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Hanford Waste-Form Release and Sediment Interaction

A Status Report with Rationale and Recommendations for Additional Studies

R. J. Serne
M. I. Wood

May 1990

Prepared for the U.S. Department of Energy
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Pacific Northwest Laboratory
Richland, Washington 99352

(a) Westinghouse Hanford Company,
Richland, Washington

ABSTRACT

This report documents the currently available geochemical data base for release and retardation for actual Hanford Site materials (wastes and/or sediments). The report also recommends specific laboratory tests and presents the rationale for the recommendations.

Currently available leach models (that predict solution concentrations of contaminants) include empirical models and solubility-, diffusion-, or desorption-controlled models. Each conceptual leach model requires that one or more parameters be quantified. This requirement dictates that laboratory testing be done to acquire the needed data. Release of contaminants from single-shell tanks is best modeled using a solubility-based conceptual model. The data base includes analyses of drainable liquors from 19 tanks for approximately 30 stable chemicals and 10 radionuclides. For grout, a release model based on diffusion has been chosen for projecting the long-term effects of contaminant release. The effective diffusion coefficients for about 30 radionuclides and stable chemicals have been determined.

Conceptual leaching models for contaminated soils have not been well established. Two conceptual models, control by desorption and by solubility, may be needed depending on the contaminant of interest. A series of sorption and empirical leach/solubility tests are recommended, using Hanford Site soils to provide ranges of sorption and solubility values for use in transport modeling. Data that quantify the chemical reactivity of solid wastes in Hanford Site soil are essentially nonexistent. The approach used to simulate contaminant migration from solid-waste burial grounds in the near term should be to treat them like contaminated soil sites.

Once contaminants are leached from the various waste forms at the Hanford Site, they may chemically interact with the soils and sediments. For most Hanford low-level wastes, adsorption processes may be the key to contaminant migration, especially outside the areas where the waste has dramatically altered the sediment's natural chemical environment.

An empirical parameter, the distribution coefficient, allows a quantitative estimate of contaminant migration. In the constant R_d model, the distribution of the contaminant between a solid adsorbent and coexisting solution is assumed

to be a constant value. Because the available Hanford-specific data base is small and the constant R_d adsorption model is simplistic, the adsorption potential of leachates from each waste form is not discussed. Instead, all available data are grouped into generic categories. Conditions at the Hanford Site suggest that most leachates can be grouped into one of three categories.

This report outlines a data collection approach that relies on feedback from performance analyses to ascertain when adequate data have been collected. The data collection scheme emphasizes laboratory testing based on empiricism.

EXECUTIVE SUMMARY

Regulations for waste disposal require performance assessment analyses before permitting or remedial actions. The groundwater pathway is generally considered to be the most important pathway when considering transport of contaminants from the disposal site to receptors. Geochemical reactions of contaminants within waste forms with pore water largely control release and transport to receptors. Consequently, data that quantify the geochemical reactions are required to adequately complete a performance assessment. This report documents the currently available geochemical data base for release and retardation for actual Hanford Site materials (wastes and/or sediments). The report also recommends specific laboratory tests and provides the rationale for the recommendations.

Currently available leach models (that predict solution concentrations of contaminants) include empirical models and solubility-, diffusion-, or desorption-controlled models. Each conceptual leach model requires that one or more parameters be quantified (e.g., a solubility limit or diffusion coefficient). In general, this requirement dictates that some laboratory testing be done to acquire the needed data.

Conceptual release models for distinct Hanford waste forms (i.e., single-shell tank wastes, grout, contaminated soils, and solid-waste burial grounds) are discussed. Release of contaminants from single-shell tanks is best modeled using a solubility-based conceptual model. Furthermore, the available data base and theoretical understanding of high ionic strength solutions preclude rigorous use of thermodynamic solubility constraints. Rather, the available data suggest that empirical solubility constraints (e.g., constant concentration limits based on empirical observations) are most appropriate. The data base includes 30 analyses of drainable liquors from 19 tanks for approximately 30 stable chemicals and 10 radionuclides. Particularly needed is a study of the effects of the relatively high content of dissolved organic material in the tanks and their effect on the solubility and adsorption of trace contaminants, such as actinides.

The low permeability exhibited by Hanford Site grout makes it reasonable to assume that any recharge water that reaches the monoliths (grout plus its concrete retaining vault) will advect around them. The pore water entrapped within the grout and the water impinging on the surface of the grout vault will act as a diffusional conduit for contaminants to reach the surface of the vault. Thus, a release model based on diffusion has been chosen for projecting the long-term effects of contaminant release. To date, leach tests on grouts prepared with three types of tank wastes have been performed by the Hanford Grout Technology Program. The effective diffusion coefficients for about 30 radionuclides and stable chemicals have been determined. The existing data base for grout leaching, knowledge of the waste inventory, and leachate-sediment adsorption data are more complete for grout than other Hanford Site waste forms. Based on general chemical principles and available data, it appears that the "problem" constituents for the grout waste forms have already been identified. To date, the organic chemical content of the liquid wastes solidified in grout has not caused any significant increases in leaching of metallic constituents or decreases in leachate adsorption.

Contaminants within contaminated soil sites exist as sorbed or precipitated radionuclides and/or hazardous chemicals that are bound in the soil column after discharged waste solutions have drained. Geochemical conditions (ambient water characteristics, soil exchange capacities, and buffering capacities) in the soil columns appear to vary widely as a function of discharge fluid chemistry and spatial proximity to the source of discharge.

Conceptual leaching models for contaminated soils have not been well established. Two conceptual models, control by desorption and by solubility, may be needed depending on the contaminant of interest. A series of sorption and empirical leach/solubility tests are recommended, using Hanford Site soils to provide ranges of sorption and solubility values for use in transport modeling. Because of the lack of available information, emphasis needs to be placed on radionuclide interactions with complexing organic compounds and the influence of pH on the chemistry of pore water at sites where acidic solutions were disposed. Parameters to be varied in the test matrix, in addition to solution or contaminated soil chemical components, should include soil types, moisture content, and flow characteristics (e.g., advective flow rates and diffusive fluxes as a function of moisture content). Stenner et al. (1988) concluded that many contaminated soil sites at the Hanford Site have released radionuclides, regulated chemicals, and organic chemicals into the unconfined aquifer; consequently, contaminated soil sites warrant the highest priority for collection of geochemical data.

Data that quantify the chemical reactivity of solid wastes and their radioactive/hazardous chemical constituents in Hanford Site soil are essentially nonexistent. Therefore, the mechanism for release of radionuclides and/or hazardous constituents is not known. The approach used to simulate contaminant migration from solid-waste burial grounds in the near term should be to treat them like contaminated soil sites. Thus, release models based on solubility and desorption processes would be used with input values based on those of contaminated soils.

The primary recommendation for determining the release of contaminants from buried solid wastes is to perform a set of laboratory leaching tests, with real or simulated solid waste, to derive an empirical leach rate or solubility that can be compared with the assumed desorption- or solubility-controlled release rates from contaminated soil. Particular attention should be given to identifying other components, particularly organic chemicals, that might enhance radionuclide mobility. Because there is no evidence that contaminants from solid-waste burial grounds at the Hanford Site have reached the water table, collection of pertinent geochemical data for this waste form should be given less priority than that for contaminated soil sites.

Once contaminants are leached from the various waste forms at the Hanford Site, they may chemically interact with the soils and sediments. The major processes that affect contaminant transport include the following: dissolution/precipitation, adsorption/desorption, filtration of colloids and small suspended particles, and diffusion into micropores within mineral grains. For most Hanford low-level wastes, adsorption processes may be the key to contaminant migration, especially outside the areas where the waste has dramatically altered the sediment's natural chemical environment.

To predict the effects of retardation using safety assessment codes, adsorption processes must be described in quantitative terms. An empirical parameter, the distribution coefficient (often called R_d or K_d), which is readily measured by laboratory testing, allows a quantitative estimate of contaminant migration rates. Whether the laboratory testing accurately represents in situ interactions between contaminants and sediments is a continuing debate.

In the constant R_d model, the distribution of the contaminant of interest between a solid adsorbent and coexisting solution is assumed to be a constant value. There is no explicit accommodation for dependence of the R_d on characteristics of the sediments, groundwater, or contaminant concentration. The limitations associated with this approach are well known to investigators, but the paucity of geochemical data specific to waste forms and sediments at the Hanford Site currently precludes a more rigorous approach to retardation.

A second practical approach for modeling adsorption is called the parametric R_d model. Numerous statistical strategies have been used to define empirical relationships that describe R_d as a function of other variables, such as the quantities and types of minerals present in the sediment, amounts and types of dissolved species in the groundwater, pH, and Eh. Because of the added complexity in solving the transport equation, explicit use of the parametric R_d model has been infrequent. On the other hand, the parametric R_d approach can be used to objectively develop a suite of time- or space-dependent, constant R_d values to be used in a given performance analysis. This latter approach is the philosophy recommended for future Hanford Site performance assessment activities.

Because the data base is small and the constant R_d adsorption model is simplistic, the adsorption potential of leachates from each waste form is not discussed. Instead, all available data are grouped into generic categories based on pH, total dissolved salt, and organic content of the waste leachate. Conditions at the Hanford Site suggest that most leachates can be grouped into one of three categories. As the leachates subsequently migrate away from the disposal facility, the resultant solution should become low in salt and organic content and neutral to slightly basic in pH.

This report outlines a data collection approach that relies on feedback from performance analyses to ascertain when adequate data have been collected. The data collection scheme emphasizes laboratory testing based on empiricism; the expected environment is simulated, and geochemical reactions between radionuclides or contaminants and the simulated environment are quantified.

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1.0 INTRODUCTION

1.1 BACKGROUND

This document was prepared by Pacific Northwest Laboratory (PNL) for Westinghouse Hanford Company under the auspices of the Hanford Site Performance Assessment (HSPA) Project in support of the Environmental Restoration Program.

The objective of the HSPA project at PNL is to assist the Westinghouse Hanford Environmental Technology Group in developing and maintaining a credible and defensible performance assessment capability (conceptual models, assumptions, computer codes, and data bases) necessary to resolve performance issues (DOE 1987a; Davis 1988) for the remediation and disposal of defense wastes at the Hanford Site.

Regulations governing waste cleanup and disposal require assessments of performance of the waste disposal systems. The pertinent regulations for waste disposed or to be disposed at the Hanford Site include U.S. Department of Energy (DOE) Order 5820.2A and the Comprehensive Environmental Response, Compensation, and Liability Act/Resource Conservation and Recovery Act (CERCLA/RCRA) legislation. DOE Order 5820.2A regulates future disposal of low-level radioactive waste; CERCLA regulates previously disposed radioactive and hazardous waste; RCRA regulates current and future disposal of hazardous waste. The DOE and CERCLA regulations demand that performance assessment analyses be completed for all types of waste buried at the Hanford Site. Performance assessments (or risk assessment, as defined by CERCLA) are analyses that predict the transport of radionuclides and/or contaminants from a source to a receptor via pathways that are considered credible. The groundwater pathway is believed to be significant, particularly when long-term effects of waste disposal are considered.

Geochemical reactions of radionuclides and hazardous chemicals with the environment of the groundwater pathway and the hydrologic characteristics of the site are the primary factor in release of contaminants to receptors. Consequently, data that quantify these reactions and the characteristics of the pathway are required for adequate analysis. The status of current geochemical data, and recommendations for additional geochemical data, are discussed in this report.

Simulations of the transport of contaminants through the groundwater pathway will be made for specific waste form and remediation programs (e.g., grouted double-shell tank wastes, single-shell tank wastes, solid wastes, and contaminated soils) to 1) help select disposal and remediation methods, 2) identify site characterization needs, 3) design engineered barrier systems, 4) develop performance goals, and 5) formally document compliance (e.g., with 4
DOE Order 5820.2A and CERCLA).

1.2 PURPOSE

The purpose of this document is threefold: to summarize currently available information, to provide a strategy for generating additional data, and to provide recommendations on specific data collection methods and tests matrices.

First, we summarize currently available conceptual models that relate to assessment of geochemical release and transport of radionuclides and contaminants from waste sources in the soils of the Hanford Site to a receptor via the groundwater. The types of information include 1) data that quantify the release of radionuclides or contaminants from a source by means of such mechanisms as solubility-controlled solution concentrations, desorption distribution coefficients, or diffusion-controlled release rates; and 2) data that quantify the retardation of radionuclides or chemical contaminants by the pathway to the receptor (e.g., sorption distribution coefficients). By means of this summary, we identify the types of data and parameters of interest needed to establish a centralized data base and identify additional data needs.

Second, the available site-specific information defines needs for additional data required to better assess performance or risk. A strategy is provided for generating the additional data by means of a rational framework that 1) allows systematic evaluation of data needs for all waste types that may be disposed of at the Hanford Site, 2) identifies data needs common to different waste sites to avoid duplication of effort, 3) sets priorities, and 4) identifies when a data set is sufficient for the identified need.

Third, recommendations are made for completing specific tests, and major elements of the associated test matrix are identified. As additional data are collected and understanding of the behavior of the environment increases, the current recommendations will likely be modified. The objective is to provide a data base of geochemical information that is approved for use in performance and/or risk assessments and which quantifies the chemical reactions affecting release and transport of radionuclides and hazardous constituents from Hanford Site waste types and waste disposal locations.

1.3 SCOPE

The scope of the work documented by this report was to review information pertinent to the release of contaminants from Hanford Site wastes and the transport of the contaminants in groundwater. The natural precipitation, recharge, waste-form leaching, contaminant transport through the unsaturated sediments and the unconfined aquifer, and subsequent uses of contaminated water were considered in defining the scope of work. Human intrusion, with consequent waste mobilization and contamination of the atmosphere, etc., was not considered. Radionuclides and selected regulated chemicals (major anions and trace metals) are addressed, and organic chemicals of potential interest are briefly discussed.

The findings of this report rely on information presented in the Hanford Defense Waste Environmental Impact Statement (HDWEIS; DOE 1987b) unless specifically stated otherwise. Additional pertinent work is in progress, but complete documentation is not currently available.

The report is organized in terms of two topics: 1) the release (leaching) of contaminants (radionuclides, trace metals, and major anions) from waste forms, and 2) the subsequent interaction between the contaminant leachates and Hanford Site sediments (retardation, adsorption, etc.). For each of these topics, the report is organized with respect to the specific waste form. The sections on contaminant release and retardation begin with general descriptions of the processes and concepts, present details on the currently used conceptual models and computer codes for each waste form, and give information on available waste-form-specific data. Finally, the report recommends specific areas for additional work to obtain needed contaminant release and retardation data.

Appendices A and B summarize current recommendations of information for entry into a contaminant release and retardation data base for near-term use in assessing performance. Appendix C discusses sophisticated concepts of adsorption.

1.4 STRATEGY

Because long-term disposal system failure cannot readily be observed, prediction of contaminant transport from waste source to receptor by groundwater must acknowledge some of the regulatory framework for evaluating safety and the level of uncertainty inherent in such predictions. To reduce uncertainty, we try to establish an appropriately comprehensive data base. For geologic environments, however, naturally occurring heterogeneities and high costs of data collection constrain the level to which one can remove uncertainty. Consequently, uncertainty about factors affecting contaminant release via the groundwater pathway (i.e., the geochemical data base) is inevitable and the results of assessments require interpretation by professional judgment and sensitivity analyses to determine what constitutes an adequate geochemical data base.

The process used to define and limit the geochemical data collection program is illustrated in Figure 1. The initial phase is subdivided into four parts that are the components of baseline data collection. Radionuclides and hazardous chemicals are identified from waste-stream records and sampling data. Geochemical data pertinent to performance assessment needs are the chemical and physical properties of the site environment that influence geochemical reactions between the radionuclides and contaminants with the pore water and sediments in the waste site environment. The reactions of interest are those affecting radionuclide and contaminant mobility, including solubility, sorption, desorption, and release rates from waste forms. The most important parameters include pore and recharge water composition, soil composition, and waste-form composition. Other parameters that influence transport by groundwater are soil porosity, and permeability, moisture content, and groundwater recharge characteristics.

