in the (VII) oxidation state once it reaches the far field.

Pertechnetate ion is highly soluble (Baes and Mesmer 1976, Pilkington 1990). In alkaline solutions and a low redox potential, the Tc(IV) species are more prevalent and its complexes are typically much less soluble, on the order of 10^{-7} to 10^{-8} mol L^{-1} over a range from pH 4 to 10 (Pilkington 1990). The solubility of Tc in contact with hydrated TcO_2 was investigated by Pilkington (1990). He found that pH had little effect on measured solubility of Tc over the pH range of 1 to 12.5. However, the presence of organic materials increased the measured solubility of Tc by a factor of 10, indicating that complexation between the dissolved organic materials and the Tc is important. Wildung et al. (1986) suggested that low molecular

weight organic ligands may increase the solubility of reduced forms of Tc, 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.

3.4.2. Precipitation and Coprecipitation

Precipitation of TcO_4^- - containing solids is not likely to be an important geochemical process affecting ^{99}Tc transport through the Hanford vadose zone. Technetium(VII) forms very soluble oxides and halide complexes (Baes and Mesmer 1976). However, if Tc(VII) is reduced to Tc(IV) in the near field, it may form a number of sparingly insoluble complexes such as TcO_2 or Tc-sulfide solids. As mentioned above, the glass weathering products formed in the short-term lab tests sequester significant amounts of Tc present in the glass as the pertechnetate species. Thus ignoring this removal process in the 2001 ILAW PA would appear to be adding a level of conservatism to the final predictions.

3.4.3. Sorption

A number of studies have shown that retention of Tc by solid phases is related to the physicochemical 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 Al/Fe 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 the soil could be extracted easily 30 days after application. Under anaerobic conditions, Cataldo et al. (1978) reported that Tc removal from solution by soils could exceed 97% in 2 to 5 weeks.

In a study of 7 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 Tc sorption. Evidence of the complexation between organic materials and Tc has also been presented by Van Loon et al. (1986). They indicated that such complexes can be readily synthesized by chemical reduction of pertechnetate in the presence of organic matter.

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

Retention of Tc is largely determined by the oxidation states of the system, due to the vast difference in the solubility between Tc(VII) and Tc(IV) containing compounds; Tc(VII) is retained appreciably less than Tc(IV).

organic matter – Tc(IV) complexation reaction can favorably compete with Tc(IV) hydrolysis reactions.

Many Hanford-specific adsorption studies with Hanford sediments and waters under oxidizing conditions have been performed and they generally show no adsorption of the pertechnetate anion. Specifics are found in this data package mainly in the tables found in Section 5.

3.5. Uranium

The natural abundance of U in geologic matter is about 3 mg/kg (Ames and Rai 1978). Naturally occurring U typically contains 99.283% ^{238}U , 0.711% ^{235}U , and 0.0054% ^{234}U by weight. Geologically, U occurs as U(IV) in minerals such as pitchblende, uraninite, carnotite, autunite, and as U(VI) in uranophane. It is also found in phosphate rock, lignite, and monazite sands at levels that can be commercially recovered. In the presence of lignite and other sedimentary carbonaceous substances, U enrichment in nature is believed to be the result of U reduction to form insoluble precipitates, such as uraninite. The U isotopes of interest in waste disposal and their respective half-lives include: ^{233}U , 162,000 years; ^{234}U , 247,000 years; ^{235}U , 7.13×10^8 years; ^{236}U , 2.39×10^7 years; and ^{238}U , 4.51×10^9 years.

3.5.1. Aqueous Speciation

Uranium can exist in the (III), (IV), (V), and (VI) oxidation states. The aqueous U(VI) uranyl cation (UO_2^{2+}) is the most stable ion in oxidizing solutions. The U(III) species easily oxidizes to U(IV) under most reducing environmental conditions, while the U(V) aqueous species (UO_2^+) readily disproportionates to U(IV) and U(VI). In aqueous systems, U(IV) species will not be present to any great extent as a result of the low solubilities of U(IV) species, such as uraninite (UO_2) or some other solids with O/U ratios between 2.3 and 2.7 (Bruno et al. 1988, Bruno et al. 1991). Average U concentrations in natural waters under reducing conditions are between 3 and 30 ppb (Bruno et al. 1991); this is consistent with equilibrium concentrations controlled by $\text{UO}_2(\text{s})$ (Bruno et al. 1988). In the absence of complexing agents, U(IV) is expected to hydrolyze to form mononuclear hydroxo complexes, $\text{U}(\text{OH})_n^{4-n}$ (Langmuir 1978). Complexation of (IV) actinides 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, (IV) actinides species form stronger organic complexes than do the (VI) actinides species (Birch and Bachofen 1990).

Aqueous U(VI) or uranyl, UO_2^{2+} , tends to form strong complexes with inorganic oxygen-containing ligands such as hydroxide, carbonate, and phosphate. Aqueous UO_2^{2+} hydrolyses 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 waters at near neutral to high pH, the carbonate complexes [UO_2CO_3^0 , $\text{UO}_2(\text{CO}_3)_2^{2-}$, $\text{UO}_2(\text{CO}_3)_3^{4-}$] will dominate, but at lower pH the hydrolysis species will dominate as CO_2 solubility decreases.

Phosphate- UO_2^{2+} complexes ($\text{UO}_2\text{HPO}_4^0$, 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 greater than 10^{-1} (Sandino and Bruno 1991, Langmuir 1978). Complexes with SO_4^{2-} , F^- , and possibly Cl^- are potentially important U(VI) species where concentrations of these anions are high. However, their stability is considerably less than that of the carbonate and phosphate complexes (Grenthe 1991). Because of the high hydroxide, high carbonate, and low organic matter concentrations expected in both the near and the far field of the Hanford ILAW disposal sites, U(VI) is likely to exist as a complexed carbonate and/or to a lesser extent, as a hydroxide-complexed species.

3.5.2. Precipitation and Coprecipitation

Precipitation or coprecipitation of a solid phase will likely not control the mobility of U(VI) in the far field vadose zone. However, reduced conditions may be created in the near field that may maintain the waste U as a uraninite precipitate, $\text{UO}_2(\text{s})$, (Rai et al. 1990). 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 2003 ILAW PA after more quantitative data are available. Besides determining the “loading” capacity of the weathering products for U and other contaminants, the long-term stability of the weathering products needs to be established. U(VI) insoluble compounds also appear to control solution concentrations of U in cementitious environments (see Brady and Kozak 1995, Krupka and Serne 1998, and Serne et al. 1996).

3.5.3. Sorption

Uranium is most mobile in oxidizing, carbonate-rich solutions. Therefore, under these conditions, one would anticipate that U would be most soluble. However, other secondary factors may affect the mobility as well. For example, in low ionic strength solutions, the uranyl ion concentrations will probably be regulated, in part, by cation-exchange adsorption process. The uranyl ion 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 Ca^{2+} , Mg^{2+} , and K^+ will displace the uranyl ion, forcing it into solution. Not only will other cations out compete the uranyl ion 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 U in solution (Yeh and Tripathi 1991). The anionic uranyl-carbonate complexes do not adsorb to the naturally negatively-charged Hanford sediments at neutral to alkaline pH conditions.

The uranyl ion is particularly mobile in high-ionic-strength solutions such as is expected to exist in the plume emanating from the Hanford LLW burial site.

Some of the sorption processes in which uranyl ion participates are not completely reversible. Sorption onto iron and manganese oxides can be a major process for extraction of U from solution. These oxide phases act as a short-term irreversible sink for U in soils. Uranium bound in these phases is not generally in isotopic equilibrium with dissolved U 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 U 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 form stable complexes. A process such as this probably accounts for a significant fraction of the organically bound U in soils, and perhaps, in sediments. Alternatively, sedimentary organics may reduce dissolved UO_2^{2+} 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-U 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. However, 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 naturally-occurring organic substances found in natural systems.

Uranium sorption to iron oxides and smectite clay has been shown to be extensive in the absence of CO_3^{2-} (Kent et al. 1988, Hsi and Langmuir 1985, Ames et al. 1982). In the presence of CO_3^{2-} and organic complexants, however, sorption was shown to be substantially reduced or severely inhibited (Hsi and Langmuir 1985, Kent et al. 1988, Ames et al. 1982). 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 and because of the presence of particulate or dissolved organic matter and dissolved carbonate.

Rancon (1973) studied the adsorption of U using four soils and three pure phase minerals. Quartz was characterized as inert ($K_d = 0$ mL/g), calcite was a poor U 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 U from solution. Acid, organic-rich soils showed higher U sorption ($K_d = 33$ mL/g) than soils containing carbonate minerals ($K_d = 16$ mL/g).

Formation of complexes between U(VI) and organic ligands such as humic and fulvic particulates has been studied most frequently because of interest in ore-forming environments. At ambient temperatures ($\sim 25^\circ\text{C}$), U 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, Szalay 1964). The adsorption is often followed by reduction to the U(IV) species followed by precipitation of UO_2 (Andreyev and Chumachenko 1964). In studies with lignite, however, the uranyl species formed a stable complex with the lignite without subsequent reduction; reduction only occurred at elevated temperatures (Nakashima et al. 1984). However, 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).

4.0 Approach

The geochemical data for both the far field and the near field were organized into five look-up tables, one for each environmental zone that was chosen to represent the ILAW pathway from the glass repository to the Columbia River. The concept and features of these five geochemical zones are presented in Table 1. A schematic representation of the five zones is presented in Figure 2. Each look-up table contains “empirical” K_d values and/or solubility data. For each contaminant in each environmental zone, a most-probable estimate, a reasonable lower-bounding estimate, and a likely range of estimates are provided. The distribution for all contaminant specific K_d and solubility parameters is assumed to be log normal for stochastic modeling. For each data entry, comments and references are provided to support the values.

Geochemical data will be organized into a number of look-up tables containing K_d values and/or solubility data for five environmental zones.

Whenever possible, the estimates provided in these tables were based on Hanford site-specific experiments. Generic literature or off-site data was 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 generate the K_d values were appropriate for the Hanford-specific zones. Consequently, expert opinion and geochemistry experience was utilized where non-site specific data was used; rationale and experimental evidence to support the expert opinion is provided. In some cases there was no generic data available and we were forced to use “expert judgement” to estimate values. The estimated values that have no actual measurements to defend the choices are marked.

Based on borehole 299-E17-21, the stratigraphy below the ILAW disposal site has two sequences, a sand-dominated sequence that exists from about 0- to 75-m depth and a gravel-dominated sequence that exists from about 75- to >475-m depth (Reidel et al. 1998). The sand-dominated sequence has essentially no gravel, except for a few gravel lenses (Reidel et al. 1998). The gravel-dominated sequence consists of about 90% gravel. Gravel-corrected K_d values (g in Equation 6 = 0.9) were used for radionuclides in the gravel-dominated layers (Zones 4 and 5 in Table 1). Little information is available about the properties and distribution of a mud layer that may exist within the gravel-dominated sequence at about 13- to 30-m below the water table (125- to 142-m below 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 core samples) clays in this zone, likely have a large sorption capacity as a result of a large cation-exchange-capacity (CEC) and surface area, and large potential for reductive precipitation. If this reducing mud layer was found to be present in a large area underneath the ILAW sites it would warrant more attention, especially for the fate of the high-dose redox-sensitive contaminants, such as Tc, U, Np, and Se discussed in Section 3.

