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Performance Assessment,
Solubility Concentration
Limits, Special Analysis

Retention: Permanent

Geochemical Data Package for Performance Assessment Calculations Related to the Savannah River Site (U)

D. I. Kaplan

February 28, 2006

Savannah River National Laboratory
Washington Savannah River Company
Savannah River Site
Aiken, SC 29808

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Acronyms

CDP	Cellulose degradation products
CIG	Components-in-Grout
CSLM	Controlled Strength Low Material
CSH	calcium-silicate-hydrate
DOC	Dissolved organic carbon
ILV	Intermediate Level Vault
LAW	Low Activity Waste
<i>K_d</i>	Distribution coefficient
MWCO	Molecular weight cut-off
PA	Performance Assessment
SRS	Savannah River Site
TRU	Transuranic

1.0 ABSTRACT

The Savannah River Site disposes of certain types of radioactive waste within subsurface-engineered facilities. One of the tools used to establish the capacity of a given site to safely store radioactive waste (*i.e.*, that a site does not exceed its Waste Acceptance Criteria) is the Performance Assessment (PA). The objective of this document is to provide the geochemical values for the PA calculations. This work is being conducted as part of the on-going maintenance program that permits the PA to periodically update existing calculations when new data becomes available.

Because application of values without full understanding of their original purpose may lead to misuse, this document also provides the geochemical conceptual model, approach used for selecting the values, the justification for selecting data, and the assumptions made to assure that the conceptual and numerical geochemical models are reasonably conservative (*i.e.*, reflect conditions that will tend to predict the maximum risk to the hypothetical recipient). The geochemical parameters describe transport processes for 38 elements (>90 radioisotopes) potentially occurring within eight disposal units (Slit Trenches, Engineered Trenches, Low Activity Waste (LAW) Vault, Intermediate Level (ILV) Vaults, TRU-Pad-1, Naval Reactor Waste Pads, Components-in-Grout Trenches, and Saltstone Facility).

This work builds upon well-documented work from previous PA calculations (McDowell-Boyer et al. 2000). The new geochemical concepts introduced in this data package follow.

- In the past, solubility products were used only in a few conditions (element existing in a specific environmental setting). This has been expanded to >100 conditions.
- Radionuclide chemistry in cementitious environments is described through the use of both the K_d and apparent solubility concentration limit. Furthermore, the solid phase is assumed to age during the assessment period (thousands of years), resulting in three main types of controlling solid phases, each possessing a unique set of radionuclide sorption parameters (K_d and solubility concentration limit).
- A large amount of recent site-specific sorption research has been conducted since the last PA (McDowell-Boyer et al. 2000). These new data have replaced previous K_d values derived from literature values, thus reducing uncertainty and improving accuracy.

Finally, because this document will be used by future PA calculations and external acceptance of the document will eventually be required, this document was extensively reviewed. The review process, including the internal review, site review, and external review process is described.

2.0 OBJECTIVE AND SCOPE

The objectives of this document are to explain the following as they relate to performance assessments (PA) conducted at the Savannah River Site (SRS):

1. the geochemical conceptual model,
2. the approach used to select values for the numerical parameters of these conceptual models,
3. the assumptions made to assure that the conceptual and numerical models are reasonably conservative,
4. the recommended geochemical input values for the PA and justification for their selection,
5. the review process of this document, and
6. identification of critical data needs.

The scope of this document follows.

1. To provide geochemical input values for PA modeling of the
 - Slit Trenches,
 - Engineered Trenches
 - Low Activity Waste (LAW) Vault,
 - Intermediate Level (ILV) Vault,
 - TRU-Pad-1,
 - Naval Reactor Waste Pads,
 - Components-in-Grout Trenches, and
 - Saltstone Disposal Facility.
2. To provide geochemical input values for PA modeling of the radionuclides of the following elements: H, Ac, Am, Ar, At, Ba, Bk, C, Cf, Cl, Cm, Co, Cs, Eu, Fr, Gd, I, Kr, Nb, Ni, Np, Pa, Pb, Po, Pu, Ra, Rb, Re, Rn, Se, Sm, Sn, Sr, Tc, Te, Th, U, and Zr.
3. The duration of interest varies between calculations but is commonly 1000 years, 10,000 years, or until the maximum dose is obtained. Thus, if geochemical conditions are expected to change with time, such as redox conditions, appropriate adjustments to the geochemical conceptual and numerical models must also be made.

3.0 PHILOSOPHY AND ASSUMPTIONS

The basic philosophy of the geochemistry applied to the PA was to utilize mechanistic studies under controlled experimental conditions to provide the paradigms for the conceptual models and empirical studies to provide input values to help quantify these conceptual models. Radionuclide partitioning between the aqueous and solid phase was described using the distribution coefficient, K_d value, and the solubility concentration limit. A series of look-up tables were prepared containing these parameters that vary with the type of solids (*e.g.*, sandy sediment, clayey sediment, cementitious material), the presence of strong complexing ligands in the groundwater (*e.g.*, cellulose degradation products), and in the case of cementitious materials, the age of the solid and the presence or absence of slag (a strong reducing agent).

The basic philosophy underpinning the geochemistry modeling was to utilize mechanistic studies to provide conceptual models and empirical studies to provide input values for these conceptual models.

Section 3.1 describes the difference between the theoretical and empirical distribution coefficients and their relation to the retardation factor, a parameter in reactive transport models that describes geochemical interactions. Section 3.1 is followed by a description of solubility constraints and how they differ from distribution coefficients (Section 3.2). Importantly, it was decided not to employ more mechanistic surface complexation models, which are discussed below in Section 3.3. While the PA has employed such models to describe limited data sets (Serkiz and Kaplan 2006), their application to the large heterogeneous systems described in the various PAs would not be appropriate at this time due to the large amount of input data required. Portions of Section 3.3 were taken from Kaplan and Serne (2000).

3.1 Theoretical Distribution Coefficients, Empirical Distribution Coefficients, and their Relation to Retardation Factors

Coupled reactive-transport modeling seeks to integrate groundwater flow with retardation of contaminants by fluid-sediment interactions to create a model capable of predicting spatial and temporal distribution of contaminants. The typical approach is to establish parameters describing fluid-sediment interactions based on the literature, or preferably based on site-specific measurements. The fluid-sediment interactions may consist of adsorption-desorption, ion exchange, and precipitation-dissolution reactions. Some models consider these reactions separately. However, the most common approach is to incorporate all of these reactions into one K_d value. The K_d value is the simplest construct describing contaminant sorption¹ 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):

¹ Sorption in this text is defined to include all processes that remove solutes from the aqueous phase, including, adsorption, absorption, partitioning into the organic matter, complexation, precipitation, and co-precipitation. These terms are described in detail by Sposito (1989).

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

where C_{solid} (mol g⁻¹) and C_{liquid} (mol mL⁻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, and not volume, as transport modelers use, or surface area, as surface chemist use.

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, (R_f , unitless) which is the ratio of the average linear velocity of water (\bullet_w , m s⁻¹) divided by the average linear velocity of the contaminant (\bullet_c , m s⁻¹). For water saturated systems, the Kd value is related to the R_f by the bulk density (ρ_b , g cm⁻³) and the porosity (η , cm³ cm⁻³) as follows (Valocchi 1984, Bower 1991):

$$R_f = \frac{u_w}{u_c} = \left(1 + \frac{Kd \rho_b}{\eta} \right). \quad (2)$$

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, such as in the vadose zone, the porosity term, η , is replaced by the volumetric water content of the vadose zone sediments.

The theoretical distribution coefficient is a thermodynamic construct. It is the ratio of the concentration of a species reversibly adsorbed/exchanged to 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 (Kd_{thermo}) is:

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

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 Kd_{thermo} is that adsorption is instantaneous, fully reversible (*i.e.*, the rate of adsorption is equal to the rate of desorption), linear (*i.e.*, the proportional adsorption of a contaminant is not influenced by the aqueous contaminant concentration) and the presence of adsorbed species does not influence subsequent adsorption of other dissolved species. Thus, a single distribution coefficient is used to represent both sorption and desorption of each contaminant species for a specific adsorbent (solid phase with one type of surface site) and for a specific macro solution chemical composition.

However, in order to apply the Kd 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

and aqueous species exists. For example, Sposito (1989; pg. 69) calculated that a typical soil solution can easily contain 100 to 200 different soluble complexes.

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 mentioned in discussion of Equation 3, 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 Kd_{thermo} 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 cannot 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 reviews by Kent et al. 1988 and Jenne 1998).

The empirical definition of the Kd 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 sum of the total concentration of all species in solution. Again, using uranyl as an example, the definition of the thermodynamic Kd construct would be for a simple system that contained three U(VI) species [UO_2^{2+} , $UO_2(OH)^+$, and $UO_2(OH)_2^0$]:

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

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

$$Kd_{empirical} = \frac{\text{total U(VI) on solid}}{\text{total U(VI) in solution}}. \quad (5)$$

In an attempt to distinguish Kd_{thermo} from $Kd_{empirical}$, researchers, especially in Europe, referred to the latter term as Rd (e.g., Bradbury and Sarott 1995). This is rarely used any longer, and $Kd_{empirical}$ is referred to simply as Kd , as is done in this text.

An important limitation of the $Kd_{empirical}$ is that it in theory describes a very limited set of conditions. It describes sorption for a specific contaminant, specific soil solution (e.g., pH, dissolved organic matter, Eh, etc.) and soil solid phase properties (e.g., cation exchange capacity, clay content, soil organic matter, etc.). Again, this definition is relaxed when it is used in contaminant transport calculations.

Among the reasons for selecting the "empirical" Kd construct for the PA, as exemplified by Equation 5, is

- 1) the bulk of the existing sorption literature on radionuclide sorption, especially at SRS can be classified as “empirical” Kd 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, Kd is a constant for a given contaminant/geological material/water composition combination under identical (geo)chemical conditions,
- 3) Kd can be used directly in all PA transport codes, and
- 4) perhaps most importantly, there is presently no thermodynamically-based conceptual model or numerical code that is robust enough to predict accurately the degree of radionuclide adsorption by natural sediments (see below).

By using site-specific materials, namely sediments or cementitious materials and groundwater from disposal areas, it is possible to gather directly relevant data and not to rely on extrapolation from other sediment and aqueous systems reported in the literature. 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” Kd values must be based. For most of the data used in the PA geochemical data package, sorption experiments have been conducted with site-specific sediment and site-specific groundwater, which also resembles natural vadose-zone porewaters.

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

Another aspect of the Kd 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 Kd 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 Kd values for a PA. Once the dominant geochemical process is identified for a specific geological and chemical environment, the range of relevant “empirical” Kd 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 radionuclide concentration. 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 Kd values. Once the dominant geochemical process is identified for a specific set of environmental conditions, the range of reasonable values for the “empirical” Kd 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 a 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 solid 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 a PA; we gain a plausible explanation of the processes governing U(VI) removal from solution. As this example illustrates, changes in the dominant chemical processes may account for an appreciable amount of variability in derived K_d values under different geochemical conditions.

3.2 Solubility Constraints

In addition to the K_d construct, the solubility product, k_{sp} , (mol/L or M,) (both thermodynamically and empirically based) are used to describe radionuclide geochemical behavior in a disposal site. A k_{sp} is used for conditions where the concentrations of the radionuclides are believed to exceed the solubility of an assumed solubility-controlling mineral phase. The selection of controlling solid phases for SRS PA activities was based on laboratory experiments, calculations, and the literature. Once the solid phase was selected, the upper limit of radionuclide concentration was calculated with the appropriate background electrolyte composition. If the background electrolyte composition remained essentially constant, then the solubility product was assumed to also be nearly constant. This has lead some transport modelers to refer to solubility products as constants but in reality the solubility product k_{sp} , varies with solution chemistry.

When radionuclide concentrations exceed the solubility limit for some mineral, precipitation can be expected and subsequent radionuclide aqueous concentrations and behavior is controlled by solubility. At concentrations below the solubility product (Point A in Figure 1), the radionuclide concentration will be controlled by the “empirical” K_d construct.

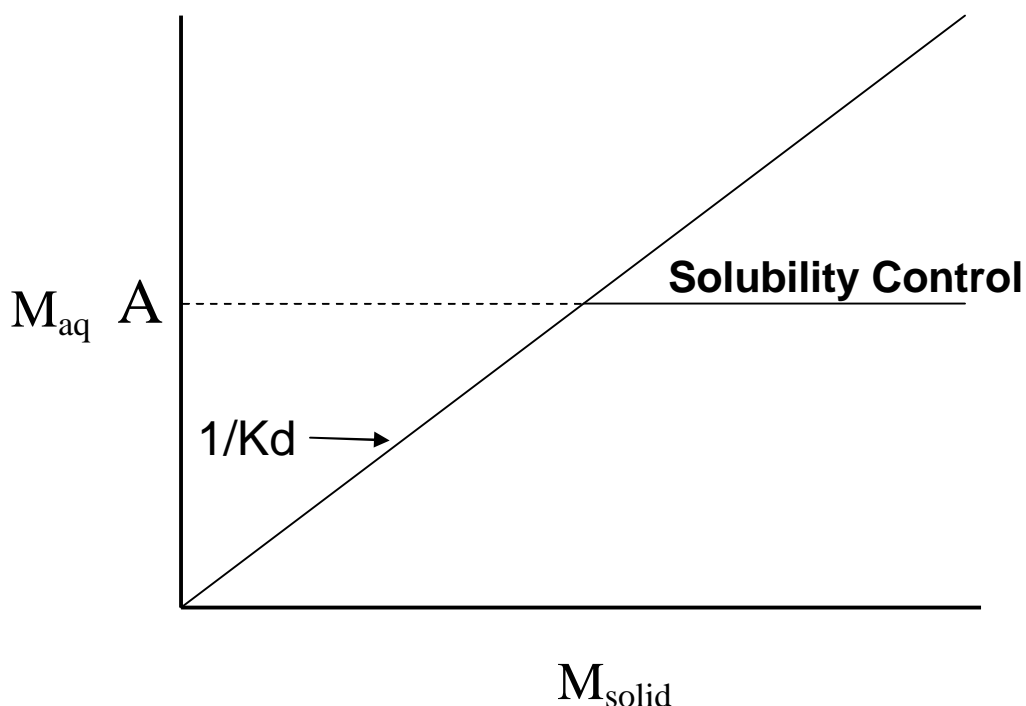


Figure 1. Effect of aqueous metal (M_{aq}) and solid metal (M_{solid}) concentrations on distribution coefficients (K_d) and solubility product. Point "A" identifies the solubility concentration limit.

When the solubility-controlling solid could not be identified but empirical solubility tests indicated that some unidentified phase was controlling solution concentration, then an empirical solubility relationship was used. An example of this is presented in Figure 2. Figure 2 presents data from Kaplan et al. (2006b) showing the desorption of Pu from a lysimeter which had been in contact with the Pu for 24 years. The Pu was originally placed in the lysimeter as dissolved $Pu^{IV}(NO_3)_4$ dried on a filter. In this batch test, portions of the lysimeter sediment were put in suspensions of varying pH and permitted to equilibrate.

The total equilibrated Pu solution concentrations were compared to data from Rai et al. (2001), showing $PuO_{2(am)}$ solubility (more specifically, this phase oxidizing to $Pu(V)$ and then solubilizing). The study by Rai et al. (2001) was conducted in the absence of sediment, simply an aqueous phase and the Pu solid phase. The main point to take from Figure 2 is that the two data sets behave very similarly with respect to pH, except that they are offset by a constant amount. Based on this and other data presented in the paper, Kaplan et al. (2006b) suggested that porewater Pu concentrations in SRS sediments are largely controlled by solubility. In this example, the solubility controlling phase is not known, and adsorption along with solubility is likely controlling the total aqueous Pu concentrations. Thus, an apparent or empirical solubility term may be appropriate to describe such data.

When the controlling solid could not be identified but empirical solubility tests indicate that some phase was controlling solution concentration, then an empirical solubility relation was constructed.

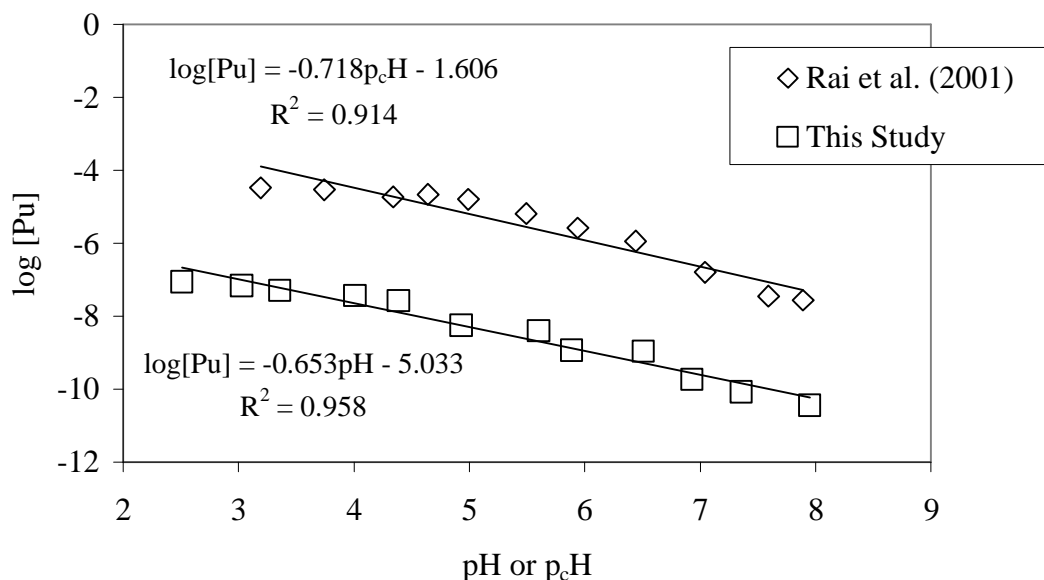


Figure 2. Comparison of sediment desorption data (this study) from a lysimeter containing SRS sediment and Pu (referred to as “This Study”) and a Pu(V)/PuO₂(am) 0.4 M NaClO₄ system (no sediment present, 0.0018- μ m filtrates; Rai et al. (2001) (taken from Kaplan et al. 2006b). Y-axis represents Pu concentrations in porewater solutions.

Finally, in some cases, the empirical solubility concentration limit data may be simplified as a constant concentration limit. This is especially true for the PA because little site/waste form/engineered barrier solubility work has been performed that identifies the solubility-controlling solids. It is also true that for short-lived radionuclides, the regulatory limits are usually far lower than the solubility limits. For example, the solubility limit for Ra-228 ($t_{1/2} = 5.7$ yr) as RaSO₄ is several orders of magnitude greater than any regulatory limit. For these short-lived constituents solubility limits rarely come into play.

3.3 Overview of Mechanistic Complexation Models

Mechanistic models explicitly accommodate the dependency of K_d values, or other sorption values, on contaminant concentration, competing ion concentrations, pH-dependent 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, from the standpoint of the PA, scientifically defensible. There are several mechanistic models that can describe 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 SRS 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 presented below. References to

excellent review articles have been included in the discussion to provide the interested reader with additional information.

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 understanding 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.

Several mechanistic models have been proposed; however, their application to complex natural sediments is not resolved (Westall and Hohl 1980, Sposito 1984, Westall 1986, Davis and Kent 1990, Sposito 1989, 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 and non-homogeneous. 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 characterization of these surfaces will remain somewhat operational in nature.

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

Mechanistic or surface-complexation models were originally designed to describe well-defined systems of little or no heterogeneity, a far cry from natural sediments. One method of addressing heterogeneous systems is an empirical approach that Davis et al. (1998) and Davis et al. (2004) refer to as the generalized composite approach. In this approach experimental data on site soils are fitted to various stoichiometric sorption reactions and model formulations based on reaction scheme simplicity and goodness-of-fit (Herbelin and Westall, 1999). This avoids the necessity of detailed mineralogical characterization required in the more general approach that Davis et al. (1998) and Davis et al. (2004) call the “component additivity” approach. It is also important to note that the authors of this approach do not assign specific binding sites (*e.g.*, Fe-oxide “B” sites or planar kaolinite sites) to the solid phases.

Data collection to support the generalized composite approach requires experimental determination of surface complexation under all mineralogical and chemical conditions expected within a plume. The resulting data permits calculating semi-empirical geochemical sorption parameters that can then be used to describe contaminant sorption for a wide range of environmental conditions at the study site. Less site-specific data is required to support the component additivity approach and this approach can simulate changing conditions more realistically than the generalized composite approach. For example, if a phase is predicted to precipitate (or disappear) in the future it cannot be accounted for in the generalized composite approach, whereas this can be incorporated into the component additivity approach. The inclusion of these geochemical models into the PA is an eventual goal and studies are presently underway to accomplish this goal (Serkiz and Kaplan 2006).

3.4 Unique Conditions Resulting in Enhanced Contaminant Transport of Radionuclides

3.4.1 Cellulose Degradation Products

Cellulosic materials (*e.g.*, wood, paper, and cardboard products) readily degrade in the environment to form cellulose degradation products (CDP) in both the solid and dissolved (*i.e.*, dissolved organic carbon; DOC) phases. Natural organic matter can greatly influence the speciation and mobility of nonradioactive elements (Perdue and Gjessing 1990, Thurman 1985, Stumm and Morgan 1981) and radioactive elements (Choppin 1989, Allard et al. 1989, Fairhurst et al. 1995; and Ledin et al. 1994). Co-disposal of radionuclides with cellulosic materials is, therefore, expected to influence nuclide fate and transport in the subsurface (Serne et al. 1993). The disposal and degradation of wood products in the E-Area Slit Trenches and the Engineered Trenches are a source of organic matter that is expected to influence radionuclide fate and transport.

A modest amount of research has been conducted to evaluate the effect of CDP on radionuclide sorption to SRS sediments (Serkiz and Myers 1996, Serkiz et al. 1998, Serkiz et al. 1999, Kaplan and Serkiz 2004, Serkiz and Kaplan 2006, and Kaplan and Serkiz 2006). Initial studies were strictly calculations describing radionuclide sorption in the presence of CDP using available literature and limited SRS site-specific data (Serkiz and Myers 1996). This initial modeling used published stability constants for reactions between low molecular-weight acids

(*i.e.*, citric acid and EDTA) and radionuclides to approximate behavior of CDP. Laboratory studies with U(VI) and Eu(III) were conducted and their results were introduced into numerical models (Serkiz et al. 1998, Serkiz et al. 1999). These elements, along with Cs data, were then used as analogues to generate recommended *Kd* values for use with a wide range of elements (Serkiz 2000).

Most recently, Kaplan and Serkiz (2004) conducted a full-factorial study evaluating the influence of varying concentrations of organic C (using fulvic acid as a surrogate for CDP), and pH on the sorption of monovalent cations (K^+ and Cs^+), divalent cations (Ni^{2+} and Sr^{2+}), trivalent cations (Ce^{3+} and Eu^{3+}) and tetravalent cations (Th^{4+} and Zr^{4+}). Analogues were matched to ~30 radionuclides based on similarities in periodicity and chemical properties and a look-up table of CDP-impacted *Kd* values were created as a function of soil type (sandy and clayey), pH and organic carbon content. This data was later modeled using a first-principles approach to provide a mechanistic geochemical understanding of the processes controlling the radionuclide-sediment-CDP system (Serkiz and Kaplan 2006). An interesting aspect of this data was that it showed that at low to moderate CDP concentrations, the sorption of several radionuclides actually increased due to the sorption of the organic matter to the sediment (with its sorbed radionuclides), which increased the sediment's sorption capacity for the radionuclides. Furthermore, this effect existed only at low pH levels ($pH < 7$), where some organic C sorbed to the sediment and did not remain in the aqueous phase. At higher pH values, the dissolved C remained in solution and acted as a ligand to complex the radionuclide, preventing it from sorbing to the sediment. This trend was true for some but not all radionuclides. CDP constituents are subject to further biodegradation as they migrate in a plume. In some cases, the enhanced migration may be a transitory effect. For example, 1) the CDP may undergo microbial degradation or 2) even though the common cations (Na, Ca, and Mg) form less strong complexes with the low molecular weight organic acids and fulvic acid with time and distance, they will out-compete the stronger but less concentrated radionuclide to form complexes with the CDP.

3.4.2 Colloid-Facilitated Transport of Contaminants

Introduction: Contaminant transport is traditionally modeled in 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 phase, a mobile solid phase, or colloidal phase. Mobile colloids consist 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 without including colloids. This mode of contaminant transport has recently come to the forefront because of the discovery of Pu on colloids 1.3 km from their source at the Nevada Test Site (Kersting et al. 1999). Reviews of colloid-facilitated transport of contaminants have been presented by McCarthy and Degueudre (1993), McCarthy and Zachara (1989), and most recently by Kretzschmar and Schafer (2006).