Hydrologic parameters used in assessing performance are generally derived from properties measured at the site of interest. Geochemical reaction values (e.g., sorption, solubility) for radionuclides or chemical contaminants are

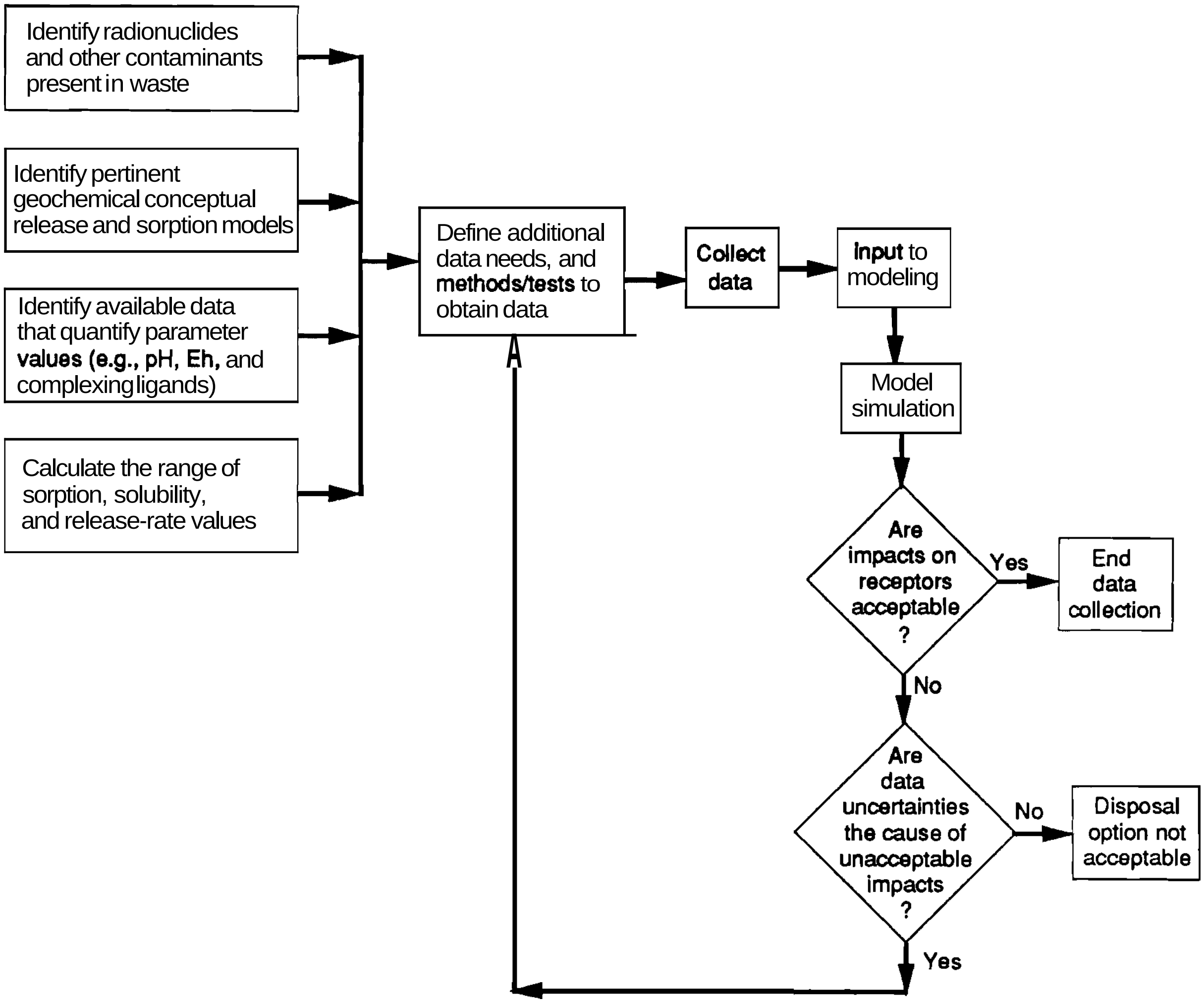

FIGURE 1. Data Collection Strategy

generally derived from laboratory studies for the range of values pertinent to the site. Solubility data are sometimes derived from thermodynamic calculations that use site-relevant chemical conditions. In this document, an initial data base has been collected based on available published information.

Having established a baseline data base, additional data needs, if any, are identified on the basis of performance assessment modeling (i.e., pathways analysis) or on an acknowledged lack of information (see Figure 1). If the pathways analysis is done on an element-by-element basis and indicates unacceptable uncertainty (e.g., on contaminant transport to a receptor or in geochemical reaction values used as input to the models), additional data will be required. Additional data may also be required to quantify parameter values that affect geochemical reaction values. For example, the effect of moisture content on the values of distribution coefficients can be calculated based on theoretical considerations, but such values need to be confirmed by test data.

Once sufficient data have been collected and the results of appropriate analyses have been used to generate model inputs, the transport analyses are performed and the impacts of contaminant release to the environment calculated. To address uncertainty, a range of input values is generally used. The results of the simulations are compared to regulatory criteria to determine if predicted releases are acceptable. If the range of parameter values used results in a predicted range of release values that is equivocal or unacceptable, then the process must be repeated to reduce or better define uncertainty.

2.0 WASTE-FORM RELEASE

Data on the release of contaminants from Hanford defense waste forms are required for simulation of disposal site performance by computer-based models. The release can be considered the source term in the overall performance assessment model.

Knowledge of the total inventory is useful, but of greater importance are data on fluxes of contaminants out of the waste form and into the surrounding vadose sediments. As described in Section 3.0, Sediment Retardation, very few contaminants release and travel at velocities coincident with the recharge waters. It is thus necessary to develop data and conceptual models on the interactions of Hanford defense waste forms (dry solids, moist contaminated soils, and liquid wastes) with surrounding packaging, container, and encapsulating materials (e.g., grout), vadose zone sediments, and pore waters.

To create a release model for a particular waste disposal site that considers recharge water as the driving force, one needs to assume one or more controlling processes and define the total mass (inventory of waste) to be considered. Controlling mechanisms can be hypothesized on the basis of physicochemical description of the waste (physical form, chemical species, density, solubility, etc.) and knowledge of the recharge water (chemical composition, quantity, velocity).

Inventory data and the spatial distribution of wastes within the disposal site provide some of the necessary data. Depending on the waste form, characterization should be more detailed than total chemical and radionuclide inventories; the physicochemical description should include a complete chemical analysis and a complete physical analysis, including separable phases (e.g., drainable liquor, salt cake, sludge, and sediment mineralogy).

After characterization of the waste form is complete, we determine what will occur when recharge waters are percolated into the waste system. In general, this will require some empirical leach testing of solids, dissolution tests on salt cakes, and recharge water mixing studies with drainable liquors. Current leach models can be categorized as empirical or mechanistic (i.e., solubility, diffusion, or desorption controlled). Different leach conceptual models for various contaminant types releasing from the same waste site are often chosen. Further, different species of the same waste constituent may require distinct release conceptual models.

2.1 CONCEPTUAL RELEASE MODELS

2.1.1 Solubility-Controlled Release

Solubility-controlled release models assume that a known solid is present, or rapidly forms, and controls the solution concentration in the aqueous phase of the constituents being released. Solubility models are thermodynamic equilibrium models and do not consider kinetics (time required to dissolve or completely precipitate). When identification of the likely controlling solid is difficult or when kinetic constraints are suspected, empirical solubility experiments are often performed to gather data that can be used to generate an empirical solubility release model (a model with the mathematical similarity to solubility but no identified thermodynamically acceptable controlling solid). It should be pointed out that a solubility limit is not a constant value in a chemically dynamic system. That is, the solubility limit (e.g., Pu, Sr, Cd, or Pb) is determined by the product of the thermodynamic activities of species that constitute the solid. If the system chemistry changes, then the individual species activities likely change. For example, if the controlling solid for plutonium is the hydrous oxide $Pu(OH)_4$, the solubility product is $[Pu]\ [OH]^4 = K_{sp}$. The value of K_{sp} is fixed, but the value of [Pu] and [OH] can vary. In fact, if the pH decreases 1 unit ([OH] decreases by 10), then for K_{sp} to remain constant [Pu] must increase by 10^4, all else held constant. A true solubility model must consider the total system and does not reduce to a fixed value for the concentration of a constituent under all conditions. Numerous constant concentration (i.e., empirical solubility) models are used in performance assessment activities that assume a controlling solid and fix the chemistry of all constituents to derive a fixed value for the concentration of specific contaminants. The value obtained is only valid for the specific conditions assumed. Currently, two commonly used Hanford performance assessment codes, TRANSS, the release code used in the HDWEIS, and Multimedia Environmental Pollutant Assessment System (MEPAS), can accommodate only the constant solubility release model.

At PNL, the geochemical code MINTEQ (Felmy et al. 1984; Peterson et al. 1987) is the current detailed solubility model/code. Less detailed, typically constant-concentration-limit models are generated from empirical studies such as Delegard and Gallagher (1983).

2.1.2 Diffusion-Controlled Release

For porous solid waste forms that bind waste within the matrix, such as grout, the currently used release model mathematically resembles mass transport theory with diffusion as the controlling process (Godbee and Joy 1974; Godbee et al. 1980). For species that chemically react in the grout, either by reaction with the cementitious matrix or by adsorption onto the clay additives, an empirical or effective diffusion coefficient, that allows predictions of solution concentrations, is measured in laboratory leach tests.

For grouts and cements containing radioactive and chemically hazardous wastes, the release of wastes is most often described as an effective diffusion process. This model is used by researchers at Brookhaven National Laboratory (Kalb and Columbo 1984), at Oak Ridge National Laboratory (Moore, Godbee and Kibbey 1977; Godbee et al. 1980; Clark 1977), at the Japan Atomic Energy Research Institute (Matsuzuru and Moriyama 1982; Moriyama, Dojiri and Matsuzuru 1977), at the United Kingdom Atomic Energy Authority, Harwell (Sambell, Smitton and Elsden 1982), and at PNL and Westinghouse Hanford (Serne et al. 1987).

The effective diffusion coefficients for reactive constituents account for the chemical retardation as well as the physical hindrance to leaching caused by the small pore sizes and tortuosity of the cement matrix. Species in the grout dissolve or desorb from the grout matrix, and the solubilized wastes then diffuse out of the grout and cement vault into the surrounding sediments. In reality, the actual processes that control grout leaching are complex, but most of the available literature on grout and cement leaching argue fairly conclusively that an effective (or lumped) diffusion model explains the observed short-term laboratory data satisfactorily. Using the effective diffusion model, most radionuclides and inorganic hazardous chemicals leaching from cementitious waste forms exhibit coefficients ranging from 10^{-6} to less than 10^{-12} cm^2/s. For comparison, most cations and anions exhibit a diffusion coefficient of approximately 10^{-5} cm^2/s in water (Dayal, Arora and Morcos 1983). The large range in the effective diffusion coefficients observed for species in grout is a reflection of the other processes, such as adsorption, precipitation, and mineral substitution, that impede the release of some constituents.

For a semi-infinite source (large inventory of contaminants), a plot of the cumulative amount of each contaminant leached versus the square root of time should be linear if diffusion is controlling and the fraction leached remains below 20%. For a cylindrical waste form of semi-infinite inventory, the governing equation is

$$\frac{\Sigma a_n}{A_o} = 2\left(\frac{S}{V}\right)\sqrt{\frac{D_e t}{\pi}} \tag{1}$$

where a_n = amount of contaminant leached during each interval
A_o = total amount of contaminant in waste form
V = volume of waste form (cm^3)
S = geometric surface area of waste form (cm^2)
t = total elapsed time of leaching; $t = \Sigma \Delta t_n$ (s)
Δt_n = time of each leach interval (s)
D_e = effective diffusion coefficient (cm^2/s).

It is often found that actual leach data indicate a much faster release in the early time periods of the leach test and later satisfy the linear dependence of $\sqrt{t}$.

Matsuzuru and Moriyama (1982), Godbee et al. (1980), Matsuzuru and Ito (1978), and Dayal, Arora and Morcos (1983) discuss leach experiments that show a similar initial rapid release. Data from these studies are analyzed using linear regression of the cumulative fraction leached versus the square root of time to provide a best-fit D_e value (from the slope) and empirical instantaneous wash-off fraction, "k_o", from the intercept at $t = 0$.

The actual mechanism or cause of the "instantaneous wash-off" has not been conclusively identified and perhaps could indicate that the experiments themselves do not satisfy all model assumptions. Some explanations offered include rapid dissolution of evaporated salts left on the waste-form surface after curing, dissolution or resuspension of very small particles of waste form clinging to the surface, or release of material in waste-form pores that directly intercept the surface (those with no tortuosity or constrictivity restraints).

The mathematical equation that describes diffusion plus instantaneous wash-off is

$$\frac{\Sigma a_n}{A_o} = 2\left(\frac{S}{V}\right)\sqrt{\frac{D_e t}{\pi}} + k_o \tag{2}$$

where k_o = constant, the intercept at $t = 0$
of' $\left(\frac{\Sigma a_n}{A_o}\right)\left(\frac{V}{S}\right)$ plotted versus $\sqrt{}$

For constituents that leach a significant portion of the total inventory during laboratory testing, the semi-infinite condition is not appropriate. ANS (1986) presents a discussion that shows Equation (1) deviates from actual data when the cumulative fraction leached exceeds 20%. For finite cylindrical waste forms that contain a uniform concentration and a surface boundary concentration of zero at all times, the following mathematical expression is valid:

$$\frac{\Sigma a_n}{A_o} = 1 - \frac{32}{\pi r^2}\sum_{n=1}^{\infty}\sum_{m=1}^{\infty}\frac{e^{-D_e[\alpha_m^2 + (2n-1)^2\pi^2/4\ell^2]t}}{(2n-1)^2\ \alpha_m^2} \tag{3}$$

where r = radius of the cylinder (cm)
ℓ = half-height of the cylinder (cm)
α_m = positive roots of the zero-order Bessel function
$J_o(r\alpha_m) = 0$ (cm^{-1}).

Côté, Constable and Moreira (1987) derive several leaching models for cement-based waste forms based on bulk diffusion [Equations (1) and (3)], bulk diffusion plus chemical reaction where the chemical reaction is either an instantaneous equilibrium linear adsorption isotherm or first-order surface dissolution (i.e., moving boundary) and interface mass resistance.

From a practical point Côté, Constable and Moreira (1987) present a semi-empirical leach model that combines the general mathematical forms of these different conceptual models. The equation is

$$\frac{\Sigma a_n}{A_o} = k_1\left(1 - e^{-k_2 t}\right) + k_3 t^{\frac{1}{2}} + k_4 t \tag{4}$$

where k_1, k_2, k_3, k_4 are empirical constants.

The first term on the right-hand side of Equation (4) describes the kinetics of exchange of species between the surface of the solid waste form and solution (pore water or leachant). When the exchange is fast, $k_2 + \infty$ and the term reduces to a constant (k_1) akin to the instaneous wash-off term in Equation (2). The second term on the right-hand side of Equation (4) is the bulk diffusion term. When diffusion dominates the semiempirical constant k_3 to related to the D_e [see Equation (1)] by the relationship $k_3 = 2\frac{S}{V}\sqrt{\frac{D_e}{\pi}}$. The third term in Equation (4) represents leaching from a slow chemical reaction such as corrosion or structural breakdown of the waste form matrix that releases species.

For leach tests in which the solution phase is not replaced periodically, the assumption that the concentration in solution remains very low compared to that in the waste form is not valid and a different mathematical approach is necessary. Equations (1) through (3) require that the solution concentration in the leachate is zero to accurately predict leach rates and effective diffusion coefficients.

For static leach tests, Godbee, Mrochek and Nestor (1989) report that the apparent effective diffusion coefficient can be determined from the equation

$$\frac{A_t}{A_f} = 1 - \sum_{n=1}^{\infty} \frac{6\alpha(\alpha + 1)e^{-[D_e q_n^2 t/9(v/s)^2]}}{9 + 9\alpha + q_n^2\alpha^2} \tag{5}$$

where A_t = mass of species in leachate at time t

A_f = mass of species in leachate at equilibrium (final steady-state value)

$\alpha = \frac{A_f}{A_o - A_f}$

q_n = non-zero roots of $\tan(q_n) = \frac{3q_n}{3+\alpha q_n^2}$

A_o, V, S, D_e, and t as previously defined.

If one assumes that bulk diffusion out of the waste-form controls leaching then Equations (1) or (3) can be used to determine the effective diffusion coefficient from leach tests where leachant replenishment is performed and Equation (5) can be used to analyze static leach tests. If other phenomena are considered (i.e., wash-off, chemical reaction), other equations, such as Equations (2) and (4) (see Godbee et al. 1980), can be used.

2.1.3 Desorption-Controlled Release

Contaminated soil sites are generally considered to retain adsorbed species from the liquid waste streams that were disposed. The release model is thus assumed to be a desorption process that removes adsorbed contaminants from the soil surfaces as the recharge water or groundwater percolates through the burial ground. Current desorption release models assume that the linear adsorption model (based on the distribution coefficient concept = R_d) applies and that the desorption R_d value is equivalent to the adsorption R_d value. This assumption is often incorrect in that desorption is often more difficult than adsorption onto the sediment (e.g., Barney 1981, 1984); that is, some contaminants bound to sediment show a high degree of irreversible adsorption.

The desorption-release model relies on the linear adsorption isotherm

$$S = R_d C \tag{6}$$

where S = concentration on solid (mass/g)

R_d = distribution coefficient (mL/g)

C = concentration in solution (mass/mL).

The value of S is measured from samples of contaminated sediment or estimated from the total inventory of wastes disposed and known or estimated volume of sediment in the disposal site. This latter approach assumes a homogeneous distribution. To calculate the flux of waste into recharge or groundwater, one must know the hydrogeologic factors (water flux, porosity, percent water saturation, etc.), the distribution coefficient for each contaminant, and the initial value of S. The value of C, concentration in the pore water leaving the disposal site, is then calculated using Equation (6). This value when coupled with the volumetric water flow rate yields the mass of contaminant removed per unit time.

Inherent in this approach is the requirement of rapid desorption kinetics, the linear relationship between S and C, and existence of only one species for each contaminant and one type of adsorption site for each sediment. It is likely that many of the radionuclides and hazardous chemicals retained in contaminated soils are actually precipitates and entrapped suspended solids as opposed to adsorbed species. Therefore, more accurate release models for contaminated soil may be needed to ensure that release estimates are not unrealistically conservative. If more realistic models are required, they should explore incorporation of other processes besides reversible adsorption-desorption. The desorption-controlled release model is now frequently used to describe the flux of contaminants from solid waste burial grounds as well as contaminated soil sites.

2.1.4 Empirical Release Models

Release models chosen to quantify the flux of contaminants may be purely empirical. A common empirical model is the constant fraction release, such as 1% of the total inventory per year; another worst case model is instantaneous release of the whole inventory. As mentioned in the discussion on diffusion, corrosion reactions and matrix dissolution often are modeled as functions of linear time. Thus a constant dissolution or corrosion rate might be approximated by a constant mass released per unit time.