Table 1. Conceptual features of the five geochemical zones			
Zone (Data Table)	Solid Phases	Aqueous Phase	Geo-chemical Parameters Used in Zone
Zone 1 – Near Field (Table 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 , solubility constraints
Zone 2 – Degraded Concrete Vault (Table 3) As of 12/01/99 this Zone may not be relevant in future repository design.	Three assemblages of minerals will exist, based on concrete age; fresh concrete with pH = 12.5, moderately aged concrete with pH ~10.5, and completely aged concrete 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 , solubility constraints
Zone 3 – Chemically Impacted Far Field in Sand Sequence (Table 4)	Sand-dominated sequence, slightly altered due to 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 4 – Chemically Impacted Far Field in Gravel Sequence (Table 5)	Same as Zone 3 except in gravel-dominated sequence	Same as Zone 3 except in gravel-dominated sequence	K _{d_{gc}}
Zone 5 – Far Field in Gravel Sequence (Table 6)	Unaltered Hanford gravel sequence (90% gravel, 10% <2-mm)	Unaltered Hanford groundwater except for trace levels of radionuclides	K _{d_{gc}}

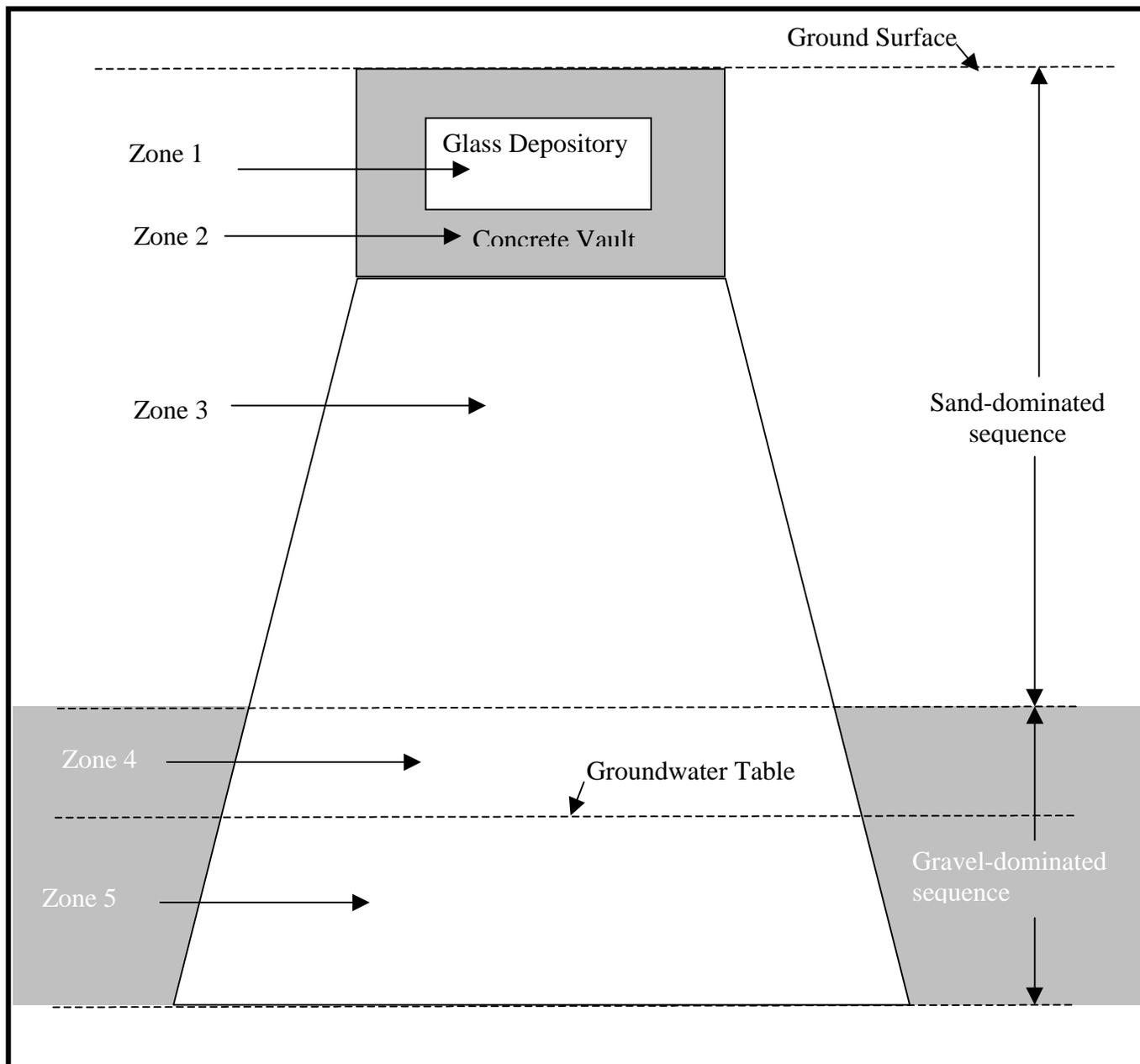


Figure 2. Schematic representation of the five geochemical zones.

The conceptual details of each of the five geochemical zones is described below.

1. **Near Field:** The chemistry in this zone is dominated by the presence of glass leachate until all the glass has dissolved. Glass leachate has high pH, ionic strength [especially soluble Na], 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. Initially, little or no contaminant adsorption will be considered on the glass. As reaction time

increases, radionuclides will be incorporated, coprecipitated, into secondary phases formed from glass-dissolution. Accounting for these processes will be closely linked with the glass waste-form leaching data package [see McGrail et al. 1999]. For the 2001 ILAW PA no credit will be taken for the coprecipitation of contaminants into the weathered glass secondary phases because we have not obtained adequate quantitative data for secondary minerals formed on the new BNFL glass formulations. We have also not determined the long-term stability of the weathering products found in the short-term hydrothermal [90 °C] tests. However, it seems clear from past [see Mattigod et al., 1998] and on-going studies on secondary phases formed from weathering other glass recipes that the coprecipitation process for trace contaminants into the zeolites and clays that form is significant. We have not presently finished determining how to take the empirical observations and generate mathematical algorithms for inclusion in the near-field transport code. Laboratory studies on determining the nature of the weathering products and trace contaminant sequestration amounts have been underway since early FY99 (Mattigod et al. 1998). Adequate data should be available for the 2003 ILAW PA.

2. **Degraded Concrete Vault:** Note that as of 12/01.99 the ILAW repository may not include concrete vaults; however crushed cement may still be used in the near field for pH control. 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 concrete 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 1. Zone 2 will also contain backfill materials. The cement weathering time evolution discussed in Krupka and Serne (1998) and Bradbury and Sarott (1995) were used to develop lookup tables for both K_d 's (onto degraded concrete/aggregate) and solubilities (in concrete porewaters and porewaters from concrete) as a function of time. Three temporal environments are being considered at present; fresh concrete with pH 12.5, moderately aged concrete with pH ~10.5, and completely aged concrete 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 ILAW PA system conceptual model. We will rely on the 2001 ILAW PA results to refine the conceptual model for this zone.

The convention of Bradbury and Sarott (1995) for the three types of physicochemical environments that all cements and concretes progress through was used for the development of a preferred database of K_d and solubility constraints. 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 Environment I with the formation of C-S-H gel [short hand for the $\text{CaO-SiO}_2\text{-H}_2\text{O}$ amorphous material that hardens

and constitutes “cement”) and portlandite [$\text{Ca}(\text{OH})_2$]. The composition of the cement pore fluid is at equilibrium with portlandite during this time. The duration of 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.

Temporal Environment II: During this period, the soluble salts of the alkali metals are all dissolved. The pH of the cement pore water is controlled at a value of 12.5 by the solubility of portlandite. The C-S-H and portlandite are the major solid phases present. Environment II may last for a long time. Its duration depends on how much water percolates through the system and the mass of cement present in the concrete structure. 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 100-10,000 years to 1,000-100,000 years.

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, Environment III can be conceptualized as leaving only silica (SiO_2) as the solubility control for the pore fluid pH. The ionic strength of the cement pore fluid during this period is low, and its pH is ~10 or less. For the sake of simplicity, the final end point of 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 Environment II is thus the longest in which the pore fluid composition is influenced by the hydration and dissolution reactions of the cement components.

3. **Chemically Impacted Far Field in Sand Sequence:** The chemistry in this zone has been impacted by the glass and concrete leachates, such that the porewater has a moderate pH between 8 (background) and 11, a moderate ionic strength between 0.01 (background) to 0.1, and low radionuclide activity (below solubility limits). This zone contains moderately altered Hanford formation sediment. This zone starts at the outside edge of the cement vault/engineered barriers and ends at the start of the gravel-dominated sequence (Figure 2). Contaminants will be controlled primarily by adsorption and not solubility constraints. However, we will consider [for the 2003 ILAW PA] the use of solubility controls in this zone should additional information become available that supports doing so. If the glass leachate and cement/engineered barrier leachates do evolve to less basic and lower ionic strength chemical solutions at long times, then the K_d values in Zone 3 will approach those in Appendix B, K_d values for the Far field in the Sand Sequence. Appendix B shows K_d values for <2 mm sized sediments for natural Hanford groundwater.
4. **Chemically Impacted Far Field in Gravel Sequence:** The chemistry in this zone has been impacted by the glass and concrete leachate, such that its pore water has a moderate pH between 8 (background) and 11, a moderate ionic strength between 0.01 (background) to 0.1, and low radionuclide activity (below solubility limits). This zone exists in the gravel-dominated sequence. The K_d values in this zone will be identical to those for Zone 3, except that the K_d values are gravel corrected. If the glass leachate and cement/engineered barrier leachates do evolve to less basic and lower ionic strength chemical solutions at long times,

then the K_d values in Zone 4 will approach those for Zone 5 at some time during the PA calculation.

5. Far Field in Gravel Sequence: This zone is located below the water table and is in the gravel-dominated sequence. The groundwater is assumed to dilute the major solutes down to natural background levels. The water in this zone is assumed to be “significantly tainted” only by contaminants and not by major common constituents of the glass and/or cement/backfill leachate. Hanford 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 1 and 2 have been completely removed by the geomedia or diluted to insignificant levels when compared to natural groundwater by the time the solution reaches Zone 5. This is equivalent to assuming that the groundwater flow is sufficiently large that it will dilute the leachate to the point that no competitive effects exist from the waste form and barrier’s leachates. The K_d values in zone 5 can be considered to be time invariant in our conceptual model.

5.0 Summary Tables

Geochemical input values for the five zones identified in Table 1 and Figure 2 are presented in Tables 2 through 6. For Zones 1 and 2, solubility constraints are provided for some contaminants where appropriate. If the near-field solution concentration of a contaminant is above the "Solubility Limit," the solubility value 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 judgement. The concept of using a central value, the statistics, and the raw data involved in identifying this central value were presented by Kaplan and Serne (1995) for I, Np, Se, Tc, and U. 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 log-normal.