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 E-Area and Z-Area disposal sites. 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, it is not clear whether environmental conditions at the SRS are conducive for colloid stabilization and subsequent transport.

Field studies of colloid facilitated transport of Pu have been studied on the SRS by two groups, the University of Georgia (Kaplan et al. 1994)² and Woods Hole Oceanographic Institution (Dai et al. 2002). Together their results indicate little or perhaps no colloidal transport of Pu occurs. Kaplan *et al.* (1994) measured Pu associated with a filterable fraction in groundwater recovered in F-Area, near the E-Area burial grounds and the Saltstone disposal facility. This filterable fraction was presumed to be a colloidal fraction based on specialized low flow collection and filtering techniques. Very little Pu was found in association with colloids, $<3 \times 10^{-15}$ Ci/L $^{239/240}\text{Pu}$. To put this concentration in perspective, the Maximum Concentration Level for $^{239/240}\text{Pu}$ is $15,000 \times 10^{-15}$ Ci/L (Federal Register, Vol. 65, No. 236, December 2, 2000). The percentage of Pu retained by filters, increased as the pH of the plume increased, which was also coincidental with distance from the point source. Inversely, the percentage of Pu that passed through the smallest membrane, 500 molecular weight cutoff (MWCO; ~ 0.5 nm) decreased with distance from the point source. The ratio between the Pu concentration of colloids in well water and liquid in the source zone did not change in a systematic manner with distance (or pH) in the field (Kaplan et al. 1994).

Dai et al. (2002) also conducted a colloid study in F-Area and concluded that colloids were not involved in Pu transport. The difference between these two results, Kaplan *et al.* (1994) reporting little colloidal Pu and Dai et al. (2002) reporting no colloidal Pu may be attributed to the latter sampling some eight years later in a somewhat more basic pH plume, and to differences in experimental technique. Dai et al. (2002) used more sensitive analytical methods but larger molecular weight cut-off membranes (permitted larger particles to pass through (1000 MWCO (~ 1 nm)) than those used by Kaplan et al. (1994).

Colloid Model: Modeling colloid facilitated transport of radionuclides in the SRS subsurface environment is greatly hindered by the paucity of data on the subject. Measurements presented by Kaplan et al. (1994) form the basis for the proposed conceptual model. This conceptual model is devoid of mechanism and is greatly simplified. As such, there is a great deal of uncertainty associated with the calculations using the conceptual model and predicted results. However, it was felt that it is important to start accounting for the possibility of this transport mechanism in the SRS PAs, with the intent of improving on the model as more

² Kaplan et al. (1994) also detected Th, U, Am, Cm and Ra on colloids, and the fraction of radionuclides associated with colloids increased as: Pu > Th > U > Am = Cm > Ra.

experimental data becomes available.³ To date, only Pu colloidal transport has been modeled in SRS Pas (Collard and Hiergesell 2004). For future PA's it is proposed that all strongly sorbing radionuclides with a $K_d > 2000$ mL/g or a solubility limit $> 10^{-6}$ M be modeled as moving in part via mobile colloids. It has been shown that radionuclides must bind strongly to colloids in order for the radionuclides to move significant distances without desorbing from the colloids and interacting with the much more abundant fixed or matrix sediment sorption sites (van der Lee et al. 1997). The assumption that colloid facilitated transport occurs in SRS modeled systems is conservative with respect to the groundwater risk calculation because it provides an additional vector for transporting radionuclides. The following is a discussion, using Pu as an example, of how to model colloid facilitate transport.

The F-area field data from Kaplan et al. (1994) were used to form the basis for estimating the concentrations of colloidal Pu, $Pu_{colloid}$, in E- or Z-Area. Kaplan et al. (1994) reported total Pu concentrations in the F-Area Seepage Basin and $Pu_{colloids}$ concentrations in the water from three wells located 30 m, 320 m and 550 m from the seepage basin. Because of considerable differences in pH and other geochemical parameters between E- and F-Area waters, the data at the 30-m and 320-m wells were not used to estimate the concentration of colloidal Pu. For simplicity, the ratio between the concentration of plutonium attached to colloids, $Pu_{colloid}$, in water from the 550-m well to the total concentration of Pu in vadose zone samples at the seepage basin is assumed to apply to the solid waste from which the Pu originated from.

The colloid conceptual model is devoid of mechanism and is greatly simplified. As such, there is a great deal of uncertainty associated with the resulting calculations. However, we felt that it is important to start accounting for the possibility of this transport mechanism in the PA, with the intent of improving on the model as more experimental data becomes available.

The ratio between the Pu concentrations on colloids in the groundwater from the 550-m well and the total Pu concentration in the porewater in the source zone was found to be 1.1×10^{-3} in the field. It will be assumed that an estimated 550-m well concentration for the $Pu_{colloids}$ in E- and Z-Area should be calculated by multiplying the total initial Pu concentration in the source zone porewater by 1.1×10^{-3} to match field observations at the other site.

The PA uses a hypothetical 100-m well to establish risk. Data presented in Kaplan et al. (1995) suggests that $Pu_{colloids}$ concentrations may be expected to be about the same at 100 m as 550 m from a well. They reported that all three wells in the sampling transect in F-Area had nearly identical concentrations of mobile colloids, 5×10^8 to 8×10^8 particles/L (Kaplan et al. 1995). Thus, no correction to $Pu_{colloid}$ concentration will be made to account for the distance between the 100-m hypothetical and the 550-m observation well.

Plutonium concentrations reported by Kaplan et al. (1994) in the source represented total Pu, and as such included both colloidal and non-colloidal Pu, while the concentrations at the distant wells consisted almost entirely of colloids. To best capture the value in the existing data, the ratio of the Pu colloid amount at the distant well to the Pu total amount at the source well will be

³ Presently, the SRNL and Woods Hole Oceanographic Institution are collaborating on a three-year DOE-funded proposal to study colloid-facilitated transport on the SRS. Also, there is ongoing research funded through the PA maintenance program to study the stability of site-specific colloidal suspensions.

directly added to modeling results for non-colloid Pu isotopes. As a conservative approach, that ratio will be applied to each and every Pu isotope. Although water from the source will not reach the 100-m well for several years, the ratio will be applied from time zero.

As the total source amount decays, the amount of the $\text{Pu}_{\text{colloids}}$ at the well will similarly decay. Progeny will be produced and included in the potential effects on a receptor. For example, if the ratio of $\text{Pu}_{\text{colloids}}$ concentration at the 100-m well to the source is 1×10^{-3} and the initial quantity of source term for Pu-238 is 1000 Ci, then 1 Ci ($1000 \text{ Ci} \times 1 \times 10^{-3}$) of Pu-238 would initially be at the well. After one half-life, the quantity of Pu-238 at the source would be reduced by one-half because of radioactive decay and reduced further by leaching and dispersion/diffusion. However, if only the decay is considered, then the quantity of Pu-238 at the source would be one-half or 500 Ci and the quantity of Pu-238 at the well attached to mobile colloids would be reduced to 0.5 Ci. Progeny at the 100-m well are assumed to be generated and that they do not migrate away from the well.

To incorporate the above assumptions, the $\text{Pu}_{\text{colloid}}$ construct will be simulated as follows.

- The Pu for the non-colloids modeled for the groundwater pathway is assigned as $\text{Source}_{\text{all}}$.
- Pu concentration fraction of the source to field measurements (Kaplan et al. 1994) is assigned as $\text{WellFrac}_{\text{colloids}}$ ($\text{Pu}_{\text{Well}}/\text{Pu}_{\text{source}}$).
- The quantity of Pu colloids at the 100-m well is the product of these two factors:
 $\text{Pu}_{\text{colloid}} = \text{Pu}_{\text{source}} * \text{WellFrac}_{\text{colloids}} = \text{Pu}_{\text{well}}$.
- The quantity of Pu in $\text{Well}_{\text{colloids}}$ is simply decayed in place, thereby reducing the parent and generating progeny.
- Transport of $\text{Pu}_{\text{colloid}}$ is not retarded by the aquifer sediment, i.e., $\text{Pu}_{\text{colloids}}$ Has a K_d value is 0 mL/g.
- $\text{Pu}_{\text{colloid}}$ does not have any assigned redox status, and as such its concentration is not influenced by the other two Pu fractions, Pu(III/IV) and Pu(V/VI).⁴
- CDPs do not influence $\text{Pu}_{\text{colloids}}$ mobility or speciation.

For precursors of Pu that generate Pu, the same method will be applied with two exceptions. First, the starting quantity at the well will be the mass concentration of the precursors' $\text{Source}_{\text{all}}$ multiplied by the $\text{WellFrac}_{\text{colloids}}$. Second, none of the quantity of precursors of Pu will be excluded from the effects that could potentially affect a receptor, because it is the $\text{Pu}_{\text{colloids}}$ being analyzed, not the ancestors.

In summary, $\text{Pu}_{\text{colloid}}$ will not be directly modeled for solid waste disposed in E- or Z-Area to determine their concentrations at a 100-m well. Rather the effects of the colloids will be captured by separately calculating the 100-m well concentration for the colloids using the ratios presented above. The well concentration for the colloids can then be summed with the well

⁴ Plutonium geochemistry is extremely sensitive to the oxidation state of the Pu. For this reason, the PA includes two oxidation states for Pu, Pu(IV) and Pu(V), which account for >97% of the Pu in the SRS subsurface environment and (Pu(III) and Pu(VI) account for the remainder (Kaplan et al. 2004; 2006a; 2006b). The PA generalizes the oxidation states of Pu to consist of two species: an oxidized species, Pu(V/VI) and a reduced species, Pu(III/IV).

concentration from the non-colloids to predict a total well concentration. Additional data and information about colloid generation is necessary before a more direct approach to modeling Pu transport by colloids is possible.

4.0 APPROACH TO SELECTING DATA

Distribution coefficients, K_d , and solubility concentration limits were assigned to the 40 elements based on their environmental settings (*e.g.*, subsurface clayey sediment, subsurface sand sediment, cementitious material, etc.) as they move with the contaminant plume. For each element and environmental setting a “best” and a “reasonably conservative” estimate of the K_d values or solubility concentration limits were provided. The “best” estimates are presented to provide guidance on what the most likely K_d values and solubility concentration limits are for a given condition. These values are based primarily on some central value of the literature, SRS site-specific experimental data, or on expert judgment. The “reasonably conservative”⁵ values represent lower-bounding values that take into consideration the range of physical, chemical, and mineralogical conditions that often lead to enhanced radionuclide migration. The “reasonably conservative” value was ideally based on the lower limit of multiple K_d value measurements or the upper limit of solubility measurements. In the absence of sufficient data, the “reasonably conservative” value was based on an assumed range of values (Section 5.0), using the “Best” value as the central point in the range. For large values (K_d or solubility concentration limits \bullet 1000 mL/g), a range of an order of magnitude was used and for small K_d values or solubility concentration limits, a range of two fold was used. The range and distribution of the K_d values and solubility concentration limits are discussed in Section 5.0.

“Reasonably conservative” and “best” values were assigned to the 40 elements based on environmental setting.

The subsurface sediments were simplified as consisting of two types of sediment, a “Clayey Subsurface Sediment” and a “Sandy Subsurface Sediment” (Phifer et al. 2006). The interaction of radionuclides with these two sediment types was described using the K_d construct, no solubility concentration values were used to parameterize dissolved species interacting with SRS sediments (Section 4.1). Radionuclide interaction in cementitious environments were described using both K_d values and solubility concentration limits that varied as a function of cementitious material age (more specifically, amount of pore volumes that flow through the system) and whether or not reducing ingredients (*e.g.*, blast furnace slag) were present (Section 4.2).

Ideally, all input data would be derived from experiments conducted under site-specific conditions. Much of the sediment K_d data was, in fact, derived from such data. Where site specific data was not available, chemical analogues were used. For example, no site-specific sorption data is available for Fr (francium) and Rb (rubidium), however, a great deal of SRS sediment sorption data is available for Cs. Cesium behaves chemically very similar to Fr and Rb, all three elements are in Group 1A in the periodic chart, have a +1 valence, form weak complexes, and exist in groundwater primarily as an uncomplexed monovalent free ion. For that reason, Fr and Rb K_d values were approximated, using the measured Cs K_d values. Where site

⁵ Throughout this text the term “conservative” is with respect to all scenarios except the intruder scenario, where, a conservative K_d may be a large value and a conservative solubility limit may be a low value.

specific data and reasonable analogues were not available, literature values were used. Careful selection of these literature values was required to make sure that the experimental conditions used to generate the K_d values were appropriate for SRS conditions. Professional opinion and geochemistry experience were used where non-site-specific data were available and where possible experimental evidence was provided to support technical judgment. There were few sediment “literature K_d values” used in the look-up tables presented in Section 5.0. Where “literature K_d values” were used, the “reasonably conservative” values were assigned greater differences with respect to the “best” values than those K_d values based on site-specific data. The cementitious material K_d values and solubility concentration limits were taken entirely from the literature. As such, they may be expected to contain more uncertainty.

In summary, a ranking of the priority for selecting K_d values and solubility concentration limits follow:

1. Site-specific measured data,
2. literature experimental data, and
3. technical judgment.

4.1 Sorption of Radionuclides to SRS Sediment

The subsurface environment beneath and near the waste units in E- and Z-Areas are assumed to consist of two primary geological strata. This simplification of the subsurface is taken from Phifer et al. (2006) and was based on particle-size distribution data and observations of several borehole specimens made in the E-Area subsurface environment. Phifer et al. (2006) describe the upper strata as extending ~7-m below the surface and having a finer texture than the lower strata, which may extend some 27-m below ground surface. The water table in E- and Z-Area is approximately 20 to 25 m below the ground surface. Additional information regarding the surface aquifer, the groundwater monitoring well program, and groundwater communication between the unconfined and confined aquifers may be found in McDowell-Boyer et al. (2000).

All radionuclide interactions with sediments were described using K_d values (Table 10). There were unique K_d values for a Clayey Subsurface Sediment and a Sandy Subsurface Sediment, meant to represent the upper and lower strata, respectively.

- The Clayey Subsurface Sediment was conceptualized as a sediment containing a clay and silt content 25 to 45 wt-%, the mineralogy composed primarily of kaolinite, hydroxyl-interlayered vermiculite, quartz, gibbsite, goethite, and hematite (most notable about its mineralogy is that it contains very low concentrations of 2:1 clays, such as smectites and vermiculites); organic matter concentration is low (<0.01 wt-%); pH is 5.5; and the sediment is covered with Fe-oxides, giving it a reddish color.
- The Sandy Subsurface Sediment was conceptualized to have identical properties as the Clayey Subsurface Sediment except the clay and silt content was <25 wt-%. Most of the sorption experiments from which data was considered for the look-up tables came from sandy sediments with clay and silt concentrations appreciably <25 wt-%, closer to 8 to 12%.

As described in Section 4.0, site-specific data were used whenever possible. However, where site-specific data were lacking, literature-derived data were used. Also important to note is that the data provided in Section 5.0 is for these conditions only. Environmental conditions that deviate from those described in this section, compromise how appropriate the data is for the scenario under study. For example, the Kd values provided for the sediments in Section 4.0 would not be appropriate for wetlands because wetlands have appreciably greater organic matter concentrations, resulting in appreciably different biogeochemistry.

4.2 Sorption of Radionuclides to Cementitious Materials as a Function of Age

The conceptual model used to describe radionuclide geochemistry in cementitious environments was taken from Bradbury and Sarott (1995). They described three types of physicochemical environments, or stages, that all cements and cementitious materials progress through as they age (Figure 3). As such, these three stages represent the progression that all types of cementitious materials would undergo as they age. The duration of each stage is controlled by how much pore water (and to some extent the water chemical composition) passes through the cement, thereby promoting cement degradation; as can be seen by the exchange cycles, or pore volumes, the X-axis of Figure 3.

Cementitious materials are assumed to progress through three stages as they age. Each stage has unique physical, mineralogical, and chemical properties, resulting in unique Kd and/or solubility concentration limits for each stage.

The advantage of using Figure 3 and the concept of exchange cycles is that it is generic in nature. Once flow models have been established for a specific facility, the exchange cycles for that facility can be quantified. Facilities with more concrete will have larger exchange cycles than those with less concrete.

Development of this conceptual model was based on laboratory studies as well as on natural analogue and ancient cement/concrete characterization studies. One of the key aqueous parameters used to identify when one stage ended and the next one started was pH (Figure 3). The pH changes are the result of mineralogical transformations that occur as the cement ages. The cement solids present in each stage are assumed to have unique sorption properties and for this reason, unique Kd values and solubility concentration limits were assigned to the cement solids in each stage. A brief description of each of the three stages is described below in Sections 4.2.1 through 4.2.3, while a more detailed discussion is presented in Bradbury and Sarott (1995) and Krupka and Serne (1998). Unique Kd values and solubility concentration limits for oxidizing and reducing cementitious materials is provided (Section 5.0). Reducing cements are used to enhance the immobilization of certain redox-sensitive radionuclides, such as Tc, U, and Np, and are created by adding blast-furnace slag to the cement mixture. Since no SRS site-specific sorption data were identified for cementitious materials, the values included in the look-up tables came entirely from the literature (Table 11 through Table 14).

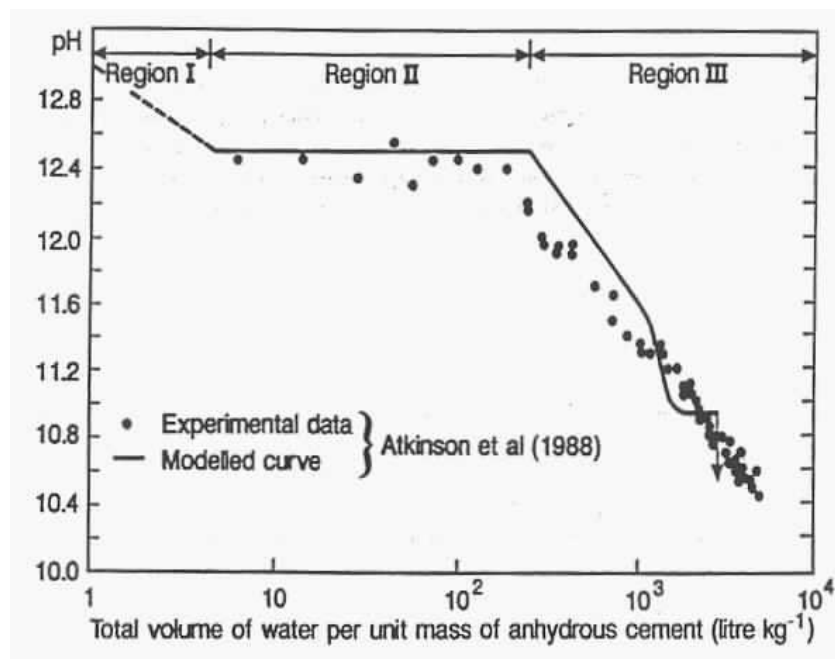


Figure 3. Conceptual model used by Bradbury and Sarott (1995) describing the influence of exchange cycles (X-axis) on pH and the designated Stages (or regions) (Atkinson et al. 1988).

4.2.1 1st Stage

The environment of the 1st Stage occurs immediately after the cement hardens and infiltrating water passes through it. The cement porewater is characterized as having a high pH (>12.5), high ionic strength, and high concentrations of potassium and sodium. The high concentrations of these monovalent cations result from the dissolution of alkali impurities in the clinker phases. Hydration continues during the 1st Stage with the formation of calcium-silicate-hydrate gels (a common shorthand for this gel is C-S-H, which is a $\text{CaO-SiO}_2\text{-H}_2\text{O}$ amorphous material that hardens and constitutes “cement”) and portlandite [Ca(OH)_2]. The composition of the cement pore fluid is at equilibrium with portlandite during this time.

Based on the modeling estimates provided by Berner (1992), the 1st Stage may last between 1 and 100 exchange cycles. An exchange cycle, or cycle, is a unit less parameter that represents the cement pore volume, *i.e.*, the length of time it takes for a pore volume to pass through a cementitious system. This in turn can be quickly converted into units of time once the water travel rate through a specific cementitious facility is established. Unfortunately, assuming a low exchange cycle value for this stage may be conservative for some elements, such as Pb, while not conservative for other elements that tend to form precipitates at high pH values (*i.e.*, have high

The concrete in the 1st Stage binds many radionuclides relatively strongly, and the porewater is characterized by a high pH (>12.5) and high ionic strength. It is anticipated to last 50 exchange cycles (pore volumes). For a 2-ft thick cement waste form, this Stage may be expected to last for 750 yr for SRS relevant recharge rates

Kd values and low solubility concentration limits). Therefore, it was assumed that the 1st Stage lasts 50 exchange cycles for SRS relevant scenarios.

For a calculation related to Pb leaching from a Components-in-Grout Trenches, Kaplan and Myers (2001) assumed the 1st Stage was 70 exchange cycles (not 50 exchange cycles as recommended here). Since this is the stage in which the lead solubility was at its highest, producing the highest dissolved lead concentrations⁶, a conservative assumption would be to assume the stage lasts 100 cycles. However, because diffusion is an important chemical process influencing the leachate chemistry, the low ionic strength and low inorganic carbon concentration of SRS groundwater will likely limit the concrete/cement aging process occurring during this stage, thereby lengthening the duration of this stage. Carbonate reacts with Ca from the calcium-silicate-hydrate gel (CHS) to promote degradation. Another reason for selecting 70 cycles for the duration of the 1st Stage was for convenience. The PA for the E-Area LLW Facility assumed the concrete infiltration rate was 4 cm/yr for the first 1050-years; 70 cycles corresponds to 1050 years (assuming 60-cm thick concrete/cycle, 4-cm/yr) (Kaplan and Myers 2001).⁷

4.2.2 2nd Stage

During this stage, the soluble salts of the alkali metals are all dissolved and washed out of the cement solids. The pH of the cement pore water is controlled at a value of 12.5 by the solubility of portlandite. The calcium-silicate-hydrate gel and portlandite are the major solid phases present. The 2nd Stage may last for a long time, and its duration depends on how much water percolates through the system and the mass of cement present in the concrete structure. The total dissolved calcium is ~20 mM/L, the pH is strongly buffered at pH ~12.5, and the silica concentration is very low, <0.03 mM/L. The flux of water must dissolve all the slightly soluble portlandite before the leachate chemistry changes.

Concrete in the 2nd Stage binds most radionuclides relatively strongly, and the porewater buffered at pH 12.5. It is anticipated to last 500 exchange cycles (pore volumes).

Berner (1992) determined that the 2nd Stage lasts between 100 and 1000 cycles. According to the Bradbury and Sarrott (1995) and adopted here, most radionuclides have higher *Kd* values and solubility concentration limits in the 2nd Stage than in the 3rd Stage. Therefore, a lower 2nd Stage lifespan is conservative. The 2nd Stage *Kd* values and solubility concentrations limits are generally higher lower than those in the 1st Stage, except in the case where cation exchange is the predominant sorption mechanism, in which case the *Kd* in the 1st Stage will be lower due to high salt concentrations in the porewater. Taking into consideration the slow dissolving attribute of the low-carbonate SRS groundwater when in contact with cementitious solids, an exchange cycle of 500 cycles was assumed.

⁶ Based on thermodynamic calculations presented in Kaplan and Myers (2001), as the pH increases from 12.2 to 12.8, the solubility of $\text{Pb}(\text{OH})_{2(\text{solid})}$ sharply increases and the concentration of $\text{Pb}(\text{OH})_4^{2-}(\text{aq})$ increases. At pH 12.8, all the Pb solid was total dissolved.

⁷ 70 exchange cycles x 60-cm cement/exchange cycle x 1/4 yr/cm = 1050 years

4.2.3 3rd Stage

In the 3rd Stage, the portlandite has been fully dissolved/reacted and the solubility or reactions of calcium-silicate-hydrate gel with the infiltrating water controls the pH of the cement porewater/leachate (Figure 3). The calcium-silicate-hydrate gel starts to dissolve incongruently⁸ with a continual decrease in pH until it reaches the pH of the background sediment, pH 5.5. At the end of this evolution, the 3rd Stage can be conceptualized as leaving only silica (SiO₂) as the solubility control for the pore water pH. The ionic strength of the cement leachate during this period is relatively low and its pH drops to ~10 and lower over long times. Solution calcium concentrations decrease to 1- to 5-mM and silica concentrations increases to 2- to 6-mM. At very high cycle numbers, other sparingly soluble solids, such as brucite [Mg(OH)₂], may buffer the solution pH and dissolved cation concentrations.

Concrete in the 3rd Stage binds radionuclides the least, and the porewater buffered by the CSH gel at pH 10 to 5.5, SRS background pH. It is anticipated to last 7000 exchange cycles (pore volumes).