A very common empirical release model, called congruent release, assumes that the major constituent in a waste controls the release of all other constituents. As the major constituent dissolves/corrodes, all other constituents within the effected volume are released in their like proportion.

That is, if the molar or weight ratios of contaminants A, B, and C to the major constituent (matrix) are 0.01, 0.05, and 0.10, then for every 100 units of matrix release, 1, 5, and 10 units of contaminants A, B, and C, respectively, are released.

2.2 RELEASE MODELS CURRENTLY USED IN HANFORD PERFORMANCE ASSESSMENT ACTIVITIES

This section details release models used on past HDWEIS and, when available, current performance assessment activities for each specific waste form (single-shell tanks, grout, contaminated soils, and solid-waste burial grounds).

To date, the HDWEIS (DOE 1987b) represents the most comprehensive use of performance assessment tools to predict the consequence of defense waste disposal at the Hanford Site. The HDWEIS does not address all low-level wastes but does provide performance assessment examples for existing tank wastes, transuranic- (TRU-) contaminated soils, and solid wastes and grout. For release model and contaminant-sediment interactions comparison, the HDWEIS activities on existing tank wastes are similar to our designation of single-shell tank wastes; the HDWEIS modeling of TRU-contaminated soils and pre-1970 TRU solid waste is similar to our contaminated soil and solid waste designations, respectively.

The HDWEIS performance assessment calculations considered several scenarios, both natural and human-induced disruptive events, and several pathways (groundwater, surface water, atmospheric, and direct ingestion). Our interest is limited to the groundwater pathway. For contaminant release from the waste forms, the HDWEIS considered two generic cases: direct leaching of wastes by infiltrating recharge water (no protective barrier in place) and diffusion-controlled release under unsaturated sediment conditions where direct infiltration is precluded by the protective barrier placed over the burial ground.

The conceptual release model and the mathematical representations for each waste form for both generic release cases are discussed next. First, we acknowledge that the HDWEIS exercises are clearly described as bounding analyses as opposed to most realistic analyses. The HDWEIS states (DOE 1987b, p. 1.20) "A bounding analysis is made with a set of data, modeling assumptions and accidental release scenarios which totaled, compounds conservatisms so that the calculated (predicted) environmental impacts should exceed those actually expected." Further, the performance assessment activities in the HDWEIS (p. 0.1, Appendix 0) use "simplistic models and rely heavily on conservative data values and modeling assumptions."

2.2.1 Single-Shell Tank Release Model

The HDWEIS uses a constant solubility release model for the scenario in which no protective barriers overlie the tank farms. Infiltrating water is assumed to freely enter and exit the tanks (the walls are considered to be highly corroded), carrying away a constant concentration (or activity for radionuclides) of each contaminant. The values of the constant concentrations for each contaminant were based on the maximum values found in tank liquors in a study of six tanks in the late 1970s (Schulz 1978). Values for F and Cd were chosen based on thermodynamic estimates of the solubility of CaF_2 (fluorite) and $CdCO_3$ (otavite) in Hanford soils and alkaline groundwater. Thermodynamic data for fluorite and otavite were taken from Lindsay (1979) and Rai et al. (1984), respectively. The radionuclides and chemicals that were considered and the selected constant solubility values are shown in Table 1 (reproduced from Table P.2, DOE 1987b). Note that the list of contaminants considered is small compared to the total number of contaminants likely present.

For the protective barrier case the release mechanism is assumed to be water vapor diffusion into the tanks and diffusion of contaminants out of the tanks. The chemicals are assumed to diffuse out of the tanks and through the vadose zone sediments either to the water table directly or to vadose zone sediments outside the vertical projection of the barrier where infiltrating water moves by advection as depicted in Figure 2 (Figure 0.4; DOE 1987b). The driving force for contaminant migration is the concentration gradient set at C_0 at the waste-form boundary and at zero where the diffusion-controlled zone intercepts the advection-controlled zone. The concentration gradient between these two points is assumed to be linear. The fixed values for C_0 are the values given on Table 1.

TABLE 1. Constant Concentration Release Values for Single-Shell Tanks (no protective barrier)

Chemical or Radionuclide	Concentration[a,b,c]
^{14}C	7.6 µCi/L
^{63}Ni	1.5×10^{3} µCi/L
^{90}Sr	1.6×10^{5} µCi/L
^{93}Zr	35 µCi/L
^{99}Tc	4.3×10^{2} µCi/L
^{129}I	0.2 µCi/L
^{137}Cs	6.7×10^{5} µCi/L
^{151}Sm	7.2×10^{3} µCi/L
^{237}Np	0.5 µCi/L
^{238}U	1.2×10^{-3} µCi/L
$^{239-240}Pu$	1.6 µCi/L
^{241}Am	1.3×10^{3} µCi/L
NO_3^-	0.3 g/mL
NO_2^-	0.14 g/mL
F^-	1.9×10^{-6} g/mL
Cr (as CrO_4^{2-})	1.1×10^{-2} g/mL
Cd	1.1×10^{-8} g/mL
Hg	3.2×10^{-4} g/mL

(a) All concentrations except those for cadmium and fluoride are from Schulz (1978).

(b) Fluoride concentration is extrapolated from Lindsay (1979).

(c) Cadmium concentration from Rai et al. (1984).

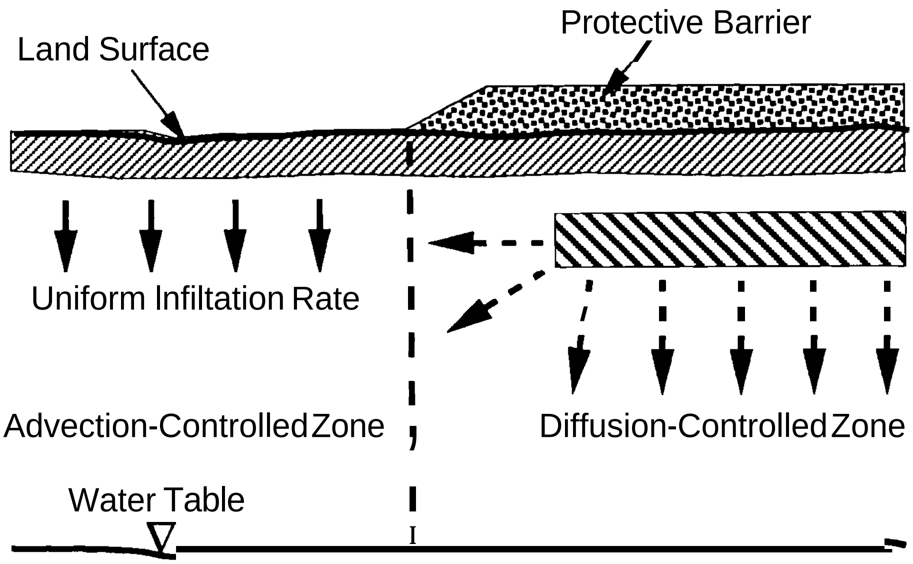

FIGURE 2. Diffusion- and Advection-Controlled Regions of the Simplified Model for Release of Waste with Barrier-Emplaced Waste

Performance assessment has recently been used to aid single-shell tank (SST) characterization planning. Recently Jim Droppo and other PNL staff projected the potential long-term impacts of the release of SST radionuclides and regulated chemicals via recharge waters dissolving waste, percolating through the vadose zone sediments to the water table, and then intercepting a drinking-water well 50 meters (m) (164 ft) downgradient. A second scenario, a farm scenario, included human exposure via eating irrigated crops and animal tissue coupled with domestic use of the contaminated water. The release, transport, and dose calculations were performed using the MEPAS model described in Whelan et al. (1987) and Buck, Hoopes and Friedrichs (1989).

MEPAS requires that the contaminant flux be input by the user in grams/year or curies/year. The flux may be changed up to 50 times in any calculation, but the user must supply each flux and the duration of the flux. MEPAS does not have any provision to track chemistry or internally modify the release flux.

For the SST calculations, the estimated inventories of each radionuclide and regulated chemical in each tank farm were assumed to be solids precipitated in the tanks. The hypothetical release from each tank farm was modeled as though the wastes for the entire tank farm were in a single tank with an expanded radius that included the same surface area as the entire tank farm. A constant concentration release model (generically called solubility-limited release) was used for the chemicals. The concentration used for each constituent was chosen from empirical data presented in Wiess (1986). A known weight (~5 g, dry basis) of core material from several tanks in the TY Tank Farm was contacted with ~15 mL of distilled water for 30 min in an ultrasonicator. The leachate was decanted and saved. A second and then a third portion (~15 mL each) of distilled water leached the core material. All three leachates were combined and the volume adjusted to ~50 mL; the resultant solution was analyzed. The average value of the concentrations of species in these leachates for all tanks tested was used in the performance assessment calculations as the constant concentration release value. For chemicals not analyzed, the performance assessment calculations were based on handbook values (the controlling compounds were not specified). Table 2 lists the constant concentration release limits chosen for chemicals. This concentration multiplied by the steady-state recharge water flow rate (separate cases considered were 0.5, 1.0, and 10.0 cm/yr) and tank farm cross section (square centimeters) yields the flux (grams per year) required by MEPAS.

For radioactive constituents, a congruent release model was used for estimating release from SST tanks. All the radionuclides are assumed to be homogeneously mixed in the predominately sodium nitrate salts. The total inventory of each radionuclide in each tank farm is conceptually mixed within the total tank farm sodium nitrate inventory. A solubility limit for $NaNO_3$ of 921 g/L of water was selected from a handbook (Weast 1988). The total time needed to leach all the sodium nitrate present in the tank farm was calculated based on total inventory, the volumetric recharge rate (steady-state recharge rate multiplied by tank farm cross section), and the 921-g/L maximum concentration that could leave the tank. The calculated leach time was then used to figure the flux of each radionuclide by dividing the total inventory (curies, Ci) by the years to deplete the sodium nitrate to get a constant flux (curies per year). For comparison purposes, Schulz (1978) found a maximum of 300 g/L NO_3 (equivalent to 411 g/L as $NaNO_3$) in tank liquors; this suggests that the 921 g/L value may never be reached in SST and that

TABLE 2. Constant Concentration Limits for Chemical Constituents

Constituent	Grams per Liter
Ag	1.73×10^{-3}
Al	3.41×10^{-1}
Ba	7.44×10^{-3}
Cl	$1.35 \times 10^{+1}$
EDTA	2.81×10^{-2}
F	3.55
Fe	1.99×10^{-1}
CN	1.10×10^{-3}
Mn	1.42×10^{-2}
NO_2	$1.25 \times 10^{+2}$
NO_3	$1.31 \times 10^{+1}$
Na	$9.19 \times 10^{+1}$
Ni	2.32×10^{-2}
Pb	7.71×10^{-3}
SO_4	8.46
Zr	3.45×10^{-1}

Droppo et al.'s calculations are definitely conservative, perhaps overly conservative in approach. Table 3 lists the fluxes calculated by Jim Droppo and other PNL staff for several key radionuclides for selected tank farms using the congruent release model with 921 g/L as the solubility limit for sodium nitrate and 1.0 cm/yr recharge. At the bottom of the table are the calculated time periods required to dissolve all the waste out of each tank farm, given the conceptual model. The leach period varies from 111 to 1433 years. For comparison purposes, the HDWEIS release scenario for SST based on a slightly different conceptual model and recharge water flux values showed that leach periods for a steady-state infiltration rate of 0.5 cm/yr vary between 2 and 1.6×10^6 years, depending on species and tank farm location. ^{137}Cs release yields the shortest leach period and fluoride yields the longest. The nitrate calculations in HDWEIS suggest complete leaching would take between 890 and 1200 years, which is skewed to the longer leach periods calculated by Droppo et al. (see Table P.2; DOE 1987b).

TABLE 3 Constant Flux Rates for Selected Radionuclides (Ci/yr) from Single-Shell Tank (SST) Farms with 1.0-cm/yr Recharge

Radionuclides	Tank Farms A	B	C	S	T	U
^{241}Am	4.06	2.53×10^{1}	7.25×10^{1}	1.65×10^{1}	1.71×10^{1}	3.32
^{14}C	8.58×10^{-1}	1.93×10^{1}	6.02	4.06	1.22×10^{1}	0.74
^{137}Cs	3.35×10^{2}	3.06×10^{4}	3.05×10^{3}	1.77×10^{4}	1.98×10^{4}	4.91×10^{3}
^{129}I	3.28×10^{-4}	5.71×10^{-2}	1.22×10^{-2}	1.75×10^{-2}	2.88×10^{-2}	$2.93 \times 10^{-}$
^{239}Pu	3.42	8.22	2.99×10^{1}	6.11	1.73×10^{1}	1.93
^{90}Sr	1.61×10^{4}	2.34×10^{4}	3.29×10^{4}	2.33×10^{4}	1.14×10^{4}	4.82×10^{3}
^{99}Tc	2.23×10^{-1}	3.57×10^{1}	6.14	1.06×10^{1}	2.21×10^{1}	2.08
^{238}U	1.13×10^{-2}	4.00×10^{-1}	0.35	4.62×10^{-2}	1.12	0.30
Time to leach all waste (yr)	1433	415	171	699	153	111

Pat Salter and co-workers at PNL recently collated the data of Weiss and Schull (1988a-i) on the fraction of selected constituents that could be leached from SST core material after the washing procedure just discussed. The results are shown in Table 4. Where no actual data were available, estimates of what percentage would likely dissolve in water are provided but Salter and co-workers do not document how the estimates were derived. Weiss and Schull's (1988) data are derived from tests on nine SST tanks: A-102, A-103, A-106, BX-104, BX-105, C-103, C-104, C-105, and C-106. Table 4 shows the range in the percentage dissolved in water is quite variable for many constituents. It is also apparent from the data that many radionuclides and chemicals do not dissolve as readily as NO_3, and thus congruent release conceptual models based on nitrate are overly conservative for many species.

2.2.2 Grout

Past performance assessment release calculations for grout waste forms relied on the computer code TRANSS (Simmons, Kincaid and Reisenauer 1986) analyses. TRANSS was also used for all types of waste-form release in the HDWEIS. TRANSS will be described in more detail in the discussions on sediment interactions. For the case of no protective barrier overlying the grout vaults, the HDWEIS used a congruent release conceptual model in which all contaminants leached proportionally with nitrate. The nitrate in grout was assumed to leach at a uniform rate of 0.007% of the total inventory per year. Thus it takes 14,286 years to completely dissolve the grout waste forms.

Where a protective barrier overlies the grout vaults, the HDWEIS used a second congruent release conceptual model in which the concentration of contaminants are held constant at the grout interface and chemicals migrate by diffusion to the interface of the water table or the advection controlled zone (see Figure 2). The concentration of each contaminant is fixed at zero at the interface of the water table or advection-controlled zone. Between the two fixed concentrations the concentration gradient is assumed to be linear. These boundary conditions and gradient assumption allow a flux for each contaminant to be calculated. The constant nitrate concentration chosen for the grout waste-form boundary was 0.30 g/mL (300 g/L or 300,000 mg/L). This value is an approximation to the solubility of $NaNO_3$ in a highly alkaline, high salt solution (Barney 1976) and observed maximum concentrations in tanks

TABLE 4. Single-Shell Tank Solids Partitioning Factors (% of constituent dissolved when water washing)

Constituents	Average %	Range Observed Minimum %	Maximum %
Ag	4	0.3	14
Al	22	0.05	89
B	48	0.0	100
Ba	0.2	0.04	0.75
Bi	23	1.6	96
Ca	2	0.2	8
Cd	38	5	100
Co	19	0.0	100
Cr	10	0.1	50
Cu	6	0.0	26
Fe	0.2	0.0	1.8
K	49	11	93
Mg	0.2	0.02	0.7
Mn	5.4	0.3	30
Na	65	14	98
Ni	9	0.5	40
NO_3	100	100	100
P	59	2.8	98
Pb	18	0.7	71
Si	1.2	0.03	3.8
TOC	91	21	100
U	6	0.01	41
Zn	11.8	0.0	100
Zr	2.3	0.02	7.1
^{241}Am	13	0.2	75
^{60}Co	10	0.0	40
^{137}Cs	50	8	99
$^{239/240}Pu$	2.2	0.04	5
^{90}Sr	0.3	0.01	1.7
^{99}Tc	56	0.8	100

TABLE 4. (contd)

Constituents	Average %
Cl	95
CN	25
CO_3	75
F	95
Hg	99
NO_2	99
Se	99
SO_4	90
^{14}C	99
^{129}I	99
Cm	1
Nb	10
Np	10
Pa	1
Pd	10
Ra	1
Sm	1
Sn	25
Th	1
La	1

(Schulz 1978). All other contaminants are released congruently to nitrate. If the contaminant is present in the grout at a concentration ratio of 10^{-4} of the nitrate, then 30 mg/L (3 x 10^5 x 10^{-4}) would be the constant concentration boundary condition at the grout surface.

Several performance assessments other than the HDWEIS have been related to grout. Performance assessment activities have been an integral part of the Hanford Grout Technology Program for at least the past 4 years. Several letter reports and a topical report (Sewart et al. 1987) have been submitted to Westinghouse Hanford Company. The following discussion describes the release model and input values used to evaluate phosphate-sulfate waste (PSW) grout.

The release model used by Sewart et al. (1987) considered that PSW grout monoliths were in direct contact with soil and that infiltrating recharge water directly contacted the monolith. The wastes within the grout were assumed to leach at a constant rate. The inventory of each regulated chemical and radionuclide was determined in both the liquid PSW waste and for the chemicals in each dry blend component (cement, fly ash, and clays). The total monolith inventory, both radioactive and the cold-cap (nonradioactive) grout, was used to assess environmental impact.