For the empirical solubility estimates only Reasonable Conservative and "Best" estimate (or most probable) values are given. No ranges or solubility distributions are given at this time. If the 2001 ILAW PA shows that solubility constraints are important then some effort will be undertaken to improve the uncertainty/sensitivity calculations during the 2003 ILAW PA. Finally, supporting references for the selection of the various K_d and solubility values or estimates is provided.

Table 2a. K_d values for Zone 1 – Near Field ^(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, I, Se, Ru, C	0	0	0 to 1.1	C, Se, Cl, and I 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).
Tc	0.1	1	0.1 to 1.2	Non-zero Tc 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).
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, cesium-137 seemed to peak at about 10 ft below the base (elevation) of the tank and nitrate at about 80ft. This implies an in situ Rf of about 8 or a K_d value of about 1 or 2 mL/g during the initial tank leak. The lack of cesium in groundwater beneath tanks suggests it has not broken through. Serne and Burke (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, Nb, Np, Pa, Sn	0.1	0.2	0.1 to 4	Estimated (4).
Sr, Ra	4	10	4 to 20	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).
Th, Zr, Pb, Pu	5	10	5 to 100	Estimated (2, 4).
U	5	20	10 to 800	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

Table 2a. K_d values for Zone 1 – Near Field^(a)

				attributed to U (co)precipitation either as uranium phases or as calcite phases. Over a 1000-year period, it is anticipated that the solutions pH of any near field would eventually decrease. Thus, over time, the K_d values would be expected to decrease as the pH increased above ~10.5 and the uranium dissolved from the solid phase.
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^(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 1 and Figure 1). No gravel correction to K_d values.

^(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.

Table 2b. Solubility Values for Designated Solids in Zone 1 – Near Field ^(a)			
Radio-nuclide	Reasonable Conservative Solubility Limit (M)	“Best” Solubility Limit (M)	Justification/References ^(b)
³ H, Cl, Tc, I, Se, Ru, C	---	-----	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 x 10 ⁻⁷	1 x 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 x 10 ⁻⁴	5 x 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 x 10 ⁻⁴	5 x 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 x 10 ⁻⁵	3 x 10 ⁻⁶	Ra sulfate is the controlling solid. Bayless et al. (4) found no precipitation for Ra at 10 ⁻⁷ M in concrete leachate.
Sr	2 x 10 ⁻⁵	1 x 10 ⁻⁷	Sr carbonate forms in cements (1, 2, and 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 x 10 ⁻⁷	1 x 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 (Ewart et al. (3)). Other assessments of these values are presented in (1,2).

Table 2b. Solubility Values for Designated Solids in Zone 1 – Near Field^(a)

U	1×10^{-6}	1×10^{-7}	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) shows 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 (co)precipitation either as uranium phases or as calcite phases.
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^(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 1 and Figure 2). 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.

Rad	Young Concrete (pH~12.5)			Moderately Aged Concrete (pH~10.5)			Aged Concrete (pH~8.5)			Justification/References ^(b)
	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)	Conser- vative K_d (mL/g)	“Best” K_d (mL/g)	K_d Range (mL/g)	
³ H, Tc	0	0	0 to 2	0	0	0 to 2	0	0	0 to 1	Tc may be slightly sorbed to concrete, albeit, very little (1, 2, 3, 4, 5, and 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 7 types of concrete samples increased gradually over 3 months, than leveled off to between 25 and 130 mL/g (10, 11). After 300 days contact with various cements, 77 to 98% iodide sorbed; even more iodate sorbed. I sorption to cement is very concentration dependent: at 10^{-8} I K_d = 1000 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 1000	5	10	5 to 1000	0	0	0	Carbon-14 chemistry is complicated in cement; C (co)precipitation more important process in concrete than adsorption. See solubility discussion in Table 3b and (18).
Ac, Am, Ce Cm, Eu	2000	5000	2000 to 40000	1000	5000	1000 to 30000	400	500	400 to 1000	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 7 different 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).
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 3000 mL/g (17).
Nb, U	700	1000	700 to 2500	700	1000	700 to 2500	70	100	70 to 250	U(VI)- K_d 's for 7 types of cement = 350 to 13,000, average = ~1000 and median = 1400 mL/g (10, 11)
Cs	2	3	2 to 5	20	30	20 to 50	20	30	20 to 50	Cs K_d 's in hardened HTS cement discs, pH ~13.3, were 3 mL/g (7). Cs K_d 's 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).
Np, Pa	1400	2000	1400 to 10000	1400	2000	1400 to 10000	140	200	140 to 500	The dominant protactinium species is assumed to be Pa O_2^+ . Np O_2^+ is assumed to be a reasonable analog (19). Np sorption test to 7 different 65-yr old cements using cement pore water reached steady state after 30 days, K_d 's ranged 1500 to 9500 mL/g (10, 11).
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 be SeO_4^{2-} and RuO_4^{2-} respectively (19). Ru K_d 's in Hanford sediment (not concrete) did not change systematically with pH; at pH 8.5 the K_d was 274 mL/g; at pH 10.4, 44 mL/g; and at pH 14, 752 mL/g (21). Using a

Table 3a. K_d Values for Zone 2 – Degraded Concrete ^(a)										
										pH 12 simulated tank waste solutions and Hanford sediment, K_d values for Ru ranged from 2.14 to 0 mL/g, averaging about 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 (co)precipitation constraints. Selenate adsorption, independent of precipitation processes would be expected to be rather large.
Pb, Pu, Th	1000	5000	1000 to 10000	1000	5000	1000 to 10000	100	500	100 to 1000	Estimated. Using 3, 65 yr-old, crushed concrete samples, and 7 different fresh concrete samples, Th- K_d were 2500 to 5500 mL/g (10, 11). Th- K_d values were: consistently less than Am- K_d 's, greater than U- K_d 's, and very similar to Np Pu K_d 's (10, 11). Pu- K_d 's ranged from 1000 to 12,000 mL/g (10, 11). Concrete containing reducing agents (BFS) did not have greater Pu K_d 's than those that did not contain reducing agents. The high K_d values are attributed to high solubility of Pu in high pH solutions, not to adsorption/absorption processes (22)
<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 = 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 = Hoglund 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 1992.</p>										

Table 3b. Solubility Limits for Designated Solids for Zone 2 – Degraded Concrete ^(a)							
Rad	Young Concrete (pH~12.5)		Moderately Aged Concrete (pH~10.5)		Aged Concrete (pH~8.5)		Justification/References ^(b)
	Conser- vative (M)	“Best” Solubility (M)	Conser- vative (M)	“Best” Solubility (M)	Conser- vative (M)	“Best” Solubility (M)	
³ H, ³⁶ Cl, Tc, I, Ru, Se	---	---	---	---	---	---	We will assume no solubility constraint 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. Carbon-14 chemistry is complicated in cement; C (co)precipitation more important process in concrete than adsorption. Calcite will be a good controlling solid and the carbon-14 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	1 x 10 ⁻⁷	1 x 10 ⁻⁹	3 x 10 ⁻⁷	3 x 10 ⁻⁸	1 x 10 ⁻⁵	1 x 10 ⁻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, and 3).
Co, Ni	5 x 10 ⁻⁴	5 x 10 ⁻⁷	5 x 10 ⁻⁴	1 x 10 ⁻⁶	1 x 10 ⁻³	2 x 10 ⁻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).

Table 3b. Solubility Limits for Designated Solids for Zone 2 – Degraded Concrete ^(a)							
Rad	Young Concrete (pH~12.5)		Moderately Aged Concrete (pH~10.5)		Aged Concrete (pH~8.5)		Justification/References ^(b)
	Conser-vative (M)	“Best” Solubility (M)	Conser-vative (M)	“Best” Solubility (M)	Conser-vative (M)	“Best” Solubility (M)	
Nb, Np, Pa, Sn	5×10^{-4}	5×10^{-6}	1×10^{-3}	5×10^{-4}	1×10^{-3}	5×10^{-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).
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. Bayless 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).

Table 3b. Solubility Limits for Designated Solids for Zone 2 – Degraded Concrete ^(a)							
Rad	Young Concrete (pH~12.5)		Moderately Aged Concrete (pH~10.5)		Aged Concrete (pH~8.5)		Justification/References ^(b)
	Conser-vative (M)	“Best” Solubility (M)	Conser-vative (M)	“Best” Solubility (M)	Conser-vative (M)	“Best” Solubility (M)	
U	1×10^{-6}	1×10^{-7}	1×10^{-6}	1×10^{-7}	1×10^{-6}	1×10^{-7}	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) shows some empirical data for solubility in cement waters. Kaplan et al. (5) reported U-Kd 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 Kd was attributed to U (co)precipitation 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).</p>							

Table 4. Kd Values for Zone 3 – Chemically Impacted Far Field in Sand Sequence ^(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	0	0	0 to 0.1	Tc and Cl are anionic. ³ H will move with H ₂ O.
Ac, Am, Ce, Cm, Eu	100	350	100 to 1500	Am-K _d 's: 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 calcrete. ¹⁴ C removed by solid phases never stabilized during 70 days, suggesting (co)precipitation reaction.
Co	150	300	150 to 2000	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 2000	Estimated. In low ionic strength Na system, K _d is 64 to 1170 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	0 to 2	Anion. Estimated.
Ni, Sn, Nb	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 's 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 (personnel communications with Tjalle T

Table 4. K _d Values for Zone 3 – Chemically Impacted Far Field in Sand Sequence ^(a)				
				(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	20-1000	Good absorber, insoluble. Estimated (4).
Pu	80	200	80 to 1000	K _d is >98 mL/g (5)
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. However, 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, and 7).
Se	2	4	2 to 10	Anionic. Se K _d measured at the ILAW disposal site had K _d values of 6.7 ± 0.4 mL/g (14). Unpublished results of a Se sorption experiment to Hanford sediments in high ionic strength (NaOH and NaOCl ₄) indicate Se K _d values of ~4 mL/g.
Th, Zr	40	300	40 to 500	Sandy soil data, K _d is 40 to 470 mL/g for Th (8).
U	2	10	2 to 500	Anionic and neutral carbonate and hydroxide species. Kaplan et al. (11) 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 (co)precipitation either as uranium phases or as calcite phases.
<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 (Table 1 and Figure 2).</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.</p>				

Radio-nuclide	Reasonable Conservative $K_{d_{gc}}$ (mL/g)	“Best” $K_{d_{gc}}$ (mL/g)	$K_{d_{gc}}$ Range (mL/g)	Justification/References ^(b)
³ H, Cl, Tc	0	0	0 to 0.01	No gravel-corrected K_d data available. Tc and Cl are anionic. ³ H will move with H ₂ O.
Ac, Am, Ce, Cm, Eu	10	35	10 to 150	No gravel-corrected K_d data available. Am- K_d 's: In low ionic strength Ca system, >1200 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 expect 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 (co)precipitation 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 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	0 to 0.2	No gravel-corrected K_d data available. Anion. Estimated.
Ni, Sn, Nb	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 's 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 (personnel communications with Tjalle 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)
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 sediments are presented in Appendix A. Based on periodicity considerations, Ra would be expected to sorb more strongly to sediments than Sr. However, 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, and 7).
Se	0.2	0.4	0.2 to 1	No gravel-corrected K _d data available. Anionic. Se K _d measured at the ILAW disposal site had K _d values of 6.7 ± 0.4 mL/g (14). Unpublished results of a Se sorption experiment to Hanford sediments in high ionic strength (NaOH and NaOCl ₄) indicate Se K _d values of ~4 mL/g.
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	0.2	1	0.2 to 50	No gravel-corrected K _d data available. Anionic and neutral carbonate and hydroxide species. Kaplan et al. (11) 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 (co)precipitation either as uranium phases or as calcite phases.