Berner (1992) suggested that the duration of the 3rd Stage is between 1000 and 10,000 cycles. Since SRS groundwater is low in carbonate concentrations, a longer duration for this stage would be appropriate; a “lifetime” of 7000 cycles was selected for the SRS PA calculations.

4.2.4 Cement Stage Lifespan

This discussion is based largely from results presented in Berner (1992). The total lifetime of the cement is somewhat arbitrarily defined by Berner (1992) as the cycle number where calcium-silicate-hydrate gel has dissolved completely. This is an arbitrary definition because this gel dissolves to form other solid phases, such as brucite [Mg(OH)₂], calcite (CaCO₃), and gypsum (CaSO₄) and silica (SiO₂). However, the physical and chemical properties of the cement change appreciably after the calcium-silicate-hydrate gel has dissolved. Berner (1992) reported that between 5,000 and 10,000 exchange cycles were required to degrade completely the calcium-silicate-hydrate gel.

Perhaps the single most important porewater constituent influencing the “lifetime” of a cement is the concentration of carbonate in the groundwater (Berner 1992, Reardon 1992). For example, calculations conducted by Berner (1992) showed that a cement interacting with a high-carbonate (4.6 mM) infiltrating groundwater had a “lifetime” of 4480 cycles, whereas the same cement interacting with a low-carbonate (0 mM) infiltrating groundwater had a “lifetime” of 7450 cycles. The sediment pore water at SRS has a total inorganic carbon concentrations of about 0.2-mM (Strom and Kaback 1992). The reason SRS pore water is low in carbonate is that our surface soils contain little or no carbonate, the result of our soils being highly weathered and acidic.

⁸ Incongruent dissolution is dissolution to give dissolved material in different proportions from those in the original solid.

The reason that groundwater carbonate concentrations are important is because the carbonate combines with the calcium released from the calcium-silicate-hydrate gel and forms calcite (CaCO_3). The calcite acts as a sink, “sucking” calcium from the calcium-silicate-hydrate gel, thereby promoting the gel’s dissolution. Berner (1992) reported that nearly 83% of the total calcium-inventory could be reprecipitated during the 3rd Stage as calcite in the cement mixture (discussed below). This transformation to calcite approximately halved the calculated “lifetime” of the calcium-silicate-hydrate gel, compared to gel degradation in pure water, where no calcite was formed.

As an example, if we were to assume that the waste was held within 60-cm of the grout (as is the case for waste disposed as Components-in-Grout), the entire lifespan of the cement waste through a 50 cycle 1st Stage (Section 4.2.1), 500 cycle 2nd Stage (Section 4.2.2), and a 7000 cycle for the 3rd Stage (Section 4.2.3) would be 12,000 years, assuming an infiltration rate of 4-cm/yr for the first 750 years before the solid has started to physically degrade, and then 40-cm/yr thereafter.⁹

For example, a 2-ft thick layer of concrete buried at SRS may be expected to have a 750 yr 1st Stage, 750 yr 2nd Stage, and a 10,500 yr 3rd Stage, for a total life span of 12,000 yr.

4.2.5 Duration of Reducing Environment Produced by Slag-Containing Cementitious Materials

Some cementitious materials have blast-furnace slag included in their formulations to promote the reductive precipitation of the radionuclide with sulfide, thus reducing the tendency of the radionuclides to leach from the solid waste form. Experimentation has shown that leaching of Cr and Tc was effectively reduced to a level that enabled all projected salt solution compositions to be processed into a non-hazardous solid waste (MMES 1992). Long-term lysimeter studies have shown that the addition of slag into the saltstone formulation essentially stopped ⁹⁹Tc leaching, but did not reduce nitrate leaching (MMES 1992). In addition to the blast-furnace slag creating a low redox status (*i.e.*, low reduction potential, which has been measured with an Eh meter), it also tends to raise the concentration of sulfides in the porewater. The net effect is that numerous metals precipitate out of solution as a result of reductive precipitation (the result of lower the Eh) and/or due to the complexation with sulfides (a strong precipitating moiety. Tc, is an example of a radionuclide that undergoes both reduction from Tc(VII) to Tc(IV) and forms insoluble precipitates with sulfides to form Tc_2S_7 (Lukens et al. 2005). Other radionuclides immobilized in the presences of blast-furnace slag include U and Np.

For purposes of the Saltstone PA, it will be assumed that reducing cementitious materials will maintain their reducing environments throughout the PA scenario. Additional calculations need to be conducted to determine the duration of the reducing environment of the Intermediate Level Vault.

⁹ 1st Cycle: 50 cycles x 60-cm cement/cycle x 0.25 yr/cm = 750 yr

2nd Cycle : 500 cycles x 60-cm cement/cycle x 0.025 yr/cm = 750 yr

3rd Cycle : 7500 cycles x 60-cm cement/cycle x 0.025 yr/cm = 10500 yr.

These infiltration rates of 4- and 40-cm/yr were taken from the E-Area LLW PA (McDowell-Boyer et al. 2000). For the first 1050 yrs, the concrete is assumed to be physically intact. The greater infiltration rate was assumed to account for the concrete crumbling into particles that were about the same size as the surrounding sediment.

Based on laboratory measurements and two-dimensional reactive transport calculations, it was estimated that the Z-Area saltstone waste form will maintain a reducing environment, and therefore its ability to sequester ^{99}Tc , for well over 10,000 years (Kaplan and Hang 2003). For example, it was calculated that ~16% of the saltstone reduction capacity would be consumed after 213,000 years (Figure 4). For purposes of comparison, two additional calculations, based on entirely different assumptions, were discussed. The first calculation conducted by Lukens et al. (2004), based on spectroscopy considerations (sans diffusion or aqueous transport considerations), yielded near identical results as above. The second calculation conducted as a first approximation and using unrealistically high groundwater flow rates, concluded that the Z-Area saltstone waste form will maintain a reducing environment likely for more than 10,000 years (Kaplan and Hang 2003). Obtaining similar conclusions by three extremely different types of calculations and sets of assumptions provides additional credence to the conclusion that the Z-Area saltstone will likely maintain a reducing environment in excess of 10,000 years.

In the past it was assumed for the Saltstone PA, that reducing cementitious materials maintained their reducing environments for the entire PA scenario, 10,000 years. In the future, as the oxidation of the reducing grout will be modeled and as it converts to the oxidized form, the Kd values or solubility concentration limits of the redox sensitive radionuclides will also change. In the case of Tc, the aqueous Tc concentration will be initially controlled within the reducing saltstone by solubility to 10^{-10} M. But once the oxidizing front reaches the saltstone, that particular node will have a Kd of 0 mL/g. (Additionally, the influence of cracking as a function of time will be integrated into the transport of oxygenated water.)

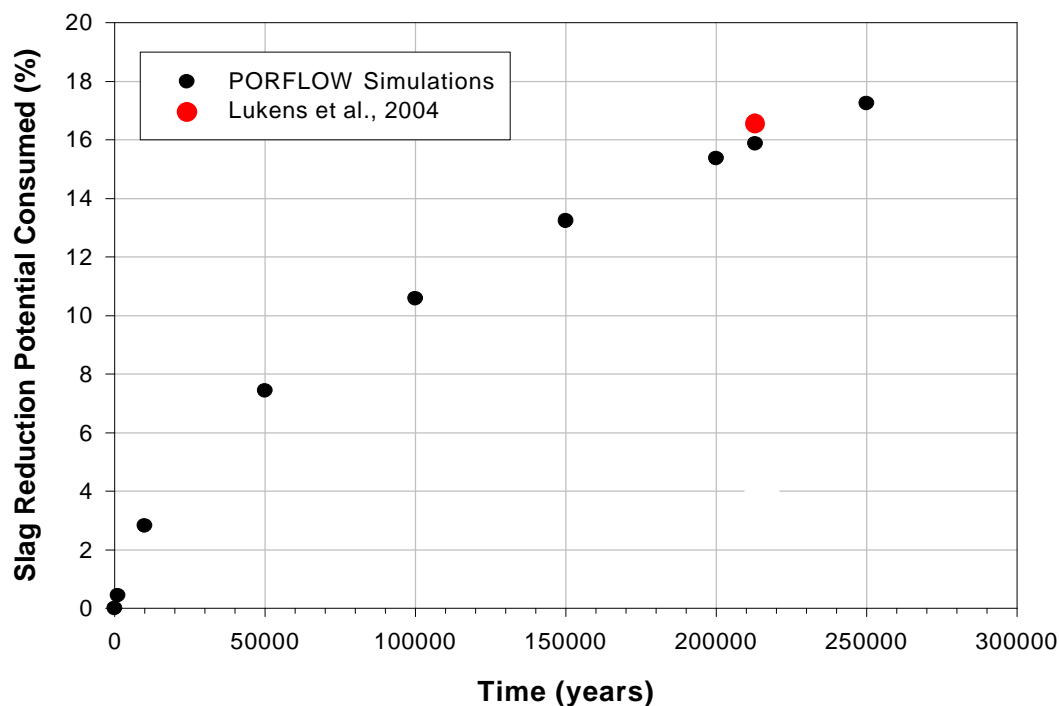


Figure 4. Consumption of slag reduction potential by diffusing dissolved oxygen in infiltrating water into the Saltstone Facility (Kaplan and Hang 2003). Results from Lukens et al. (2004) is also presented (value corrected for diffusion from four sides).

4.3 Radionuclide Leaching from Waste Materials

There are a large number of different types of solid phases that are disposed within the various E-Area facilities, especially, in the trenches. They include paper, plastics, wood, cloth, spent ion exchange resins, metal, concrete debris, and glass. The degree to which the various radionuclides sorb to each material is largely unknown. Therefore, the following simplifying assumption was made. Unless waste-form specific data is available, the extent that a radionuclide sorbs to the waste form is assumed to be similar to the extent that the radionuclide sorbs to the solid phase immediately in contact with the waste. For example, the leaching rate of Th associated with paper disposed in the Slit Trench Facility will be calculated using the Th K_d value reported in the Clayey Sediment look-up table. The Clayey Sediment, is the solid phase in contact with the waste. There are some, not many, waste-specific K_d values and solubility concentration limits, especially for anions sorbing to anionic resins (*e.g.*, Kaplan and Serkiz 2000). The extent that radionuclides desorb from waste can be estimated through the use of K_d values and solubility concentration values. The use of these parameters to estimate desorption, is simply the reverse of adsorption. One of the assumption of

Unless waste-form specific data is available, the extent that a radionuclide sorbs to the waste form will be set equal to the extent that the radionuclide sorbs to the solid phase (sediment or cement) immediately in contact with the waste.

the Kd construct is that it is fully reversible, meaning that adsorption occurs at the same rate as desorption.

5.0 DATA TABLES

This section describes the key features of each waste facility that influence the geochemical conceptual models. For each facility, there is a schematic, followed by a table containing the conceptual geochemical features of the facility and the associated parameters used to describe the radionuclide as it interacts with these features. At the end of this section, are the various look-up tables containing the Kd values and solubility concentration limits. The schematic and description of the geochemical features for each disposal facility are:

- Slit and Engineered Trenches (Figure 6 and Table 1),
- Low Activity Waste (LAW) Vault (Figure 7 and Table 2),
- Components-in-Grout Trenches (Figure 8 and Table 3),
- Intermediate Level (ILV) Vault (Figure 9 and Table 4),
- Naval Reactor Waste Pads (Figure 11 and Table 5),
- TRU-Pad-1 (Figure 12 and Table 6), and
- Saltstone Disposal Facility (Figure 13 and Table 7).

A summary table follows the description of these disposal units that states whether CDP is present and whether the unit was or will be constructed of reducing or oxidizing cementitious materials. Following these facility descriptions are a list of the elements of interest and their assumed oxidation states and speciation under different environments (A description of whether cellulose degradation products (CDP) are present and if reducing and oxidizing cementitious materials were used during the construction of the disposal unit/facility).

Disposal Unit	CDP(a)	Constructed with Reducing Cementitious Materials(b)	Constructed with Oxidizing Cementitious Materials
Slit Trenches	Yes	No	No
Engineered Trenches	Yes	No	No
Low-Activity-Waste Vault	Yes	No	Yes
Components-in-Grout Trench	Yes	No	Yes
Intermediate Level Vault	Yes	Yes	Yes
Navel Reactor Waste Pad	Yes	No	No
TRU-Waste Pad	Yes	No	Yes
Saltstone Facility	No	Yes	Yes
^(a) Cellulose degradation products are released from wood, cardboard, and paper products. The amount of cellulosic materials contained in each of these disposal facilities is expected to vary greatly. Consequently the duration that CDP-correct Kd values will be used prior to using simple Kd values will also vary greatly between facilities. ^(b) Reducing cementitious materials contain slag to create the reducing environment for immobilizing redox-sensitive radionuclides, such as Tc and Pu.			

Table 9). Distribution coefficients for the Clayey Sediment and Sandy Sediment Layers are presented in Table 10 and K_d values and solubility concentration limits for the various cementitious environments are presented in Table 11 through Table 14.

There has not been any work done to date regarding geochemical parameter input variability as it relates to the SRS PA. However, activity to understand variability and uncertainty associated with these parameters is presently underway. Wieland and Van Loon (2003) suggested that the low range value of K_d values be set to 2 fold the mean if the K_d value was <1000 mL/g and an order-of-magnitude if the K_d value was ≥ 1000 mL/g. This decision was largely based on professional judgment, rather than on a rigorous statistical analysis of data. Furthermore, Wieland and Van Loon (2003), as well as Krupka et al. (2004), recommend that the parameters have a normal distribution. Again, this decision appears to be largely based on professional judgment.

For the look-up tables, a “best” value is provided and then a “reasonably conservative” value. When the K_d value was <1000 mL/g and there was little data available to evaluate the range of values, the “reasonably conservative” value was set to be about half of the “best” value, or the lowest measured value, to yield a range of two fold. When the K_d value was ≥ 1000 mL/g, the “reasonably conservative” value was approximately half an order-of-magnitude less than the “best” value, yielding a range of one-order-of-magnitude for the overall distribution around the mean. In all cases, these general guidelines were overruled when data in the literature showed contradictory information. Site-specific data that showed a wider range was reported rather than using these general guidelines. The systematic approach to selecting data for the look-up tables is presented in Section 4.0.



Figure 5. E-Area Slit Trench Facility showing a range of waste materials. Also note the red clayey sediment, characteristic of the upper sediment strata.

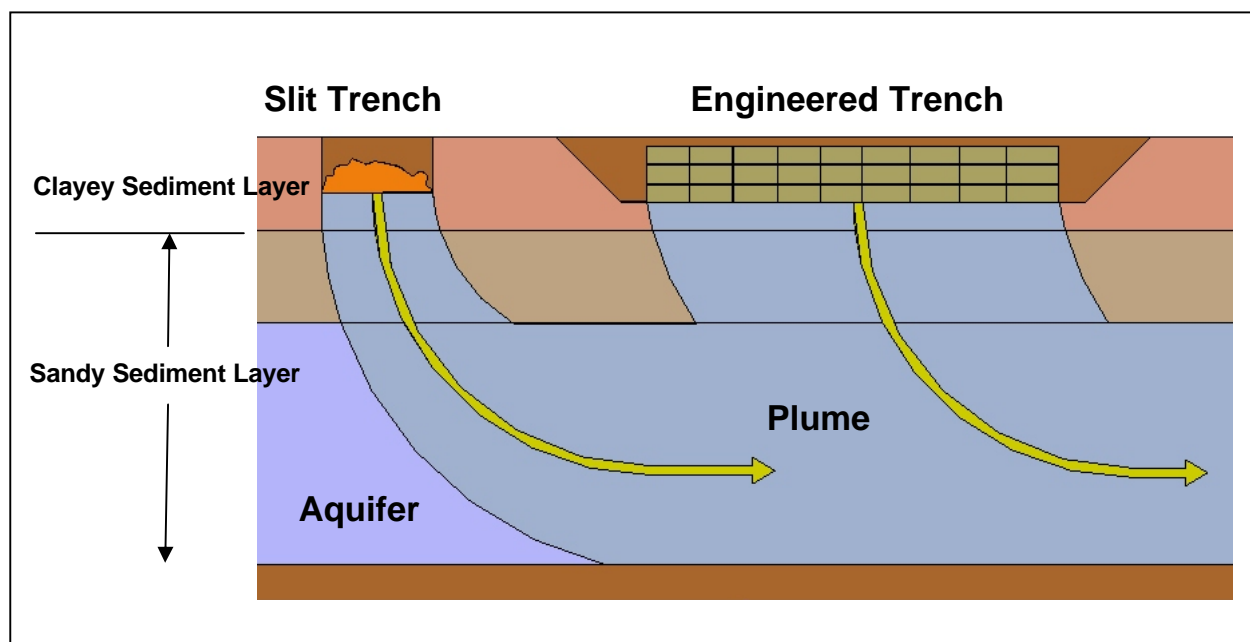


Figure 6. Schematic representation of the geochemical conceptual model of a Slit and Engineered Trench Units. Not shown is that a multilayered-closure cap will be added above these units during Post-Institutional Control. See Table 1 for facilities description.

Table 1. Slit and Engineered Trenches: Conceptual geochemical features and parameters (See Figure 6).

Solid Phases	Aqueous Phase	Geochemical Parameter
Waste Zone ^(a)	SRS ground water: pH 5.5, ionic strength 0.01 M ¹⁰ , except for possible trace levels of radionuclide concentrations and CDPs	Initially use Clayey Sediment Kd_{CDP} until all the CDP ^(b) has leached from the Waste Zone. Then use Clayey Sediment Kd . Will assume waste has characteristics of Clayey Sediment, the nearest solid phase to the Waste Zone.
Clayey Sediment Layer	As above.	Initially use Clayey Sediment Kd_{CDP} until all the CDP ^(b) has leached from the Waste Zone. Then use Clayey Sediment Kd .
Sandy Sediment Layer	As above.	Initially use Sandy Sediment Kd_{CDP} until all the CDP ^(b) has leached from the Waste Zone. Then use Sandy Sediment Kd .
^(a) Slit Trenches are approximately 6-m x 6-m x 200-m and receive a wide range of materials that contain very low concentrations of radioactivity, including from environmental restoration and building decommissioning. The Engineered Trenches are about 218-m long by 50-m wide and 7-m depth and received similar types of waste materials as the Slit Trenches. All waste from the Engineered Trenches are placed in metal boxes (<i>e.g.</i> , B-25 boxes) that are stacked on top of each other. ^(b) $Kd_{CDP} = Kd$ for cellulose degradation products.		

¹⁰ Ionic strength of a solution is a measure of the amount of ionic species in solutions and is proportional to the salt content. Its influence on radionuclide sorption is complex and non-linear. In simple cation exchange systems, as described by Kd values, an increase in ionic strength results in greater desorption, and this general rule holds true in most natural environments. Above a critical concentration, and depending on the ions in solution, precipitation may occur.

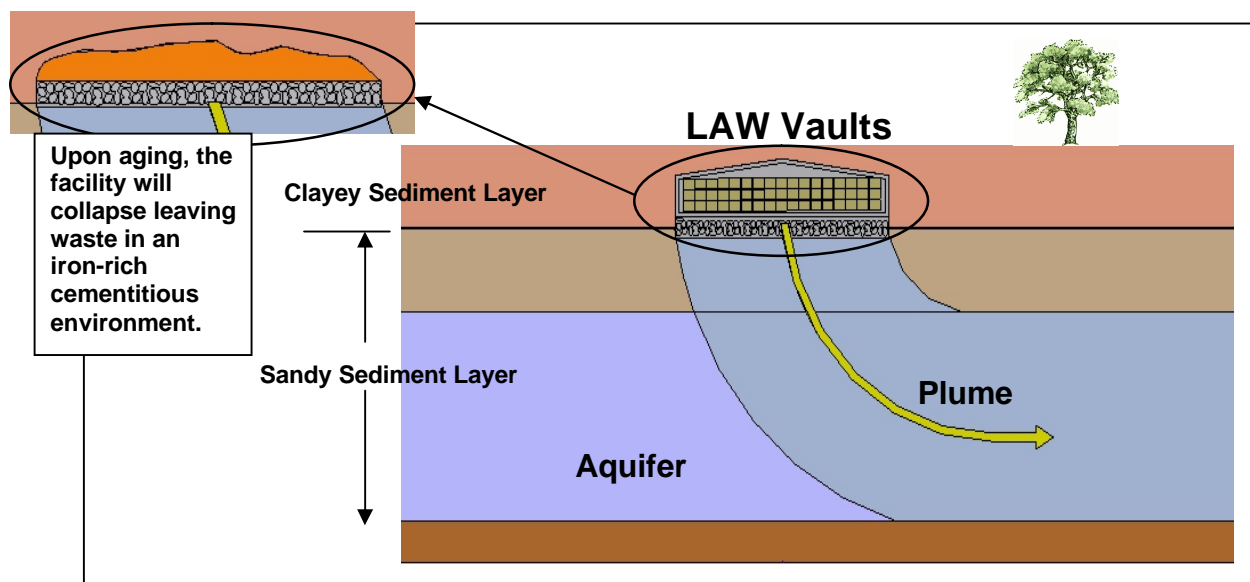


Figure 7. Schematic representation of the geochemical conceptual model of the Low-Activity Waste Vault. Not shown is that a multilayered-closure cap will be added above the vault during Post-Institutional Control. See Table 2 for facility description.

Table 2. LAW Vault: Conceptual geochemical features and parameters (See Figure 7).

Solid Phases	Aqueous Phase	Geochemical Parameter
Waste Zone ^(a) : Aged metal boxes (B-25 boxes) containing waste. Over time the boxes rust and release radionuclides. Eventually concrete vault structure and B-25 boxes collapse leaving waste in an Fe-rich cementitious environment.	Concrete leachate enters metal boxes or into collapsed rusted Fe. Higher pH and ionic strength in this environment compared to natural rain water/ groundwater.	Clayey Sediment K_d . These K_d values are generally for background sediments with a pH of 5.5. Clayey sediments on the SRS are typically red in color as a result of being covered by Fe-oxides. These Fe-oxides coatings will provide a conservative (less abundant) approximation of pure Fe-oxides. Also applying Clayey Sediment (which have an assumed pH of 5.5) K_d values to a system with a higher pH (concrete pH is typically >10) will be conservative because metal sorption (K_d values) will be greater in high pH than in low pH systems.
Concrete: concrete roof, walls, & floor.	Cementitious: Three types of concrete leachate chemistries controlled by different aged solid phases: young concrete leachate pH 12.5, then pH 10.5, final pH 5.5; generally higher in ionic strength than SRS groundwater (Figure 3).	Oxidizing Concrete K_d or Oxidizing Concrete solubility concentration limits
Crushed stone: used beneath LAW Vault facility. ^(c)	Cementitious (as above).	See footnote (c).
Clayey Sediment Layer	Typical SRS groundwater: pH 5.5, ionic strength 0.01, except for possible trace levels of radionuclide concentrations and CDPs.	Initially use Clayey Sediment K_{dCDP} until all the CDP ^(b) leached from the waste has been flushed from clay layer. Then use Clayey Sediment K_d .
Sandy Sediment Layer	Typical SRS groundwater (as above).	Initially use Sandy Sediment K_{dCDP} until all the CDP ^(b) leached from the waste has been flushed from sand layer. Then use Sandy Sediment K_d .
<p>^(a) This waste contains greater radioactivity than the waste disposed in the Slit Trenches. Some cellulosic materials will be disposed in the vaults. Waste is placed in large metal boxes (B-25 & B-12 boxes) which are stacked and stored in large concrete vaults. The vault consists of concrete roof, walls, and floor, which are generally about 1-ft thick.</p> <p>^(b) $K_{dCDP} = K_d$ for cellulose degradation products.</p> <p>^(c) A 1.1-m layer of crushed stone exists immediately beneath the concrete floor of the LAW Vault. It has not been included in previous PA modeling efforts, presumably because it was believed that this layer would become "silted in" within a relatively short period of time. For this same reason, it is not included in the conceptual geochemical model of this disposal site and will be modeled as behaving like the Clayey Sediment Layer.</p>		

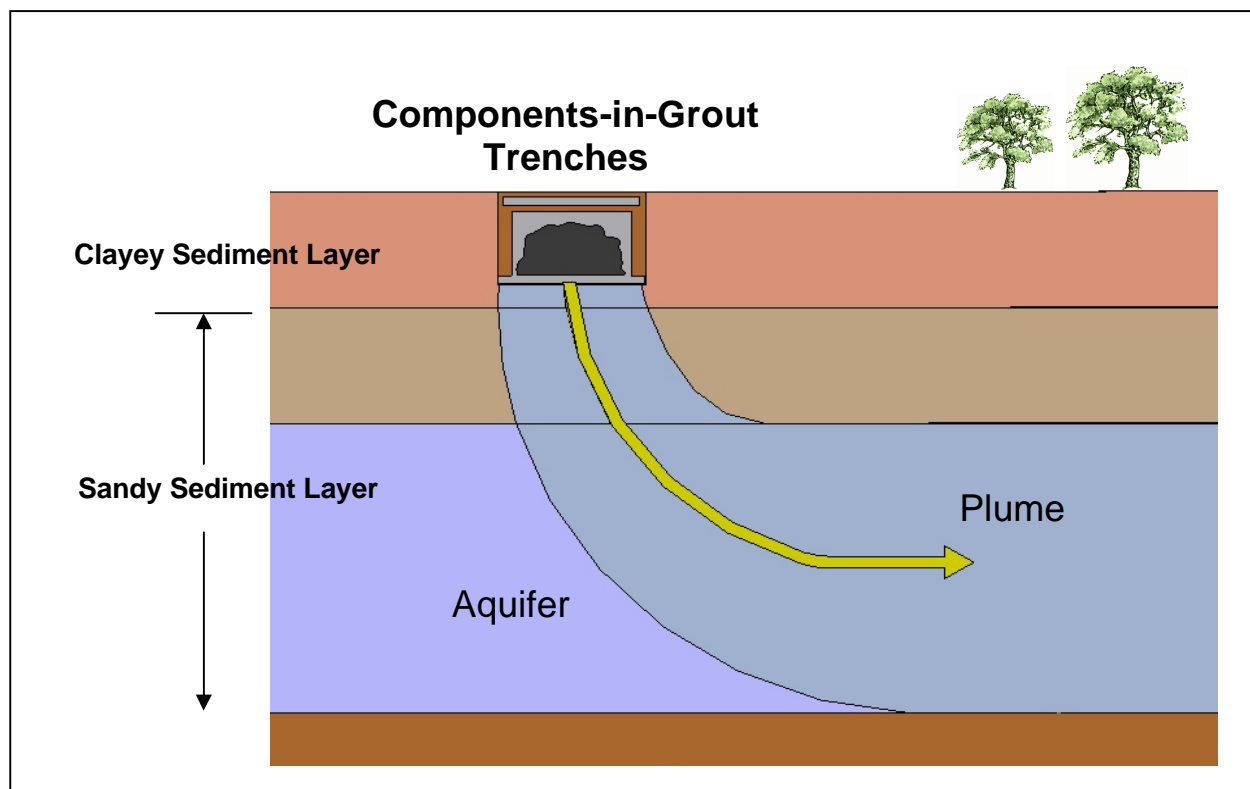


Figure 8. Schematic representation of the geochemical conceptual model of a Components-in-Grout Trenches. Not shown is that a multilayered-closure cap will be added above the vault during Post-Institutional Control. See Table 3 for facility description.