Release from the grout monoliths was modeled in two ways, depending on the contaminant under consideration. Contaminants that were not selected as solubility limited were modeled as being released at a constant rate and the solubility-limited contaminants were assumed to be released according to a fixed concentration. The fixed concentration times the annual volume of recharge water defined the mass flux.

The constant rate of release of contaminants that were not solubility controlled was determined from an analysis of laboratory data on small PSW grout cylinders (see Serne et al. 1987). The laboratory tests suggested that mobile contaminants were released from the grout by diffusion processes and that Equation (1) could estimate the effective diffusion coefficient. The value chosen for the PSW performance assessment was $D_e = 1 \times 10^{-9} cm^2/s$. Using Equation (1), this value of D_e and the appropriate value for the surface area to volume ratio for a PSW monolith ($3.8 \times 10^{-3} cm^{-1}$), a calculation was performed to determine the fraction released in the first 70 years. The result was that 0.7% (0.007) of the contaminant would be released in 70 years or 0.01% (0.0001) would be released per year, assuming a constant release rate. This analysis was considered conservative because contaminant release that is actually controlled by diffusion is not constant with time; rather, release is faster in early time because the concentration gradient is higher.

To determine which chemicals in PSW grout were potentially solubility controlled, the chemical composition of soil pore water outside the grout vaults was input to the geochemical computer code MINTEQ (see Felmy, Girvin and Jenne 1984; Peterson et al. 1987). If one assumes the potential controlling solids and the pore water composition shown in Table 5, 10 regulated chemicals were deemed to be solubility limited at the concentrations listed in Table 5.

TABLE 5 Solubility-Limited Concentrations for Phosphate-Sulfate Waste PSW) Grout

Element	Controlling Solid	Maximum Predicted Concentration, mg/L	Assumed Soil Pore Water Composition
Manganese	$MnHPO_4$	0.02	pH, 8.1
Iron	$Fe_3(OH)_8$	0.025	Eh, 295 mV
Chromium	$Cr(OH)_3$	0.09	Potassium, 7.8 mg/L
Copper	CuO (tenorite)	0.06	Sodium, 25 mg/L
Barium	$BaSO_4$ (barite)	0.04	Magnesium, 14.4 mg/L
Zinc	Zn_2SiO_4 (willemite)	0.02	Calcium, 56 mg/L
Cadmium	$CdCO_3$ (otavite)	0.002	Chloride, 22 mg/L
Silver	AgCl (cerargyrite)	0.075	Sulfate, 85 mg/L
Lead	$PbCO_3$ (cerussite)	0.29	H_4SiO_4, 54 mg/L
Fluoride	CaF_2 (fluorite)	2.04	Total carbonate, 86 mg/L

These values were used as constant release concentrations that are combined with the annual recharge volume to determine the mass flux.

Other grout performance assessment activities have been performed for Hanford grouts but as yet have not been documented in publicly available reports. These efforts have been used to develop criteria and standards for permanent disposal of grouted waste. Criteria and standards are technical, quantitative limits for waste disposal. The ultimate purpose of establishing such limits is to protect the public health and the environment far into the future after the waste is disposed. The efforts for criteria and standards used the same constant release conceptual models for the grout waste form as Sewart et al. (1987); that is, either the solubility- (constant concentration) controlled release or the constant fraction (0.0001/yr) rate, based on scaling the laboratory test results over the first 70 years for an effective diffusion coefficient of $1 \times 10^{-9} cm^2/s$, were used. For some analyses the concrete vault and a diffusion barrier (either gravel or asphalt) were considered as additional barriers with fluxes controlled by diffusion at $5 \times 10^{-8} cm^2/s$ over 0.7-m thickness and $1 \times 10^{-9} cm^2/s$ over 1.0-m thickness, respectively. The ratio of the cumulative amount of a contaminant leached with barriers in place versus no barriers in place were determined when the flux out of the grout, out of the vault, and through the gravel were assumed to be at steady state (i.e., the same through each barrier). Further, by assuming that the grout monolith is a semi-infinite slab and that the concentration of all contaminants at the diffusion barrier-soil interface is set at zero (soil pore water carries leached products rapidly away), simple equations can be used to describe release with and without barriers.

The flux ratio of a contaminant with the barrier(s) present to the case with no barriers at any specified time (t) or the integrated ratio from $t = 0$ to a specified time, t, are, respectively:

$$\frac{N\ \mathrm{with}}{N\ \mathrm{wo}} = \frac{1}{\left[1 + \Theta_m \left(L_g/D_{eg} + L_c/D_{ec}\right) \sqrt{D_{em}/\pi t}\right]} \quad (7)$$

and

$$\frac{\bar{N}\ \mathrm{with}}{\bar{N}\ \mathrm{wo}} = 1 - \frac{\theta_m\left(L_g/D_{eg} + L_c/D_{ec}\right)}{\sqrt{\pi t/D_{em}}} \mathrm{Ln}\left[1 + \frac{\sqrt{\pi t/D_{em}}}{\theta_m\left(L_c/D_{ec} + L_g/D_{eg}\right)}\right] \quad (8)$$

where N with = instantaneous flux when barrier(s) in place, m/l^2t

N wo = instaneous flux when barriers not present, m/l^2t

$\bar{N}$ wo, $\bar{N}$ with = integrated fluxes from $t = 0$ to $t = t$

θ_m = volumetric moisture content of grout monolith, l^3/l^3

L_g, L_c = thickness of gravel cocoon and concrete vault respectively, l

D_{em}, D_{ec}, D_{eg} = effective diffusion coefficients for contaminant through grout monolith, cement vault, and gravel cocoon respectively, l^2/t.

With knowledge of the fraction leached with no barriers present [see Equation (1)] and the ratio of fluxes with barriers present, the fraction remaining value for a contaminant can be calculated and input to TRANSS.

Current grout performance assessment activities are taking a new approach and use new computer codes. Current methodology will be documented in late 1989. Release of contaminants from grout is now performed simultaneously for the entire system (grout, vault, cocoon, and vadose zone sediments) in two dimensions. Contaminant-specific effective diffusion coefficients form the basis of the release calculations from the grout. Effective diffusion coefficients are also used for the vault, gravel cocoon, and unsaturated soils but one value is assumed to be valid for all contaminants in each media. At present effective diffusion coefficients out of the grout for each contaminant are categorized as falling into four regions: $D_e = 10^{-8}$, 10^{-9}, 10^{-10}, or 10^{-12} cm^2/s. The concrete vault is given a constant value of 5×10^{-8} cm^2/s for all constituents. The cocoon treats all wastes as the same and for sensitivity analyses, values of 10^{-9}, 10^{-10}, and 2 x 10'' cm^2/s have been used. In the unsaturated sediments underneath the protective barrier where contaminants are considered to migrate predominately by diffusion the effective diffusion coefficient (all contaminants are given the same value) is varied as a function of soil moisture content:

$$D_{soil} = D_o a e^{b\theta} \tag{9}$$

where D_{soil} = effective diffusion coefficient in soil (cm^2/s)

D_o = diffusion coefficient of a typical species in dilute water
= 2.5×10^{-5} cm^2/s
a = empirical constant = 0.003
b = empirical constant = 10
θ = volumetric moisture content of soil (cm^3/cm^3).

See Kemper and Van Schaik (1966), Olsen, Kemper and Van Schaik (1965), Olsen and Kemper (1968), and Porter et al. (1960) for details on this empirical relationship.

For unsaturated zone sediments outside the protective barriers, advective flow predominates. The water flow field for the entire system (grout, vault, cocoon, protective barrier, and Hanford unsaturated sediments) is simultaneously calculated for two dimensions using TRACER3D (Travis 1984). The calculated flow field is input to a convective-dispersive flux code S-301 (Farmer 1984, 1985, 1987; Farmer and Norman 1986) that considers contaminant retardation in two dimensions via the linear adsorption isotherm. Finally flow and transport in the Hanford unconfined aquifer (two dimensions) is predicted using the code SLAEM (Strack 1988) with input from S-301 and the regional hydrology data base.

The determination of the effective diffusion coefficient category of each contaminant is based on laboratory leaching studies of Hanford-specific grouts (e.g., Serne et al. 1987, 1989 a,b; Tallent et al. 1988). More details will be presented in late 1989 when the performance assessment efforts of the Hanford Grout Technology program are published.

2.2.3 Contaminated Soils

We assume that the TRU-contaminated soils in the unsaturated Hanford sediments discussed in the HDWEIS are representative (in regards to release processes) of all low-level-waste- (LLW-) contaminated soils present at Hanford.

The release conceptual model used in the HDWEIS for the case when no protective barrier is present was a combination of constant solubility- and desorption-controlled release. The radionuclides Pu and Am were considered solubility controlled, while C, Sr, Cs, and Np were modeled using desorption as the controlling process. These six elements were the only constituents for contaminated soils considered in the HDWEIS. The release predictions used the estimated geometric surface area of contaminated soil disposal units and the chosen steady-state net infiltration rate to calculate the volume of water/per unit time fluxing through the burial ground. Solubility-limited radionuclides are released into this flux of water at a rate that allows the leachate to leave the burial ground at the chosen constant concentration until all contaminant mass is removed from the soil. For the desorption-controlled nuclides, the total inventory of each is assumed to be homogeneously distributed within the total cross-sectional area of the burial ground to a depth dependent on the inventory. This homogeneous distribution yields the value of S in Equation (6). When one chooses a value for R_d for each nuclide, the desorption-release equation [Equation (6)] allows calculation of the solution concentration that will leave the disposal site.

Alternatively, a contaminant-specific effective depth of contamination can be constructed on the basis of estimates of the total inventory disposed, burial site cross section, R_d for each contaminant, and an assumed waste influent concentration. The total mass of contaminant is then adsorbed onto the disposal site soil based on Equation (6). Contaminants with low R_d values will travel deeper into the soil before being totally adsorbed. Less mobile contaminants will be completely adsorbed in the shallower depths. Using this contaminant-specific distribution, the initial conditions of a burial site can be approximated and subsequent release modeled in a similar fashion; S and R_d are known and C is the parameter calculated [see Equation (6)].

The product of the retardation factor, a function of the R_d, and contaminant deposit thickness show the sensitivity of the adsorption-desorption model. If the thickness of the contaminated zone is increased while the total inventory and R_d value are held constant, release will be slowed because the value of S must decrease to accommodate the fixed inventory in a growing volume. As S decreases, with R_d constant, C must also decrease, thus slowing release.

The values of the constant solubility and linear desorption release parameters used for TRU-contaminated soils are shown in Table 6 (taken from Tables P.6, P.26, and P.27 in the HDWEIS). The values for the constant solubility concentrations for Am and Pu were based on data in Rai et al. (1981) and Rai, Serne and Moore (1980b), respectively. The Am value comes from

TABLE 6. Values Chosen for Contaminated Soil Release

Radionuclide	Constant Concentration (Ci/L)	Desorption Distribution Coefficient (mL/g)
^{241}Am	1.5×10^{-8}	
$^{239-240}$Pu	2.6×10^{-7}	
^{90}Sr		0.64
^{137}Cs		26
^{237}Np		16
^{14}C		0

empirical solubility data for a dilute solution in contact with contaminated Hanford crib soils. The value selected (1.5×10^{-8} Ci/L) is equivalent to 1.9×10^{-11} M ^{241}Am. The value for Pu was chosen based on laboratory tests on the solubility of amorphous plutonium oxides in dilute solutions. The value selected (2.6×10^{-7} Ci/L) is equivalent to 1.8×10^{-8} M ^{239}Pu. The distribution coefficients are conservative values from adsorption studies of synthetic tank solutions and dilute waste solutions onto typical 200 Area Hanford sediments (Delegard and Barney 1983; Routson et al. 1981).

For the TRU-contaminated soils no performance assessment analyses were made for the scenario where a protective barrier is placed over the burial site. The predicted consequences of the no-barrier case were below regulatory concern such that additional work considering the barrier (which would lower release further) was deemed unnecessary.

Currently, the desorption release model used in the HDWEIS for contaminated soil sites is based on adsorption tests, not desorption tests using contaminated soils. To our knowledge no performance assessment activities that predict release and migration from contaminated soil sites have been performed since the HDWEIS.

2.2.4 Solid-Waste Burial Grounds

The conceptual release model and parameter values for solid wastes used in the HDWEIS are identical to those used for contaminated soils. In essence the solid waste is assumed to be homogeneously disaggregated and mixed within the soil. Infiltrating water contacts the pieces of solid waste and removes (dissolves) material based on a constant solution constraint or linear desorption constraint.

To our knowledge no other work on the development of release or transport models or other performance assessment calculations for solid wastes have been performed at Hanford.

2.3 CURRENT ESTIMATE OF RELEASE RATES

The purpose of this section is to document any available Hanford Site-specific data that could be used to develop waste-form release conceptual models or data that provide actual values for input parameters to available release models. The section has four subsections, one for each distinct Hanford waste form. Further, each subsection includes a discussion of recommended values for release parameters for selected radionuclides and regulated chemicals that should be used in future performance assessment activities. The rationale for choosing each value is also given in accompanying appendices. Our goals in this exercise are to document actual data, extrapolate reasonable values if data are lacking, and offer a consistent and referenceable data base to the various performance assessment practitioners. The fourth section in the report complements these goals by offering strategies, testing protocol, and priorities for improving conceptual models and data bases.

2.3.1 Single-Shell Tanks

We assume that the release of contaminants from single-shell tanks (SST) occurs either by existing liquors draining through cracks in tank walls or bottoms or from dissolution of tank salt cake and sludge into recharge waters that invade the tanks and then drain through existing cracks.

There are three sources of actual measurements of the drainable liquor in tanks and water leaches of tank solids; Schulz (1978), Weiss (1986), and Weiss and Schull (1988a-i). Weiss and Schull also report acid- (5 M HCl) leachable fractions of composite core from 15 separate tanks (25 total analyses of 25 separate cores). Finally, Delegard and Gallagher (1983) and Delegard, Barney and Gallagher (1984) report laboratory determinations of the solubility of cobalt, strontium, neptunium, plutonium, and americium in simulated tank liquor.

The material in Hanford SST consists of drainable liquor (<5% by weight of total material), salt cake, and sludge. Hanford salt cake is an admixture of large amounts of $NaNO_3$ and lesser amounts of $NaNO_2$, $NaAl(OH)_4$, Na_2CO_3, Na_2CrO_4, Na_3PO_4, Na_2SO_4, NaOH, and numerous trace constitu-ents both stable and radioactive. Sludge includes hydrated oxides of Al, Fe, Mn, Zr, $Sr_3(PO_4)_2$, and $Ni_2[Fe(CN)_6]$, as well as many radionuclides.

Schulz (1978) concluded that residual liquid (drainable liquor) contained higher concentrations of ^{106}Ru, ^{125}Sb, NO_2^-, EDTA, and other complexants than salt cake. Schulz (1978) also inferred that ^{79}Se and SeO_4^{2-} could also concentrate in the drainable liquor. Schulz conjectures that drainable liquors become concentrated with trace impurities as the salt cake crystallizes and purifies salt minerals.

A complete listing of chemical analyses of separable liquid (drainable liquor) is found in Tables 7 and 8; Table 7 lists the chemical constituents and Table 8 the radionuclides. In general, drainable liquors exhibit high pH values (10 to greater than 12), but several tanks in the TY Farm appear to be less alkaline. The liquors are predominately sodium, nitrate, nitrite, and carbonate with significant dissolved organic carbon (>2 g/L) and often Cr (>1 g/L). The highest nitrate concentration in drainable liquors is found in Tank TY-102, a value of 362.7 g/L, which exceeds the constant concentration limit chosen in the HDWEIS (300 g/L).

The median value of nitrate found in 26 drainable liquors was 165 g/L and the arithmetic average was 161 ± 85 g/L. Droppo and co-workers used a solubility value of 921 g/L for $NaNO_3$ as given in Weast (1988). The combined concentration of sodium and nitrate in drainable liquor is generally between 400 and 450 g/L for tanks with high total dissolved salts. It would appear that the environment in the tanks restricts sodium nitrate solubility to a value much less than the handbook value for pure sodium nitrate. Assuming that the tank liquors with high dissolved salts are in fact saturated in respect to $NaNO_3$, a tank-empirical solubility limit would be 450 to 500 g/L. When pure $NaNO_3$ dissolves the nitrate makes up 73% of the solutes weight and sodium makes up 27%. The ratios observed in drainable liquor range from 40 to 53% nitrate and 47 to 60% sodium, suggesting that the vast array of other solutes complicate the solubility calculations.