^(a) The aqueous phase is moderately altered from the cement and glass leachate emanating from Zones 1 and 2; pH is between 8 (background)

Table 5. Gravel-corrected Kd Values ($K_{d_{gc}}$) for Zone 4 – Chemically Impacted Far Field in Gravel Sequence^(a)

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 1 and Figure 2).

^(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.

Table 6. Gravel-corrected Kd Values (Kd _{gc}) for Zone 5 – Far Field in Gravel Sequence ^(a)				
Radio-nuclide	Reasonable Conservative Kd _{gc} (mL/g)	“Probable” Kd _{gc} (mL/g)	Kd _{gc} Range (mL/g)	Justification/References ^(b)
³ H, Cl, Tc	0	0	0 to 0.06	No laboratory results of gravel-K _d values available. 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 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 Kd less negative by a factor of 0.9 because of reduced surface area that would create the anion exclusion.
Ac, Am, Ce, Cm, Eu	6	30	6 to 130	No laboratory results of gravel-K _d values available. Am-K _d : 67 to >1200 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 1250	No laboratory results of gravel-K _d values available. Na system, 1290 to 2120 mL/g (11); Ca system, 2000 to 3870 mL/g (11); Hanford sediment/groundwater system 11600 to 12500 mL/g (12)
Cs	50	200	50 to 400	No laboratory results of gravel-K _d values available. Na system, 1410 to 1590 mL/g (11) Hanford sediment/groundwater system, 540 to 3180 mL/g (12).). Most recent results using ILAW specific borehole sediments [299-E17-21] yielded K _d of 2,030 ± 597(18).
I	0	0.01	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). Most 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, Nb	5	30	5 to 250	No laboratory results of gravel-K _d values available. Ni: Hanford sediment/groundwater system, 440 to 2350 mL/g (12) Ni: A study of a broad range of sediments, including those from Hanford had Ni-K _d 's of 50 to 340 mL/g (13).
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 4 observations; median was 17.8 mL/g (1). Later studies increased the K _d 's 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 (personnel communications with Tjalle 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	800	1000	800 to 8000	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 >1980 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

Table 6. Gravel-corrected Kd Values ($K_{d_{gc}}$) for Zone 5 – Far Field in Gravel Sequence ^(a)				
				of 14.3 ± 1.6 mL/g (18). See Appendix A for Sr K_d values measured with sediments containing gravel. Based on periodicity considerations, Ra would be expected to sorb more strongly to sediments than Sr. However, 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	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 laboratory 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 >2000 mL/g (15)
U	0.05	0.06	0.01 to 8	No laboratory results of gravel- K_d values available. 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).
<p>^(a) The aqueous phase is untainted Hanford groundwater except for trace levels of radionuclides; the solid phase is composed of the unaltered gravel-dominated sequence material (Table 1 and Figure 2). $K_{d_{gc}}$ is the gravel-corrected K_d value as defined in Equation 6. K_d values for the far field, without a gravel correction, are presented in Appendix B.</p> <p>^(b) References: 1 = Kaplan and Serne 1995b; 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. 1984; 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.</p>				

6.0 Review Process

6.1. Internal PNNL Review

Scientists from the Applied Geology and Geochemistry group that are not contributors to the ILAW project performed an internal peer review concurrent with the Hanford Review and to cover the required PNNL/DOE document clearance process. The Data Package was created in the format of a typical PNNL topical report.

6.2. Hanford Review

The Hanford Personnel who reviewed this data package are:

- Fred Mann, Fluor-Daniel Northwest
- Harry Babad, WHC retired (private consultant)
- Tom E. Jones, MacTec-Meier

We have received and addressed the comments of the Internal Hanford Review Team in the September 10, 1999 version of the document. The comments were not contentious enough to warrant a comment resolution meeting prior to submittal for review by the other Hanford organizations [DOE/BHI/LMHC].

The September 10, 1999 version of the Geochemical Data Package was then sent concurrently to DOE-RL/ORP [Richland Operations Office of River Protection], BHI, and LHMC project management for review. Their comments were minor. The Data Package was revised a second time on September 20, 1999. This revision was sent to the external review team.

6.3. External Review

We solicited review comments from external reviewers. The members of the External Review were:

- Patrick V. Brady, Sandia National Laboratory
- Steve Serkiz, Westinghouse Savannah River Company
- Tjalle T. (Chuck) Vandergraaf, Atomic Energy of Canada, Limited at Pinawa, Manitoba, Canada.

Resumes for these three reviewers are available from R. J. Serne at PNNL. The reviewers were given the Data Package and instructions on what is expected of them. After they reviewed the instructions and had all questions answered, the review process started in FY00. The three sets

of review comments were considered and our responses to the individual questions were shared among all external reviewers. This occurred in mid-December 1999. A final review was performed by Fred Mann prior to submittal to Lockheed and DOE-RL on December 20, 1999. Each reviewer prepared comments on the electronic September 20, 1999 draft and in emails. Our responses to the main comments were prepared and an electronic file [Respon~2.doc] was circulated. The final draft of the data package December 20, 1999 and the response file will be used by the reviewers to finalize any comments. These final comments, the Respon~2.doc electronic file and the data package will become part of the public record associated with this data package.

6.4. Scope of the Work Reviewed

The reviewers (both internal and external) were given the data tables of Kd and solubility controls for each of the six geochemical zones for each contaminant, the reference to the publicly available documents that were used, and the rationale for the choice of each value. The rationale, for those values that were chosen by relying on expert judgment and generic literature, were especially clearly documented. We also prepared a general description of our overarching philosophy on approaching the selection of geochemical parameters for the ILAW PA in chapter 2. In the final version of the data package public record we will include an assessment of how satisfied we are with the technical defensibility of each selected value and a priority listing on which parameters deserve the attention of future funding. The prioritization will also include a brief discussion of the types of test that would best be performed to improve technical defensibility and what key parameters should be controlled, varied or monitored in the experimental test program.

6.5. Review Criteria

The reviewers were given all the above material and were asked to review/comment on several levels including:

- understandability of the overall geochemical approach from a “layman’s “ and “systems PA” approach
- technical defensibility of the overall geochemical approach (peer to peer technical comments)
- technical opinion on the particular Kd and solubility constraints provided for each geochemical zone and contaminant
- request for missing/overlooked data that the reviewers think would improve selected values
- opinion on our assessment of satisfaction of the “defensibility” for each value or contaminant’s overall geochemical data base
- assessment of our choice and prioritization for future work regarding contaminants that need more study and on the type of tests to perform and what are the key parameters to vary, monitor, or control.

6.6. Schedule

TABLE 7. SCHEDULE FOR GEOCHEMICAL DATA PACKAGE APPROVAL		
	Item	Date
1	Send Data Package Plan to Technical Representative for Review	March 30, 1999
2	Final Plan, Incorporating Comments Issued By The Tech. Rep.	April 30, 1999
3	Inform technical representative by electronic message that Kd selection of Zones 3, 4, 5 and 6 have been completed	June 30, 1999
4	Send out Draft Data Package for Internal Hanford Review	July 1, 1999
5	Get comments back from Hanford Technical Review	July 12, 1999
6	Send out Draft Data Package to DOE/BHI/LHMC	September 30, 1999
7	Get comments back from other Hanford Organizations	October 15, 1999
8	Respond to Hanford Reviewers' comments	October 31, 1999
9	Send final Hanford Reviewed Draft to Outside Reviewers	October 8, 1999
10	Respond to Outside Reviewers First Round of Comments	November 15, 1999
11	Respond to Outside Reviewers 2 nd Round of Comments	December 10, 1999
12	Get final/formal letter comments back from Reviewers and Complete Data Package	December 31, 1999

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8.0 Appendices

Appendix A: A Less Conservative Approach to Correcting Kd Values for the Presence of Gravel

Appendix B. Kd Values For Far-Field Sediment Conditions

Appendix C. Discussion on Double Layer and Film Thickness

Appendix D. Information Requested For Near Field Geochemical Transport Modeling

Appendix A: A Less Conservative Approach to Correcting Kd Values for the Presence of Gravel

An alternative approach to correcting Kd values that 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. A manuscript of this research has been submitted for publication and is included in this appendix.

The equation used for gravel-corrected Kd values was:

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

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

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

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

An attempt was made to apply Equation A-2 to the gravel corrections. We have laboratory data on Sr and Cs for $Kd_{>2mm}$, i.e., for 2 of the 26 radionuclides for which Kd data is needed for the data package. The ratio of $Kd_{>2mm}/Kd_{<2mm}$ for Sr and Cs were 0.23 and 0.42, respectively.

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

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

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

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

Thus, gravel corrected Kd 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. However, and perhaps more importantly, more uncertainty is associated with the approach presented in A-4, due to the lack of $Kd_{<2mm}$ for each radionuclide.

DRAFT
Gravel-Corrected Kd Values

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Gravel-Corrected Kd Values

Abstract

Standard measurements of solute sorption to sediments are typically made on the <2-mm sediment fraction. This fraction is used by researchers to standardize the method, and to ease experimental protocol, whereby large labware is not required to accommodate the large gravel fraction (>2-mm particles). Since sorption is a phenomenon directly related to surface area, sorption measurements based on the <2-mm fraction would be expected to underestimate actual whole-sediment values for sediments containing gravel. This inaccuracy, referred to as the Gravel-Kd Issue, is a problem for ground water contaminant transport modelers who use laboratory-derived sorption values, typically expressed as a distribution coefficients (Kd), to calculate the retardation factor (Rf), a parameter that accounts for solute-sediment chemical interactions. The objectives of this laboratory study were to quantify the effect of gravel on Kd and Rf values and to develop an empirical method to calculate gravel-corrected Kd values. Three gravel corrections, Kd_{gc} values, were evaluated: 1) a correction based on the assumption that the gravel simply diluted the $Kd_{<2mm}$ and had no sorption capacity ($Kd_{gc,g=0}$), 2) a correction based on the assumption that the Kd of the intact sediment (Kd_{tot}) was a composite of the $Kd_{<2mm}$ and the $Kd_{>2mm}$ ($Kd_{gc,g=x}$), and 3) a correction based on surface area ($Kd_{gc,surf}$). On average, $Kd_{<2mm}$ tended to overestimate Kd_{tot} by 28 to 47%; $Kd_{gc,g=x}$ overestimated Kd_{tot} by only 3 to 5%; $Kd_{gc,g=0}$ and $Kd_{gc,surf}$ underestimated Kd_{tot} by 10 to 39%. Although, $Kd_{gc,g=x}$ provided the best estimate of actual values (Kd_{tot}), $Kd_{gc,g=0}$ was appreciably easier to acquire. These results have important implications regarding the traditional approach to modeling contaminant transport which uses $Kd_{<2mm}$ values. Such calculations may overestimate the ability of gravel-containing sediments to retard contaminant migration, thereby overestimating lower-bounding limits of contaminant migration. Use of gravel-corrected Kd values will improve such lower-bounding estimates.