Table 3. Components-in-Grout Trenches: Conceptual geochemical features and parameters (Figure 8).

Solid Phases	Aqueous Phase	Geochemical Parameter
Waste Zone ^(a)	Cementitious: Three types of concrete leachate chemistries controlled by different aged solid phases: young concrete leachate pH 12.5, then pH 10.5, final pH 5.5; higher in ionic strength than SRS groundwater	Oxidizing concrete Kd or Oxidizing concrete solubility concentration limits
Concrete: 0.3-m-thick concrete/grout walls & floor of trench, concrete/grout poured over waste to encapsulate waste.	Cementitious (as above)	Oxidizing concrete Kd or Oxidizing concrete solubility concentration limits
Clayey sediment layer	Typical SRS groundwater: pH 5.5, ionic strength 0.01, except for possible trace levels of radionuclide concentrations and CDPs	Initially use Clayey Sediment Kd_{CDP} until all the CDP ^(b) leached from the waste has been flushed from clay layer. Then use Clayey Sediment Kd .
Sandy sediment layer	Typical SRS groundwater (as above).	Initially use Sandy Sediment Kd_{CDP} until all the CDP ^(b) leached from the waste has been flushed from sand layer. Then use Sandy Sediment Kd .
^(a) This waste is too bulky and too large to place in the Low-Activity Waste Vault or the Intermediate Level Vault and typically contains more radioactivity than the waste that is placed in Slit Trenches. A hole is dug in the ground to act as a form, a grout floor is poured, and the waste is placed in the floor, ~1-ft of grout is poured over the waste, and then sediment backfill is added to fill the hole. A reinforced concrete slab is installed over new Components-in-Grout sediments for support of the final closure cap. It is expected that negligible cellulosic material is included this material. ^(b) $Kd_{CDP} = Kd$ for cellulose degradation products.		

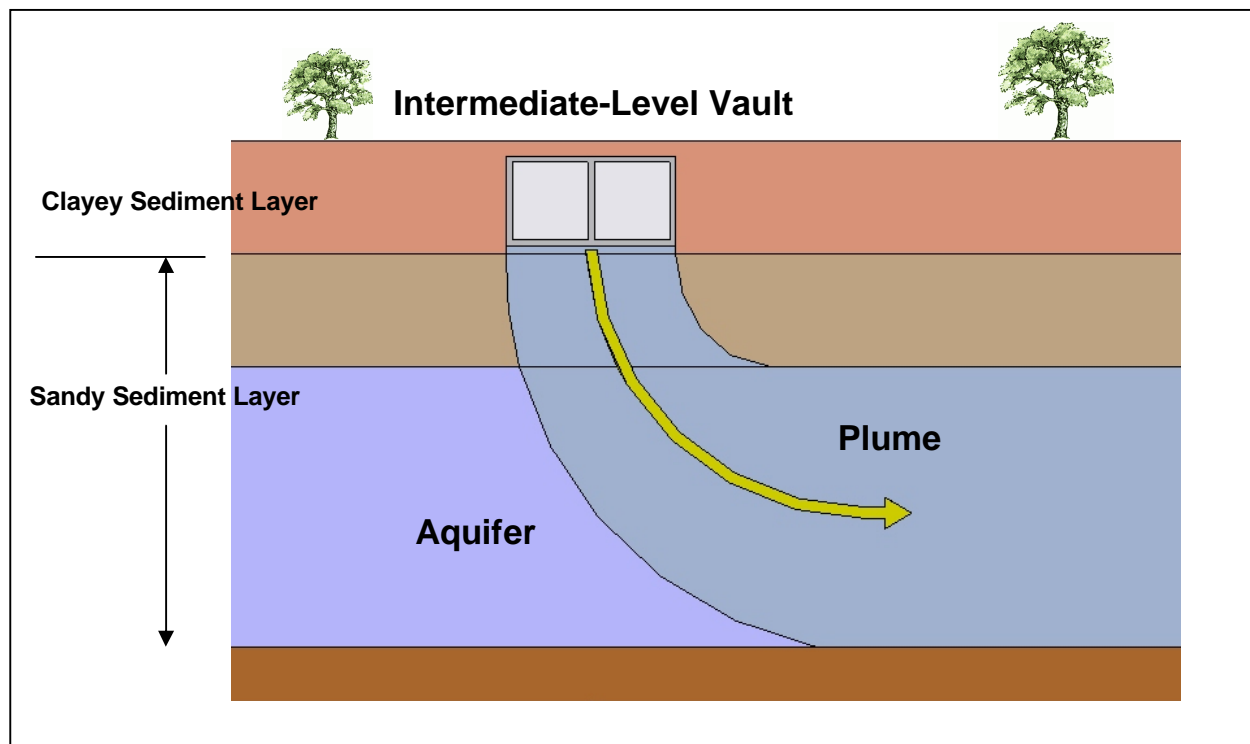


Figure 9. Schematic representation of the geochemical conceptual model of the Intermediate-Level Vault Facility. Not shown is that a multilayered-closure cap will be added above the vault during Post-Institutional Control. See Table 4 for facility description.

Table 4. Intermediate-Level Vault: Conceptual geochemical features and parameters (Figure 9).^(a)

Solid Phases	Aqueous Phase	Geochemical Parameter
Waste Zone ^(a)	Reducing Cementitious ^(c) : Three types of concrete leachate chemistries controlled by different aged solid phases: young concrete leachate pH 12.5, then pH 10.5, final pH 5.5 (Figure 3); generally higher in ionic strength than SRS groundwater. Leachate will contain sulfides released from slag (Angus and Glasser 1985).	Reducing concrete Kd & reducing concrete solubility concentration limits ^(c)
Reducing concrete ^(c) : Slag added to concrete used in floor and walls. Roof truss steel structure will be replaced with reducing concrete.	Reducing Cementitious Environment: (as immediately above)	Reducing concrete Kd & reducing concrete solubility concentration limits ^(b)
Clayey sediment layer	Typical SRS groundwater: pH 5.5, ionic strength 0.01, except for possible trace levels of radionuclide concentrations and CDPs	Initially use Clayey Sediment Kd_{CDP} until all the CDP ^(d) leached from the waste has been flushed from clay layer. Then use Clayey Sediment Kd .
Sandy sediment layer	Typical SRS groundwater (as above).	Initially use Sandy Sediment Kd_{CDP} until all the CDP ^(d) leached from the waste has been flushed from sand layer. Then use Sandy Sediment Kd .
<p>^(a) This waste contains more radioactivity than Slit- and Engineered-Trench waste. It is placed in the vault in layers and is grouted/concreted/CSLMed in place. The facility includes Intermediate-Level Non-Tritium Vault and the Intermediate-Level Tritium Vault. The latter is used for disposal and storage of tritium-bearing waste packed in 10-gallon drums, or spent tritium extraction crucibles, and tritium job control waste.</p> <p>^(b) Some oxidizing concrete may have been used to anchor B-25 metal waste containers as reducing concrete or CSLM was added to cover waste within vault, but a majority of the cementitious material contains slag.</p> <p>^(c) Reducing cementitious materials are those that contain slag and change the pore water chemistry sufficiently to require unique geochemical parameters (see Section 4.2.5).</p> <p>^(d) $Kd_{CDP} = Kd$ for cellulose degradation products.</p>		



Figure 10. Photo showing partially covered Naval Reactor Waste Pad and components of various sizes. Earth and a clay cap will be mounded over Naval Reactor Waste prior to final disposal. There are two such facilities, the “old” and “new” facilities.

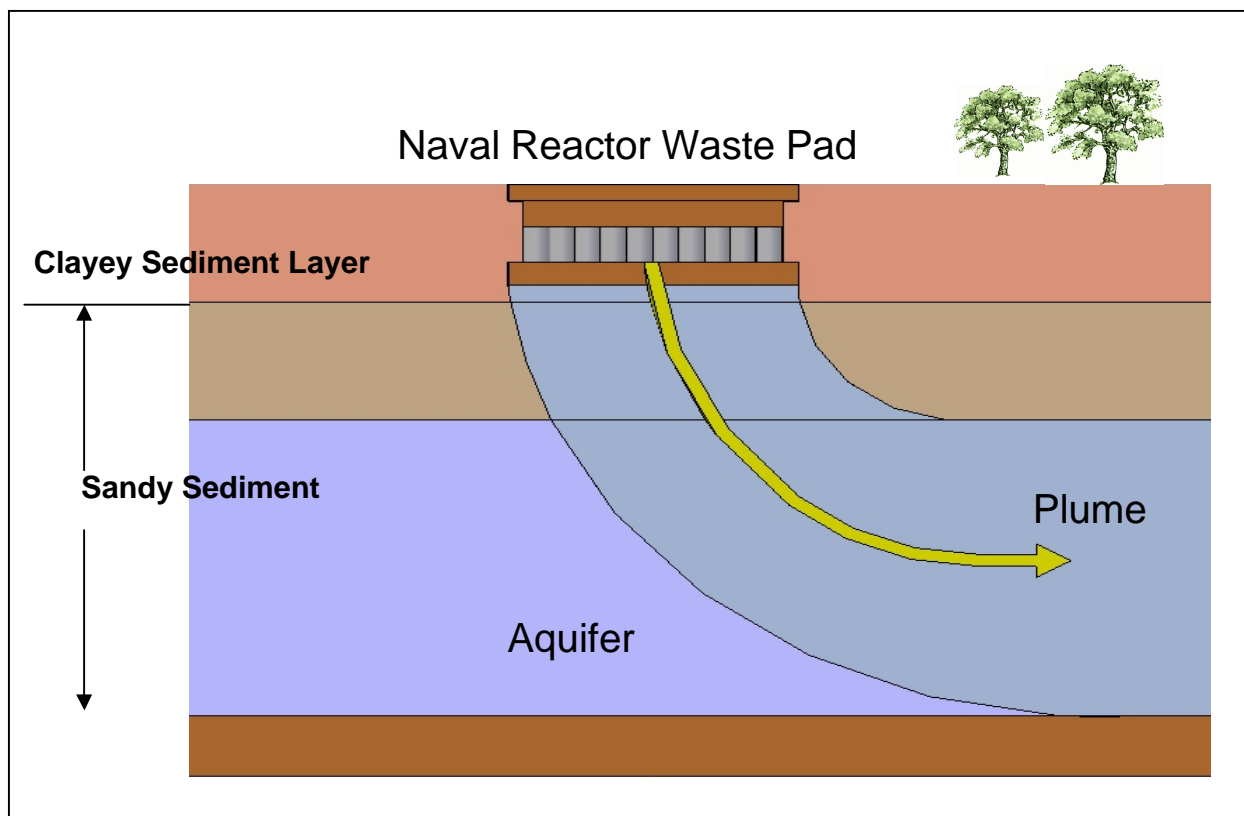


Figure 11. Schematic representation of the geochemical conceptual model of the Naval Reactor Waste Pad Facility. Not shown is that a multilayered-closure cap will be added above the pads during Post-Institutional Control. See Table 5 for facility description.

Table 5. Naval Reactor Waste Pads: Conceptual geochemical features and parameters (See Figure 11).

Solid Phases	Aqueous Phase	Geochemical Parameter
Waste Zone: Activated metal waste. It is assumed that the metal waste will rust to form Fe-oxides and that the radionuclides will sorb to these Fe-oxides. ^(a)	Typical SRS ground water & rainwater: pH 5.5, ionic strength 0.01, except for possible trace levels of radionuclide concentrations.	Clayey Sediment K_d . It is assumed that the geochemistry of the clayey sediment will approximate that of the rusted metal waste form. In reality the rusted waste form will contain much greater Fe-oxide content than the typical clayey SRS sediment, the use of clayey sediment K_d is a conservative assumption.
Clayey sediment layer	Typical SRS groundwater: pH 5.5, ionic strength 0.01, except for possible trace levels of radionuclide concentrations and CDPs	Initially use Clayey Sediment K_{dCDP} until all the CDP ^(d) leached from the waste has been flushed from clay layer. Then use Clayey Sediment K_d .
Sandy sediment layer	Typical SRS groundwater (as above).	Initially use Sandy Sediment K_{dCDP} until all the CDP ^(d) leached from the waste has been flushed from sand layer. Then use Sandy Sediment K_d .
^(a) This waste contains large pieces of activated metal naval reactor components encased in heavily shielded shipping containers (See photos in Figure 10. The waste consists of core barrels, adapter flanges, closure heads and other similar equipment. There are two NRW Pads. The casks are placed on an earthen pad and will be covered with a minimum of 4.1 m of backfill and a moisture barrier (clay, gravel, and geotextile fabric layers). There are negligible amounts of cellulosic materials included amongst this waste. ^(b) $K_{dCDP} = K_d$ for cellulose degradation products.		

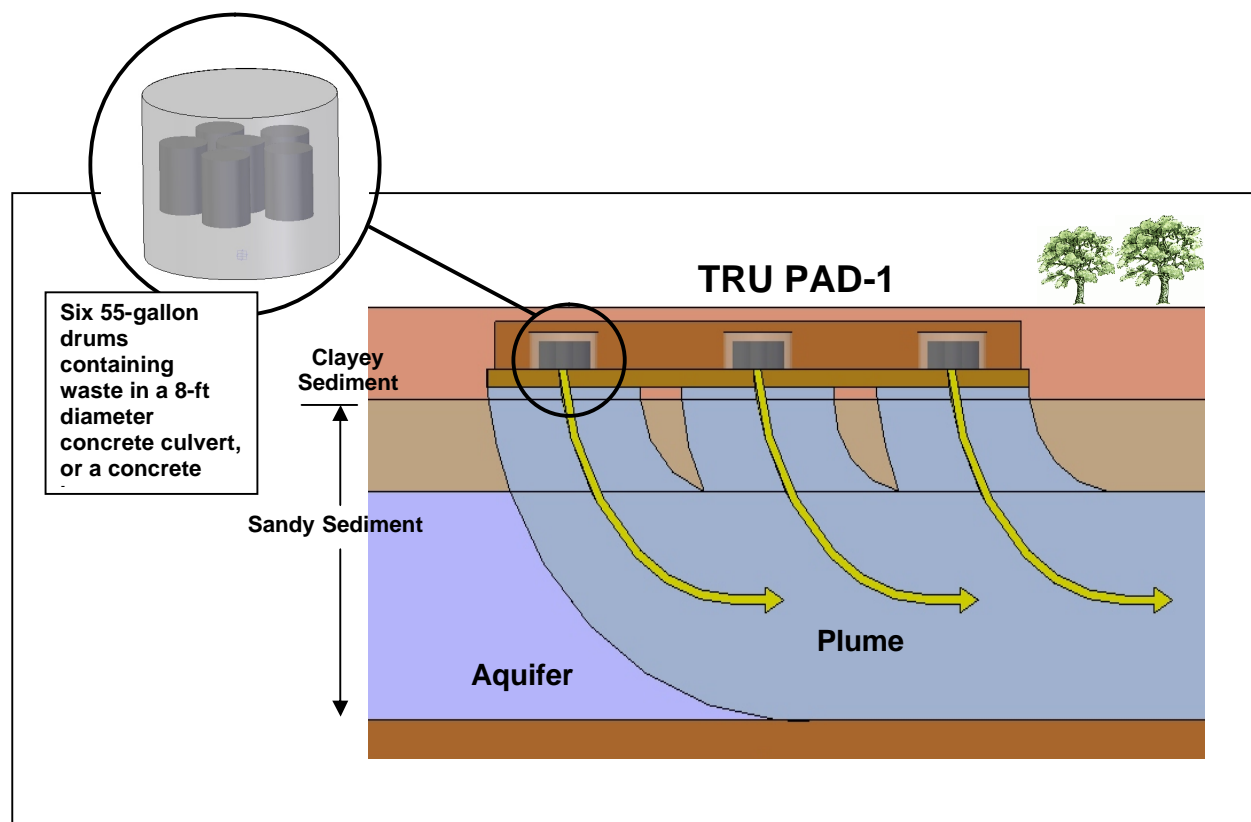


Figure 12. Schematic representation of the geochemical conceptual model of the TRU PAD-1. Not shown is that a multilayered-closure cap will be added above the pads during Post-Institutional Control. See Table 6 for facility description.

Table 6. TRU PAD-1: Conceptual geochemical features and parameters (See Figure 12).

Solid Phases	Aqueous Phase	Geochemical Parameter
Waste Zone ^(a)	Oxidizing Concrete: Three types of concrete leachate chemistries controlled by different aged solid phases: young concrete leachate pH 12.5, then pH 10.5, final pH 5.5 (Figure 3); higher in ionic strength than SRS groundwater	Oxidizing Concrete K_d or Oxidizing Concrete solubility concentration limits
Concrete: 1-ft-thick concrete/grout walls & floor of trench, concrete/grout poured over waste to encapsulate waste.	Oxidizing Concrete (as immediately above)	Oxidizing Concrete K_d or Oxidizing Concrete solubility concentration limits
Clayey sediment layer	Typical SRS groundwater: pH 5.5, ionic strength 0.01, except for possible trace levels of radionuclide concentrations and CDPs	Initially use Clayey Sediment K_{dCDP} until all the CDP ^(d) leached from the waste has been flushed from clay layer. Then use Clayey Sediment K_d .
Sandy sediment layer	Typical SRS groundwater (as above).	Initially use Sandy Sediment K_{dCDP} until all the CDP ^(d) leached from the waste has been flushed from sand layer. Then use Sandy Sediment K_d .
<p>^(a) This waste form includes six 55-gallon drums that are placed in an 8-ft-diameter concrete culvert or concrete box. The drums will be arranged with one drum in the middle and the remaining five surrounding it. Concrete will be poured between the drums to hold them in the culvert or concrete box. Approximately 2 ft of concrete will be poured between the outside of the drums and the inside of the culvert/box. The waste-containing concrete culverts/boxes will be placed on a concrete pad and will be covered with a minimum of 4.1 m of backfill and a moisture barrier (clay, gravel, and geotextile fabric layers).</p> <p>^(b) Some protective clothing and a small amount of cellulosic material is included in this waste, thus CDP-K_d values need to be applied for the appropriate length of time, as discussed in section 3.4.1 ($K_{dCDP} = K_d$ for cellulose degradation products).</p>		

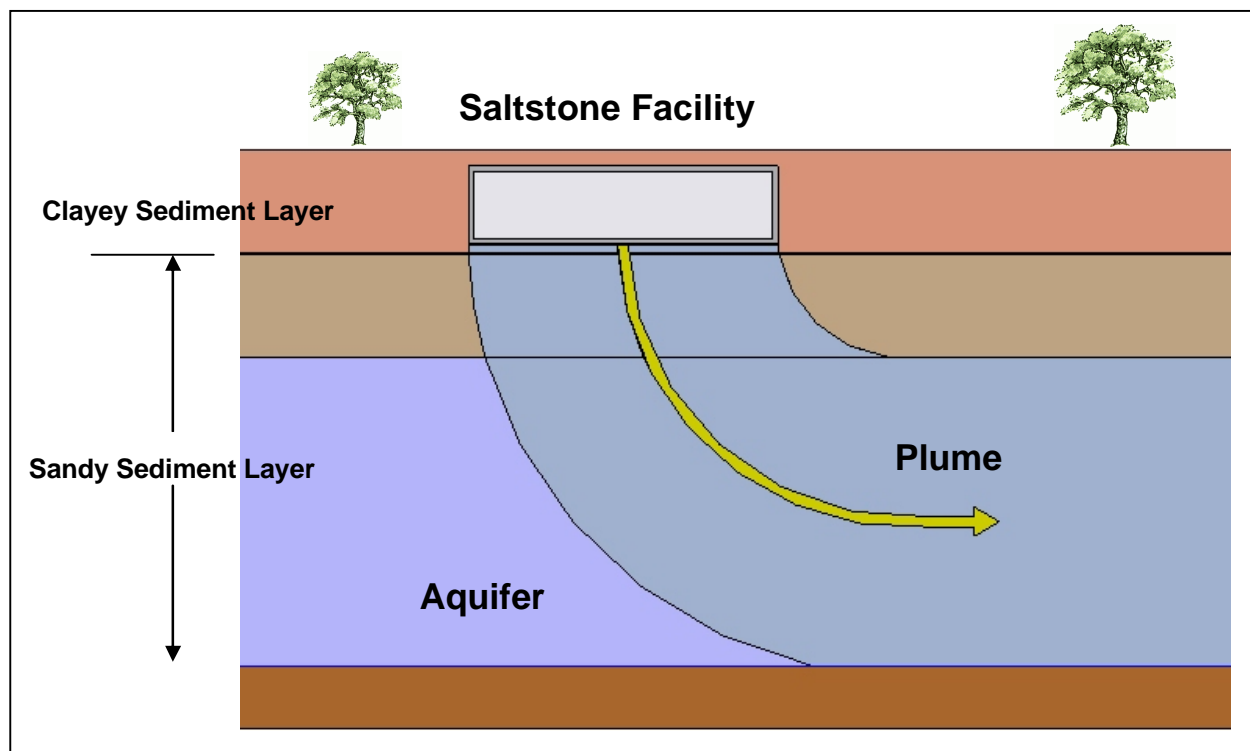


Figure 13. Schematic representation of the geochemical conceptual model of the Saltstone Facility. Not shown is that a multilayered-closure cap will be added above the Saltstone Facility during Post-Institutional Control. See Table 7 for facility description.

Table 7. Saltstone Facility: Conceptual geochemical features and parameters (See Figure 13).