TABLE 7. Chemical Composition of Drainable Liquor in Single-Shell Tanks (g/L)

						Riser 5	Riser 5	Riser 5	Riser 5	Riser 8	Riser 8	Riser 7	Riser 7	Riser 7	Riser 15
Constituent	S-110	U-106	U-111	S-102	TX-118	TY-106	N-104	TY-104	TY-104	TY-103	TY-103	TY-103	TY-103	TY-103	TY-103
pH						9.15	12.2	12.1	12.1	10.0	10.9	10.4	12.2	11.1	9.48
Al	34.6	17.0	23	11.6	21.1		0.51	0.63	0.57						
Ba	<0.012						0.00014	0.0002	0.0001						
Bi							<0.0002	0.0026	<0.001						
B															
Cd							<0.0005	<0.0005	<0.0002						
Ca	<0.14														
Cr	10.92		<0.5	3.8	6.76		1.46	1.89	1.66						
Co															
Cu															
Fe	0.06	1.68	1.28	1.34	0.2		0.21	0.26	0.23						
Pb							0.0007	<0.0016	0.001						
Mg	<0.02														
Mn							<0.004	<0.004	<0.002						
Ni							0.0018	0.0267	0.0177						
P							3.620	4.1	4.04						
K															
Si							0.041	0.0086	0.006						
Ag							0.004	0.0072	0.0047						
Na	237		110.2	175.7	194.6		87.1	74.8	88.1						
Sr	<0.05														
Zn	<0.6														
Zr							<0.0009	<0.0009	<0.0005						
NO_3^-	161	301		153.1	216.4		85.6	114.1	97.3		219.	179.2	187.0	278.4	230.0
NO_2^-	62.5	57.5		<0.9	40.5		15.7	6.9	11.22	16.6	13.7	10.4	12.4	18.2	18.0
CO_3^{2-}	19.8	29.4	3.7	39.0	30.0		30.8	40.0	35.2	4.02	4.08				
PO_4^{3-}	<9.6		<0.3	7.2	<0.9		11.1(a)	12.56(a)	12.4(a)						
SO_4^{2-}	3.06			0.3	14.4		4.7	6.24	5.4		10.94	7.2	8.64	13.06	14.4
OH^-	60.	16.	23.	10.0	19.7		0.27	0.22	0.22	0.000	0.017			0.017	0.000
TOC	16.3	130.	47.5	31.6	41.9		1.86	2.05	2.41		1.94		0.30		
U						0.006	0.022	0.037	0.04		0.039				
Cl							1.2	1.5	1.3		2.2	0.17	1.88	2.52	2.00
F							<0.46	0.6	<0.5		<0.5	<0.5	<0.5	<0.5	<0.5
Source(b)	Sc	Sc	Sc	Sc	Sc	W6	W6	W6	W6	W6	W6	W6	W6	W6	W6

TABLE 7. (contd)

Constituent	Riser 5 TY-102	Riser 8 TY-105	Riser 17 ~~A-103~~	Riser 12 ~~A-103~~	Riser 8 ~~C-104~~	Riser 17 ~~A-106~~	Riser 20 ~~A-106~~	Riser 4 ~~A-102~~	Riser 1 ~~BX-105~~	Riser 8 ~~EX-105~~	Riser 2 ~~C-103~~	Riser 8 C-105	Riser 1 C-106	Riser 1 ~~BX-104~~	Riser 8 ~~EX-104~~
pH	8.71	7.01	12.94	>12.0		>12.0	>12.0	>12.0	>12.0	>12.0	9.91	9.69	9.81	>12.00	>12.00
Al			34	37.12		2.7	26.0	38.0	5.3	6.6	<0.014	<0.009	<0.034	4.49	3.50
Ba			<0.01	<0.01		<0.01	<0.01	0.06	0.0007	0.0009	0.002	0.003	<0.005	<0.005	<0.005
Bi			<0.22	<0.22		<0.22	<0.22	<0.22	<0.01	<0.01	0.161	0.101	<0.111	<0.012	<0.012
B				0.03			0.06	0.032	0.013	0.014	0.004	0.003	0.010	0.015	0.024
Cd			<0.05	0.05		<0.05	<0.05	0.003	0.011	0.014	<0.01		<0.025	0.008	0.005
Ca			0.14	0.15		0.07	0.09	0.04	0.16	0.13	0.015	0.004	0.011	0.014	0.128
Cr			0.26	0.33		0.85	1.16	0.08	0.29	0.20	0.067	1.12	0.006	1.895	0.092
Co							0.001		0.001				0.001		
Cu						0.01			0.008	0.007	0.197	0.004	0.003	0.057	0.005
Fe			<0.02	<0.02		<0.02	<0.02	0.003	0.004	0.005	0.010	0.003	0.012	0.003	0.004
Pb			<0.16	<0.16		<0.16	<0.16	0.069	0.043	0.060	<0.033	<0.012	<0.082	0.018	0.045
Mg				0.003				0.0006	0.0002	0.0005	0.005	0.006	0.013	0.0002	0.0005
Mn			<0.4	<0.4		<0.4	<0.4	<0.02	<0.02	<0.02	<0.082	<0.014	<0.202	<0.02	<0.02
Ni			0.084	0.11		0.04	0.05	0.03	0.088	0.100	0.060	<0.006	0.072	0.062	0.040
P			1.02	1.37		1.5	1.67	1.2	1.6	1.8	1.45	2.56	0.344	1.768	2.106
K			5.06	5.82		3.3	4.62	6.92	2.69	2.50	0.351	1.57	0.422	1.982	1.520
Si			0.17	0.51		0.11	0.16	0.65	0.088	0.19	0.129	0.103	0.105	0.156	0.124
Ag			<0.02	<0.02		<0.02	<0.02	<0.001	<0.001	<0.001	0.024	<0.002	<0.001	<0.001	<0.001
Na			252.	188.		213.	255.	168.	128.	120.	40.2	114.8	94.9	163.	102.
Sr								<0.0001	0.002	0.002	0.0005			0.0002	0.0001
Zn				0.048		0.026	0.023	0.009	0.003		0.007				
Zr			<0.09	<0.09		<0.09	<0.09	<0.005	<0.005	<0.005	0.36	0.36	0.293	<0.005	<0.005
NO_3^-	362.7	128.31	202.1	203.4		185.4	194.7	168.	107.	128.	4.7	34.3	1.4	145.7	99.2
NO_2^-	15.2	6.5													
cOf -															
PO_4^{3-}			3.13[(a)]	4.2[(a)]		4.6[(a)]	5.13[(a)]	3.68[(a)]	4.9[(a)]	5.5[(a)]	4.44[(a)]	7.85[(a)]	1.05[(a)]	5.42[(a)]	6.45[(a)]
SO_4^{2-}	20.5														
OH^-	0.000	0.000													
TOC			8.36	8.26	10.3	5.64	<0.13	8.06	9.12	9.75	7.37	2.87	2.52	6.18	5.62
U			0.0024	0.0064	0.025	0.003	0.002	0.003	0.0046	0.0044	2.630	0.966	0.958	0.0034	0.0036
Cl	1.7	0.96													
F	<0.51	<0.51													
Source(b)	W6	W6	W8	W8	W8	W8	W8	W8	W8	W8	W8	W8	W8	W8	W8

(a) Calculated from ICP data for P.

(b) Sc, Schulz 1978; W6, Weiss 1986; W8, Weiss and Schull 1988 a-i.

TABLE 8 Radionuclide Composition of Drainable Liquor in Single-Shell Tanks (μCi/L)

Constituent	S-110	U-106	U-111	S-102	TX-118	Riser 5 TY-106	Riser 5 TY-104	Riser 5 TY-104	Riser 5 TY-104	Riser 8 TY-103
^{14}C							0.93	1.17	1.02	
^{60}Co		3.02×10^{3}	2.90×10^{3}	1.63×10^{3}	4.63×10^{2}	<0.23	<2.1	<2.4	7.14	
^{90}Sr	1.5×10^{4}	1.0×10^{5}	1.63×10^{5}	8.57×10^{3}	7.28×10^{3}		82.8	111.	88.5	
^{99}Tc	1.9×10^{2}					5.43	44.9	59.9	48.6	
^{106}Ru	9.6×10^{3}	6.78×10^{3}		89.4						
^{125}Sb	4.6×10^{2}	4.52×10^{2}								
^{129}I	0.2									
^{134}Cs	3.1×10^{3}	6.32×10^{2}	2.79×10^{3}	1.22×10^{3}	1.18×10^{3}					
^{137}Cs	5.2×10^{5}	4.1×10^{5}	5.43×10^{5}	2.81×10^{5}	3.51×10^{5}	7.33×10^{3}	1.62×10^{4}	1.91×10^{4}	1.71×10^{4}	9.26
^{154}Eu		6.68×10^{3}	1.13×10^{4}	8.57×10^{3}	2.64×10^{3}					
^{155}Eu		1.33×10^{4}								
$^{239,240}Pu$					16		1.45	1.91	1.49	
^{241}Am	1.31×10^{3}				≤68	<5.3	<0.3	<0.3	<0.3	<0.4
Source[(a)]	Sc	Sc	Sc	Sc	Sc	W6	W6	W6	W6	W6

(a) Sc, Schulz 1978; W6, Weiss 1986; W8, Weiss and Schull 1988 a-i

TABLE 8 (contd)

Contituent	Riser 7 TY-103	Riser 7 TY-103	Riser 7 TY-103	Riser 15 TY-103	Riser 5 TY-103	Riser 8 TY-102	Riser 17 TY-105	Riser 12 A-103	Riser 8 A-103	C-104
^{14}C								1.1	0.94	1.33
^{60}Co	1.7	<0.4	<0.5	<2.0	4.1	<1.8	<0.5	<22	<16	$3.98x10^{2}$
^{90}Sr	16.2							$3.21x10^{3}$	$2.57x10^{3}$	$1.30x10^{4}$
^{99}Tc								$2.61x10^{2}$	$2.16x10^{2}$	27.8
^{106}Ru										
^{125}Sb										
^{129}I								$7.9x10^{-2}$	0.12	
^{134}Cs										
^{137}Cs	$2.96x10^{3}$	$3.17x10^{3}$	$4.54x10^{3}$	$2.12x10^{3}$	$6.43x10^{2}$	$1.62x10^{4}$	$3.58x10^{3}$	$3.87x10^{5}$	$4.06x10^{5}$	$1.18x10^{5}$
^{154}Eu										
^{155}Eu										
$^{239,240}Pu$								28.5	25.2	7.73
^{241}Am	<4.2	<13.1	<15.5	<10.6	<2.2	<58.4	<11.8	<1.5	<1.7	<0.8
Source(a)	W6	W6	W6	W6	W6	W6	W6	W8	W8	W8

(a) Sc, Schulz 1978; W6, Weiss 1986; W8, Weiss and Schull 1988 a-i

TABLE 8. (contd)

Contituent	Riser 17 A-106	Riser 20 A-106	Riser 4 A-102	Riser 1 BX-105	Riser 8 BX-105	Riser 2 C-103	Riser 8 C-105	Riser 1 C-106	Riser 1 BX-104	Riser 8 BX-104
^{14}C	0.98	1.09	0.94	0.63	0.58	0.37	2.82	0.35	1.61	0.84
^{60}Co	<125	<13	<47	1.8x10^{2}	1.77x10^{2}	<57	17	<12.7	<100	<90
^{90}Sr	3.04x10^{3}	3.91x10^{3}	1.55x10^{3}	1.1x10^{4}	1.2x10^{4}	1.95x10^{3}	5.12x10^{3}	1.65x10^{3}	2.71x10^{3}	2.35x10^{3}
^{99}Tc	1.9x10^{2}	1.51x10^{2}	3.18x10^{2}	1.2x10^{2}	1.09x10^{2}	37.	258	1.41x10^{2}	1.22x10^{2}	1.18x10^{2}
^{106}Ru										
^{125}Sb										
^{129}I	0.18	0.18	0.22	0.05	0.056	0.27	0.27	<0.014	0.11	0.11
^{134}Cs										
^{137}Cs	1.15x10^{4}	3.91x10^{5}	4.34x10^{5}	1.71x10^{5}	1.79x10^{5}	2.21x10^{4}	4.42x10^{5}	2.78x10^{4}	2.21x10^{4}	143x10^{5}
^{154}Eu										
^{155}Eu										
^{239,240}Pu	0.29	0.26	5.65	18.9	15.4	33.2	155.	97.8	17.9	18.4
^{241}Am	<4.9	<4.7	7.13	19.4	29.6	<3.74	<5.7	<13.9	<8.1	<3.7
Source$^{(a)}$	W8	W8	W8	W8	W8	W8	W8	W8	W8	W8

(a) Sc, Schulz 1978; W6, Weiss 1986; W8, Weiss and Schull 1988 a-i.

The radionuclide composition of drainable liquor is dominated by ^{137}Cs activities, which range between 10^2 to 5×10^5 $\mu Ci/L$ with a median value about 5×10^4 $\mu Ci/L$ and an arithmetic mean 1.72×10^5 $\mu Ci/L$. ^{90}Sr activities are generally second largest at values that range from 10 to $1 \times 10'$ $\mu Ci/L$ with a median value of 3×10^3 and an arithmetic mean of 1.6×10^4 $\mu Ci/L$. Of the other radionuclides commonly measured, drainable liquors generally contain about 1 $\mu Ci/L$ ^{14}C, 100 $\mu Ci/L$ ^{99}Tc, and 1 to 20 $\mu Ci/L$ $^{239,240}Pu$. The entire core generally also contains about 0.1 $\mu Ci/kg$ ^{129}I.

Schulz (1978), Weiss (1986), and Weiss and Schull (1988a-i) report data on water leaching of tank core material. Their data are presented in Tables 9 and 10. Schulz (1978) does not provide details on the time allocated for water leaching, and he used a low solution-to-solids ratio of about 2 mL/g of tank solids. Weiss and Schull used three successive leaches (30 min each at about 2 to 3 mL/g). All three leachates were combined to yield a final solution-to-solids ratio of about 7 to 10 mL/g of tank solids. The chemical nature of water leachates is similar to drainable liquors in that sodium, nitrate, and nitrite predominate and significant concentrations of Cr and total organic carbon are present. Water leachates also often contain between 10 and 50 g/L phosphate.

One leachate of core taken from riser 5 in TY-102 dissolved 494 g/L nitrate, considerably above the assumed upper limit of 300 g/L used as the constraint in HDWEIS performance assessments. This value is atypical of all other water leaching data that show the next highest nitrate concentration at 250 g/L. The range in concentrations in leachable nitrate is 0.1 to 494 g/L; the median value is 50 g/L, and the average is 100 g/L. The water-leachable sodium ranges from 0.003 to 198 g/L with a median value of about 70 g/L and an average of 59 g/L.

The water-leachable concentrations of nitrate and sodium are highest when the water-to-solids ratio is smallest. Schulz's data on water leaching are very similar to the concentrations found in drainable liquors suggesting that solubility limits may in fact be reached in Schulz's data. Weiss and Schull's data on water leachable concentrations show lower values than drainable liquors, suggesting that they did in fact dissolve all the salt cake

TABLE 9. Chemical Composition of Water Leachates of Tank Solids (g/L in leachate)

								Riser 5	Riser 5	Riser 3	Riser 15
	S-110	S-109	B-105	S-105	SX-102	SX-103	TX-116	TY-104	TY-104	TY-104	TY-104
pH			9.					12.0	11.9	11.7	12.0
Al	3.24	3.78	<0.11	2.65	2.40	1.48	0.03	0.28	0.32	0.705	0.354
Ba	<0.019	<0.034	<0.059	<0.007	<0.118			8.0007	0.0008	(0.0009	0.001
Bi								(8.010	<0.010	(0.009	<0.011
B											
Cd								<0.002	(0.002	(0.005	(0.002
Ca	<0.002	<0.009	<0.008	<0.002	0.006						
Cr	0.68	1.04	<0.007	0.728	0.728	0.348	0.120	0.624	0.664	1.18	1.12
Cu											
Fe	<0.004	<0.015	<0.009	<0.003	<0.004	<0.004	<0.10	8.869	0.075	0.167	0.032
Pb								(0.007	<0.008	(0.018	(0.008
Mg											
Mn	<0.003	<0.008	<0.004	<0.003	<0.001	<0.004		<0.019	(0.019	<0.003	<0.020
Ni	0.004	0.004	0.002	<0.003	0.006	0.006	<0.023	8.011	0.012	0.013	0.031
P								35.8	18.7	5.01	12.4
K											
Si	0.03	0.025	0.025	0.022	0.172		<0.21	8.073	8.084	0.027	0.467
Ag								8.803	0.003	8.005	0.001
Na	105.3	120.8	126.0	112.5	103.3	97.1	155.5	123.	81.6	66.6	73.4
Sr	<0.007	<0.006	<0.005	<0.032							
Zn	0.011	0.0007	0.004								
Zr								<0.004	<0.004	(0.006	(0.804
NO_3^-	248.6	249.9	56.3	243.0	238.7	247.4	170.5	33.1	34.7	80.5	58.4
NO_2^-	13.8	<0.9	54.7	5.06	6.9	4.14	1.24	9.3	9.77	16.9	12.9
CO_3^{2-}	3.3	16.8	<0.6	2.28	8.4	6.60	8.94	14.6	16.4	23.9	19.9
PO_4^{3-}		<0.95	46.5	2.56	0.72	0.62		107.3(a)	57.3(a)	15.4(a)	38.0(a)
SO_4^{2-}	1.2	4.61			1.92	0.84	36.9	<7.0	<2.71	3.68	<2.77
OH^-	4.2	6.12		3.4	2.9	0.66	3.6	1.58	1.24	0.778	1.56
TOC		0.64			2.52	2.52		1.81	2.27	1.73	0.741
U				0.0048	0.001	0.0001		0.092	0.026	0.019	0.015
Cl^-								<0.846	0.463	0.809	0.672
F^-								10.2	5.54	1.06	4.61
Water/Solids mL/g	2.80	2.00	2.00	2.13	2.13	2.13	1.53	9.31	9.56	9.12	9.62

(a) Calculated from ICP data for P

TABLE 9. (contd)