Introduction

The extent that contaminants sorb to sediments is typically measured in the laboratory using a batch test in which the <2-mm particle size fraction of the sediment is placed into contact with an aqueous phase containing the contaminant of interest. The <2-mm fraction is used to standardize the method and to ease the experimental protocol, whereby large labware is not required to accommodate the gravel (>2-mm particles). 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 1):

$$K_d = \frac{C_{solid}}{C_{liquid}} \quad (1)$$

where C_{solid} ($M\ kg^{-1}$) and C_{liquid} ($M\ L^{-1}$) are the concentration in the solid and liquid phases, respectively. Since sorption is typically a surface reaction phenomenon (Sposito 1984), the extent of sorption based on the <2-mm fraction will overestimate the true extent of sorption for the entire sediment, especially in sediments dominated by gravel.

The discrepancy between the laboratory K_d value and the true field value due to excluding the gravel from the laboratory samples is referred to as the “gravel- K_d issue.” 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 ($m\ s^{-1}$) divided by the average linear velocity of the contaminant ($m\ s^{-1}$). The K_d value is related to the retardation factor (R_f , unitless) by the bulk density (ρ_b , $kg\ m^{-3}$) and the porosity (η , $m^3\ m^{-3}$) as follows (Valocchi 1984, Bouwer 1991):

$$R_f = \left(1 + \frac{K_d \rho_b}{\eta} \right) \quad (2)$$

As gravel concentrations in a sediment increase, the K_d value would be expected to decrease because the specific surface area of the sediment decreases; the bulk density would be expected to increase. These changes in sediment properties have opposite effects on the magnitude of the retardation factor (Equation 2). Bulk density values in the subsurface typically vary between $2650\ kg\ m^{-3}$ (the density of a solid quartz crystal) to $1180\ kg\ m^{-3}$ (the density of closely packed clay-size particles). K_d values of many metals and cationic radionuclides often vary by several orders of magnitude as a function of particle size (reviewed by Ames and Rai 1978 and Thibault et al. 1990). Thus, it is likely that the introduction of gravel to a system will cause the actual retardation factor to decrease because the K_d values will decrease to a greater extent than bulk density values will increase. An important implication of this conclusion is that transport modelers using traditional K_d values measured with the <2-mm sediment fraction will likely overestimate the ability of a gravel-containing sediment to retard contaminant movement, thereby overestimating lower-bounding limits of contaminant migration.

The objectives of this study were to: 1) quantify the effect of gravel on K_d and R_f values, and 2) develop a method to calculate gravel-corrected K_d values ($K_{d_{gc}}$). The intent of this research was to conduct batch-sorption experiments to develop a $K_{d_{gc}}$ that would be beneficial to contaminant transport modelers. Thus, we wanted the corrections to be based on the traditional K_d value, $K_{d_{<2mm}}$, for which there is an extensive literature base. Also, any additional parameters needed for the correction had to be easily obtainable, which would rule out extensive solid phase characterization.

Materials and Methods

Two laboratory experiments were conducted using similar experimental protocols. In the Natural Sediment Experiments, Sr sorption to various size fractions of eight natural, gravel-containing sediments was measured. In the Gravel-Amended Experiment, Sr sorption to sediments amended with varying amounts of gravel was measured. Three gravel corrections were evaluated: 1) a correction based on the assumption that the gravel simply diluted the $K_{d_{<2mm}}$ and had no sorption capacity ($K_{d_{gc,g=0}}$), 2) a correction based on the assumption that the K_d of the intact sediment ($K_{d_{tot}}$) was a composite of the $K_{d_{<2mm}}$ and the $K_{d_{>2mm}}$ ($K_{d_{gc-g=x}}$), and 3) a correction based on surface area ($K_{d_{gc,surf}}$). Strontium was selected as a trace solute because its geochemistry is relatively simple. It exists almost exclusively as the Sr^{2+} species between pH 3 to 9.5 and it sorbs to sediments almost exclusively by cation exchange (Ames and Rai 1978, Kaplan et al. 1998). It was anticipated that the relative simplicity of Sr geochemistry would ease data interpretation.

General Sorption Procedure

The general procedure used in the two experiments was identical. The solid phases (natural sediment or gravel-amended sediment) was first pre-equilibrated with an uncontaminated ground water collected from the Hanford Site located in Richland, Washington (Well 600-S3-25, Table 1). This was accomplished by adding the ground water to the solid phases (typically in a 40:1 solution to solid ratio), shaking the suspensions overnight, centrifuging, decanting the supernatant, and then measuring the supernatant pH. This was repeated until the pH of the wash solution did not change by more than ± 0.05 units before and after contact with the solid phase. Equilibration by this method typically required three washings. The purpose of the pre-equilibration step was to isolate the Sr-adsorption reaction from other reactions that may occur while sediments and solutions came to chemical equilibrium.

A portion of the equilibrated ground water solution was amended with $25\text{-}\mu\text{Ci L}^{-1} \text{ }^{85}\text{Sr}$, as carrier-free Sr^{2+} , and then mixed overnight on a platform shaker. The ^{85}Sr -amended solution was then placed in contact with the solids. The solid-to-solution ratio was 1:30 (wt:wt). This relatively low solid-to-solution ratio provided optimal sensitivity for measuring K_d values in the range of 10 to 30 L kg^{-1} . The aqueous ^{85}Sr /sediment suspensions were placed on a slow-moving platform shaker to equilibrate for 14 days. After equilibration, the suspensions were centrifuged and then passed through $0.45\text{-}\mu\text{m}$ filters. The ^{85}Sr activity and pH of the filtrates were measured. The ^{85}Sr activity was measured with a germanium detector. All radiological counting was performed to a 3% total error.

Distribution coefficients (K_d , $L\ kg^{-1}$) were calculated using Equation 3. This equation accounts for the dilution of the initial ^{85}Sr -amended solution by the interstitial ground water remaining in the sediment after the final pre-equilibrating wash (i.e., the ^{85}Sr -free ground water left in the tube after pre-equilibration):

$$Kd = \frac{(C_{initial} \times V_{initial}) - C_{final} (V_{initial} + V_{interstitial})}{C_{final} \times M_{sediment}} \quad (3)$$

where $V_{interstitial}$ is the volume of the interstitial solution left after the final pre-equilibration wash (L), $M_{sediment}$ is the sediment mass (kg), $V_{initial}$ is the volume of the ^{85}Sr -amended solution added to the sediment (L), C_{final} is the ^{85}Sr concentration in the effluent solution after contact with the sediment ($\text{Ci}\ L^{-1}$), and $C_{initial}$ is the ^{85}Sr concentration in the ^{85}Sr -amended solution added to the solids ($\text{Ci}\ L^{-1}$).

Two types of control treatments were included in these experiments: a negative and a positive control. The positive control consisted of the ^{85}Sr -amended aqueous phase, $C_{initial}$, and no solid phase. This control monitored Sr sorption to labware and filters. The negative control consisted of the solid and aqueous phases without added ^{85}Sr . This control quantified the amount of ^{85}Sr in the uncontaminated aqueous and solid phases or introduced into the experiment through laboratory activities. Four replicates of controls and of each treatment were included in the experimental design.

The ground water used in this study was characterized by standard methods. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was used to determine dissolved cation concentrations. It had an analytical precision of $\leq \pm 4\%$ at $5\ \text{mg}\ L^{-1}$ cation concentrations. Ion chromatography (IC) was used to determine dissolved anion concentrations. It had an analytical precision of $\leq \pm 4\%$ at $5\ \text{mg}\ L^{-1}$ anion concentrations. A carbon analyzer was used to determine total and inorganic carbon (Nelson 1987).

Sediment characterization was conducted using standard methods. Cation exchange capacity (CEC) was determined by the Na^+ - ion exchange method that is specifically designed for arid sediments (Rhodes 1987). Particle size distribution was determined by the sieve and pipette method (Gee and Bauder 1987). Bulk density and porosity were determined gravimetrically by repacking dry sediments in a column assembly (Klute and Dirksen 1986). pH was determined by the 1:1 solid:solution method (McLean 1987).

Three gravel corrections, $K_{d_{gc}}$ values, were evaluated: a correction based on the assumption that the gravel simply diluted the $K_{d_{<2\text{mm}}}$ and had no sorption capacity ($K_{d_{gc,g=0}}$), a correction based on surface area ($K_{d_{gc,surf}}$), and a correction based on the assumption that the K_d of the entire sediment ($K_{d_{tot}}$) was a composite of the $K_{d_{<2\text{mm}}}$ and the $K_{d_{>2\text{mm}}}$ values ($K_{d_{gc,g=x}}$). $K_{d_{gc,g=0}}$ was defined as:

$$Kd_{gc,g=0} = (1 - f)Kd_{<2mm} \quad (4)$$

where f is the weight fraction of gravel in the total sediment.

$Kd_{gc,g=x}$ was defined as:

$$Kd_{gc,g=x} = (1 - f)Kd_{<2mm} + (f)Kd_{>2mm} \quad (5)$$

One important disadvantage of $Kd_{gc,g=x}$ compared to $Kd_{gc,g=0}$ is that it requires $Kd_{>2mm}$, a parameter that may be difficult to measure. The additive approach would be expected to overestimate the extent of actual sorption because it does not account for masking of sorption sites by particles contacting each other.

The definition of $Kd_{gc,surf}$ is:

$$Kd_{gc,surf} = (1 - f)(Kd_{<2mm}) + (f) \left[(Kd_{<2mm}) \left(\frac{SA_{>2mm}}{SA_{<2mm}} \right) \right] \quad (6)$$

where $SA_{>2mm}$ and $SA_{<2mm}$ is a specific surface-area estimate ($m^2 kg^{-1}$) of the greater-than and less-than 2-mm fractions of the sediment, respectively (further defined below). The first term on the right side of Equation 6 is the weight-averaged Kd value of the <2-mm fraction. The second component on the right side of the equation accounts for the Sr sorption to the >2-mm fraction. Such a correction to the $Kd_{<2mm}$ assumes that the sorptive surfaces and sorption site density of the <2-mm and >2-mm fractions are similar. Furthermore, it assumes that the cause for differences between $Kd_{<2mm}$ and $Kd_{>2mm}$ values is due to the differences in the surface areas of the >2-mm and <2-mm fractions. These may be reasonable simplifying approximations in systems where the surfaces are coated with Fe-oxyhydroxides, organic matter, or carbonates.