Solid Phases	Aqueous Phase	Geochemical Parameter
Waste Zone ^(a)	Reducing Cementitious ^(c) : Three types of concrete leachate chemistries controlled by different aged solid phases: young concrete leachate pH 12.5, then pH 10.5, final pH 5.5 (Figure 3); generally higher in ionic strength than SRS groundwater. Leachate will contain sulfides released from slag (Angus and Glasser 1985).	Reducing Concrete K_d or Reducing Concrete solubility concentration limits ^(b)
Reducing Concrete ^(c) : 1-ft-thick concrete/grout walls and 2-ft thick floor of vault.	Reducing Concrete (as immediately above)	Reducing Concrete K_d or Reducing Concrete solubility concentration limits ^(b)
Clayey sediment layer	Typical SRS groundwater: pH 5.5, ionic strength 0.01, except for possible trace levels of radionuclide concentrations and CDPs	Initially use Clayey Sediment K_{dCDP} until all the CDP ^(d) leached from the waste has been flushed from clay layer. Then use Clayey Sediment K_d .
Sandy sediment layer	Typical SRS groundwater (as above).	Initially use Sandy Sediment K_{dCDP} until all the CDP ^(d) leached from the waste has been flushed from sand layer. Then use Sandy Sediment K_d .
<p>^(a) The waste zone consists of a vault made from reducing concrete that has walls that are ~0.3-m thick and a floor that is ~0.6-m thick. The Saltstone contains blast-furnace slag (a strong reducing agent). Their dimension vary; three vaults have dimensions of 60-m x 180-m long vault to a height of 7.6-m; 30 x 180 x 7.6 m; and 30 x 30 x 7.6 m. On top of the Saltstone is a 0.3-m thick grout fill layer that sits between the Saltstone and the 0.3-m thick concrete roof.</p> <p>^(b) Kaplan and Hang (2003) estimated that reducing conditions in the Saltstone facility will exist for an extremely long time. They calculated that after 10,000 years, <3% of the total reduction capacity of the Saltstone waste had been oxidized. Therefore, to assume that reducing condition exist during the entire duration of the PA simulation is acceptable (See Section 4.2.5). Additional research needs to be conducted in this area and is proposed in Section 7.0.</p> <p>^(c) Reducing cementitious materials are those that contain slag and change the pore water chemistry sufficiently to require unique geochemical parameters (see Section 4.2.5).</p>		

Table 8. A description of whether cellulose degradation products (CDP) are present and if reducing and oxidizing cementitious materials were used during the construction of the disposal unit/facility.

Disposal Unit	CDP ^(a)	Constructed with Reducing Cementitious Materials ^(b)	Constructed with Oxidizing Cementitious Materials
Slit Trenches	Yes	No	No
Engineered Trenches	Yes	No	No
Low-Activity-Waste Vault	Yes	No	Yes
Components-in-Grout Trench	Yes	No	Yes
Intermediate Level Vault	Yes	Yes	Yes
Navel Reactor Waste Pad	Yes	No	No
TRU-Waste Pad	Yes	No	Yes
Saltstone Facility	No	Yes	Yes
<p>^(a) Cellulose degradation products are released from wood, cardboard, and paper products. The amount of cellulosic materials contained in each of these disposal facilities is expected to vary greatly. Consequently the duration that CDP-correct Kd values will be used prior to using simple Kd values will also vary greatly between facilities.</p> <p>^(b) Reducing cementitious materials contain slag to create the reducing environment for immobilizing redox-sensitive radionuclides, such as Tc and Pu.</p>			

Table 9. Radionuclides of interest and their assumed oxidation states or speciation under varying environments.

	Group ^(b)	Sandy Sediment, Clayey Sediment, Crushed Stone	Oxidizing Cement	Reducing Cement
tritium (T)		HTO	HTO, OH ⁻	HTO, OH ⁻
Inorganic C			CO ₃ ²⁻ , HCO ₃ ⁻	
Co, Ni	Divalent Transition	+2	+2	+2
Se, Te	VIB Elements	XO ₄ ²⁻ , XO ₃ ²⁻ (c)	XO ₄ ²⁻ , XO ₃ ²⁻	XO ₃ ²⁻
Kr, Rn, Ar	Noble Gas	0	0	0
Sr, Ra, Ba	Alkali-earth metals	+2	+2	+2
Zr, Th	Group VI Elements	+4	+4	+4
Nb		Nb(OH) ₆ ⁻	Nb(OH) ₆ ⁻	Nb(OH) ₄ ⁻ (a)
Tc, Re	XO ₄ ^{-(c)}	XO ₄ ⁻	XO ₄ ⁻	X ⁴⁺
Sn		+4	+4	+4
Cl, I, At	VIIB, Halides	-1	-1	-1
Cs, Fr, Rb	Alkali metal	+1	+1	+1
Ac, Am, Bk, Cf Cm, Eu, Gd, Sm	Trivalent Actinides & Rare Earth Elements	+3	+3	+3
Pb, Po	Soft, divalent cation	+2	+2	+2
U		UO ₂ ²⁺	UO ₂ ²⁺	U ⁴⁺
Np, Pa		XO ₃ ^{-(c)}	XO ₃ ⁻	X ⁴⁺
Pu		Pu ^{VI} O ₂ ²⁺ , Pu ^V O ₂ ⁺ , colloid	Pu ^{VI} O ₂ ²⁺ , Pu ^V O ₂ ⁺ , colloid	Pu ⁴⁺ , colloid

(a) Nb likely exists as Nb(III) under reducing conditions, but little sorption data is available for this species (Baes and Mesmer 1976).

(b) These groupings of radionuclides will be used in the following *Kd* and solubility limit value tables in the absence of experimental data. These groupings are based on basic chemical considerations including periodicity and basic aqueous chemical properties.

(c) X = generic metal

Table 10. Distribution coefficients (*Kd* values, mL/g): Sandy Sediment Layer (<25 wt-% silt + clay) and Clay Sediment Layer (25 to 45 wt-% silt + clay)

Radio-nuclide	Sandy Sediment		Clayey Sediment		Comments/References ^(a)
	Conser-vative	“Best”	Conser-vative	“Best”	
³ H, Kr, Rn, Ar	0	0	0	0	<u>Tritium & Noble Gases</u> : No sorption experiments were found to have been conducted on SRS sediments or other sediments with these elements. Tritium is assumed to be water species and the inert noble gases should also not interact with the sediments..
Cl, Nb	0	0	0	0	<u>Anions</u> : Unless site specific data is available, assume that anions do not sorb to SRS sediments.
Ac, Am, Bk, Cf, Cm, Eu, Gd, Sm	550	1100	4250	8500	<u>Trivalent Cations</u> : Kaplan and Serkiz (2004) reported that SRS sandy sediment Ce(III) <i>Kd</i> = 1220 ± 1040 mL/g at pH 5.3; SRS clayey sediment Ce(III) <i>Kd</i> = 8697 ± 4980 mL/g at pH 5.3 (Ce(III) is being used here as a chemical analogue for the trivalent radionuclides of interest). Kaplan and Serkiz (2004) reported SRS sandy sediment Eu(III) <i>Kd</i> = 1168 ± 1159 mL/g at pH 5.3; SRS clayey sediment Eu(III) <i>Kd</i> = 9020 ± 3526 mL/g at pH 5.3. Both trivalent cations had very similar <i>Kd</i> values for a given sediment.
Inorganic C	0	0	0	0	No inorganic C sorption data related to SRS sediments was found in the literature. C is assumed to exist primarily as HCO ₃ ⁻ and CO ₂ -gas. The <i>Kd</i> construct does not describe any speciation of gases. Consideration of CO ₂ -gas will require a special analysis and some site-specific measurements. In the aqueous phase, C is anticipated to exist as an anion, and little sorption is expected. Little carbonate exists in the upper aquifers of the SRS due to the low pH.
Cs, Rb, Fr	15	50	180	250	<u>Monovalent (Group 1A)</u> : Hoeffner (1985) reported that Cs sorption to SRS sediments is very pH dependent. Under ambient conditions, <i>Kd</i> values = 410 mL/g. Bibler and Marson (1992) reported Cs <i>Kd</i> values for: an E-Area sediment (TF1, 40-60 mesh) of 34 mL/g, a second E-area sediment (TF2, 40-60 mesh) of 37 mL/g, and an ETF sediment of 7 to 8 mL/g. It should be noted that had the entire soil been used, including the <40 mesh fraction, that the <i>Kd</i> values would be larger than those reported by Bibler and Marson (1992). Johnson (1995; Figure 5-18) reported Cs <i>Kd</i> values of 800 mL/g in aged samples with initial Cs concentrations of 1e-8 M Cs at pH 5. In field observations (squeezed porewater out of aquifer sediment), he measured a <i>Kd</i> of 29 mL/g at pH 5. Johnson (1995; Figure 5-17), using subsurface F-area sediments, showed that the Cs sorption to SRS sediments was very pH dependent and that there was a steep increase in sorption from pH 4.2 to 6.4, between which the <i>Kd</i> increased from about 5 to 95 mL/g. At pH 5.5 the <i>Kd</i> values ranged from 20 to 35 mL/g. Findley (1998) conducted sequential extraction studies and reported that field contaminated sediments did not desorb Cs until extremely harsh acids were used, whereas in lab tests where Cs was added during adsorption (followed by desorption) tests, a majority of the Cs desorbed using relatively mild extractants. This suggests that Cs may become more strongly bound by SRS sediment with time. This same finding has been reported for Hanford and

Radio-nuclide	Sandy Sediment		Clayey Sediment		Comments/References ^(a)
	Conser-vative	“Best”	Conser-vative	“Best”	
					Chernobyl sediments. Goto (2001) conducted >200 Cs sorption experiments with 5 SRS sediments of varying clay content. She showed a strong Cs- <i>Kd</i> dependency on Cs concentrations at environmental-relevant concentrations. The <i>Kd</i> values ranged from 226 ± 51 to 21 ± 7 mL/g at ambient pH levels; varying directly with clay content (Goto 2001; Table 5-3). Sediments with clay content >10% had Cs <i>Kd</i> values >139 mL/g. Those with clay content <10% had <i>Kd</i> values of 73 to 15 mL/g. In distilled water, Cs <i>Kd</i> values were as high as 1500 mL/g, underscoring the importance of using appropriate background electrolytes when conducting sorption experiments.
Co	5	7	21	30	Hoeffner (1985) reported that a SRS sandy sediment (9% clay) had a Co <i>Kd</i> = 4.6 mL/g, pH ~4.7; SRS clayey sediment (23% clay) had a Co <i>Kd</i> = 29 mL/g, pH ~4.7; Co <i>Kd</i> values in SRS sediments were independent of Co concentration between 1e-12 to 1e-6 M Co; Co <i>Kd</i> values in SRS sediments decreased in presence of high divalent cation concentrations but not in presence of high monovalent cation concentrations; strong pH dependency with a slight increase in <i>Kd</i> from pH 2 to 4.8 (background) then sharp increase in <i>Kd</i> as pH increases to pH 7 (<i>Kd</i> = 20,000 mL/g), than as pH increased to 9.5 the <i>Kd</i> steadily decreased to ~20 mL/g (thus concrete <i>Kd</i> values should be appreciably higher than background sediment <i>Kd</i> values (background pH <i>Kd</i> = 7 and cement pH <i>Kd</i> = 30) (2). Oblath et al (1983) reported that SRS lysimeters studies calculated <i>Kd</i> values of 10 to 20 mL/g based on flow calculations.
I, At	0	0	0.3	0.6	Stone et al. (1985) reported iodide (I^-) <i>Kd</i> values based on column studies to be 0.6 mL/g, which was at the low range of <i>Kd</i> values measured by the batch method, which ranged from 0.5 to 6.6 mL/g (texture of sediment is unknown). The column studies likely reflect non-equilibrium conditions and thus did not provide sufficient time for the iodide to sorb. Kaplan (2002) reported a similar <i>Kd</i> of 0.6 mL/g at pH ~5 in an upland sandy sediment and 1.2 mL/g in a wetland sediment at pH 5. Hoeffner (1985) reported appreciably higher <i>Kd</i> values in a sediment that contained 31% silt+clay content of 10, 5.35, and 3.62, mL/g for initial I^- concentration of 5, 50 and 500 $\mu\text{g/L}$ I^- . Iodide sorption to a clayey subsurface SRS sediment (no fulvic acid added) and SRS uncontaminated groundwater was (units of mL/g): <i>Kd</i> = -0.2 ± 0.2 at pH 3.9, <i>Kd</i> = 0.1 ± 0.4 at pH 5.3, and 0.2 ± 0.1 at pH 6.7 (24). Similar experimental setup, except to a sandy subsurface SRS sediment <i>Kd</i> values were always ~0 mL/g between pH 3.9 and 6.7 (Kaplan and Serkiz 2006). These latter studies had too much variability, making it impossible to discern whether the <i>Kd</i> values were significantly different than 0 mL/g.
Ni	5	7	21	30	Kaplan and Serkiz (2004) reported that SRS sandy sediment Ni <i>Kd</i> = 7 ± 2 mL/g at pH 5.3; SRS clayey sediment Ni <i>Kd</i> = 30 ± 1 mL/g at pH 5.3. Using 3 clayey sands (>19% clay) from the SRS, Neiheisel (1983) reported Ni <i>Kd</i> values of 115, 116, and 120. The results from these two studies vary greatly. The lower, more conservative values will be used until additional work warrants using larger values.
Np, Pa	0.2	0.6	25	35	The only Np sorption study using SRS sediments found in the literature was Sheppard et al (1979).

Radio-nuclide	Sandy Sediment		Clayey Sediment		Comments/References ^(a)
	Conser-vative	“Best”	Conser-vative	“Best”	
					In this study, Np <i>Kd</i> values for a soil (pH = 5.1, cation exchange capacity = 2.5 meq/100 g, 3.6% silt, 0.5% clay, CaCO ₃ = <0.2 mg/kg) were 0.25 and 0.16 mL/g. This sediment is lower in clay content and pH than our assumed typical sediments for the “Sandy Sediment” or “Clayey Sediment”. Therefore higher values were chosen herein. Np will exist primarily as NpO ₂ ⁺ (21). It has been shown that Np: 1) sorbs moderately to iron oxides and clays, 2) does not compete favorably with dissolved Ca or other divalent ions, 3) sorption is strongly pH dependent, and 4) does not readily convert to Np(IV) under ambient groundwater conditions (21). Due to lack of experimental data, extra conservatism is included in “Conservative” estimates.
Pu(V/VI)	11	16	2500	5000	A great deal of Pu sorption studies has recently been completed by SRNL and Clemson University (10–19; 26, 27). In these papers the conceptual model for how Pu subsurface transport of Pu is believed to occur at SRS is described. These studies include batch equilibrium, kinetic, and 11 year field lysimeter studies containing sources of Pu of known oxidation state. Wet chemistry and spectroscopic methods (X-ray Absorption Spectroscopy) were conducted to determine Pu oxidation state on aqueous and solid phase samples. Briefly, the dominant Pu oxidation state in the aqueous phase was shown to be Pu(V) and on the solid phase Pu(IV), irrespective of what was the starting Pu oxidation of the solid or aqueous phases. (Note: Although most of Pu in the aqueous phase consist of Pu(V), only trace concentrations of Pu exist in the aqueous phase compared to the solid phase, which is primarily Pu(IV).) After 11 yr, Pu(IV) moved only a couple centimeters in the field, with >95% remaining within 2 cm of the source material (10, 15). Sediment Pu concentration profiles were modeled using <i>Kd</i> sorption terms for a Pu(III/IV) and Pu(V/VI) and kinetic terms to describe the oxidation of Pu(III/IV) to Pu(V/VI) and a reduction term to describe the opposite reaction. Irrespective of what oxidation state Pu is added to SRS sediment, it quickly (within a day) is converted to Pu(IV) sorbed onto sediment (15). Most recently, aqueous Pu concentrations appear to be more controlled by solubility constraints than by adsorption (19). Powell et al. (2002) measured Pu(V) sorption to 4 end-member (extreme geological types) SRS sediments, two of which would be appropriate for consideration here, the “Subsurface Sandy” and “Subsurface Clayey” sediments. Sorption values in the “Subsurface Sandy” most representative of Pu(V) (<i>i.e.</i> , before all of the Pu was reduced to Pu(IV)) may be those measured after “1-day contact time”: at pH 5.3 the <i>Kd</i> was 9 mL/g, at pH 5.72, the <i>Kd</i> was 20 mL/g, at pH 5.94, the <i>Kd</i> was 30 mL/g and at pH 5.90, the <i>Kd</i> was 60 mL/g. The following are taken from the “33-day contact” Subsurface Sandy sediment and likely are more representative of Pu(IV) in the system: pH 5.41/ <i>Kd</i> 4900, and pH 5.62/ <i>Kd</i> 3100. Similarly, for the Subsurface Clayey sediment after 1 day contact (<i>Kd</i> units mL/g): pH 4.81/ <i>Kd</i> 2100, pH 5.82/ <i>Kd</i> 6600, and pH 5.98/ <i>Kd</i> 9000. For the “33-day contact” Subsurface Clayey sediment: pH 5.32/ <i>Kd</i> 10,000, and pH 5.68/ <i>Kd</i> 4700. It was shown through speciation studies that during the 33 days of time that the Pu(V) had in fact reduced to Pu(IV). Thus, the <i>Kd</i> value in this case is not the true exchange

Radio-nuclide	Sandy Sediment		Clayey Sediment		Comments/References ^(a)
	Conser-vative	“Best”	Conser-vative	“Best”	
					Pu(V) <i>Kd</i> value and it is clear that Pu(V) is unstable in the SRS subsurface. If the presence of both Pu(IV) and Pu(V) are not included in the transport model, it is more accurate to assume that all the Pu exists as Pu(IV) since >97% of the Pu exists as Pu(IV) (19). Prout's (1958) frequently referenced research with Pu is purposely not applied here because of compromised experimental procedures. Furthermore, emphasis of the selection of data was placed on the most recent data, where controls of the Pu speciation were monitored and attempts were made to understand the differences between the sorption behavior of the various Pu oxidation states.
Pu(III/IV)	200	300	3000	6000	Powell et al. (2002) using a subsurface SRS sandy sediment and adding Pu(IV), reported a <i>Kd</i> of 220 at pH 4.5 and 390 mL/g at pH 5.85. Using a SRS subsurface clay sediment and adding Pu(IV), they report <i>Kd</i> values of 2100 mL/g at pH 4.81, 6600 mL/g at pH 5.82, and 9000 mL/g at pH 5.98. The “typical” sediment is assumed to have a pH of 5.5. (Also, see the Comments/References for Pu(V) in this table).
Pu(combo)	180	270	2950	5900	Pu is a single geochemical parameter for Pu. It is a hybrid value of 90% of the Pu(III/IV) and 10% Pu(V/VI) measured <i>Kd</i> values. Kaplan et al. (2004), in a laboratory experiment showed that after 50-hr that 99% of the Pu added as Pu(V) had converted to Pu(IV) in the sediment/water system. Demirkanli et al (2006) using computer simulation of a lysimeter study reported that during a 24 yr simulation that 99.99% of the Pu existed as Pu(III/IV). But reported that the the short periods of time that Pu existed in the oxidized form, it moved appreciably faster than Pu in the reduced form, Pu(III/IV), but clearly much slower than Pu(V/VI).
Th, Zr	75	900	100	2000	<u>Tetravalent Cations</u> : Kaplan and Serkiz (2004) reported that SRS sandy sediment had a Zr(IV) <i>Kd</i> = 991 ± 352 mL/g at pH 5.3; SRS clayey sediment had a Zr(IV) <i>Kd</i> = 1969 ± 561 mL/g at pH 5.3 (1). Kaplan and Serkiz (2004) reported that SRS sandy sediment had a Th(IV) <i>Kd</i> = 245 ± 0 mL/g (the standard error is in fact zero) at pH 5.3; SRS clayey sediment Th(IV) <i>Kd</i> = 99 ± 48 mL/g at pH 5.3 (1). The latter Th(IV) data appears suspect in that greater sorption to sand than clay is inconsistent with basic principles of surface chemistry. This latter value will drive the uncertainty high and the “Conservative” estimates low. Thibault et al. (1990) in their <i>Kd</i> compilation of sorption values from throughout the world provide a very wide range of Th <i>Kd</i> values, with almost all values being >10,000 mL/g, however, a few values were as low as 35 mL/g.
Pb, Po, Sn	500	2000	2500	5000	<u>Divalent Soft Metals</u> : Bibler and Marson (1992) reported that Pb <i>Kd</i> values for a SRS burial ground sediment (TF1, 40-60 mesh) was generally >10,000 mL/g, a second burial ground sediment (TF2 40-60 mesh) was 63 to 925 mL/g, and a sediment from near the ETF (40-60 mesh) facility had Pb <i>Kd</i> values generally >2,000,000 mL/g. It appears quite likely that all these experiments were conducted at concentrations above the solubility of Pb, and thus reflect precipitation more than adsorption; the experiments were conducted at an initial Pb concentration of 5 mg/L Pb ²⁺ . Furthermore, the <40-mesh fraction of the sediment was not included in these experiments, thus greater sorption would likely have been measured with the entire sediment. In a

Radio-nuclide	Sandy Sediment		Clayey Sediment		Comments/References ^(a)
	Conser-vative	“Best”	Conser-vative	“Best”	
					compilation put together for groundwater modelers throughout the world, the estimated range of <i>Kd</i> values for sediments with a pH of 4 to 6.3 was 940 to 8,650 mL/g. Finally, these elements tend to have low solubility values. Solubility limits can easily be exceeded by these elements. Therefore it is especially important to consider using solubility constraints rather than <i>Kd</i> values when concentrations are slightly elevated for these elements.
Sr, Ra, Ba	4	5	12	17	<u>Alkaline Earth Elements (Group IIA)</u> : Kaplan and Serkiz (2004) reported that SRS sandy sediment <i>Sr Kd</i> = 5 ± 1 mL/g at pH 5.3; SRS clayey sediment <i>Sr Kd</i> = 17 ± 0 mL/g at pH 5.3. Hoeffner (1985) reported SRS sandy sediment (9% clay) <i>Sr Kd</i> = 3 mL/g, pH ~4.7; SRS clayey sediment (23% clay) <i>Sr Kd</i> = 9 mL/g, pH ~4.7; very strong pH effect on <i>Sr Kd</i> values on SRS sediments: for sandy sediment (9% clay) between pH 2 to 4.8 (background) <i>Kd</i> slightly increased from 4 to 19, then increased sharply from pH 4.8 to 6.0-7.0, where the <i>Kd</i> became 2000 mL/g, then the <i>Kd</i> decreased gradually to 100 mL/g as the pH increased to pH 11 (2). Prout's work (1958) with Sr is purposely not applied here because of compromised experimental procedures. Sr sorption is almost entirely by cation exchange (25), and as such, is readily reversible upon changes in groundwater chemistry. Estimates in look-up table reflect this weak-sorption mechanism.
Se, Te	800	1000	800	1000	Selenate (SeO_4^{2-}) sorbs strongly to SRS sediments between the pH values of 3.9 and 6.7 (24). With 0 mg/L C from fulvic acid added to SRS groundwater, selenate <i>Kd</i> values for a clayey subsurface SRS sediment were 1041 ± 0.7 mL/g at pH 3.9; 1041 ± 0.4 mL/g at pH 5.3, and 1041 ± 0.3 mL/g at pH 6.7 (24). The authors remarked that there appeared to be an upper sorption limit reached yielded such similar <i>Kd</i> values as a function of pH. Under similar experimental conditions but using a subsurface sandy sediment, selenate <i>Kd</i> values were 1041 ± 0 mL/g at pH 3.9, 1311 ± 384 mL/g at pH 5.3, and 601 ± 65 mL/g at pH 6.7 (24). The sandy sediment, but not the clayey sediment, showed the characteristic decrease in <i>Kd</i> values as the pH increased. Troubling, is that the sandy sediment also had larger <i>Kd</i> values than the clayey sediment.
Tc, Re	0.05	0.1	0.1	0.2	TcO_4^- exists in oxidized systems, including vadose zone. Hoeffner (1985) reported correlation between clay content in SRS sediments and Tc <i>Kd</i> : <10% clay <i>Kd</i> =0.17 mL/g, ~10% clay <i>Kd</i> = 0.14 mL/g, ~10% clay <i>Kd</i> = 0.23 mL/g, 11% clay <i>Kd</i> =0.10 mL/g, 30% clay <i>Kd</i> =0.33 mL/g, 43% clay <i>Kd</i> =1.31 mL/g, 45% clay <i>Kd</i> = 1.16 mL/g. Kaplan (2005) reported TcO_4^- sorption to an SRS sediment occurred only when the pH was <4.3; the <i>Kd</i> values to this sandy subsurface sediment increased from 0 at pH 4.3 to ~0.11 at pH 3.7. Sorption studies with ReO_4^- to a clayey subsurface SRS sediment in SRS groundwater as a function of pH all had a <i>Kd</i> of ~0 mL/g: -0.6 ± 0.6 mL/g at pH 3.9; -0.3 ± 0.1 mL/g at pH 5.3; -0.1 ± 0.3 mL/g at pH 6.7(24). Similar studies conducted with sandy subsurface SRS sediment also showed no sorption between the pH of 3.9 and 6.7: <i>Kd</i> = -0.4 ± 0.3 mL/g at pH 3.9, <i>Kd</i> = -0.2 ± 0.4 mL/g at pH 5.3, and <i>Kd</i> = 0 ± 0.2 mL/g at pH 6.7 (24). The variability in these latter studies was quite high due to the limited number of replicates, two. However, they indicate that Tc or Re sorption is either non-existent or very limited to SRS

Radio-nuclide	Sandy Sediment		Clayey Sediment		Comments/References ^(a)
	Conser-vative	“Best”	Conser-vative	“Best”	
					sediments.
U	100	200	150	300	<p>Johnson (1995) and Serkiz and Johnson (1994) conducted several field studies and laboratory studies to determine the processes controlling U sorption to SRS sediments. A portion of this work involved the collection of paired sediment-pore water samples from F-Area, within a U contaminated plume. Using the sequential extraction data (as defined by the sum of the concentrations of the first 6 extraction steps divided by the porewater U concentration in a saturated paste extract; see Johnson 1995): at pH 4.7 the K_d was 87 mL/g, at pH 4.75 the K_d was 100 mL/g, at pH 5.05 the K_d was 37 mL/g, and at pH 5.12 the K_d was 93 mL/g. The lack of trend with pH can be attributed to the fact that this was field data and reflects several different sediments. In an (ad)sorption test to a sandy subsurface F-Area sediment as a function of pH, at pH 4.82, 4.87, 5.01, and 5.04, the K_d values were 116, 153, 198, and 238 mL/g. At pH 5.5, the assumed background pH, the K_d is likely going to be greater than 238 mL/g (the K_d at pH 5.04) or 100 mL/g (the K_d measured at pH 4.75).</p> <p>Using all the U in the solid phase to calculate in situ K_d values resulted in K_d values that were 2000 to 10,000 mL/g (Serkiz and Johnson (1994); see Figure 4-12). This will clearly overestimate K_d values appropriate for use in reactive transport modeling. They reported K_d values of (presented as sample ID/pH/K_d (mL/g)): A-52/pH5.47/K_d 2,200, C-32/pH5.53/K_d >6300, C-42/pH5.27/K_d >14,000, F-42/pH5.2/K_d 34,000, F-52/pH5.91/K_d 5500, F-53/pH5.63/ K_d 27,000. The data across the entire pH range of 3.0 to 6.8 suggest that U was solubility controlled in this field site. Additional work needs to be conducted to further understand this process to permit inclusion of solubility constraints, if appropriate, into PA modeling. Additional U sorption mechanistic experiments have been conducted with SRS sediments (8, 9). Bibler and Marson (1992) U sorption data could not be used for this review because it was conducted at pH 3.</p>
^(a) References: (1) = Kaplan and Serkiz 2004 ; (2) = Hoeffner 1985; (3) = Oblath et al. 1983; (4) = Prout 1958 ; (5) = Kaplan 2003 ; (6) = Rai and Serne 1978 ; (7) = Bibler and Marson 1992 ; (8) = Johnson 1995; (9) = Bertsch et al. 1994 ; (10) = Kaplan et al. 2006a (11) = Powell et al. 2005 (12) = Serkiz et al. 2005 (13) = Powell et al. 2004 (14) = Kaplan et al. 2004 ; (15) = Fjeld et al. 2004 ; (16) = Powell et al. 2006; (17) = Kaplan et al. 2001; (18) = Kaplan and Wilhite 2001; (19) = Kaplan et al. 2006b; (20) = Sheppard et al. 1979; (21) = EPA 2004; (22) = Findley 1998; (23) = Goto 2001; (24) = Kaplan and Serkiz (2006); (25) = EPA 1999; (26) = Kaplan et al. 2001; (27) = Kaplan et al. 2004.					