	Riser 8	Riser 8	Riser 5	Riser3	Riser 8	Riser 5	Riser 7	Riser 4	Riser 4	Riser 17	Riser 12
	TY-103	TY-103	TY-102	TY-101	TY-105	TY-106	TY-106	A-102	A-102	A-103	A-103
pH	11.2	10.9	8.53	8.20	8.68	8.81	7.51				
Al	0.014	0.004	<0.003	0.039	<0.002	<0.004	<0.002	1.6	1.65	1.85	1.94
Ba	0.0003	0.007	0.006	<0.0004	0.003	0.015	0.0005	<0.0003	<0.0005	<0.0006	<0.0006
Bi	0.007	<0.007	<0.010	<0.009	<0.007	<0.012	<0.007	<0.007	<0.012	<0.011	<0.011
B								0.002	0.002	0.004	0.002
Cd	<0.002	<0.002	<0.002	<0.002	<0.002	<0.003	<0.002	<0.002	<0.003	<0.009	<0.009
Ca								0.010	0.014	0.019	0.017
Cr	0.353	0.406	0.008	0.042	0.023	0.002	0.001	0.016	0.020	0.007	0.005
Cu									<0.001	0.0003	0.0006
Fe	0.071	0.156	0.001	0.053	<0.0006	0.008	<0.0006	<0.0005	<0.0003	<0.0008	<0.0008
Pb	<0.005	<0.005	<0.007	<0.006	<0.005	<0.009	<0.005	<0.005	<0.001	<0.033	<0.033
Mg								0.0001	0.0003	0.0005	0.0003
Mn	<0.012	<0.013	<0.018	<0.016	<0.013	<0.023	<0.013	0.012	<0.022	<0.004	<0.004
Ni	0.043	0.064	0.001	0.077	<0.001	<0.002	<0.001	0.002	0.002	0.005	0.005
P	9.88	6.31	8.59	5.39	2.62	6.05	2.32	0.64	0.566	0.246	0.298
K								0.32	0.347	0.310	0.293
Si	0.070	0.073	0.079	0.322	0.069	0.068	0.044	0.015	0.020	0.035	0.063
Ag	0.0006	<0.0006	<0.0009	<0.0008	<0.0007	<0.001	<0.0007	<0.0006	<0.001	<0.0003	<0.0003
Na	78.2	73.9	198.	75.0	81.8	103.	56.2	23.9	22.9	25.1	26.9
Sr									<0.0001		
Zn								0.0009			
Zr	<0.003	<0.003	<0.004	<0.004	<0.003	<0.005	<0.003	<0.005	<0.005	<0.002	<0.002
NO_3^-	129.	149	494	145	178	205	128	28.6	19.5	14.5	14.4
NO_2^-	7.51	8.10				7.03					
CO_3^{2-}	7.32	4.78				1.25					
PO_4^{3-}	30.3(a)	19.3(a)	26.3(a)	16.5(a)	8.03(a)	18.54(a)	7.11(a)	1.96(a)	1.73(a)	0.75(a)	0.91(a)
SO_4^{2-}	7.81	9.26		5.49		14.8					
OH^-	0.17	0.087	0.0005	0.212	0.053	0.001	0.00004				
TOC	0.50	0.99	0.130	0.253	0.471	1.70	1.40	0.935	1.13	1.02	0.992
U	0.058	0.041	0.009	0.011	0.014	0.005	<0.0006	0.001	0.001	0.001	0.001
Cl^-	1.04	1.20		0.757		1.51					
F^-	1.91	<0.86		3.37		<0.866					
Water/Solids mL/g	6.26	6.43	8.35	9.05	7.0	11.5	6.62	7.70	7.02	7.88	7.79

(a) Calculated from ICP data for P

TABLE 9. (contd)

	Riser 17	Riser 20	Riser 4	Riser 8	Riser 1	Riser 8	Riser 2	Riser 8	Riser 8	Riser 8	Riser 1
	A-106	A-106	BX-105	BX-105	BX-104	BX-104	C-103	C-103	C-104	C-105	C-106
pH											
Al	1.52	1.22	0.261	0.184	0.218	0.238	0.001	0.002	0.054	0.0009	0.003
Ba	<0.0003	<0.0003	0.0003	<0.0003	0.0001	0.0003	0.0003	0.0005	<0.0003	<0.0003	0.0004
Bi	<0.007	<0.007	<0.002	<0.002	<0.002	<0.002	0.012	0.013	<0.006	<0.006	0.002
B	0.003	0.002	0.001	0.0007	0.001	0.001			0.0003	0.0003	0.0006
Cd	<0.002	<0.0015	<0.0005	<0.0005	<0.0005	<0.0005	<0.002	0.0008	0.007	<0.005	<0.002
Ca	0.009	0.008	0.016	0.011	0.008	0.014	0.008	0.006	0.002	0.006	0.006
Cr	0.061	0.049	0.025	0.022	0.146	0.081	0.005		0.005	0.040	0.0002
Cu	0.0006	0.0006	0.0004	0.0005	0.003	0.0003	0.005		0.0003		0.0002
Fe	<0.0005	<0.0005	0.0004	0.0003	0.0002	0.0002	0.001	0.002	0.0007	<0.0004	<0.0001
Pb	<0.005	<0.005	0.006	0.007	<0.002	<0.002	<0.006	<0.003	<0.018	<0.018	<0.006
Mg	0.00008	0.0001	0.0004	0.0008	0.00007	0.0003	0.002	0.002	0.0005	0.002	0.002
Mn	<0.012	<0.012	0.004	<0.004	<0.004	0.004	0.002	0.003	0.002	<0.002	<0.0006
Ni	0.002	0.001	0.005	0.003	0.003	0.004	0.005	0.014	0.008	<0.0009	0.004
P	2.23	2.19	3.717	1.100	0.743	0.477	0.140	0.153	0.009	0.112	0.059
K	0.245	0.207	0.134	0.118	0.094	0.098	0.030	0.036	0.035	0.033	0.021
Si	0.009	0.011	0.154	0.069	0.026	0.024	0.009	0.032	0.213	0.004	0.003
Ag	<0.0006	<0.0006	<0.0002	<0.0002	<0.0002	<0.0002	0.002	0.003	0.0001	0.0001	0.0002
Na	6.45	20.7	16.4	8.35	10.3	8.53	0.003	3.76	5.79	2.97	6.08
Sr	<0.00006		0.0001	0.102		0.00002					
Zn	0.0005										
Zr	<0.003	<0.003	<0.0009	<0.0009	<0.0009	<0.0009	0.002	0.015	<0.001	<0.001	0.015
NO_3^-	10.85	9.92	5.58	4.774	8.000	6.70	0.248	0.992	2.36	0.87	0.124
NO_2^-											
CO_3^{2-}											
PO_4^{3-}	6.83(a)	6.71(a)	11.39(a)	3.37(a)	2.28(a)	1.46(a)	0.43(a)	0.47(a)	0.028(a)	0.343(a)	0.181(a)
SO_4^{2-}											
OH^-											
TOC	0.833	0.946	0.593	0.275	0.340	0.516	0.583	0.678	0.440	0.085	0.617
U	0.001	0.002	0.000	0.000	0.001	0.001	0.315	0.181	0.003	0.055	0.001
Cl^-											
F											
Water/Solids mL/g	7.48	7.56	6.35	8.53	5.24	5.23	6.69	3.88	10.03	11.75	7.48

(a) Calculated from ICP data for P.

TABLE 10. Radionuclide Composition of Water Leachates of Tank Solids (μCi/L in leachate)

Constituent	S-110	S-109	B-105	S-105	SX-102	SX-103	TX-116	Riser 5[a] TY-104	Riser 5[b] TY-104	Riser 3 TY-104	Riser15 TY-104
^{14}C								0.049	0.20	0.10	<0.05
^{60}Co	<1.1	0.08		<2.2	4.8	3.2		<1.7	<2.1	<3.1	<4.3
^{90}Sr	6.42×10^2	3.40×10^2	4.64×10^2	22.9	4.57×10^Z	1.78×10^3	9.18	1.1×10^2	60.2	1.2×10^2	61.2
^{99}Tc	13.1	3.0	0.6	9.3	13.3	9.3		2.0	1.75	3.1	2.71
^{106}Ru	93	6.23×10^2		2.1×10^2	1.82×10^3	2.20×10^2					
^{125}Sb	<35	4.8		<64	<61	1.2					
^{129}I				0.0005	0.006	0.002		<47[a]	<0.03[a]	<90[a]	<0.06[a]
^{134}Cs	23.5		<0.7	26.1	78.5		16.7				
^{137}Cs	1.36×10^4	3.79×10^4	2.68×10^2	1.51×10^4	3.54×10^4	2.1×10^4	5.89×10^3	7.05×10^3	7.97×10^3	1.15×10^4	3.93×10^4
^{154}Eu	<4.5	<0.7			12.3	14.9					
^{155}Eu	20.4	2.1		<20	82	14.9					
^{239,240}Pu	0.20		<0.07	0.47	0.41	0.18		<0.71	<0.76	<0.76	0.35
^{241}Am	0.009		<0.007	<0.002	0.41	0.84		<1.9	<1.9	<1.8	<2.2
^{237}Np				<0.006	0.004	0.006					
Water/Solids (ml/g)	2.00	2.00	2.00	2.13	2.13	2.13	1.53	9.31	9.56	9.12	9.62

(a) ^{129}I was measured on bulk solid sample not just water leachate (for conservatism one could assume all ^{129}I would dissolve in water)

TABLE 10. (contd)

	Riser 8	Riser 8	Riser 5	Riser 3	Riser 8	Riser 5	Riser 7	Riser 4	Riser 4	Riser 17	Riser 12
Constituent	TY-103	TY-103	TY-102	TY-101	TY-105	TY-106	TY-106	A-102	A-102	A-103	A-103
^{14}C	<0.04	<0.04	(0.02	(8.02	<0.02	0.03	(0.02	0.22	fl.09	0.33	0.32
^{60}Co	1.2	0.9	<0.85	<0.11	<0.6	<0.25	1.91	<1.02	<0.34	4.66	<3.9
^{90}Sr	28.9	19.7	$1.23x10^{2}$	<0.4	44.5	91.2	$1.62x10^{2}$	92.1	$1.39x10^{2}$	$2.34x10^{2}$	$2.24x10^{2}$
^{99}Tc	1.01	1.1	0.05	0.04	2.58	20.6	0.44	14.6	12.4	15.5	14.4
^{106}Ru											
^{125}Sb											
^{129}I	<49(a)	<2.7(a)	<0.02(a)	<0.05(a)	<0.03(a)	<13(a)	<120(a)	<0.04(a)	<0.035(a)		0.019(a)
^{134}Cs											
^{137}Cs	1.13	<0.5	$2.62x10^{3}$	0.26	$6.46x10^{3}$	$4.69x10^{3}$	$1.57x10^{3}$	$2.03x10^{4}$	$5.39x10^{3}$	$2.54x10^{4}$	$2.56x10^{4}$
^{154}Eu											
^{155}Eu											
^{239,240}Pu	<0.18	<0.17	<0.63	<0.57	<0.76	<0.73	<0.46	7.41	10.9	5.43	6.12
^{241}Am	<1.28	<0.96	<1.97	<0.36	<1.5	<10.2	<1.7	<0.52	<0.16	<0.97	7.65
^{237}Np											
Water/Solids (ml/g)	6.26	6.43	8.35	9.05	7.0	11.5	6.62	7.70	7.02	7.88	7.79

(a) ^{129}I was measured on bulk solid sample not just water leachate (for conservatism one could assume all ^{129}I would dissolve in water)

TABLE 10. (contd)

Constituent	Riser 17 A-106	Riser 20 A-106	Riser 4 BX-105	Riser 8 BX-105	Riser 1 EX-104	Riser 8 BS-104	Riser 2 C-103	Riser 8 C-103	Riser 8 C-104	Riser 8 C-105	Riser 1 C-106
^{14}C	0.14	0.08	0.335	(0.067	0.120	<0.067	0.057	0.075	0.062	0.056	0.031
^{60}Co	(0.75	(0.28	7.86	4.45	2.87	5.42	15.1	14.4	2.72	(0.02	3.73
^{90}Sr	4.25×10^{2}	5.16×10^{2}	4.46×10^{2}	2.95×10^{2}	37.6	69.2	1.91×10^{2}	2.06×10^{2}	2.85	36.6	27.3
^{99}Tc	15.3	14.4	5.72	4.68	6.39	6.18	3.17	3.41	2.27	5.77	4.72
^{106}Ru											
^{125}Sb											
^{129}I	0.14(a)	0.82(a)	<0.037(a)	<0.023(a)	0.052(a)	<0.035(a)	<0.023(a)			0.12(a)	0.081(a)
^{134}Cs											
^{137}Cs	2.33×10^{4}	4.69×10^{3}	7.72×10^{3}	6.31×10^{3}	1.13×10^{4}	1.23×10^{4}	3.97×10^{3}	5.72×10^{3}	4.92×10^{2}	1.02×10^{3}	8.32×10^{3}
^{154}Eu											
^{155}Eu											
^{239,240}Pu	6.7	12.8	2.98	0.497	0.404	0.254	1.40	1.12	0.419	0.361	32.8
^{241}Am	<0.41	<0.50	3.35	0.50	<0.39	1.10	<1.52	<1.66	<0.62	96.0	<2.0
^{237}Np											
Water/Solids (ml/g)	7.48	7.56	6.35	6.53	5.24	5.23	6.69	3.88	10.03	11.75	7.48

(a) ^{129}I was measured on bulk solid sample not just water leachate (for conservatism one could assume all ^{129}I would dissolve in water).

and added water that only diluted the solutes. Weiss and Schull's data mightaccurately reflect the mass of constituents readily dissolved by water but likely do not reflect solubility-limited conditions where excess solids must be present (i.e., the data ensure undersaturation of sodium nitrate and other readily dissolvable salts by using excess water to dilute/dissolve all salts). Water leachates of tank solids contain the same radionuclides as drainable liquors. ^{137}Cs again dominates with values ranging from 0.26 to 3.93 x 10^4 μCi/L. The median value is 5.4 x 10^3 μCi/L, and the average value is 1 x 10^4 μCi/L. The median and average values are factors of 10 and 20 lower, respectively, than values for drainable liquor.

^{90}Sr is the second most abundant radionuclide found in water leachates of tank solids. Water leachates range from 0.4 to 1780 μCi/L ^{90}Sr with median and mean values of 120 and 226 μCi/L, respectively. These values are 25 and 70 times lower than values in drainable liquors. Water leachates also contain <0.1 μCi/L ^{14}C, ~5 μCi/L ^{99}Tc, and, infrequently, small amounts of plutonium and cobalt.

The radionuclide data also suggest that the water leachates are more dilute than drainable liquors. The data also suggest that radionuclides such as ^{90}Sr, Pu, and ^{60}Co are not as prone as ^{137}Cs and ^{99}Tc to partition into water. It is not possible to judge whether solubility reactions are limiting water leaching of any radionuclides from Weiss and Schull's data.

Delegard and Gallagher (1983) and Delegard, Barney and Gallagher (1984) performed laboratory experiments on simulated high-level waste (HLW) solutions to determine empirical solubility limits for Co, Sr, Np, Pu, and Am. Twelve components of HLW solutions were studied: $NaNO_3$, $NaNO_2$, NaOH, $NaAlO_2$, Na_2CO_3, Na_2SO_4, Na_3PO_4, NaF, HEDTA, EDTA, sodium hydroxyacetate, and trisodium citrate.

In the first set of tests two levels were chosen for each of these 12 components as shown in Table 11. An experiment was then performed where 20 different solution combinations of the 12 components were traced with radionuclides. The tracers were radionuclides in nitric acid. Small aliquots of the nitric acid stock solution were taken to dryness and 5 mL of the synthetic HLW solution added. Dissolution of the dried stock solution into the synthetic HLW solution was allowed to occur over 2 weeks. After the 2-week contact time the solutions were filtered through 0.003-μm-pore-size ultrafilters to

TABLE 11. Component Concentration Values for Screening Tests

Components	Concentration (M)	
	High	Low
$NaNO_3$	2	0
$NaNO_2$	2	0
NaOH	4	1
$NaAlO_2$	0.5	0
Na_2CO_3	0.05	0
Na_2SO_4	0.01	0
Na_3PO_4	0.01	0
NaF	0.01	0
Na_3HEDTA	0.1	0
Na_4EDTA	0.05	0
Na hydroxyacetate	0.1	0
Na_3 citrate	0.03	0

remove undissolved solids. The filtered solutions were analyzed (gamma ray for ^{60}Co, ^{85}Sr, ^{237}Np, and ^{241}Am, and low-energy x-ray for ^{238}Pu).

The original activity of spike added was known and each filtrate's activity was determined. Plackett-Burman (1946) statistics were used to analyze the data to see which components in the HLW significantly increased or decreased solubility. In many experiments all the cobalt, strontium, and americium was dissolved. In no cases did all the Np and Pu dissolve. Initial activities used are shown in Table 12.

The results suggest up to 7500 μCi/L ^{60}Co, 7070 μCi/L of ^{241}Am, and less than 1230 μCi/L of ^{237}Np could be found in solution in SST liquors. The largest actually observed values, presented in Tables 8 and 10, are one-fourth the values that Delegard and Gallagher (1983) report. The activities of ^{85}Sr and ^{238}Pu used in the lab tests are small (on a mass basis) compared to the actual ^{90}Sr and ^{239}Pu concentrations found in drainable liquors such that comparisons cannot be made.

TABLE 12. Initial Activities of Tracers (μCi/L)

	7500
^{85}Sr	832
^{237}Np	1230
^{238}Pu	9004
^{241}Am	7070

In general, Delegard and Gallagher's laboratory tests to do not set upper-limit empirical solubility limits but they do suggest which variables increase or decrease the concentrations found in solution. Both EDTA and HEDTA were found to increase the solution concentrate of Co, Sr, and Am. Hydroxyacetate and citrate also increase Am solution concentrations.