In the absence of direct measurement, specific surface area can be approximated by assuming spherical particles, and from the particle surface area, volume, and particle density,

$$SA_i = (4\pi r_i^2) \left[\left(\frac{1}{4/(3\pi r_i^3)} \right) \left(\frac{1}{\rho_{p-i}} \right) \right], \quad (7)$$

where r is the average particle radius, ρ_p is the particle density, and the subscript i refers to either the <2-mm or >2-mm fraction. The term within the square brackets in Equation 7 converts the surface area of one particle ($m^2 \text{ particle}^{-1}$) to the specific surface area of a particle ($m^2 kg^{-1}$). By assuming that $\rho_{p-<2mm}$ is equal to the $\rho_{p->2mm}$, the ratio of $SA_{>2mm}/SA_{<2mm}$ in Equation 6, simplifies to $r_{<2mm}/r_{>2mm}$. For this study, $r_{<2mm}$ was estimated by multiplying the percent clay, silt, and sand in each sediment by 1.025, 0.026 and 0.001 mm, respectively, and then averaging these three numbers. $r_{>2mm}$ were assumed to be 3 mm.

Natural Sediment Experiment

Eight subsurface sediment samples were collected from the walls of a 20-m deep trench located in the 200 East Area of the Hanford Site, Richland, Washington. Samples were collected from sediment layers exposed by the trench to provide a wide range of gravel concentrations. At each sampling location, the surface 0.2-m of sediment was discarded prior to collecting approximate 1-kg sample. Samples were collected within 200 m of each other, in the same geologic formation and appeared to be composed of similar mineral assemblages. The samples were air-dried and then characterized for CEC, pH, bulk density, and porosity. Strontium-sorption tests were conducted on total, <2-mm, and >2-mm fractions following the General Sorption Procedure described above. There were four replicates for each gravel-amendment and both controls. Gravel-corrected K_d values were calculated using Equations 4 through 7.

Gravel-Amended Experiment

The solids used in these Sr-sorption experiment were composites created by combining varying amounts of gravel with the <2-mm sediment fraction from Sediment F of the Natural Sediment Experiment. The composite samples contained 0, 20, 40, 60, 80, and 100% (wt) gravel. The gravel used to make these samples was itself a composite of the gravel-fractions isolated from the sediments used in the Natural Sediment Experiment. The air-dried samples were characterized for CEC, pH, bulk density, and porosity. Strontium-sorption tests were conducted on the entire composite sample following the General Sorption Procedure described above. There were four replicates of each gravel-amendment and both controls. Gravel-corrected K_d values were calculated using Equations 4 through 7.

RESULTS AND DISCUSSION

Natural Sediment Experiment

Selected physical and chemical properties of the sediments used in the Natural Sediment Experiment are presented in Table 2. The gravel, sand, and silt-plus-clay (<50 μm fraction) fractions varied greatly between the sediments, ranging from 11.5 to 64.8 % (wt) gravel, 35.1 to 88% sand, and 0.1 to 25 % (wt) silt-plus-clay. Sediment pH, porosity, and bulk density did not vary greatly; pH ranged by <1 pH unit, porosity by <0.12-m³ m⁻³, and bulk density by 280 kg m⁻³. There was no significant correlation ($P \leq 0.05$ at 7 degrees of freedom) between gravel concentrations and CEC, porosity or bulk density. One would expect that as the gravel concentrations increased that bulk density would increase, and CEC and porosity would decrease. There was also no significant correlation between pH and CEC. There were significant differences between the bulk density and porosity values of the <2-mm and >2-mm fractions. The bulk density for the <2-mm fraction was always less than the bulk density for the whole sediment (except Sediment H). The porosity for the <2-mm fraction was always greater than the porosity for the whole sediment (again, except for Sediment H).

The various measured K_d values and gravel-corrected K_d values are presented in Table 3. Means and standard deviations for four replicates of the measured K_d values, K_{d_{tot}}, K_{d_{<2mm}}, and K_{d_{>2mm}}, are presented. No estimate of the variance associated with the gravel-corrected values is

available because they had to be calculated from averaged $Kd_{<2mm}$ and gravel concentration (f) values. All the gravel corrected Kd values were significantly correlated to Kd_{tot} , with $Kd_{gc,g=x}$ and $Kd_{<2mm}$ having the largest correlation coefficients (Table 3). However, based on the percent difference with Kd_{tot} (Equation 8), the accuracy of the various gravel-corrected Kd values for estimating Kd_{tot} varied appreciably.

$$\% \Delta Kd_x = \left(\frac{Kd_x - Kd_{tot}}{Kd_{tot}} \right) \times 100 \quad (8)$$

where Kd_{tot} is the Kd value measured using the entire sediment sample, Kd_x is a measured or gravel-corrected Kd value (Equations 4 – 7), and $\% \Delta Kd_x$ is the percent difference between Kd_x and Kd_{tot} . On average, $Kd_{<2mm}$ was 28% greater than Kd_{tot} , indicating that the $Kd_{<2mm}$ overestimated the Kd of the entire sediment sample by 28% (Table 3). Conversely, $Kd_{>2mm}$ was on average 45% smaller than Kd_{tot} . On average, $Kd_{gc,g=0}$ underestimated Kd_{tot} by 10%, indicating that the >2 -mm fraction had some sorptive capacity. This is not surprising in light of the fact that Hanford subsurface sediments typically contain iron-oxyhydroxide and carbonate coatings. Kaplan and Serne (1998) reported that three subsurface Hanford Site sediments contained about 0.3% (wt) Fe_2O_3 and 1.8% $CaCO_3$. These coatings may enhance the sorptive capacity of the feldspar, and quartz particles that typically comprise the larger particles of Hanford Site sediments. On average, $Kd_{gc,g=x}$ overestimated Kd_{tot} by only 5%. On average, $Kd_{gc,surf}$ values underestimated Kd_{tot} by 13%.

The average ratio of $Kd_{>2mm}$ to $Kd_{<2mm}$ for these sediments was 0.42 ± 0.08 (Table 3). Stated differently, the Kd value of the gravel was 42% of the Kd value of the <2 -mm fraction. By using Equation 9, which assigns the $Kd_{>2mm}$ a value 0.42 times $Kd_{<2mm}$, it was possible to calculate precisely the average Kd_{tot} (Table 3).

$$Kd_{gc,g=0.42} = (1 - f)Kd_{<2mm} + (f)0.42Kd_{<2mm} \quad (9)$$

Equation 9 provides the most accurate average gravel correction. Although Equation 8 requires only the knowledge of f and $Kd_{<2mm}$, it is limited insofar that the robustness of the 0.42 factor is not known. The 0.42 factor is likely not applicable to other contaminants or even to Sr in other sediment systems, since other sorption processes will often be involved.

Retardation factors were calculated (Equation 2) using the various measured and calculated Kd values (Table 3). For these calculations, the porosity and bulk density values of the total sediment (Table 2) were used because these parameters are essentially always measured on the entire sediment sample, as opposed to the <2 -mm sieved fraction used for the Kd measurement. The Rf value for the sediments, Rf_{tot} , averaged 231 ± 64 , meaning that Sr would be expected to move through these sediments at an average rate that was 231 times slower than water. The various Rf values varied proportionally to their respective Kd values, since the difference between the two constructs is a scalar (i.e., the ratio of ρ_b/η was constant for a given sediment). Thus, the % differences and correlation coefficients between the various Rf values and Rf_{tot} are identical to those listed in Table 3 for their respective Kd values.

The relation between sediment properties and the various K_d values were evaluated through linear regression analyses and correlation coefficients (Table 4). As expected, gravel fraction (f) and bulk density were generally inversely related to the various K_d and $\% \Delta\text{-}K_{d_x}$ values, whereas porosity and CEC were generally directly related to these parameters. Increases in gravel concentrations could decrease Sr K_d values by a number of processes, including reducing the sediment surface area. Increases in bulk density would be expected to result in decreased Sr K_d values because bulk density tends to increase in coarse sediments (Hillel 1980) and coarse sediments tend to have low specific surface areas (or low binding site concentrations) for Sr sorption. Conversely, increases in porosity would be expected to result in increased Sr K_d values because porosity tends to decrease in coarse sediments (Hillel 1980). The positive correlation coefficients with CEC may be attributed to the greater number of sorption sites available for Sr sorption.

Gravel-Amended Experiment

This experiment provided an estimate of the effect of gravel on sediment Sr- K_d values under more controlled conditions than in the Natural Sediment Experiment. In this experiment, the gravel fractions and the <2-mm fractions of each of the composite sediments had identical mineralogy, particle-size distributions, and surface chemistry. The only thing that changed between the samples was the proportion of the two size fractions.

The sediment properties used in the Gravel-Amended Experiment varied in an expected manner consistent with the amount of gravel added to the sediments (Table 4). As more gravel was added, the cation exchange capacity decreased ($r = -0.999$, $P \leq 0.001$), porosity decreased ($r = -0.990$, $P \leq 0.001$), and the bulk density increased ($r = 0.66$, $P \leq 0.05$). Unexplainably, pH also increased with increasing gravel additions ($r = -0.991$, $P \leq 0.001$).

$K_{d_{gc,g=x}}$ estimates most closely reflected the measured $K_{d_{tot}}$ values; overestimating the $K_{d_{tot}}$ values on average by $3 \pm 3\%$ (Equation 8 and Figure 1). $K_{d_{gc,surf}}$ underestimated $K_{d_{tot}}$ values on average by $-33\% \pm 32\%$, the degree of underestimation increased as the amount of gravel added increased. Similarly, $K_{d_{gc,g=0}}$ underestimated $K_{d_{tot}}$ values on average by $-39 \pm 37\%$, the degree of underestimation also increased as the amount of gravel added increased. A ranking of the K_d values by percent difference with $K_{d_{tot}}$, i.e., by their overall accuracy in estimate $K_{d_{tot}}$, is consistent with the ranking for the Natural Sediment Experiment (Figure 2): $K_{d_{<2mm}} > K_{d_{gc,g=x}} > K_{d_{tot}} > K_{d_{gc,g=0}} \geq K_{d_{gc,surf}} > K_{d_{>2mm}}$. For this experiment, $K_{d_{>2mm}}$ was 15.2 L kg^{-1} and $K_{d_{<2mm}}$ was 29.5 L kg^{-1} (Figure 1). The $K_{d_{>2mm}}/K_{d_{<2mm}}$ was 0.52, compared to the average ratio in the Natural Sediment Experiment of 0.42 (Table 3).