Table 11. Apparent solubility concentration limits (mol/L or M) for Oxidizing Cementitious Solids

Radio-nuclide	Young Cement 1 st Stage (pH ~12.5)		Moderately-aged Cement, 2 nd Stage (pH ~10.5)		Aged Cement ^(b) 3 rd Stage (pH ~5.5)		Comments/References ^(a)
	Conser- vative	“Best”	Conser- vative	“Best”	Conser- vative	“Best”	
³ H, Cl, Tc, Re, Kr, Rn, Ar, Nb, Se, Te, I, At, Cs, Fr, Rb	NA	NA	NA	NA	NA	NA	No solubility constraints are assumed to exist with these radionuclides. Ochs et al. (15) reported that SeO_4^{2-} may substitute for sulfate in ettringite, but more recent reports (3) indicate that this substitution on ettringite is quantitatively unimportant. Johnson et al. (2000) has also recently conducted some Se partitioning research with various cements.
C	5×10^{-5}	10^{-6}	5×10^{-3}	10^{-4}	5×10^{-3}	10^{-4}	¹⁴ C chemistry is influenced by carbon dioxide gas/water/solid phase equilibrium, isotopic exchange, adsorption, precipitation, aqueous chemistry, and coprecipitation. To be conservative the role of gas phase and isotopic exchange (two very important processes for removing ¹⁴ C from groundwater) will not be considered. For young concrete, assumed that portlandite controls Ca to 10^{-3} M and CO_3^{2-} to 10^{-6} M (1). Ca concentrations are set by the solubility of calcite to “fix” the carbonate concentration. For moderately aged cement the Ca is controlled at 10^{-2} M by some undefined reactions (1). Subsurface C chemistry in a cementitious environment is discussed by Dayal (16, 17) and modeling gaseous C-14 in cementitious environments in the SRS subsurface has been discussed by Kaplan (18).
Ac, Am, Bk, Cf, Cm, Eu, Gd, Sm	5×10^{-10}	10^{-11}	5×10^{-7}	10^{-8}	5×10^{-6}	10^{-7}	<u>All +3 oxidation state:</u> <u>Young Concrete:</u> Am solubility in concrete rinsate at pH 12 = 8×10^{-11} M, at pH 13 = 1×10^{-11} to 7×10^{-12} M Am (2). Solid phase controlling solubility assumed to be $\text{Am}(\text{OH})_3$ or $\text{Am}(\text{OH})\text{CO}_3$ (2,4); Using a variety of cements and contact times of 100 days under oxidizing conditions measured Am solubility average was 1×10^{-11} M (5). Experiments with sulfate resistant Portland cement consistently had Eu concentrations $< 1 \times 10^{-11}$ M. Time-resolved laser fluorescence spectroscopy (TRLFS) showed that Eu was incorporated within CSH and another fraction had properties suggesting it was within a structure like $\text{Eu}(\text{OH})_3$ (11). Similarly, Cm was shown to be incorporated into the structure of calcium-silicate-hydrate (CSH) gels (6). <u>Moderately Aged Concrete:</u> Am solubility in concrete rinsate (no solid phase) at pH 10 to 11 was 1×10^{-8} to 1.5×10^{-10} M Am (2).

Radio-nuclide	Young Cement 1 st Stage (pH ~12.5)		Moderately-aged Cement, 2 nd Stage (pH ~10.5)		Aged Cement ^(b) 3 rd Stage (pH ~5.5)		Comments/References ^(a)
	Conser- vative	“Best”	Conser- vative	“Best”	Conser- vative	“Best”	
Co,Ni	5×10^{-6}	10^{-7}	5×10^{-6}	10^{-7}	5×10^{-5}	10^{-6}	Solid phase assumed to control solubility is $\text{Co}(\text{OH})_2$ (5, 6). Experiments with sulfate resistant Portland cement had Co solubility values of 5×10^{-8} and 2×10^{-7} M at pH 13.3 (6). The solubility of $\text{Co}(\text{OH})_2$ was calculated to be 6.5×10^{-5} M (6). Calculated values are considered less reliable than experimental values. Experiments and calculations have also been done with aged cement end members under alkaline cement conditions (2, 4, 7). Several experiments show solubility controls (6, 2, 4, 7). Solubility controls of Ni are shown by (8, 9, 10). Ni concentrations consistently in range of 5×10^{-8} to 2×10^{-7} M regardless of the solid/liquid ratio (6).
Np, Pa	5×10^{-7}	10^{-8}	5×10^{-7}	10^{-8}	5×10^{-6}	10^{-7}	Oxidation state of radionuclides is +5. Assume that NpO_2^+ and PaO_2^+ is the controlling solid. There is empirical data in Ewart et al. (2) that predicts much lower concentrations than thermodynamic predictions (2,4,7). Allard et al. (1984) added Np(V) to a variety of cements & measured solubility after 100 days of 4×10^{-9} M. Solubility of Np(IV) is $\sim 1 \times 10^{-8}$ M for pH 9.75 through pH 12.6 (3). Thus, according to Allard et al. (1984) and Ewart et al (1992) solubility of Np is about the same in concrete whether it is in +4 or +5 state.
Ra	5×10^{-5}	10^{-6}	5×10^{-5}	10^{-6}	5×10^{-5}	10^{-6}	RaSO_4 is the controlling solid (1, 14). Bayliss et al. (1989) found no precipitation for Ra at $\sim 1 \times 10^{-7}$ M in concrete leachate. When appropriate, such as in the Salstone Facility, it may be necessary to use sulfate controlling solubility phases, i.e., BaSO_4 and SrSO_4 .
Sr, Ba	5×10^{-4}	10^{-5}	5×10^{-4}	10^{-5}	NA	NA	SrCO_3 is solubility controlling phase. However, Sr may coprecipitate as $(\text{Ca,Sr})\text{CO}_3$ which has an even lower solubility value (12). But solubility controls are only important at pH < 11, i.e., in the absence of $\text{Ca}(\text{OH})_2$ and high ratios of calcium-silicate-hydrate gel (12). Therefore, coprecipitation is unlikely in the paste matrix, but may occur at the cement/leachate interface. For this reason Atkins and Glasser (12) recommend a minimum Sr solubility of $\sim 2 \times 10^{-5}$ M. This solubility value is likely to decrease even further if coprecipitation occurs (13). No solubility data is provided for “Aged Cement in the 3 rd Stage” because it is believed that it will likely not precipitate in this stage.
Pb, Po, Pu(V/VI) Pu(III/IV), Pu(combo)	5×10^{-7}	10^{-8}	5×10^{-7}	10^{-8}	5×10^{-6}	10^{-7}	Assumed solubility controlling phase are hydroxide/hydrous oxides for Th, Zr, Pu and hydroxycarbonates for Pb. The following is from (2) and was conducted by adding Th(IV) to water equilibrated with concrete and pH adjusted: solubility ranged from 1×10^{-8} M to 4×10^{-9} M as pH increased

Radio-nuclide	Young Cement 1 st Stage (pH ~12.5)		Moderately-aged Cement, 2 nd Stage (pH ~10.5)		Aged Cement ^(b) 3 rd Stage (pH ~5.5)		
	Conser- vative	“Best”	Conser- vative	“Best”	Conser- vative	“Best”	Comments/References ^(a)
Th, Zr, Sn							from 8.3 to 12.9. In essence, the solubility didn't change for Th. Sn exists in the tetravalent state, (Sn(IV)), under the cementitious conditions and readily hydrolyses in the pH range >8. It sorbed to the same extent as Th(IV) to sulfate resistant Portland cement (2). Calculations of Pb, Pu, Th, and Zr solubility under cementitious conditions have been conducted (4, 7).
U(VI)	5×10^{-6}	10^{-7}	5×10^{-6}	10^{-7}	5×10^{-5}	10^{-6}	Solubility controlling phases are likely U(VI) hydrous oxide [schoepite] and uranophase [calcium U(VI) silicate] (4, 7). Brady and Kozak (7) calculated a solubility of 1×10^{-8} M U(VI).
^(a) References: (1) = Krupka et al. 2004; (2) = Ewart et al. 1992; (3) = Baur and Johnson 2003; (4) = Brady and Kozak 1995; (5) Allard et al. 1984; (6) = Wieland & Van Loon 2003; (7) = Krupka and Serne 1998; (8) = Hietanen et al. 1984; (9) = Pilkington and Stone 1990; (10) = Atkins et al. 1993; (11) = Pointeau et al. 2001; (12) = Atkins and Glasser 1992; (13) = Smith and Walton 1991; (14) = Bayliss et al. 1989; (15) = Ochse et al. 2002; (16) = Dayal and Reardon 1992; (17) = Dayal et al. 1989; (18) = Kaplan 2005. ^(b) Making the same assumptions about the solid phase changes in the cementitious materials as Bradbury and Sarott (1995) and as described in Section 4.2, the solubility concentration limits values in the Aged Concrete (3 rd Stage) were set to an order of magnitude higher (more soluble) than those in the Moderately Aged Concrete (2 nd Stage). This same approach to assigning solubility concentration limits values to the 3 rd Stage was used by Bradbury and Sarott (1995).							

Table 12. Apparent solubility concentration limits (mol/L or M) for Reducing Cementitious Solids

Radio-nuclide	Young Cement 1 st Stage (pH ~12.5)		Moderately-aged Cement, 2 nd Stage (pH ~10.5)		Aged Cement ^(b) 3 rd Stage (pH ~5.5)		Comments/References ^(a)
	Conser- vative	“Best”	Conser- vative	“Best”	Conser- vative	“Best”	
³ H, Cl, Kr, Rn, Sr, Ra, Zr, Th, Nb, Sn, I, Cs, Ac, Am, Cf, Cm, Eu, Po, Se, C, Co, Ni, Pb, Bk, Sm, Fr, Gd, At, Ar, Te, Ba,	These radionuclides are assumed to have the same apparent solubility values as for the Oxidizing Cementitious Solids (Table 11).						The solubility of a number of other metals would likely be further lowered in a concrete that contains blast furnace slag (BFS) because BFS greatly increases the concentration of sulfides (S ²⁻) in the porewater (1). Sulfide concentrations in BFS concrete porewater have been measured as high as 1100 mg/L (1). However, there hasn't been any experimental or theoretical work to substantiate the assertion that metal sulfides form and lower the solution concentrations of metals in this group below concentrations presented in Table 11.
Tc(IV), Re (IV)	10 ⁻⁹	10 ⁻¹⁰	10 ⁻⁹	10 ⁻¹⁰	10 ⁻⁹	10 ⁻¹⁰	Bayliss et al. (2) adsorbed Tc onto Portland cement or concrete in an anoxic glove box with 0.05 M dithionite in 1.5 M NaCl for 28 days in 50:1 water:crushed cement: $K_d = 5000$ mL/g and measured Tc solution concentration was 1e-11 M. Assuming Tc ₂ S ₇ as the solubility controlling phase, MMES (1992; Appendix D) calculated that reducing grout used in the SRS saltstone program would maintain Tc at a concentration of 1.4e-20 M (2.4e-8 pCi/L). Allard (4) calculated that reducing concrete would maintain Tc at a concentration <1e-10 M. It is assumed that the SRS cementitious materials containing blast furnace slag remain reducing throughout all three stages.
Np(IV), Pa(IV)	5x 10 ⁻⁵	10 ⁻⁶	5x 10 ⁻⁵	10 ⁻⁶	5x 10 ⁻⁴	10 ⁻⁵	Under reducing conditions, both Np and Pa are reduced from +5 to +4. In the tetravalent form they would be expected to sorb very strongly or be insoluble. Assume that metal hydroxide is the controlling solid. The empirical laboratory data generated by Ewart et al. (1992) is much lower than thermodynamic predictions (2,4,7). Berry et al. 1988 reported that Pa sorbed very strongly, but due to experimental problems (sorption to glassware and filters) was unable to come up with reliable cement sorption values. It is assumed that the cementitious materials remain reducing throughout all three stages.
Pu(III/IV)	5x 10 ⁻⁹	10 ⁻¹⁰	5x 10 ⁻⁹	10 ⁻¹⁰	5x 10 ⁻⁸	10 ⁻⁹	Pu(IV) solubility measured by adding Pu(IV) spike into concrete rinsate under reducing conditions without solid phase and adjusting pH: from 9 to 11 the solubility was 1e-10 to 5e-11; essentially not changing (8). Assumed Pu(OH) ₄ controlled solubility. Based on thermodynamic calculations,

Radio-nuclide	Young Cement 1 st Stage (pH ~12.5)		Moderately-aged Cement, 2 nd Stage (pH ~10.5)		Aged Cement ^(b) 3 rd Stage (pH ~5.5)		Comments/References ^(a)
	Conser- -vative	“Best”	Conser- -vative	“Best”	Conser- -vative	“Best ”	
							solubility limits under reducing cementitious conditions were estimated to be less than 10^{-9} to 10^{-10} M Pu (9). It is assumed that the cementitious materials remain reducing throughout all three stages.
Pu(combo)	5×10^{-9}	10^{-10}	5×10^{-9}	10^{-10}	5×10^{-8}	10^{-9}	Pu(combo) is a single geochemical parameter for Pu taking into account its many oxidation states. For this system, all Pu is assumed to exist in the +4 oxidation state.
U	5×10^{-5}	10^{-6}	5×10^{-6}	10^{-7}	5×10^{-6}	10^{-7}	U(IV) solubility measured by adding U(IV) spike into concrete rinsate under reducing conditions without solid phase and adjusting pH: from 5 to 13 the solubility was 8×10^{-7} to 2×10^{-7} ; essentially not changing over that entire pH range (8). This wide pH range suggests that the solubility concentration limits does not change as a function of cement Stage. Assumed UO_2 (crystal) and UO_2 (amorph) were the solubility controlling phases. Based on thermodynamic calculations, solubility limits of U under reducing cementitious conditions were estimated to be less than 10^{-9} to 10^{-10} M U(IV) (9). It is assumed that the cementitious materials remain reducing throughout all three stages.
^(a) References: (1) = Angus and Glasser 1985; (2) = Bayliss et al. 1991; (3) = MMES 1992; (4) = Allard 1984; (5) = Bajt et al. 1993; (6) = Macias et al. 1997; (7) = Rai and Szelmeczka 1990; (8) = Ewart et al. 1992; (9) = Brady and Kozak 1995.							
^(b) Discussion of the age of each of the stages is facility specific because it depends on the amount of water that passes through the cementitious material (see Section 4.2.4).							

Table 13. Distribution coefficients (*Kd* values, mL/g): Oxidizing Cementitious Solids

Radio-nuclide	Young Cement 1 st Stage (pH ~12.5)		Moderately-aged Cement, 2 nd Stage (pH ~10.5)		Aged Cement ^(b) 3 rd Stage (pH ~5.5)		Comments/References ^(a)
	Conser- vative	“Best”	Conser- vative	“Best”	Conser- vative	“Best”	
Tc(VII), Re, Kr, Rn, Ar	0	0	0	0	0	0	TcO ₄ ⁻ adsorption to cementitious material has been measured between 1 and 10 mL/g (1). CrO ₄ ²⁻ (an anion analogue) immobilization as a result of carbonation (the natural process by which concrete becomes coated with CaCO ₃) has been documented (5). Until studies are conducted to prove otherwise (such as tritium (see below)), it will be necessary to assume their <i>Kd</i> values = 0 mL/g.
³ H	0	0	0	0	0	0	A great deal of recent research has been conducted using careful measurements of tritium sorption to cement (reviewed by Wieland and Van Loon 2003 and Tits et al. 2003). Through the use of batch sorption and through-diffusion experiments they have arrived at essentially the same <i>Kd</i> value, 0.8 ± 0.2 mL/g and 0.8 ± 0.1 mL/g, respectively. In Wieland and Van Loon's (2003) look-up table for cement <i>Kd</i> values, they suggest using a value of 1 mL/g for tritium (this value would be equivalent to a “Best” value in this table). However, there is also a great deal of data indicating that tritium really doesn't sorb and that experimental evidence indicating so is, in some cases, actually errors in mass balance (reviewed by Krupka et al. 2004). That is, during diffusion tests or batch sorption test, researchers incorrectly assign tritium existing in the concrete/cement pore water as “sorbed tritium” during their mass balance calculations (<i>Kd</i> calculations).
Cl	0.4	0.8	1.4	2	0	0	Based on diffusion studies with French sulfate-resistant cement Cl <i>Kd</i> values were 25 mL/g (2). Atkins and Glasser (3) also reported Cl sorption to cement, but it was not possible to calculate a <i>Kd</i> based on the data provided in the paper. Cl <i>Kd</i> to cement powder after 24 h contact time = 0.8 mL/g (4). (This latter value is not especially reliable considering the experimental technique.) Decreased <i>Kd</i> values in “Young Concrete” because of high concentration of aqueous salts. In 1 st Stage <i>Kd</i> values were decreased because high ionic strength likely resulted in anion exchange (desorption).
I, At	6	8	14	20	0	0	I assumed to be present as iodide (I ⁻). Iodide sorbed stronger to cement than Cs (1). I- <i>Kd</i> measured on 7 types of concrete samples increased gradually over 3-mo, then leveled off at 25 to 130 mL/g (1, 6). Iodide sorption to

Radio-nuclide	Young Cement 1 st Stage (pH ~12.5)		Moderately-aged Cement, 2 nd Stage (pH ~10.5)		Aged Cement ^(b) 3 rd Stage (pH ~5.5)		Comments/References ^(a)
	Conser- vative	“Best”	Conser- vative	“Best”	Conser- vative	“Best”	
							cement is highly reversible when Cl is added to aqueous phase, suggesting it adsorbed and was not precipitated (3). Increasing pH, decreased I ⁻ sorption (3; therefore Stage 3 <i>Kd</i> values will be slightly greater than other stages). Iodide sorption on CSH varies with its C/S ratio, increasing towards high C/S ratios (3). Decreased <i>Kd</i> values in “Young Concrete” because of high concentration of aqueous salts. In 1 st Stage <i>Kd</i> values were decreased because high ionic strength likely resulted in anion exchange (desorption).
Inorganic C ^(c)	14	20	7	10	0	0	¹⁴ C chemistry is very complicated and is not well characterized by the <i>Kd</i> construct. It is influenced by carbon dioxide gas/water/solid phase equilibrium, isotopic exchange, adsorption, precipitation, and coprecipitation. To be conservative the role of gas phase and isotopic exchange (two very important processes for removing ¹⁴ C from groundwater) will not be considered. Inorganic C exists as an anion, CO ₃ ²⁻ (1). Subsurface C chemistry in a cementitious environment is discussed by Dayal (7, 8) and how it has been applied to the SRS by Kaplan (9).
Ac, Am, Bk, Cf, Cm, Eu, Gd, Sm	2500	5000	2500	5000	360	500	Trivalent cation <i>Kd</i> values for concrete exceed those for sediments (3). Am <i>Kd</i> > 10,000 mL/g (10). Am <i>Kd</i> value was 12,000 mL/g based on diffusion tests in cement (11). Am <i>Kd</i> values ranged from 2,500 to 35,000 mL/g for 7 fresh concrete blends (1, 6). Am <i>Kd</i> for 65-yr old concrete sample = 10,000 mL/g (1, 6). Fresh cement Am <i>Kd</i> = 2000 for 24-h contact time (12). Eu <i>Kd</i> = 2,400 mL/g for 24-h contact time (12). Very large <i>Kd</i> values may reflect precipitation reaction that occurred during the adsorption measurements.
Co, Ni	500	1000	500	1000	360	500	Three studies were found that included adsorption data for Ni onto cement/concrete. Hietanen et al (15) reported <i>Kd</i> values that ranged from 500 to 3000 mL/g, Kato and Yanase (12) reported a Ni <i>Kd</i> value of 1500 mL/g, and Pilkington and Stone (16) reported <i>Kd</i> values that ranged from 500 to 3000 mL/g.
Ra, Ba	70	100	70	100	50	70	Bayliss et al. (11) and Berry et al. (13) measured Ra <i>Kd</i> values onto ordinary Portland cement and as a function of Ra concentration. They reported <i>Kd</i> that ranged from 50 to 530 mL/g.
Sr	0.2	1	0.5	1	0.2	0.8	Jakubick et al. (14) reported Sr <i>Kd</i> values of 0.8 to 1.6 mL/g for high density and normal density concretes, and 1.3 to 3 mL/g for the same concretes, but in lower ionic strength solutions. Ewart et al. (14) reported <i>Kd</i> values between 1 and 4 mL/g. Kato and Yanase reported a Sr <i>Kd</i> value of 56 mL/g for an experiment involving 24 h contact time, dried cement powder, pH 11