Nine of 12 components statistically influence Np solution concentrations but $NaNO_2$ effects are most dominant. Nitrite appears to reduce Np(V) to Np(IV), which lowers solubility. Plutonium solution concentrations were more sensitive to NO_3^-, OH^-, and AlO_2^- contents than organic chelating agent contents. This observation is somewhat surprising.

More detailed testing using three-level factorial design was performed for Sr, Am, and Pu isotopes, and again Sr and Am solution concentrations were strongly dependent on HEDTA and EDTA concentrations. The plutonium solution concentration was most sensitive to NaOH concentration. Delegard and Gallagher (1983) present solubility predictor equations based on the three-level factorial design tests that are reproduced in Table 13. We used the predictor equations and data from Schulz (1978) and Weiss and Schull (1988a-i) to compare predicted activities with actual tank liquor values. To do this comparison for Sr and Am would require that the available dissolved organic carbon value (see Table 7) could be distributed among HEDTA, EDTA, citrate, and hydroxyacetate.

For Pu predictions it is possible to compare the predictor equation with available data (Table 7) for OH^-, NO_3^-, and AlO_2^- contents if we assume that all the Al in tank liquors is present as aluminate. [Weiss (1986) and Weiss and Schull (1988a-i) do not present data for free hydroxide content, so it is impossible to make direct comparisons.] Schulz (1978) contains three drainable

TABLE 13. Radioelement Solubility Prediction Equations[(a)]

Radioelement	Solubility Prediction Equation (log M)[(b)]	R^2
Sr	$\log(\mathrm{Sr}) = -1.1211 + 0.5015\log(\mathrm{HEDTA}) + 0.4830\log(\mathrm{EDTA}) + 0.0502[\log(\mathrm{HEDTA})]^2 + 0.0451[\log(\mathrm{EDTA})]^2 - 0.0282[\log(\mathrm{HEDTA}][\log(\mathrm{EDTA})]$	0.918
Pu	$\log(\mathrm{Pu}) = -5.6688 + 0.1385\log(\mathrm{NaNO_3}) - 0.1794\log(\mathrm{NaOH}) + 0.1175\log(\mathrm{NaAlO_2}) + 0.0125[\log(\mathrm{NaNO_3})]^2 + 2.0957[\log(\mathrm{NaOH})]^2 + 0.00090[\log(\mathrm{NaAlO_2})]^2$	0.975
Am	$\log(\mathrm{Am}) = -3.2202 + 0.3132\log(\mathrm{HEDTA}) + 0.1537\log(\mathrm{OAc})^{(c)} + 0.5082\log(\mathrm{citrate}) + 0.0388[\log(\mathrm{HEDTA})]^2 + 0.0206[\log(\mathrm{OAc})]^2 + 0.0475[\log(\mathrm{citrate})]^2 - 0.0296[\log(\mathrm{HEDTA})][\log(\mathrm{OAc})] - 0.0433[\log(\mathrm{HEDTA})][\log(\mathrm{citrate})]$	9.056

(a) See Delegard and Gallagher (1983) for details.

(b) To convert mol/L total strontium to Ci ^{90}Sr/L, change the constant in equation from -1.1211 to 2.5187.

To convert mol/L total plutonium to Ci ^{239,240}Pu/L, change the constant in equation from -5.6688 to -4.4161.

To convert mol/L total americium to Ci ^{241}Am/L, change the constant in equation from -3.2202 to -0.3025.

(c) OAc, hydroxyacetate.

TABLE 14. Comparison of Predicted Pu Activity Versus Observed in Tank Liquors (μCi/L)

Tank	Predicted	Observed
SY 101	60.1	0.032
TX 118	44.4	1.6
Composite	57.2	0.4

liquors (tank SY-101, TX-118, and a composite of several tanks) with all thenecessary data to predict Pu activity based on Table 13. The results are shown in Table 14. The predicted Pu activities cluster between 45 and 60 μCi/L but the observed values range from 0.03 to 1.6 μCi/L.

In general, it appears that the Delegard and Gallagher (1983) laboratory data on solubility are only qualitatively useful in that they point out important parameters that influence nuclide solution concentrations but do not agree with actual tank liquor observations. A measure of free hydroxide and actual composition of the dissolved organic carbon would be useful analyses to perform in future tank liquor characterizations to allow further comparisons with Table 13 predictor equations. At present there does not seem to be a better or more defensible method for choosing an empirical release limit (constant concentration or solubility limit) than relying upon the maximum or some statistical percentile such as the 95% percentile value actually measured in drainable tank liquor.

The data presented in Tables 15 and 8 (drainable liquor values) could be used as empirical solubility limits for selected contaminants. This was the approach used in the HDWEIS but only the data on six tanks (Schulz 1978) were available. Table 15 compares the HDWEIS constant solubility release limits to values observed in the combined data base (Schulz 1978; Weiss 1986; Weiss and Schull 1988a-i). The values in the first column of Table 15 are our recommendation for the values to use for future performance assessment activities on release from SST when the release model chosen is a constant concentration-limited release. The values are derived from measurements on actual tank liquors as discussed. For convenience we compare these values to those used by the HDWEIS and Droppo and co-workers' recent efforts.

TABLE 15. Comparison of Constant Concentration Constraint Values(a)

Chemicals	This Paper	HDWEIS	Droppo and Co-workers
Al	40		0.34
Ba	0.06		0.007
Bi	0.2		
B	0.06		
Cd	0.02	1.1×10^{-5}	
Ca	0.2		
Cr	10.	4.9	
Co	0.001		
Cu	0.2		
Fe	2		0.2
Pb	0.1		0.0077
Mg	0.01		
Mn	0.2		0.014
Ni	0.2		0.023
K	10		
Si	1		
Ag	0.02		0.0017
Na	300		91.9
Sr	0.01		
Zn	0.01		
Zr	0.4		0.345
NO_3	360	300	13.1
NO_2	60	14	125
CO_3	40		
PO_4	15		
SO_4	15		8.46
TOC	10 - 100(a)		
C1	5		13.5
F	0.5	0.002	3.55
U	2.6	3.6×10^{-3}	

TABLE 15. (contd)

Radionuclides	This Paper	HDWEIS
^{14}C	3	7.6
^{60}Co	3×10^3	
^{90}Sr	1.5×10^5	1.6×10^5
^{99}Tc	300	430
^{106}Ru	1×10^4	
^{125}Sb	500	
^{129}I	0.3	0.2
^{137}Cs	5×10^5	6.7×10^5
^{154}Eu	1×10^4	
$^{239,240}Pu$	100	1.6
^{241}Am	50 - 1500(b)	1.3×10^3
^{63}Ni	1.5×10^3	1.5×10^3
^{93}Zr	35	35
^{151}Sm	7.2×10^3	7.2×10^3
^{237}Np	140(c)	0.5

(a) Units for chemicals, g/L; for radionuclides, μCi/L.
(b) Highly variable; dependent on tank selected.
(c) Experimental value from Delegard and Gallagher (1983).

We further recommend that these constant concentration release values be coupled with data available from Weiss and Schull that show the percentage of total tank inventory that is water soluble (see Table 4). That is, the preferred conceptual release model would allow a constituent to release at the concentration listed in Table 15 until the percentage of total tank mass that is water leachable (Table 4) is reached. At this point no more mass would leach. This approach would lead to a different leach period for each species as opposed to a uniform leach period as dictated by nitrate-based congruent depletion.

2.3.2 Grout

Hanford grouts are formed by mixing liquid low-level nuclear waste with dry solids, including cement, blast furnace slag, fly ash, clay, and sometimes other additives. The cement and blast furnace slag act as a binder and the fly ash is added to react with excess calcium hydroxide from the cement, thereby reducing permeability and leach rates. Fly ash also improves the pumpability of the slurry. Clays are used as suspending agents and to adsorb or sequester specific contaminants. For each specific liquid waste type, a grout formulation will be developed to optimize the waste form's processibility, stability, and long-term leaching characteristics.

During hydration and curing, the permeability of the grout decreases significantly. This serves to physically isolate waste components inside the grout from future water contact. Furthermore, some of the waste constituents chemically react with the grout minerals or additives and become more strongly bound in the grout matrix. Cations that hydrolyze at high pH, such as many metals and the actinides, could be expected to form highly insoluble hydroxides in the high pH environment inside the grout. Many Hanford tank wastes contain appreciable concentrations of phosphate, which also forms very insoluble compounds with Ca, Sr, Pb, Am, and several other metals. Certain clay additives adsorb cations such as cesium. Matsuzuru and Ito (1977) show that the addition of 10% to 20% by weight zeolite (similar to clay) to the dry grout ingredients can decrease the effective leach rate of cesium by two to three orders of magnitude. Thus, some waste constituents are sequestered in the grout by strong chemical bonds but other waste constituents are physically isolated in the small pores of the grout.

Water percolating through Hanford sediments may contact and leach waste constituents from the grout. The amount of percolating water in the Hanford shallow land burial setting is controlled largely by the amount of recharge in the overlying vadose sediments and the efficacy of the gravel cocoon that surrounds the vault.

Qualitative permeability tests conducted at PNL have shown that more than 110 lb/in.^{2} overpressure is required to force water to flow through grout. Thus, it seems reasonable that any recharge water not diverted by water barriers that will be a part of the original emplacement will advect around the grout monoliths (provided that they are not fractured). Because the surrounding sediments are rather coarse and permeable, any water flow should be through the sediments. The pore water at the grout surface will allow diffusion into and out of the grout, but will not flow through the grout. Thus, a waste-release model based on diffusion and chemical reaction processes seems appropriate for the purpose of projecting the long-term impacts of grout disposal.

An effective diffusion model is used because it is simple and yet satisfactorily describes most laboratory leach data over the months to a few years during which tests have been conducted. The leach rate is related to the square root of the effective diffusion coefficient, D_e. Data collection for the release of contaminants from Hanford grout is occurring through the Hanford Grout Technology Program at PNL, Oak Ridge National Laboratory (ORNL), and Westinghouse Hanford Company.

To date, leach results on three generic tank wastes [phosphate/sulfate waste (PSW), cladding removal waste (CRW), and double-shell slurry feed (DSSF) waste] have been published. The double-shell slurry feed waste grout studies continue. The liquid waste streams that constitute PSW, CRW, and DSSF are generally neutralized slurries of high-salt wastes replete with suspended solids. Generic compositions for such wastes used in PNL grout leaching studies are found in Table 16. Each type of liquid waste stream is solidified in an optimized blend of liquid waste and dry materials. Grout recipes used at PNL are listed in Table 17. The recipes used at ORNL and Westinghouse Hanford Company are similar, and specific details can be found in Tallent et al. (1988) and Rebegay and Dodd (1989).

TABLE 16. Chemical Composition of Liquid Waste Streams That Were Solidified into Grouts (mg/L)

	Phosphate-Sulfate Waste			Double-Shell Slurry Feed	
	60% to 40%	70% to 30%	CRW	T-106AN	Generic
pH	12	12	>12	>12	>12
Al		5	35	10,800	40,500
B		0.07	<0.02	28.6	210
Ba		0.07	--	--	1,247
Ca		9.7	0.3	70	400
Co		<0.1	<0.1	--	--
Cr		3.9	0.2	662	2,309
Cu		0.2	--	1.5	12.7
Fe		208	<0.5	--	2,815
K		<4	25	1,150	19,433
Li		0.2	<0.05	--	<0.5
Mg		0.6	<0.06	--	<0.5
Mn		17.2	<0.02	--	5,494
Mo		--	0.33	31	97
Na	7,400	12,872.0	19,900.	93,800	241,500
Ni		1.1	<0.2	27	58.6
Pb		<0.6	<0.6	--	5.1
Si		0.3	31	55	110
Sr		0.04	--	--	--
Zn		1.24	0.07	--	3,250
Zr		0.10	1.2	--	<1
F		47	10,617	170	1,120
Cl		26	507	2,438	7,730
NO_3		498	2,540	88,500	308,760
NO_2	727	--	400	38,250	45,954
PO_4	8,607	18,200	<1	2,650	10,080
SO_4	1,152	1,300	--	15,225	11,305
NH_4	--	--	12,582	--	<1
CO_3	--	--	--	22,920	17,940
TOC	--	--	--	5,292	320

TABLE 17. Recipes to Solidify Hanford Grouts

Phosphate-Sulfate Waste (PSW)

Solids	Wt%
Portland type I and II cement	41
Class F fly ash	40
Attapulgite clay	11
Indian red pottery clay	8

Ratio: 840 g solid blend/liter of liquid waste

Cladding Removal Waste (CRW)

Solids	Wt%
Portland type III LA cement	42
Class F fly ash	40
Calcium hydroxide	10
Indian red pottery clay	8

Ratio: 840 g solid blend/liter of li'quid waste

T106-AN

Solids	Wt%
Portland type 1/1I cement	5
Class F fly ash	47.5
Ground blast furnace slag	47.5

Ratio: 1080 g solid blend/liter of liquid waste

Double-Shell Slurry Feed (DSSF)

Solids	Wt%
Portland type 1/11 cement	6
Class F fly ash	47
Ground blast furnace slag	47

Ratio: 1080 g solid blend/liter of liquid waste

The effective diffusion coefficients for selected radionuclides and chemicals for the three generic liquid waste streams are shown in Table 18. Table 18 also lists currently preferred values for species that have not been studied as yet but are of interest to performance assessment activities. Specific details can be found in Serne et al. (1987, 1989a,b and Serne (1989)). The effective diffuson coefficients vary more than seven orders of magnitude (from 5×10^{-8} to below 10^{-15} cm^2/s). Much of the variation is likely caused by chemical reaction (e.g., solubility reactions) between contaminants and grout-forming material. For other constituents, such as nitrate, there appear to be almost two orders of magnitude variation between grouts, perhaps an indication of differences in physical attributes such as porosity and tortuosity. Some of the variation is also caused by the variable length of time each experiment was performed, effects of temperature during curing, and length of curing time before starting leach tests.

The values reported in Table 18 are calculated using Equation (1) that requires D_e to remain constant with time. The actual data show leaching to slow down with time. It is not clear at present whether the data are better treated by alternative expressions such as Equation (4).

Two other issues, whether grout specimens of differing sizes yield similar effective diffusion coefficients and whether the D_e value is sensitive to starting inventory, are being addressed. There are data that suggest nitrate, nitrite, sodium, potassium, molybdenum, chromium, fluoride, sulfate, boron, cesium, and technetium are released from cementitious waste forms of variable size (1 cm in diameter x 1 cm long to 55 cm in diameter x 55 cm long) in proportions that yield a relatively constant D_e value. Specifics are discussed Kalb and Columbo (1984), Dayal, Arora and Morcos (1983), Morcos, Dayal and Weiss (1982), Morcos and Dayal (1982), Pietrzak et al. (1989), and Serne (1989). Currently there are no reports that show data in which D_e for constituents vary significantly with specimen size.

The effects of variable inventories are less well studied. For major waste constituents, changing the loading (waste liquid to solid blends ratio) generally impacts the solid waste's leachability. Increasing the liquid waste portion increases waste-form leaching. For trace contaminants, the effects of variable waste loading is less well defined. Matsuzuru and Moriyama

TABLE 18. Review of Available D_e Values for Hanford Grouts (cm^2/s)

Species	PSW	CRW	T-106 AN	DSSF	Default Value(a)
H	------------	------------	------------	------------	5x10^{-8} conservative estimate
B	<10^{-12} to 5x10^{-12}	10^{-12}x to 5x10^{-10}	------------	5x10^{-10}	5x10^{-10}
C	5x10^{-14}	2x10^{-13}	<10^{-11}	------------	10^{-12}
NO_3, NO_2	10^{-10} to 10^{-9}	1.5±0.5x10^{-9}	7±0.5x10^{-9}	3±3x10^{-8}	grout dependent
F	------------	10^{-12} to 5x10^{-11}	8.5±0.1x10^{-9}	1x10^{-11}	1x10^{-10}
Na	1 to 3 x 10^{-9}	6±2x10^{-9}	6±1x10^{-9}	4±2x10^{-8}	grout dependent
SO_4	10^{-12} to 10^{-11}	10^{-9} to 10^{-8}	------------	4±2x10^{-8}	grout dependent
Cl	------------	------------	9±1x10^{-9}	------------	1x10^{-8}
K	4 to 9x10^{-10}	1.3±0.4x10^{-9}	------------	2±1x10^{-8}	1x10^{-8}
Cr	10^{-12} to <10^{-10}	------------	------------	6±5x10^{-11}	1x10^{-10}
Mn	10^{-13} to 10^{-11}	------------	------------	------------	5x10^{-11} conservative estimate
Fe	------------	------------	------------	------------	5x10^{-11} conservative estimate
Co	10^{-13} to 10^{-11}	------------	<2x10^{-11}	------------	5x10^{-11}
Ni	------------	------------	4.3±0.2x10^{-10}	------------	5x10^{-10} conservative estimate
Cu	------------	------------	------------	------------	5x10^{-10} conservative estimate
Zn	------------	------------	------------	------------	5x10^{-10} conservative estimate
As	<10^{-12} to <10^{-10}	------------	------------	------------	5x10^{-10} conservative estimate
Se	10^{-12} to 5x10^{-11}	------------	------------	1.5±0.5x10^{-10}	2x10^{-10} conservative estimate
Sr	10^{-13} to 10^{-12}	10^{-12} to 10^{-10}	2x10^{-15}	------------	5x10^{-11}

TABLE 18. (contd)

Species	PSW	CRW	T-106 AN	DSSF	Default Value(a)
Zr	------------	$<10^{-12}$	------------	------------	$1x10^{-12}$
Mo	------------	------------	$9\pm1x10^{-9}$	$1.4\pm0.8x10^{-8}$	$2x10^{-8}$
Tc	$4x10^{-11}$	10^{-12} to 10^{-10}	$<7x10^{-8}$(b)	$5\pm4x10^{-9}$	grout dependent
Ag	10^{-13} to $5x10^{-11}$	------------	------------	------------	$5x10^{-11}$
Cd	$<10^{-12}$ to $<10^{-10}$	------------	------------	------------	$5x10^{-10}$ conservative estimate
I	10^{-10} to $5x10^{-9}$	3.4 to $34x10^{-9}$	5 to 8 x 10^{-8}	$2\pm2x10^{-8}$	$5x10^{-8}$
Cs	10^{-14} to 10^{-12}	1 to $5x10^{-15}$	$3x10^{-10}$	------------	$5x10^{-10}$ conservative estimate
Ba	------------	------------	------------	------------	$5x10^{-11}$ Sr analog
Hg	$<10^{-10}$ to $<10^{-8}$	------------	------------	------------	$5x10^{-10}$ conserative estimate
Pb	$<10^{-11}$ to $<10^{-18}$	------------	------------	------------	$1x10^{-11}$
Lanthanides (Ce-Lu)	------------	------------	------------	------------	$5x10^{-11}$ Sr analog
Th	------------	------------	------------	------------	$1x10^{-12}$ U analog
U	10^{-15} to 10^{-11}	------------	------------	------------	$1x10^{-12}$
Np	------------	------------	------------	------------	$1x10^{-11}$ conservative estimate
Pu	------------	10^{-16} to 10^{-15}	------------	------------	$5x10^{-13}$
Am	------------	10^{-17} to 10^{-16}	$2x10^{-13}$	------------	$5x10^{-13}$
Cm	------------	------------	------------	------------	$5x10^{-13}$ Am analog

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(a) Default values should be used for generic grout performance assessment calculations when actual grout-specific data are lacking.