Strontium retardation factors calculated with $K_{d_{tot}}$ values (Equation 2) varied from 235 for the <2-mm fraction treatment (0% gravel-added sediments in Figure 2) to 166 for the gravel amended (100% gravel-added sediments in Figure 2). $Rf(K_{d_{gc,g=x}})$ values estimated actual Rf values, $Rf(K_{d_{tot}})$, very closely. $Rf(K_{d_{<2mm}})$ overestimated and $Rf(K_{d_{gc,surf}})$ and $Rf(K_{d_{gc,g=0}})$ underestimated $Rf(K_{d_{tot}})$. All of these trends are consistent with those observed for the respective K_d values (Figure 1). Unlike the other Rf values, $Rf(K_{d_{<2mm}})$ values increased as the percent of added gravel increased. Since the value of $K_{d_{<2mm}}$ used to calculate $Rf(K_{d_{<2mm}})$ remained constant for the various added-gravel treatments, the increase in Rf values reflects

changes in the ratio of bulk density to porosity (Equation 2). The bulk density to porosity ratio varied from 7.84 to 11.37 as the percent of added gravel increased from 0 to 100% (Table 5). This is an increase of 45% with respect to the ratio of the 0% added-gravel treatment. Since an increase in Rf is not expected as more gravel is added to a system, this illustrates an intrinsic error with keeping the Kd constant while varying the bulk density and porosity values. Since bulk density and porosity are more easily measured or estimated by empirical relations, it is not improbable that a modeled system would make this error.

Conclusions

Two experiments were conducted to quantify the gravel-Kd issue. Additionally, these experiments sought to evaluate methods an empirical method or formula to permit the conversion of the $Kd_{<2mm}$ value traditionally collected from laboratory experiments to gravel-corrected Kd values. The worse estimate of the actual Kd and Rf values for gravel-containing sediments was the traditional $Kd_{<2mm}$. On average, $Kd_{<2mm}$ over estimated actual Kd values by 28% in the Natural Sediment Experiment and 47% in the Gravel-Added Experiment. In one experiment, $Rf(Kd_{<2mm})$ values actually increased as the actual Rf values decreased. Of the various gravel-corrected Kd values, $Kd_{gc,g=x}$ provided the best estimate of the actual Kd value, Kd_{tot} , slightly overestimating Kd_{tot} values on average by between 3 and 5%. In both experiments, $Kd_{gc,x=0}$ and $Kd_{gc,surf}$ underestimated actual Kd values, the disparity systematically increased as the amount of gravel in the sample increased. This suggests that the gravel corrections for both constructs are less than perfect and therefore become systematically worse as the amount of gravel in the sample increases.

Although $Kd_{gc,g=x}$ clearly provided the best estimate of the actual Kd value, it has the important disadvantage in that it requires knowledge of the Kd value for the $>2mm$ fraction. This is experimentally difficult to measure and requires additional resources to acquire. When this information can not be acquired, the $Kd_{gc,g=0}$ or $Kd_{gc,surf}$ constructs may be a reasonable alternative. $Kd_{gc,g=0}$ has the advantage over $Kd_{gc,surf}$ in that the former requires knowledge of the percent gravel, whereas the latter requires knowledge of percent gravel and mean particle sizes in the $<2\text{-mm}$ and $>2\text{-mm}$ fractions. Percent gravel in a sediment may be inexpensively acquired by sieve analysis or if need be, estimated from common stratigraphic descriptions of well boreholes.

The findings in this study have important implications regarding the traditional approach to modeling contaminant transport using $Kd_{<2mm}$ values because such modeling may overestimate the ability of gravel-containing sediments to retard contaminant migration. This is a problem insofar that lower-bounding estimates, that is, conservative estimates, of contaminant migration may not be in fact truly lower-bounding and therefore worse-case scenarios may be improperly estimated. Use of gravel-corrected Kd values will improve such lower-bounding estimates.

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Table 1. Ground water (<0.45- μ m Filter) Chemical Composition

<i>Constituent</i>	<i>Concentration (mg L⁻¹)</i>
pH	8.3 (unitless)
Cl ⁻	22
NO ₃ ⁻	1.7
SO ₄ ⁻²	108
Total Organic C	0.73
Total Alkalinity (as CO ₃ ²⁻)	67.5
Al	0.14
B	0.05
Ba	0.069
Ca	67.5
Fe	0.14
K	3
Mg	16.4
Mn	0.046
Na	27.6
Si	16.2
Sr	0.28
Sum of Cations ^a	0.0065 M
Sum of Anions ^a	0.0054 M
Equilibrium Ionic Strength ^a	0.00918

^a Calculated by the geochemical thermodynamic code MINTQA2 (Allison et al. 1991).

Table 2. Properties of Sediments Used in the Natural Sediment Experiment

<i>Sediment Code</i>	<i>Total Sediment</i>					<i><2-mm Fraction</i>			<i>>2-mm Fraction</i>
	<i>Gravel/Sand/Silt+Clay (wt. %)^a</i>	<i>pH</i>	<i>Bulk Density (kg m⁻³)</i>	<i>Porosity (m³ m⁻³)</i>	<i>CEC (meq kg⁻¹)</i>	<i>Bulk Density (kg m⁻³)</i>	<i>Porosity (m³ m⁻³)</i>	<i>CEC (meq kg⁻¹)</i>	<i>CEC (meq kg⁻¹)</i>
A	11.5 / 88.0 / 0.5	8.34	1900	0.30	46.7	1860	0.31	59.2	26.2
B	39.0 / 54.0 / 7.0	9.01	2140	0.22	22.6	1840	0.28	16.8	16.9
C	28.0 / 69.5 / 2.5	9.03	2000	0.21	22.3	1820	0.26	14.5	6.1
D	44.0 / 55.6 / 0.4	9.25	2100	0.22	20.0	1840	0.30	13.1	18.2
E	44.0 / 53.7 / 2.3	9.02	2030	0.19	15.5	1800	0.27	16.7	6.0
F	21.0 / 54.0 / 25.0	8.38	2030	0.24	23.5	1960	0.25	19.1	6.0
G	52.0 / 43.0 / 5.0	9.18	2180	0.20	19.6	1700	0.27	17.0	NA
H	64.8 / 35.1 / 0.1	8.20	1930	0.31	73.0	1810	0.31	81.0	19.0

^a Gravel is ≥ 2 -mm; Sand is <2-mm and ≥ 50 - μ m; Silt +Clay is <50- μ m.

Table 3. Sr Kd Values, Retardation Factors and Correlation Coefficients from the Natural Sediment Experiment

	Kd_{tot}	$Kd_{<2mm}$	$Kd_{>2mm}$	$Kd_{gc,g=x}^a$	$Kd_{gc,g=0}^a$	$Kd_{gc,surf}^a$	$Kd_{gc,x=0.42}^a$
Sediment A	38 ± 3	50 ± 2	22 ± 1	47	44	45	47
Sediment B	37 ± 4	51 ± 3	20 ± 1	39	31	34	39
Sediment C	20 ± 4	34 ± 1	12 ± 4	28	24	25	28
Sediment D	19 ± 3	23 ± 0	13 ± 1	19	13	14	17
Sediment E	18 ± 3	21 ± 1	10 ± 1	16	12	13	15
Sediment F	31 ± 4	33 ± 3	13 ± 3	29	26	27	29
Sediment G	23 ± 3	27 ± 1	13 ± 6	20	13	15	19
Sediment H	27 ± 2	31 ± 1	10 ± 2	27	31	15	19
Avg. Kd	27 ± 8	34 ± 11	14 ± 4	28 ± 11	24 ± 11	24 ± 11	27 ± 11
Avg. % Δ - Kd_{tot} ^b	0	28 ± 21	-45 ± 10	5 ± 19	-10 ± 27	-13 ± 25	0 ± 24
Corr. Coef. with Kd_{tot} ^c	1.00	0.91***	0.83**	0.91***	0.85**	0.78*	0.87**
Avg Rf ^d	231 ± 64	296 ± 96	126 ± 38	241 ± 74	204 ± 70	203 ± 81	231 ± 86

^a Equations 4 through 7 and 9 were used to calculate these Kd values.

^b Equation 8 was used to calculate % Δ - Kd_{tot} .

^c Correlation coefficients between the various Kd constructs and Kd_{tot} . *, **, and *** indicate significance at the 5% level ($P \leq 0.05$), 1% level ($P \leq 0.01$), and 0.1% level ($P \leq 0.01$), respectively, for 7 degrees of freedom.

^d Retardation factors were calculated using Equation 2, Kd values from this table, and porosity and bulk density of the entire sediment from Table 2.

Table 4. Correlation Coefficients Between Sr Kd Values and Sediment Properties for the Natural Sediment Experiment

	<i>Gravel Fraction (f)</i>	<i>Bulk Density of Entire Sediment</i>	<i>Porosity of Entire Sediment</i>	<i>CEC of Entire Sediment</i>
Kd_{tot}	-0.46	-0.23	0.56	0.35
$Kd_{<2mm}$	-0.51	-0.22	0.44	0.26
$Kd_{>2mm}$	-0.59* ^a	-0.06	0.31	0.04
$Kd_{gc,g=x}$	-0.61*	-0.42	0.59*	0.37
$Kd_{gc,g=0}$	-0.48	-0.64*	0.79**	0.63*
$Kd_{gc,surf}$	-0.79**	-0.36	0.42	0.14
% Δ - $Kd_{<2mm}$ ^b	-0.28	-0.08	-0.15	-0.13
% Δ - $Kd_{>2mm}$	-0.21	0.32	-0.47	-0.56
% Δ - $Kd_{gc,g=x}$	-0.51	-0.47	0.23	0.15
% Δ - $Kd_{gc,g=0}$	-0.31	-0.78*	0.67*	0.64*
% Δ - $Kd_{gc,surf}$	-0.81**	-0.33	0.03	-0.16

^a * and ** indicate significance at the 5% level ($P \leq 0.05$) and 1% level ($P \leq 0.01$), respectively, for 7 degrees of freedom.

^b Equation 8 was used to calculate % Δ - Kd_x .