Radio-nuclide	Young Cement 1 st Stage (pH ~12.5)		Moderately-aged Cement, 2 nd Stage (pH ~10.5)		Aged Cement ^(b) 3 rd Stage (pH ~5.5)		Comments/References ^(a)
	Conser- vative	“Best”	Conser- vative	“Best”	Conser- vative	“Best”	
							cement equilibrated water. We elected to disregard this value because it is an order-of-magnitude greater than those reported by other researchers and the nature of the solid phase was not clearly described by the author. In 1 st Stage <i>Kd</i> values were decreased because high ionic strength likely results in competitive exchange (desorption).
Sn	2000	4000	2000	4000	1000	2000	Sn exists in cementitious environments in the +4 state (17) and as such readily hydrolyses. Using sulfate resistant Portland cement, Sn <i>Kd</i> values were >30,000 mL/g; this likely reflected some precipitation (17).
Cs, Fr	1	2	2	4	1	2	Cs <i>Kd</i> values in hardened HTS cement discs, pH 13.3 were close to 3 mL/g (15). Wieland and Van Loon (17) reviewed Cs <i>Kd</i> values onto various cementitious materials and they had a very narrow range: from 0.2 to 5.0 mL/g. In 1 st Stage <i>Kd</i> values were decreased because high ionic strength likely results in competitive exchange (desorption). This has been shown experimentally (17).
Nb	500	1000	500	1000	360	500	Krupka and Serne (18) review Nb <i>Kd</i> values and concluded that there was a great deal of variability related in Nb sorption data to cementitious materials. They reported <i>Kd</i> ranges of 11 to 69,000 mL/g (from studies that had problems with the blanks, <i>i.e.</i> , the blanks indicated Nb sorbed to the glassware). We defer to their best values (1000 mL/g) and add conservatism to these values.
Np, Pa	1000	2000	1000	2000	140	200	These radionuclides are assumed to exist in the +5 oxidation state. Np sorption test to 7 different 65-yr old cements using cement pore water reached steady state after 30 days, <i>Kd</i> values ranged from 1500 to 9500 mL/g (1, 6). As is the case with all large <i>Kd</i> values, these values may reflect some precipitation occurring during the adsorption measurement.
Se, Te	100	300	210	300	110	150	Twenty-seven cementitious formulations (varying water/solid, silica fume %, and clay concentration) were used to measure selenate (SeO_3^{2-}) <i>Kd</i> values from an alkaline solution (Johnson et al. 2000). <i>Kd</i> values ranged from 250 to 930 mL/g. Sorption was irreversible. At high selenate (SeO_4^{2-}) concentrations, sorption to ettringite, monosulfate, calcium-silicate-hydrate (all mineral constituents of concrete) resulted in selenate substitutes for sulfate (23). Selenite <i>Kd</i> values measured in sulfate resistant Portland cement ranged from 30 to 100 mL/g (Wieland and Van Loon 2003). It is not clear why these latter <i>Kd</i> values were so much lower than those reported by Johnson et al (2000). This variability in results requires that conservative

Radio-nuclide	Young Cement 1 st Stage (pH ~12.5)		Moderately-aged Cement, 2 nd Stage (pH ~10.5)		Aged Cement ^(b) 3 rd Stage (pH ~5.5)		Comments/References ^(a)
	Conser- vative	“Best”	Conser- vative	“Best”	Conser- vative	“Best”	
							values in table be lowered.
Pb, Po	250	500	250	500	180	250	Soft divalent cations: Bayliss et al. (1988) conducted a series of sorption experiments with Pb and crushed sulfate resisting Portland cement and ordinary Portland cement/blast furnace slag pastes with an Eh of +50 to -500 mV. The main findings were that sorption was concentration and cement composition dependent. Data strongly suggested solubility controls on Pb aqueous concentrations. “Best” estimates taken from (19).
Pu(III/IV), Pu(V/VI), Pu(combo) Th, Zr	1000	5000	1000	5000	250	500	Concrete containing reducing agents (blast furnace slag, BFS) did not have greater Pu <i>Kd</i> values than those that did not contain BFS. High <i>Kd</i> values are attributed more to low solubility of Pu in high pH systems, than to adsorption/absorption processes. Using three 65-yr-old crushed concrete samples and seven fresh concrete samples, Th- <i>Kd</i> values were 2,500 to 5,500 mL/g (1, 6). Th- <i>Kd</i> values were consistently less than Am <i>Kd</i> values, greater than U- <i>Kd</i> values, and very similar to Np and Pu <i>Kd</i> values (1, 6). Pu- <i>Kd</i> values ranged from 1,000 to 12,000 mL/g (1, 6). Using a sulfate resistant Portland cement, Th <i>Kd</i> values were measured to be 100,000 mL/g (17).
U	500	1000	500	1000	50	70	U(VI)- <i>Kd</i> values for 7 types of cement were 350 to 13,000 mL/g; median = 1400 mL/g (1,6).
^(a) References: (1) = Allard et al. 1984; (2) = Sarott et al. 1992 ; (3) = Atkins and Glasser 1992 ; (4) = Brodda 1988 ; (5) = Macias et al. 1997; (6) = Hoglund et al. 1985 ; (7) = Dayal and Reardon 1992; (8) = Dayal et al. 1989; (9) = Kaplan 2005; (10) = Ewart et al. 1988; (11) = Bayliss et al. 1991; (12) = Kato and Yanase 1993; (14) = Ewart et al. 1986; (15) = Sarott et al. 1992; (16) = Pilkington and Stone 1990; (17) = Wieland and Van Loon 2003; (18) = Krupka and Serne 1998; (19) = Bradbury and Sarott 1995; (20) = Tits et al. 2003; (21) = Krupka et al. 2004; (22) = Johnson et al. 2000; (23) = Baur and Johnson 2003. ^(b) The age of each of the stages is facility specific because it depends on the amount of water that passes through the cementitious material (see Section 4.2.4). ^(c) Inorganic carbon geochemistry is very complicated. The use of only the <i>Kd</i> value without the associated solubility value in a cementitious environment will greatly overestimate the true mobility of C through this environment.							

Table 14. Distribution coefficients (*Kd* values, mL/g): Reducing Cementitious Solids

Radio-nuclide	Young Cement (pH ~12.5)		Moderately-aged Cement (pH ~10.5)		Aged Cement (pH ~5.5)		Comments/References ^(a)
	Conser-vative	“Best”	Conser-vative	“Best”	Conser-vative	“Best”	
³ H, Cl, Kr, Rn, Sr, Ra, Zr, Th, Nb, Sn, I, Cs, Ac, Am, Cf, Cm, Eu, Po, Se, C, Co, Ni, Pb, Bk, Sm, Fr, Gd, At, Ar, Te, Ba, Np, Pa, Pu, Rb, Pu(IV), Pu(V), Pu(combo)	(Same values as reported in Table 13 for Oxidizing Cementitious Solids)						Concrete containing reducing agents (blast furnace slag, BFS) did not have greater Pu , Np , or Pa <i>Kd</i> values than those that did not contain BFS (1, 2, 3).
Tc, Re	2500	5000	2500	5000	2500	5000	Tc ^{VII} O ₄ ⁻ gets reduced to Tc ⁴⁺ , which like other tetravalent cations sorbs strongly to surfaces. “Best” values taken from Bradbury and Sarott (1995).
U	2500	5000	2500	5000	2500	5000	UO ₂ ²⁺ gets reduced to U ⁴⁺ , which like other tetravalent cations sorbs strongly to surfaces. “Best” Values taken from Bradbury and Sarott (1995).
^(a) References: (1) = Wieland and Van Loon 2003; (2) = Krupka and Serne 1998; (3) = Bradbury and Sarott 1995.							

5.1 Cellulose Degradation Product Corrected Kd Values, Kd_{CDP}

Cellulose degradation products, CDP, will influence the tendency of radionuclides to sorb to sediments, and therefore to move away from the buried waste. Several laboratory studies and surface complexation models have been conducted to evaluate this phenomenon (Serkiz et al. 1998, Serkiz et al. 1999, Kaplan and Serkiz 2004, Serkiz and Kaplan 2006). From these studies, the amount of sediment clay content, pH, organic C content, contact time, and order of addition were evaluated. CDP-Correction Factors, $f_{CDP,pH,C}$, were estimated from this work that varied as a function of pH and organic carbon content:

$$f_{CDP,pH,C} = \frac{Kd_{CDP,pH,C=x}}{Kd_{pH,C=0}} \quad (3)$$

As is the case with all Kd values, $f_{CDP,pH,C}$ values are also very sediment specific. The numerator, $Kd_{pH,C=x}$, is a measure of the radionuclide Kd value with a sediment at a given pH and organic carbon content dissolved in the solution. The denominator, $Kd_{pH,C=0}$ is a measure of the radionuclide Kd value with the same sediment and the same pH, but without any cellulose degradation products present in the solution. The CDP-correction factor was used to calculate a CDP-corrected Kd value, Kd_{CDP} :

$$Kd_{CDP} = f_{CDP} \times Kd . \quad (4)$$

For the purposes of this document, the Kd values used to calculate Kd_{CDP} were taken from Table 10 and the $f_{CDP,pH,C}$ values (Table 15) were taken from Serkiz and Kaplan (2006).

It is important to note that the sorption of all radionuclides with f_{CDP} values >1 (e.g., Cs, Ni, and Sr) increased in the presence of CDPs. Therefore, the assumption associated with modeling CDPs in the PA must be carefully considered and what may be a conservative assumption for one radionuclide, may not be for another radionuclide.

The experimental work (Kaplan and Serkiz 2004) upon which the surface complexation speciation modeling work of Serkiz and Kaplan (2006) was based on evaluated monovalent (Cs^+), divalent (Ni^{2+} , and Sr^{2+}), trivalent (Ce^{3+} and Eu^{3+}) and tetravalent (Zr^{4+} and Th^{4+}) cations at three pH and 5 organic C concentrations. The sorption results for these specific species were then applied as analogues to provide estimates of how other radionuclides with similar chemical properties may behave. The laboratory results were consistent with expected results based on considerations of the relative strengths of ligand bonds between radionuclides and organic matter, versus organic matter-sediment surface bonds, versus radionuclide-sediment surface bonds. In some cases an increase in dissolved organic C concentrations resulted in a systematic decrease in Kd values. In other

Carbon from the CDPs will be released into the groundwater at a constant rate of 95 mg/L C, a concentration measured to decrease many Kd values. Once the carbon from the CDP has been exhausted, Kd_{CDP} values will be replaced by the regular Kd values.

cases, the presence of dissolved cellulosic materials resulted in an increase in Kd values at low organic C concentrations (≤ 95 mg C/L) and a decrease in Kd values at highest organic C concentration (222 mg C/L; except for Cs). This occurred because the organic carbon partitioned onto the sediment surfaces and increased the sorption capacity of the sediment (which has a relatively very poor sorption capacity, a cation exchange capacity of SRS sediment is commonly between 1 and 3 meq/100 g).

The Kd_{CDP} will be employed as long as cellulosic degradation materials emanate from the waste. For each waste source containing CDP (see Table 8 for a list of disposal units that contain CDP), the total amount of CDP (in units of mass of organic carbon) will need to be estimated. Reactive transport models will release carbon into the groundwater from the CDP at a constant concentration (rate) of 95 mg/L C until all the carbon in the CDP is exhausted. This concentration was selected to provide a generally conservative estimate and is not based on organic C values measured in groundwater samples. It was selected after looking at the resulting Kd data and noting which organic C concentrations caused generally the greatest decreases in Kd values. (All the CDP-correction factors for varying organic C concentrations are presented in Appendix A.) Short-term laboratory leach experiments with various solids containing the precursors to CDPs can create a wide range of organic C concentration in solution depending on the solid to liquid ratio, types of solids used, and age of suspension (Serkiz et al. 1998, Serne et al. 1993). To provide some context, a 20 mg/L organic C solution has a slight yellow color to it. A 95 mg/L organic C solution is highly colored and in our case produced a translucent yellowish-orange solution.

Table 15. CDP Correction Factors (f_{CDF}).

Radionuclides	Analog	$f_{CDF}^{(a)}$
Kr, Ar, Rn, ^3H , Nb, Cl,	N/A	N/A
Ac, Am, Bk, Cf Cm, Eu, Gd, Sm	Ce & Eu	0.049
C	None	0.5 ^(b)
Cs, Rb, Fr	Cs	1.66
I, At, Se, Te, Tc, Re,	None	0.5 ^(b)
Ni	Ni	1.41
Np, Pa	Cs	1.66
Pb, Po	Ni	1.41
Pu	Th	0.51
Sn	Ni	1.41
Sr, Ba, Ra	Sr	1.89
Th	Th	0.51
U	Sr ^(c)	1.89
Zr	Zr	0.08
^(a) CDP correction Factor at pH 5.5 and 95 mg/L organic C from CDP (defined in Equation 1).		
^(b) Estimated value based on profession opinion. It is believed that these radionuclides would sorb rather weakly (compared to tetravalent or trivalent metals). So a conservative value of 0.5 was selected.		
^(c) U is expected to exist most of the time as UO_2^{2+} , similar to Sr^{2+} (under reducing conditions U exists as U^{4+}).		

6.0 REVIEW PROCESS

The objective of the review process is not only to improve the quality of this document, but also to enhance its credibility. Performance Assessments must undergo a number of evaluations, including technical reviews from the outside scientific community. There will be three levels of review before issuing this report and each level will target various aspects of a review. Of course reviewers will be encouraged to comment on any aspect of the document, but focusing their attention to their specialty, was intended to save the reviewers' time and improve the quality of their reviews. This review process will include:

The objective of the review process is to improve the quality and credibility of the document.

- an **internal review** (based on “Technical Report Design Check Guidelines, WSRC-IM-2002-00011, Rev.2”),
- a **site review**, from on-site personnel with strong facility and site knowledge, and finally,
- an **external review**, from knowledgeable professionals outside the site.

It is understood that the author has the overall responsibility for the report quality while the reviewers will have the primary responsibility for quality of the technical review. There will be two reviewers during this stage of the process. All review instructions, comments, and manner in which the review comments were addressed will be documented and archived. The process will be taken full cycle, *i.e.*, all comments will be resolved to the reviewers' satisfaction. Responses to the individual questions will be shared among the reviewers.

6.1 Internal Review

The internal review follows the guidelines outlined in WSRC (2004). Tailoring this guideline to the needs of this document, the following primary elements will be asked of the internal reviewers:

1. Approaches: Are the various approaches used in selecting geochemical parameters logical, consistent, and appropriate? Conduct a complete check.
2. Mathematical Check: Check mathematical calculations. Conduct a complete check.
3. Correct use of Input: Ensure that information was correctly transferred from the original text into the document. Conduct a spot check.
4. Justification of Assumptions: All assumptions must be justified. Conduct a complete check.
5. Reasonableness of Output: Do results make sense? Conduct a complete check.
6. Cross-check for Accuracy of Transcription: Check that no transcription errors within document have occurred. Conduct a spot check.

They will also be asked to provide the following:

- Is there any missing or overlooked data that would improve the selected values?

The SRNL reviewer will be:

- Dr. Miles Denham

6.2 Site Review

The Internal-Reviewed draft document will then be reviewed by two people knowledgeable about geochemistry and the SRS waste-disposal facilities:

- Dr. Maurice Ades, Waste Management Area Project
- Mr. Jeffry Newman, Tank Closure Planning

They will be asked to concentrate on items #1 (Approach), #4 (Assumptions) and #5 (Reasonableness of Output) above (Section 6.1). They will also be asked to provide the following:

- Is there any missing or overlooked data that would improve the selected values?

6.3 External Review

The SRS-Reviewed document will then be forwarded to the following people for external review:

- R. Jeffrey Serne, Pacific Northwest National Laboratory
- Dr. David Kosson, Vanderbilt University

R. Jeffrey Serne has been working on radiological waste disposal issues, including PAs, at the Hanford site for 37 years and has been on several national and international committees to address topical problems associated with safe geological disposal of radiological waste. He is also an author of the most recent geochemical data package developed by the Hanford Integrated Disposal Facility (IDF) PA effort (Krupka et al. 2004). Dr. Kosson has conducted extensive research related to waste-form leaching and modeling and is very familiar with DOE-specific waste problems through his various DOE-funded programs (<http://www.cee.vanderbilt.edu/facultystaff/kosson.html>).

The external reviewers will be asked to concentrate on items #1 (Approach), #4 (Assumptions) and #5 (Reasonableness of Output) above (Section 6.1). They will also be asked to provide the following:

- Is there any missing or overlooked data that would improve the selected values?
- Was there any data that was misinterpreted?

7.0 FUTURE RESEARCH AND DATA NEEDS

In the process of collecting these input data for the PA modeling effort, several data needs were identified. The identification of data needs is part of the PA maintenance program which provides a vehicle to update PA calculations when new or improved data become available or when new information is learned that requires additional modeling scenarios be conducted. The following is a list of the key areas that require additional research to gather new and improved data.

1. Reactive Transport Modeling: Although K_d and solubility concentration limits values are convenient for inclusion in transport models, they may not always captures a full picture of the actual geochemistry believed to be occurring in the system (Sections 3.1 and 3.3). For this reason, it is necessary to rely on site-specific and condition-specific experiments to provide insight into how the radionuclides interact with the solid phase. It is the express goal of the PA to move towards a reactive transport model where important aqueous solutes can be included in the model. It is also the interest of the PA to incorporate more process-driven (mechanistic) approaches to describing the geochemistry in the PA. Important advances have been made towards this end with regards to Pu geochemistry and how it has been incorporated into performance assessment and special analysis calculations (Kaplan et al. 2001, 2004, 2006a, 2006b; Fjeld et al. 2004; Powell et al. 2005, 2006). Additional work needs to be conducted to incorporate reactive transport modeling into the PA, including in cementitious environments.
2. Colloids: The PA is presently modeling colloid facilitated transport of Pu and its approach is entirely empirical and based on two SRS field studies (Section 3.4.2). The conceptual and numerical models need to be improved based upon field and laboratory studies designed to develop a numerical model. Also, the role of strong pH gradients (such as at cement/soil interfaces) and cellulose degradation products on colloid generation needs to be evaluated.
3. Saltstone/Grout/Concrete Sorption Values: All the K_d and solubility concentration limits values for cementitious materials are grouped together and are taken from the literature. It is necessary to have solid-specific sorption values, especially for saltstone. Sorption measurements will also need to be made on aged saltstone/grout/concrete materials. The use of surrogate mineral assemblages (minerals components of concrete expected to exist during each of the three stages) may be appropriate to approximate aged cementitious materials.
4. Technetium Interaction with Reducing Grout: The geochemistry describing the interaction of Tc with reducing grout/saltstone is extremely important to the PA. It is described here as a solubility controlled process, however, other reactions may also be important. Additional work needs to be conducted to more completely describe this system of reactions, including the reduction and oxidation kinetics of Tc(IV) and Tc(VII) conversions, and the influence of dissolved oxygen (in groundwater) on sulfide and sulfate conversions. Additional measurements of solubility concentration limits values are also required to determine variability associated between Saltstone batches. Tests

must also be developed to determine good experimental protocols for determining the reduction capacity of a reducing cement/saltstone.

5. Degradation Rate of Cellulosic Materials: No site-specific work has been done to describe the degradation rate of cellulosic materials that is co-disposed with the radiological waste (Sections 3.4.1 and 5.1). Since soil microbes play an important role in cellulose degradation, it is especially necessary to conduct these studies under site-specific conditions. This information is necessary for more accurately including the role of cellulose-degradation-products on Kd values.
6. Uncertainty: At present, only an estimate as to this variability is provided in this report, actual measured values are required (Section 5.0). The variability associated with Kd values and solubility concentration limits must be measured to provide input into uncertainty calculations. Additionally, the distribution of the values must also be determined, for instance, whether the values log-normally or normally distributed? These values will be used in probabilistic modeling. Additionally, work needs to be conducted to address the uncertainty associated with our conceptual geochemical models (uncertainty separate from that associated with parameter input and natural variability).
7. Cs, C, Np, and I Waste-Form Chemistry and Geochemistry: The geochemistry associated with Cs, C, Np, and I is more complicated than can be readily described by a single Kd or solubility concentration value. Additional research needs to be directed at integrating existing with needed data to provide a geochemical correct conceptual model of these contaminants. Among, but not limited to, the processes to be included are Cs dual sorption domain (“irreversible mica sites” and “reversible sites”), carbonate chemistry in the presence of cementitious materials (aqueous, solid, and gaseous), Np redox chemistry, and iodine biogeochemistry. Finally, non-linear sorption isotherms (such as the Freundlich equation, as opposed to the Kd value) will be evaluated.

8.0 REFERENCES

- Allard, B., L. Eliasson, S. Hoglund, and K. Andersson. 1984. *Sorption of Cs, I and Actinides in Concrete Systems*. SKB Technical Report SKB/KBS TR-84-15, SKB, Stockholm, Sweden.
- Allard, B., Moulin, V., Ballo, L., Tran, M.T., Stammose, D. 1989. Americium Adsorption on Alumina in the Presence of Humic Materials. *Geoderma*. 44:181-187.
- Angus, M. J. and F. P. Glasser. 1985. The Chemical Environment in Cement Matrices. *Mat. Res. Soc. Symp. Proc.* 50:547–556.
- Atkins, M., and F. P. Glasser. 1992. Application of Portland Cement-Based materials to Radioactive Waste Immobilization. *Waste Management*. 12:105–131.
- Atkins, M., F. P. Glasser, L. P. Moroni, and J. J. Jack. 1993. *Thermodynamic Modeling of Blended Cements at Elevated Temperatures (50-90°C)*. DoE/HMIP/RP/94.011. UK Nirex Ltd., Harwell, UK.
- Atkinson, A., N. Everett, and R. Guppy. 1988. *Evolution of pH in a Radwaste Repository: Internal Reactions Between Concrete Constituents*. AERE-R12939, UKAEA, Harwell, UK.
- Baes, C. F., Jr., and R. E. Mesmer. 1976. *The Hydrolysis of Cations*. John Wiley and Sons, New York, NY.
- Bajt, S., S. B. Clark, S. R. Sutton, M. L. Rivers, and J. V. Smith. 1993. Synchrotron X-ray Microprobe Determination of Chromate Content using X-ray Absorption Near-edge Structure. *Analytical Chemistry*. 65:1800-1804.
- Baur, I., C. A. Johnson. 2003. Sorption of Selenite and Selenate to Cement Minerals. *Environ. Sci. Technol.* 37:3442-3447.
- Bayliss, S., F. T. Ewart, R. M. Howse, S. A. Lane, N. J. Pilkington, J. L. Smith-Briggs, and S. J. Williams. 1989. The Solubility and Sorption of Radium and Tin in a Cementitious Near-field Environment. *Mat. Res. Soc. Symp. Proc.* 127: 879-885.
- Bayliss, S., A. Haworth, R. McCrohon, A. D. Moreton, P. Oliver, N. J. Pilkington, A. J. Smith, and J. L. Smith-Briggs. 1991. Radioelement Behavior in a Cementitious Environment. In *Scientific Basis for Nuclear Management XV*, C. G. Sombret (ed) Materials Research Soc. Symposium Proceedings Vol. 257:641-648. Materials Research Society, Pittsburgh, PA.
- Berner, U. R. 1992. Evolution of Pore Water Chemistry during Degradation of Cement in a Radioactive Waste Repository Environment. *Waste Management*. 12: 201-215.

- Bertsch, P. M., D. B. Hunter, S. R. Sutton, S. Bajt, and M. L. Rivers. 1994. In Situ Chemical Speciation of Uranium in Soils and Sediments by Micro X-ray Absorption Spectroscopy. *Environ. Sci. Technol.* 28:980-984.
- Bibler, J. P., and D. B. Marson. 1992. *Behavior of Mercury, Lead, Cesium, and Uranyl Ions on Four SRS Soils*. WSRC-RP-92-326. Westinghouse Savannah River Company, Aiken, SC.
- Bower, H. 1991. Simple Derivation of the Retardation Equation and Application to Preferential Flow and Macrodispersion. *Ground Water*. 29:41-46.
- Bradbury, M. H., and F. A. Sarott. 1995. *Sorption Databases for the Cementitious Near-field of a L/ILW Repository for Performance Assessment*. PSI Bericht Nr. 95-06. Paul Scherrer Institut, Villigen, Switzerland.
- Brady, P. V., and M. W. Kozak. 1995. Geochemical Engineering of Low Level Radioactive Waste in Cementitious Environments. *Waste Management*. 15:293-301.
- Brodda, B. G. 1988. Leachability of Technetium from Concrete. *The Science of the Total Environment*. 69:319-345.
- Choppin G.R. 1989. Soluble Rare Earth and Actinide Species in Seawater. *Mar. Chem.* 28: 19-26.
- Collard, L. B., and R. A. Hiergesell. 2004. 2004 General Revision of Slit and Engineered Trench Limits. WSRC-TR-2004-00300. Westinghouse Savannah River Site, Aiken, SC.
- Dai, M., J. M. Kelley, and K. O. Buesseler. 2002. Sources and Migration of Plutonium in Groundwater at the Savannah River Site. *Environ. Sci. Technol.* 36:3690-3699.
- Davis, J.A. and D. B. Kent. 1990. Surface Complexation Modeling in Aqueous Geochemistry. In. *Review in Mineralogy: Mineral-Water Interface Geochemistry*, eds. M. F. Hochella and A. F. White, Mineralogy Society of America, Washington, DC, pp. 177-260.
- Davis, J. A., J. A. Coston, D. B. Kent, and C. C. Fuller. 1998. Application of the Surface Complexation Concept to Complex Mineral Assemblages. *Environ. Sci. Technol.* 32:2820-2828.
- Davis, J. A., D. E. Meece, M. Kohler, and G. P. Curtis. 2004. Approaches to Surface Complexation Modeling of Uranium(VI) Adsorption on Aquifer Sediments. *Geochem. Cosmochem.* 68:3621-3641.
- Dayal, R., H. Johnston, and Z. Zhou. 1989. *Reactor Operating Waste Disposal Program, 1989 Progress Report*. 89-226-K. Ontario Hydro, Ontario, Canada.
- Dayal, R., and E. J. Reardon. 1992. Cement-Based Engineered Barriers for Carbon-14. Isolation. *Waste Management* 12:189-200.

- Demirkanli, D. I., F. J. Molz, D. I. Kaplan, R. A. Fjeld, and S. M. Serkiz. 2006. Long-Term Vadose Zone Plutonium Transport at the Savannah River National Laboratory. *Vadose Zone Journal* (submitted).
- EPA. 1999. *Understanding Variation in Partition Coefficient, K_d, Values. Volume II: Review of Geochemistry and Available K_d Values for Cadmium, Cesium, Chromium, Lead, Plutonium, Radon, Strontium, Thorium, Tritium, and Uranium*. EPA 402-R-9-004B, US EPA, Washington, DC.
- EPA. 2004. *Understanding Variation in Partition Coefficient, K_d, Values. Volume III: Review of Geochemistry and Available K_d Values for Americium, Arsenic, Curium, Iodine, Neptunium, Radium, and Technetium*. EPA 402-R-04-002C, US EPA, Washington, DC.
- Ewart, F. T., J. L. Smith-Briggs, H. P. Thomason, and S. J. Williams. 1992. The solubility of Actinides in a Cementitious Near-Field Environment. *Waste Management*. 12:241–252.
- Ewart, F. T., R. M. Howse, H. P. Thomason, S. J. Williams and J. E. Cross. 1986. The Solubility of Actinides in the Near-field, pp. 701-708. *Scientific Basis for Nuclear Waste Management IX*, ed. L. O. Werme. Materials Research Society Symposium Proceedings, Volume 50, Materials Research Society, Pittsburgh, PA.
- Ewart, R., S. Pugh, S. Wisbey, and D. Woodward. 1988. *Chemical and Microbiological Effects in the Near-Field: Current Status*. Report NSS/G103, U.K. Nirex Ltd., Harwell, United Kingdom.
- Fairhurst A.J., Warwick P., Richardson S. 1995. The Effect of pH on Europium-Mineral Interaction in the Presence of Humic Acid. *Radiochim. Acta*. 69: 103-111.
- Findley, M. 1998. Characterizing the Environment Availability of Trace Metals in Soils at the Savannah River Site. Masters' Degree Thesis, Clemson University, Clemson, SC.
- Fjeld, R. A., S. M. Serkiz, P. L. McGinnis, A. Elci, and D. I. Kaplan. 2004. Modeling the Effect of Surface-Mediated Reduction of Pu(V) to Pu(IV) on Plutonium Transport Behavior. *J. Contam. Hydrol.* 67:79-94.
- Goto, M. 2001. Development of a Quantitative Model for Binding Cesium to SRS soils. Masters' Degree Thesis. Georgia Institute of Technology, Atlanta, GA.
- Herbelin, A. L., and J. C. Westall. 1999. *FITEQL: A Computer Program for the Determination of Chemical Equilibrium Constants from Experimental Data. Version 4.0*. Report 99-01, Chemistry Department, Oregon State University, Corvallis, OR.
- Hietanen, R., E. -L. Kamarainen, and M. Aluusua. 1984. *Sorption of Cesium, Strontium, Iodine, Nickel and Carbon in Concrete*. Nuclear Waste Commission of Finnish Power Companies, Report YJT 84-04, Helsinki, Finland.

- Hoeffner, S. L. 1985. *Radionuclide Sorption on Savannah River Plant Burial Ground Soil A Summary and Interpretation of Laboratory Data*. DP-1702. E.I. DuPont de Nemours & Co. Savannah River Laboratory, Aiken, SC.
- Hoglund, S., L. Eliasson, B. Allard, K. Andersson, and B. Torstenfelt. 1985. Sorption of some Fission Products and Actinides in Concrete Systems. *Mat. Res. Soc. Symp. Proc.* 50:683-690.
- Jenne, E. A. (Ed.) 1998. *Metal Adsorption by Geomedia*. Academic Press, San Diego.
- Johnson, E. A., M. J. Rudin, S. M. Steinberg, and W. H. Johnson. 2000. The Sorption of Selenite on Various Cement Formulations. *Waste Management*. 20:509-516.
- Johnson, W. H. 1995. Sorption Models for U, Cs, and Cd on Upper Atlantic Coastal Plain Soils. A Thesis Presented to the Academic Faculty at Georgia Institute of Technology. Atlanta, GA.
- Kaplan, D. I. 2002. Influence of Surface Charge of an Fe-oxide and an organic Matter Dominated Soil on Iodide and Pertechnetate Sorption. *Radiochim. Acta*. 91:173-178.
- Kaplan, D. I. 2005. *Estimate of Gaseous ¹⁴Carbon Concentrations Emanating from the Intermediate-Level Vault Disposal Facility*. WSRC-TR-2005-00222, Westinghouse Savannah River Company, Aiken, SC.
- Kaplan, D. I., and T. Hang. 2003. *Estimated Duration of the Subsurface Reducing Environment Produced by the Z-Area Saltstone Disposal Facility*. WSRC-RP-2003-00362, Rev. 2, Westinghouse Savannah River Company, Aiken, SC.
- Kaplan, D. I., J. L. Myers. 2001. Long-Term Dynamics of Lead Solubility in a Cementitious Groundwater Environment. WSRC-TR-2000-00416, Westinghouse Savannah River Company, Aiken, SC.
- Kaplan, D. I., and S. M. Serkiz. 2000. *¹²⁹Iodine Desorption from Resin, Activated Carbon, and Filtercake Waste Generated from the F- and H-Area Water Treatment Units*. WSRC-TR-2000-00308. Westinghouse Savannah River Company. Aiken, SC.
- Kaplan, D. I., and S. M. Serkiz. 2004. *Influence of Dissolved Organic Carbon and pH on Contaminant Sorption to Sediment*. WSRC-RP-2004-00593, Westinghouse Savannah River Company, Aiken, SC.
- Kaplan, D. I., and S. M. Serkiz. 2006. *Influence of Dissolved Organic Carbon and pH on Anion Sorption to Sediment*. WSRC-RP-2006-00005, Westinghouse Savannah River Company, Aiken, SC.
- Kaplan, D. I., and R. J. Serne. 2000. *Geochemical Data Package for the Hanford Immobilized Low-Activity Tank Waste Performance assessment (ILAW PA)*. PNNL-13037, Rev. 1, Pacific Northwest National Laboratory, Aiken, SC.

- Kaplan, D. I., B. A. Powell, D. I. Demirkanli, R. A. Fjeld, F. J. Molz, S. M. Serkiz, J. T. Coates. 2004. Enhanced Plutonium Mobility During Long-Term Transport Through an Unsaturated Subsurface Environment. *Environ. Sci. Technol.* 38:5053–5058
- Kaplan, D. I., D. I. Demirkanli, L. Gumapas, B. A. Powell, R. A. Fjeld, F. J. Molz, and S. M. Serkiz. 2006a. 11-Year Field Study of Pu Migration from Pu III, IV, and VI Sources. *Environ. Sci. Technol.* (In press).
- Kaplan, D. I., B. A. Powell, R. A. Fjeld, L. Gumapas, and J. T. Coates. 2006b. Influence of pH on Plutonium Desorption and Oxidation State in Sediment. *Environ. Sci. Technol.* (Submitted).
- Kaplan, D. I., P. M. Bertsch, and D. C. Adriano. 1995. Facilitated Transport of Contaminant Metals Through an Acidified Aquifer. *Ground Water* 33:708-717.
- Kaplan, D. I., P. M. Bertsch, D. C. Adriano, and K. A. Orlandini. 1994. Actinide Association with Groundwater Colloids in a Coastal Plain Aquifer. *Radiochimica Acta* 66/67:181–187.
- Kaplan, D. I., S. M. Serkiz, R. A. Fjeld, and J. T. Coates. 2001. *Influence of pH and Oxidation State on Plutonium Mobility through an SRS Sediment*. WSRC-TR-2001-00472, Rev. 0, Westinghouse Savannah River Company, Aiken, SC.
- Kaplan, D. I., T. L. Gervais, and K. M. Krupka. 1998. Uranium(VI) sorption to Sediments Under High pH and Ionic Strength Conditions. *Radiochimica Acta*. 80:201-211.
- Kato, S., and Y. Yanase. 1993. *Distribution Coefficients of Radionuclides in Concrete Waste for Coastal Soil and Concrete Powder*. JAERI-M 93-113. Japan Atomic Energy Research Institute, Ibaraki-ken, Japan.
- Kent, D. B., V. S. Tripathi, N. B. Ball, J. O. Leckie, and M. D. Siegel. 1988. *Surface-Complexation Modeling of Radionuclide Adsorption in Subsurface Environments*. NUREG/CR-4807 and SAND86-7175. U.S. Nuclear Regulatory Commission, Washington, DC.
- Kersting, A. B., D. W. Efur, D. L. Finnegan, D. J. Rokop, D. K. Smith, and J. L. Thompson. 1999. Migration of Plutonium in Groundwater at the Nevada Test Site. *Nature*. 397:56–59.
- Kretzschmar, R., and T. Schafer. 2006. Metal Retention and Transport on Colloidal Particles in the Environment. *Elements*. 1:205–210.
- Krupka, K. M., and R. J. Serne. 1998. *Effects on Radionuclide Concentrations by Cement/Ground-water Interactions in Support of Performance Assessment of Low-level Radioactive Waste Disposal Facilities*. NUREG/CR-6377, PNNL-11408.
- Krupka, K. M., R. J. Serne, and D. I. Kaplan. 2004. *Geochemical Data Package for the 2005 Hanford Integrated Disposal Facility Performance Assessment*. PNNL-13037, Rev. 2, Pacific Northwest National Laboratory, Richland, WA.

- Ledin A., Karisson S., Düker A., Allard B. 1994. The Adsorption of Europium to Colloidal Iron Oxy-hydroxides and Quartz – The Impact of pH and an Aquatic Fulvic Acid. *Radiochim. Acta*, vol.66/67, 213-220.
- Lukens, W. W., J. J. Bucher, D. K. Shuh, and N. M. Edelstein. 2004. Evolution of Technetium Speciation in Reducing Grout. *Environ. Sci. Technol.* 39:8064-8070.
- Macias, A., A. Kindness, and F. P. Glasser. 1997. Impact of Carbon Dioxide on the Immobilization Potential of Cemented Wastes: Chromium. *Cement & Concrete Research*. 27:25-225.
- McCarthy, J. F., and C. Degueudre. 1993. Sampling and Characterization of Colloids and Particles in Groundwater for Studying Their Role in Contaminant Transport. In: J. Buffle and J. P. van Leeuwen (eds.) pp. 247-315. *Environmental Particles*. Boca Raton, Lewis Publishers.
- McCarthy, J. F., and J. M. Zachara. 1989. Subsurface Transport of Contaminants. *Environ. Sci. Technol.* 23:497-502.
- McDowell-Boyer, L. A. D. Yu, J. R. Cook, D. C. Kocher, E. L. Wilhite, H. Holmes-Burns, and K. E. Young. 2000. Radiological Performance Assessment for the E-Area Low-Level Waste Facility, WSRC-RP-94-218, Rev. 1. Westinghouse Savannah River Company, Aiken, SC.
- MMES (Martin Marietta Energy Systems, Inc., EG&G Idaho, Inc., Westinghouse Hanford Company, and Westinghouse Savannah River Company). 1992. *Radiological Performance Assessment for the Z-Area Saltstone Disposal Facility*, WSRC-RP-92-1360, Westinghouse Savannah River Company, Aiken, South Carolina.
- Neiheisel, J. 1983. *Prediction Parameters of Radionuclide Retention of Low-Level Radioactive Waste Sites*. EPA 520/1-83-025. Office of Radiation Programs, U.S. Environmental Protection Agency, Washington DC.
- Oblath, S. B., J. A. Stone, and J. R. Wiley. 1983. *Special Wasteform Lysimeter Program at the Savannah River Laboratory*. Proceedings of the Fifth Annual Participant's Information Meeting, DOE Low-Level Waste Management Program, CONF-8308106, p. 441. EG&G Idaho, Inc., Idaho Falls, ID.
- Ochs, M., B. Lothenbach, and E. Giffault. 2002. Uptake of Oxo-anions by Cements through Solid-solution Formation: Experimental Evidence and Modeling. *Radiochim. Acta* 90:639-645.
- Parson, R. 1982. Surface Properties of Oxides. *J. Electroanal. Chem.* 118:2-18.
- Perdue, E.M. and Gjessing, E.T. 1990. *Dahlem Workshop Reports: Organic Acids in Aquatic Ecosystems*. Wiley & Sons, New York.

- Phifer, M., M. R. Millings, and G. P. Flach. 2006. *E-Area and Z-Area Hydraulic and Diffusional Material Properties Summary*. SRNL-EST-2006-00016. Washington Savannah River Company, Aiken, SC.
- Pilkington, N., and N. Stone. 1990. *The Solubility and Sorption of Nickel and Niobium under High pH Conditions*. UK Nirex Ltd., Report NSS/R186, Harwell, UK.
- Pointeau, I., B. Piriou, M. Fedoroff, M. G. Barthes, N. Marmier, and F. Fromage. 2001. Sorption Mechanisms of Eu^{3+} on CSH Phases of Hydrated Cement. *J. Colloid Interface Sci.* 236:252-259.
- Powell, B. A., M. C. Duff, D. I. Kaplan, R. A. Fjeld, D. B. Hunter, P. M. Bertsch, J. T. Coates, P. Eng, M. Newville, M. L. Rivers, S. M. Serkiz, S. R. Sutton, I. R. Triay, and D. T. Vaniman. 2006. Plutonium Oxidation and Subsequent Reduction by Mn(IV) Minerals in Yucca Mountain Tuff. *Environ Sci. Technol.* (Submitted).
- Powell, B. A., R. A. Fjeld, D. I. Kaplan, J. T. Coates, and S. M. Serkiz. 2004. Kinetics of $^{239}\text{Pu}(\text{V})\text{O}_2^+$ Reduction by Synthetic Magnetite (Fe_3O_4). *Environ. Sci. Technol.* 38:6016-6024.
- Powell, B. A., R. A. Fjeld, D. I. Kaplan, J. T. Coates, and S. M. Serkiz. 2005. $\text{Pu}(\text{V})\text{O}_2^+$ Adsorption and Reduction by Synthetic Hematite ($\bullet\text{-Fe}_2\text{O}_3$) and Goethite ($\bullet\text{-FeOOH}$). *Environ. Sci. Technol.* 39:2107-2114.
- Powell, B. A., R. A. Fjeld, J. T. Coates, D. I. Kaplan, and S. M. Serkiz. 2002. *Plutonium Oxidation State Geochemistry in the SRS Subsurface Environment*. WSRC-TR-2003-00035, Rev. 0, Westinghouse Savannah River Company, Aiken, SC.
- Prout, W. E. 1958. Adsorption of Radioactive Wastes by Savannah River Plant Soil. *Soil Sci.* 86:13-17.
- Rai, D. and R. W. Szelmezcza. 1990. Aqueous Behavior of Chromium in Coal Fly Ash. *Journal of Environ. Qual.* 19:378-82.
- Rai D., Moore D.A., Felmy A. R., Choppin G. R., and Moore R.C. 2001. Thermodynamics of the $\text{PuO}_2^+-\text{Na}^+-\text{OH}^--\text{C}^--\text{ClO}^--\text{H}_2\text{O}$ system: Use of NpO^{2+} Pitzer parameters for PuO_2^+ . *Radiochim. Acta.* 89:491-498.
- Ramsay, J. D. F. 1988. The Role of Colloids in the Release of Radionuclides from Nuclear Waste. *Radiochim. Acta* 44/45:165-170.
- Reardon, E. J. 1992. Problems and Approaches to the Prediction of the Chemical Composition in Cement/Water Systems. *Waste Management.* 12:221-231.
- Sarott, F. A., M. H. Bradbury, P. Pandolfo, and P. Spieler. 1992. Diffusion and Adsorption Studies on Hardened Cement Paste and the Effect of Carbonation on Diffusion Rates. *Cement Concr. Res.* 22:439-444.

- Schindler, P. W., and G. Sposito. 1991. Surface Complexation at (Hydro)oxide Surfaces. pp 115–145. In *Interactions at the Soil Colloid-Soil Solution Interface*. G. H. Bolt, M. F. DeBoodt, M. H. B. Hayes, and M. B. McBride (eds.). Kluwer Academic Press.
- Serkiz S. M. and Myers J.L. 1996. *Additional Information for E-area Vault Performance Assessment, Appendix I “Suspect Soil Performance Analysis” – Results of Modeling the Effects of Organic Matter on the Mobility of Radionuclides as it Relates to the Disposal of Wood Products in E-Area Slit Trenches*. WSRC-TR-98-00049. Westinghouse Savannah River Company. Aiken, SC.
- Serkiz, S. M., and D. I. Kaplan. 2006. Modeling the Influence of Dissolved Organic Carbon and pH on Cation Sorption to SRS Sediments. WSRC-RP-2005-01597. Westinghouse Savannah River Company. Aiken, SC.
- Serkiz S. M., Knaub D., and Lee C. 1999. *Phase II Nuclide Partition Laboratory Study Influence of Cellulose Degradation Products On the Transport of Nuclides from SRS Shallow Land Burial Facilities*. WSRC-TR-99-00298. Westinghouse Savannah River Company. Aiken, SC.
- Serkiz S. M., Knaub D., and Uhal H. 1998. *Phase I Nuclide Partition Laboratory Study Influence of Cellulose Degradation Products On the Transport of Nuclides from SRS Shallow Land Burial Facilities*. WSRC-TC-98-00460. Westinghouse Savannah River Company. Aiken, SC.
- Serkiz, S. M., 2000. *Recommended Partition Coefficient (Kd) Values for Nuclide Partitioning in the Presence of Cellulose Degradation Products*. WSRC-TR-2000-00262. Westinghouse Savannah River Company, Aiken, SC.
- Serkiz, S. M., and W. H. Johnson. 1994. *Uranium Geochemistry in Soil and Groundwater at the F and H Seepage Basins*. EPD-SGS-94-307. Westinghouse Savannah River Company, Aiken, SC.
- Serkiz, S. M., B. W. Gibbs, R. A. Fjeld, J. T. Coates, and D. I. Kaplan. 2005. Influence of pH and Oxidation State on Plutonium Transport Through a Low-Carbonate Coastal-Plain Soil. *Radiochim. Acta*. *Radiochim. Acta* (In press).
- Serne, R.J., Conca, J.L., LeGore, V.L., Cantrell, K.J., Lindenmeier, C.W., Campbell, J.A., Amonette, J.E. and Wood, M.I. 1993. *Solid-Waste Leach Characteristics and Contaminant-Sediment Interactions, Volume 1: Batch Leach and Adsorption Tests and Sediment Characterization*. PNL-8889 Vol. 1. PNNL, Richland, WA.
- Sheppard, J. C., M. J. Campbell, J. A. Kittrick, and T. L. Hardt. 1979. Retention of Neptunium, Americium, and Curium, by Diffusible Soil Particles. *Environ. Sci. Technol.* 13:680–684.
- Sposito, G. 1984. *The Surface Chemistry of Soils*. Oxford University Press, New York.
- Sposito, G. 1989. *The Chemistry of Soils*. Oxford University Press, New York.

- Stone, J. A., S. B. Oblath, R. H. Hawkins, M. W. Grant, S. L. Hoeffner, and C. M. King. 1985. *Waste Migration Studies at the Savannah River Plant Burial Ground*. DP-MS-85-86, Westinghouse Savannah River Company, Aiken, SC.
- Strom, R. N., and D. W. Kaback. 1992. *SRP Baseline Hydrogeologic Investigation: Aquifer Characterization, Groundwater Geochemistry of the Savannah River Site and Vicinity*. WSRC-RP-92-450. Westinghouse Savannah River Company, Aiken, SC.
- Stumm W. and Morgan, J.J. 1981. *Aquatic Chemistry*. Wiley & Sons, New York.
- Thibault, D. M., M. I. Sheppard, and P. A. Smith. 1990. *A Critical Compilation 2nd Review of Default Soil Soil/Liquid Partition Coefficients, K_d , For Use in Environmental Assessment*. AECL-10125. White Shell Nuclear Research Establishment, Pinawa, Manitoba, Canada.
- Thurman, E.M. (1985). *Organic Geochemistry of Natural Waters*. Kluwer Academic, Hingham, MA.
- Tits, J., A. Jakob, E. Wieland, and P. Spieler. 2003. Diffusion of Tritiated Water and $^{22}\text{Na}^+$ Through Non-Degraded Hardened Cement Pastes. *J. Contam. Hydrol.* 61:45–61.
- Valocchi, A.J. 1984. Validity of Equilibrium Assumption for Modeling Sorbing Solute Transport Through Homogeneous Soils. *Water Resour. Res.* 21:808–820.
- Van der Lee, J., E. Ledoux, G. De Marsily, A. Vinsot, H. van de Weerd, A. Liejnse, B. Harmand, E. Rodier, M. Sardin, J. Dodds, A. Harnandez Nenitex. 1997. *Development of a Model for Radionuclide Transport by Colloids in the Geosphere*. EUR 17480, Office for Official Publications of the European Communities, Luxembourg.
- Wang, F., J. Chen, and W. Forsling. 1997. Modeling Sorption of Trace Metals on Natural Sediments by Surface Complexation Model. *Environ. Sci. Technol.* 31:448-453.
- Westall, J. C. 1986. Reactions at the Oxide-Solution Interface: Chemical and Electrostatic Models. In *Geochemical Processes at Mineral Surfaces*. ACS Symposium Series 323, pp. 54-78. American Chemical Society, Washington, DC.
- Westall, J. C. 1994. Modeling of the Association of Metal Ions with Heterogeneous Environmental Sorbents. In *XVIII International Symposium on the Scientific Basis for Nuclear Waste Management*, pp. 1-12. Materials Research Society, Warrendale, PA.
- Westall, J.C., and J. Hohl. 1980. A comparison of Electrostatic Models for the Oxide Solution Interface. *Adv. Colloid. Interface Sci.* 12:265–294.
- Wieland, E., and L. R. Van Loon. 2003. *Cementitious Near-Field Sorption Data Base for Performance Assessment of an ILW Repository in Opalinus Clay*. PSI Bericht 03-06, Paul Scherrer Institut, Villigen, Switzerland.

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9.0 APPENDIX A: CELLULOSE -DEGRADATION-PRODUCT CORRECTION FACTORS FOR K_d VALUES

Table 16. Cellulose-degradation-products correction factors, f_{CDP} , for K_d values.

Radionuclides	10 mg/L C	20 mg/L C	95 mg/L C	222 mg/L C
Ac	2.9	0.77	0.049	0.015
Am	2.9	0.77	0.049	0.015
Cf	2.9	0.77	0.049	0.015
Cm	2.9	0.77	0.049	0.015
Cs	1.14	1.14	1.66	1.49
Eu	2.65	0.55	0.04	0.01
Ni	1.13	1.82	1.41	0.88
Np	1.14	1.14	1.66	1.49
Pa ^(a)	1.14	1.14	1.66	1.49
Pb	1.13	1.82	1.41	0.88
Pd	1.13	1.82	1.41	0.88
Po	1.13	1.82	1.41	0.88
Pu	1.89	2.92	0.51	0.12
Ra	1.22	2.38	1.89	0.44
Rb	1.14	1.14	1.66	1.49
Sn	1.13	1.82	1.41	0.88
Sr	1.22	2.38	1.89	0.44
Th	1.89	2.92	0.51	0.12
U	1.22	2.38	1.89	0.44
Zr	5.17	6.07	0.08	0.02

F_{CDP} = defined in Equation 3 in this document; this table is taken from Serkiz and Kaplan (2006).
^(a) In Serkiz and Kaplan (2006), they assumed that Pa had an oxidation state of +4 (Pa^{+4}), for this PA, it was assumed Pa had an oxidation state of +5 (PaO_2^{+}). The values reported in this table are appropriate for Pa(V).

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