Table 5. Properties of Sediments Used in the Gravel-Amended Sediment Experiment

<i>Gravel Added</i> (%, wt)	<i>CEC</i> (<i>meq kg⁻¹</i>)	<i>pH</i>	<i>Bulk Density</i> (<i>kg m⁻³</i>)	<i>Porosity</i> (<i>m³ m⁻³</i>)
0	140.3	8.38	1960	0.25
20	118.2	8.44	1980	0.24
40	95.9	8.52	2010	0.23
60	73.3	8.61	2050	0.22
80	51.6	8.67	2100	0.21
100	29.5	8.7	2160	0.19

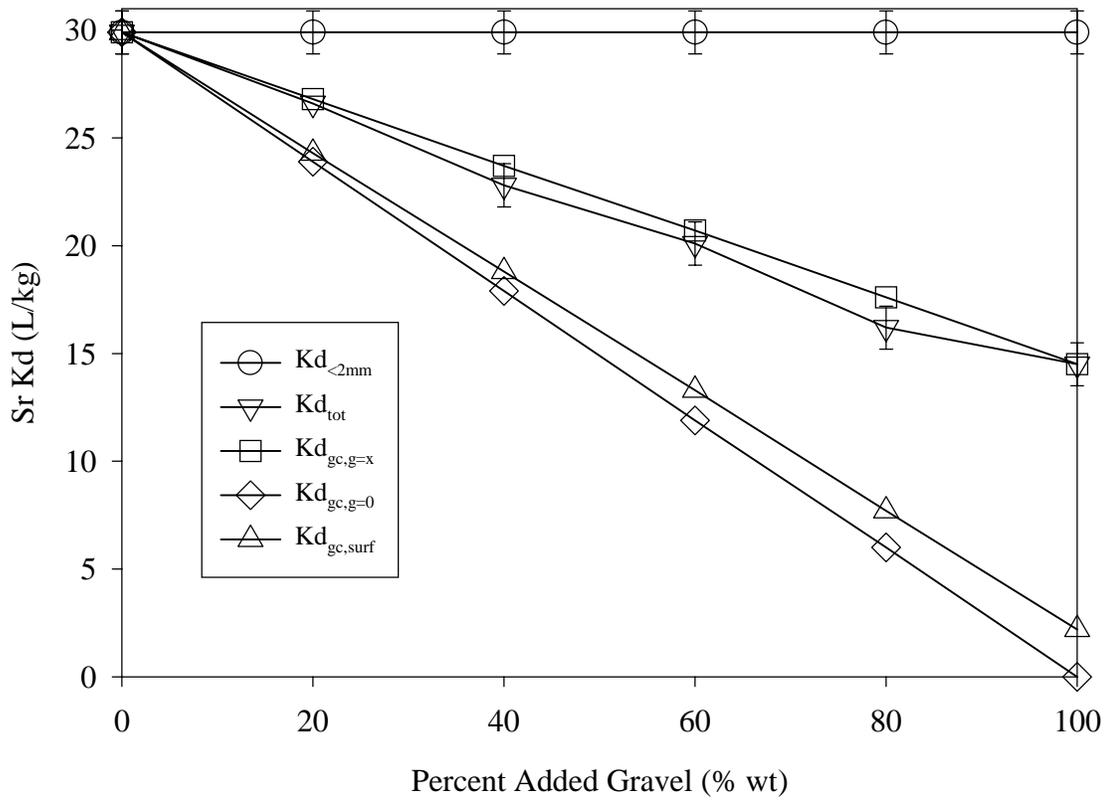


Fig. 1. Measured and gravel-corrected Sr Kd Values from the Gravel-Amended Experiment. $Kd_{<2mm}$ is 29.9 L kg^{-1} ; $Kd_{>2mm}$ is 15 L kg^{-1} . Kd_{tot} is the mean and standard deviation of 4 replicates. $Kd_{gc,g=0}$, $Kd_{gc,g=x}$, and $Kd_{gc,surf}$ calculated from Equation 4, 5, and 6, respectively.

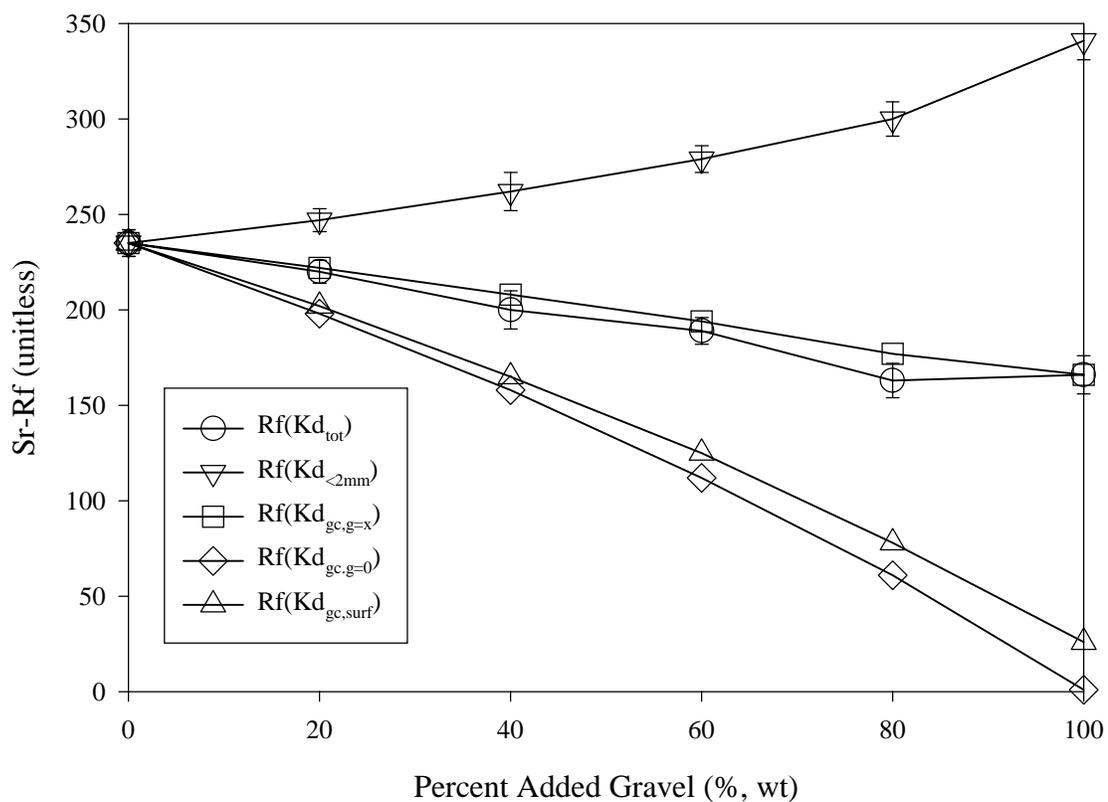


Fig. 2. Strontium retardation factors (Rf) as a function of added gravel. Rf values calculated with Kd_{tot} , $Kd_{<2mm}$, $Kd_{gc,g=0}$ (Equation 4), $Kd_{gc,g=x}$ (Equation 5), and $Kd_{gc,surf}$ (Equation 6), and measured bulk density and porosity values (Table 4). $Rf(Kd_{tot})$ is the mean and standard deviation of 4 replicates. Rf values from gravel-corrected Kd values were calculated using means, therefore no measure of variability is available.

Appendix B. Kd Values for Far-field Sediment Conditions

Appendix B. Kd Values for Far-field Sediment Conditions ^(a)				
Radio-nuclide	Reasonably Conservative Kd (mL/g)	“Best” Kd (mL/g)	Kd Range (mL/g)	Justification/References ^(b)
³ H, Cl, Tc	0	0	0 to 0.6	Tc exists predominantly as TcO ₄ ⁻ . A review of Hanford sediment Tc-Kd 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 Kd values are physically 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-Kd of 0 mL/g. See Kaplan et al. (18) for details.
Ac, Am, Ce, Cm, Eu	60	300	60 to 1300	Am-Kd: 67 to >1200 mL/g (3). Am-Kd: 125 to 833 mL/g (4)
C	0.5	5	0.5 to 1000	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 Kd should be used to account for the isotopic dilution/precipitation reaction that may occur. A Kd of 100 mL/g would be appropriate for such a system. Since most of the 100 and 200 plateau areas contain <1% carbonate, lower Kd 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	1000 to 12500	Na system, 1290 to 2120 mL/g (11) Ca system, 2000 to 3870 mL/g (11) Hanford sediment/groundwater system 11600 to 12500 mL/g (12)
Cs	500	2000	500 to 4000	Na system, 1410 to 1590 mL/g (11) Hanford sediment/groundwater system, 540 to 3180 mL/g (12). . Most recent results using ILAW specific borehole sediments [299-E17-21] yielded Kd of 2,030 ± 597. See Kaplan et al. (18) for details.
I	0	0.1	0.0 to 15	A review of Hanford sediment I-Kd 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). Most recent results using ILAW specific borehole sediments [299-E17-21] yielded Kd of 0 mL/g (18).

Ni, Sn, Nb	50	300	50 to 2500	Ni: Hanford sediment/groundwater system, 440 to 2350 mL/g (12) Ni: A study of a broad range of sediments, including those from Hanford had Ni-Kd's of 50 to 340 mL/g (13).
Np	2	15	2 to 25	A review of Hanford sediment Np-Kd 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).
Pb	8000	10,000	8000 to 80000	pH 6 and no competing ions: 13,000 to 79,000 mL/g (14)
Pu	50	150	50 to 2000	Pu(V, VI): pH 4 to 12: 80 to >1980 mL/g (15)
Ra, Sr	5	14	5 to 200	Sr Kd 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) Most recent data using ILAW borehole sediment [299-E17-21] yielded 14.3 ± 1.6 . See (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 Kd values ranging from 3.75 to 10.85 mL/g and had an average of 6.7 ± 1.9 mL/g (18).
Th, Zr	40	1000	40 to 2500	Estimated. Zr: pH 6 to 12 : 90 to >2000 mL/g (15)
U	0.5	0.6	0.1 to 80	A review of Hanford sediment U-Kd 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 Kd of 0.6 ± 0.1 . See (18).

^(a) Kd 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.

^(b) References: 1 = Kaplan and Serne 1995b; 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. 1984; 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 1957; 16 = Nelson 1959; 17 = Rhodes 1957a,b; 18 = Kaplan et al. 1998.

Appendix C. Discussion on Double Layer and Film Thickness

Double Layer Thickness vs. Film Layer Thickness

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

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

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 A is $1.5\text{e-}9$ m.**

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

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

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, the **film thickness (λ) = $2.4 \mu\text{m}$.**

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Appendix D. Information Requested For Near Field Geochemical Transport Modeling

Reactive transport modeling of the waste form leaching and 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. The Geochemical Data Package provides guidance in this appendix. The mineralogy of the Hanford sand sediments that might be used for backfill and the native Hanford formation sands and gravels have not been characterized at the ILAW site. However some quantitative mineralogy of Hanford formation sediments taken from outcrops and from the sides of other solid waste disposal facilities in the 200E and 200W areas have been reported. The data in Serne et al. (1993) pages 5-28 list detailed mineralogical, geochemical, hydrologic and physical characterization information for four sediments. This information can be used as input to STORM.

In FY00 about ten of the 21 samples from the ILAW borehole [299-E17-21] drilled in FY98 will be characterized for quantitative mineralogy and perhaps amorphous hydrous oxide content 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 FY98-99. These data have been documented in topical reports [Kaplan et al. 1998 and Reidel et al. 1998] and companion 2001 Data Packages [Khaleel 1999 and Reidel and Horton 1999].

Mineralogy data needed for the STORM code reactive transport calculations for cement and concrete and are available in the following topical reports [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 the Near Field Hydrology 2001 Data Package [Myer and Serne 1999] and references cited therein.

For the 2001 ILAW PA all chemical dissolution/precipitation reactions for the backfill sediments, natural sediments, cements and concrete are assumed to reach equilibrium in each time step during the transport modeling. There is limited kinetic data available for the dissolution/precipitation reactions for these minerals/materials but the geochemists could not tabulated the information in time for the 2001 data packages. However kinetic data will be tabulated and made available to the STORM transport modelers in time for the 2003 PA activity. The amount of effort expended in tabulating kinetic information will be determined based on the importance of kinetics deciphered from critically analyzing the results of the near field transport modeling in the 2001 PA.

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