(b) Value is questionable based on difficulty in measuring original waste inventory (see Serne et al. 1989a).

(1982) found ^{3}H and ^{90}Sr leach rates increased but ^{137}Cs, ^{60}Co, and ^{144}Ce leach rates were unaffected as leaching increased. Tests where only the inventory of trace constituents is changed have been performed by Stegemann and Côté (1989) and Serne (1989). Stegemann and Côté (1989) varied the mass of chromium and phenol solidified in a grout and Serne (1989) varied the mass of selenium and activity of ^{125}I and ^{99}Tc in a Hanford DSSF grout. The calculated D_e values for selenium, ^{125}I, and phenol remained constant with inventory changes while chromium D_e values decreased as chromium loading increased. ^{99}Tc D_e values showed a complicated variation with larger D_e values when the liquid waste contained 1 mCi/L and smaller D_e values at both 0.1 mCi/L and 10 mCi/L loadings.

Stegemann and Côté (1989) attribute the apparent chromium leaching decrease to solubility processes. Because they loaded quite large concentrations (1, 8, 50, and 100 g/L) of Cr in their liquid waste, it might not be surprising that solubility reactions were important. The concentrations of trace metals in Hanford liquid waste streams destined for grout disposal generally do not exceed 1 g/L so the relevancy of Stegemann and Côté's results is not certain. Serne (1989) used approximately 0.005, 0.05, and 0.5 g/L selenium in inventory scale-up tests and found no effect on calculated D_e values.

A third issue is curing temperature effects on grout leaching. Recently Lokken (personal communication, PNL) observed that the leach rates (leach tests at room temperature) of nitrate, nitrite, sodium, and organic carbon from DSSF are quite variable and depend on the temperature history of curing the specimens. The leach rates tend to steadily increase for these constituents as the curing temperature was raised from room temperature to 95°C, but at curing temperatures above 105°C resultant leach rates were dramatically lower. However, the effects of elevated temperature during curing could have volatilized constituents such that the leach data could be misleading. Alternatively, the data may suggest that higher temperature promotes reactions that form a better waste form. A key question is whether the same reactions occur at lower temperatures at later times. This question is related to the following issue warranting further study, that is, effects of grout aging on contaminant leach rates. The issue is whether grout that has fully hydrated and existed in the environment for hundreds or thousands of years shows contaminant leach rates similar to "fresh" grout.

2.3.3 Contaminated Soil Sites

The Hanford soils/sediments have been used to dispose numerous types of liquid wastes, ranging from low ionic strength, slightly radioactive cooling waters to high-salt, high-acid (pH ≤ 1), or neutral to basic laboratory and process wastes. Some of the liquid wastes also contained organic solvents and organic complexing agents. Many of the waste streams, especially those that were neutralized, contain suspended particles of insoluble compounds such as plutonium, americium, iron, etc. Disposal schemes for most liquid wastes included injection into reverse wells, covered French drains, and cribs (covered drain fields). Several of these disposal facilities have been studied to understand the distribution of plutonium, americium, strontium, and cesium in the surrounding sediments. The concentrations of these radionuclides were determined both by borehole logging (gamma and neutron counting), and actual sediment counting (characteristic x-ray counting, gamma ray analysis, and total digestion and alpha or beta counting). In some instances the sediment particle size was also measured. For selected studies sediment moisture content, total calcium carbonate content, and saturated paste pH were recorded.

Most studies describe the spatial distribution of radionuclides but do not address potential for further release with wetting by recharge water. Only a few studies address how the radionuclides may have become attached to the sediments or how the contaminated sediments react on rewetting with recharge water.

Smith and Kasper (1983) discuss field data on cribs 216-A-8, 216-A-10, 216-A-30, 216-A-36B, 216-A-37-1, and 216-U-12. All six have been gamma ray logged, while four have had ^{90}Sr desorption determined ($R_{d_{Sr}}$ = 0.2 to 64, dependent on pH and composition of liquid waste) from contaminated sediments, and for one (216-A-36B) a desorption cesium R_d value ($R_{d_{Cs}}$ = 5.7) was measured.

Crib 216-A-8 received low-salt liquid wastes and condensates from self-boiling tanks. Volatile organics also reached the crib as evidenced by organic-rich (3-m-thick) sediments below the crib bottom, based on core analyses. At the time of Smith and Kasper's investigation the crib had received the inventory listed in Table 19 (decay corrected to 1/1/81). The gamma profiles show that the bulk of the ^{137}Cs activity remains within 2 m of the crib bottom and has a peak activity of 90 nCi/g.

Crib 216-A-10 received acidic (pH ~ 2) high-salt wastes from the PUREX process. Organics apparently were also disposed and could be the cause of partial plugging from the crib bottom to a depth of 4 m (18 m total depth below ground surface). A distinct band of ^{137}Cs with a concentration of 3nCi/g is found from the crib bottom (14 m) to 27 m in depth. A more diffuse peak of ^{90}Sr with a maximum content of 0.2 nCi/g reaches to 43 m depth. The saturated paste pH of sediments just below the crib bottom (15 to 20 m total depth) is 4; the pH of sediments at 28 to 40 m is 7.7. In situ R_d values (sediment content/pore water content) for ^{90}Sr in the 28- to 40-m depth sediments varied from 0.8 to 2.7 mL/g depending on depth. The apparent cause of the more rapid migration of ^{90}Sr is that acidic wastes interact with the Hanford sediments and release high concentrations of Ca that compete with ^{90}Sr for adsorption sites.

Studies at 216-A-30 crib show slight vertical migration of ^{90}Sr and ^{137}Cs below the crib bottom (migration from 2.3 to 5.3 m). The crib had received steam condensate and floor drainage from equipment disposal operations (all wastes low salt and neutral pH). A desorption R_d value for ^{90}Sr determined by contacting contaminated sediments with groundwater was 17 mL/g.

Crib 216-A-36B received ammonia scrubber wastes (high salt, basic pH wastes). Core samples suggest that ^{137}Cs and ^{90}Sr have migrated to 14 m below the crib bottom (18 m total depth). As the bulk of the cesium was disposed 4 years previously, an averaged rate of travel for ^{137}Cs is 3.5 m/yr. Desorption R_d values on actual sediment contacting groundwater were 5.7 and 64 mL/g, respectively, for Sr and Cs. Smith and Kasper (1983) warned that future disposal of NH_4^+-rich liquid (0.3 M NH_4OH) wastes could lower ^{137}Cs R_d values to 3 mL/g.

Crib 216-U-12 received stack drainage from 291-U-1 and process condensate from 224-U building. In October 1965 a slug of contaminated water from 244-WR vault was also disposed. Core analyses show a distinct ^{137}Cs plume from the crib bottom (4.3 m below grade) to 12-m depth with a peak concentration of 20 nCi/g. A more diffuse ^{90}Sr peak has reached to a depth of 48 m with the bulk being present at depths 27 to 48 m with a peak concentration of 0.7

TABLE 19. Inventories of Selected Radionuclides Disposed to Cribs (decay corrected to 1/1/81)

Crib	Liquid Volume (L)	Pu (g)	^{90}Sr (Ci)	^{106}Ru (Ci)	^{137}Cs (Ci)	^{60}Co (Ci)	U (kg)
216-A-8	1.2×10^{9}	5×10^{1}	6.4×10^{1}	2×10^{-2}	6.4×10^{2}	<0.1	3.7×10^{2}
216-A-10	2.9×10^{9}	3.4×10^{2}	1.0×10^{2}	0.5	9.8×10^{1}	1.7×10^{1}	2.0×10^{2}
216-A-30	4.3×10^{9}	$<7.3\times10^{1}$	1.3×10^{2}	$3\ 4\times10^{-2}$	1.4×10^{2}	1.5	$<2.\times10^{2}$
216-A-36B	9.4×10^{7}	1.8×10^{2}	4.1×10^{2}	4.1	4.3×10^{2}	$<1.2\times10^{1}$	1.2×10^{2}
216-A-37-1	1.0×10^{8}	$<2.8\times10^{-2}$	$<1.2\times10^{-2}$	$<3\ 9\times10^{-3}$	$<2.2\times10^{-2}$	$<4\times10^{-2}$	$<2.7\times10^{1}$
216-U-12	1.3×10^{8}	1.	6.9×10^{1}	9×10^{-4}	$<6.8\times10^{-2}$	$<1\times10^{-2}$	1.8×10^{3}
216-S-1,-2	1.6×10^{8}	1.2×10^{3}	1.6×10^{3}	5.2×10^{4}	1.4×10^{3}	3.2×10^{-1}	2.3×10^{3}
216-B-5	3.1×10^{7}	4.3×10^{3}	3.3×10^{1}	$<10^{-8}$	3.7×10^{1}	--	--
216-Z-12	2.8×10^{8}	2.51×10^{4}					
216-Z-1A	6.2×10^{6}	5.74×10^{4}	$<1\ 5\times10^{-1}$	$<3\times10^{-2}$	$<1.5\times10^{-1}$	$<4\times10^{-2}$	<0.15
216-Z-9		3.8×10^{4}					

nCi/g. Because the bulk of the ^{90}Sr activity can be attributed to the 1965 incident, an average ^{90}Sr migration rate of 6 mlyr was estimated. Again acid disposal is suggested as the cause for strontium migration. Table 20 lists saturation paste pH values and in situ Rd values for ^{90}Sr on core material.

Van Luik and Smith (1982) report on borehole scintillation and gamma ray spectroscopy logs in boreholes around and in cribs 216-S-1 and 216-S-2. They compared logs from 1959, 1967, and 1980. The comparisons confirm that after active liquid discharge ceased (1956) that little movement in radionuclides (^{137}Cs, predominant gamma emitter) occurred. An estimate of the volume and inventory released to 216-S-1 and 216-S-2 is shown in Table 19. The waste was high salt and acidic (pH -2.1) in nature. Active disposal occurred from 1952 to 1956. During monitoring well deepening in June 1955, liquid waste flooded the well casing and reached the water table. At various times since 1955, above-background levels of ^{90}Sr, ^{139}Cs, and ^{3}H have been found in the unconfined aquifer. Well deepening by pushing casing deeper into the sediments apparently has also caused some movement of contamination to levels 50 to 60 m below the surface. Generally, ^{137}Cs is found between 10 and 20 m below the surface (crib bottoms, ~10 m) with peak concentrations to 2000 nCi/g. Below 20 m, activities are <10 nCi/g, excepting areas where well casing contamination was driven deeper or where the well flooded. Strontium-90 migration has been more pervasive because of the acidic nature of the liquid waste. Van Luik and Smith estimate an in situ R_d for Cs at 300 mL/g.

Smith (1980) reports on the distribution of Pu, ^{137}Cs, and ^{90}Sr in sediments around a reverse well (216-B-5). The reverse well was drilled to 92 m and was perforated from 74 to 92 m below ground surface (*i*.e., just barely into the water table). Monitoring wells drilled nearby in 1979 show that Pu and ^{90}Sr above 10 nCi/g are confined within a cylinder with a 6-m radius around the well. ^{137}Cs may have moved further (>8 m) but a second source, BY-cribs 900 m to the north, may be the actual cause of the large Cs plume. The liquid waste was low in salt [<0.15 M $Na(NO_3,F)$] and alkaline. Volume disposed and estimated inventories are shown in Table 19. Before disposal the liquid was discharged to a settling tank to remove particulates, and the well received waste from April 1, 1945, to September 20, 1947. The authors also infer that

TABLE 20. Sediment pH and Sr R_d Value Below Crib 216-U-12

Sample Depth (m)	pH	In Situ R_d (mL/g)
6.7	3.9	--
33.2	6.1	1.25
38.7	6.3	0.25
44.2	6.6	2.75
Background	7.5 - 8.0	--

the presence of phosphate and the alkaline nature of the liquid waste wouldrestrict the mobility of ^{90}Sr and plutonium.

Kasper (1982) describes the distribution of Am and Pu in sediments beneath 216-2-12 crib used to dispose low-salt, neutral liquid wastes. He determined that Am in the sediments is the direct result of ^{241}Pu decay and that no ^{241}Am was likely present in the original liquid wastes. Plutonium activity decreases rapidly with distance from the bottom of the crib. At the crib bottom, 1 to 5 µCi/g of ^{239}Pu was measured. Three meters below the crib bottom. 1 nCi/g values were common, and 10 m below the crib bottom the activities were background (<1 pCi/g). There is a slight increase in Pu content (to 20 pCi/g) at a depth of 30 to 36 m below the crib bottom because there is a high-silt-content lens present. Groundwaters in nearby wells show no detectable alpha activity (<0.017 pCi/mL).

The sediments immediately below the crib bottom (with highest actinide content) were reddish-brown from a coating of precipitates likely from the waste solution. Hydrous iron oxides are generally reddish-brown and are known to be strong adsorbers/coprecipitators of metals.

Marratt, Kasper and Van Luik (1984) determined the Pu and Am distribution beneath the 216-2-8 French drain from borehole sediment samples but no leaching or desorption tests were performed. The liquid waste stream disposed was low in salt and nearly neutral in pH. During the active disposal period, October 1957 to April 1962, about 10,000 L was disposed. A single well was drilled less than 1 m away from the French drain. The bottom of the drain was at 5.3 m.

Results of sediment plutonium and americium activities determined by total digestion and alpha energy analysis are shown in Table 21. The observed ^{241}Am comes from the decay of ^{241}Pu rather than from americium in the liquid waste. Background values of ^{239}Pu are about 1 pCi/g, and results suggest plutonium has migrated about 5 m below the drain bottom. The ^{241}Am at a constant ratio of 0.1 compared to ^{239}Pu shows the same trend.

Price et al. (1979) and Delegard, Gallagher and Kasper (1981) performed studies to determine the distribution of Pu and Am in sediments beneath 216-Z-1A crib and their leachability from the contaminated sediments, respectively. The liquid waste stream disposed to the 216-Z-1A crib contained high salt (3.6 M nitrates of sodium, calcium, magnesium, and aluminium), acid (pH < 1.0), and organic materials (<5% by volume: CCl_4, TBP, DBBP). Price et al. (1979) drilled 16 new wells (24 wells already existed) through or near the crib to characterize the actinide distribution. The highest concentrations of $^{239-240}$Pu (40μCi/g) and ^{241}Am (2.5 μCi/g) occurred in sediments immediately beneath the crib bottom. The maximum vertical penetration of actinides (defined as 10^{-5} μCi/g) was found 30 m below the crib bottom. Note that the deepest vertical migration remains 30 m above the water table. The estimated lateral extent of contamination was less than 10 m beyond the perimeter of the crib. The pattern of waste beneath the crib was attributable to both chemical and

TABLE 21. Sediment Analyses from Below 216-Z-8 French Drain (pCi/g dry)

Depth (m)	^{238}Pu	^{239}Pu	^{241}Am
5.3	0.014	1.32	0.085
6.1	0.734	4410	457
6.9	6.03	341	45.8
7.6	70.6	4290	370
8.4	1.37	75.4	7.7
9.1	0.20	2.47	0.18
9.9	0.02	2.6	0.122
10.7	0.24	0.82	0.104

physical processes: 1) physical filtering of disposed PuO_2 particles at the crib bottom; 2) pH-mediated precipitation as the soil carbonates, alumino-silicates, and silicates neutralized the acid; and 3) unsaturated flow patterns at the interface of different strata.

The ^{241}Am content in the sediments nearly equals the Pu content and is too large to have come solely from decay of ^{241}Pu; thus, Am must have been present in the original waste. The Am distribution in the sediments is very similar to plutonium.

Delegard, Gallagher and Kasper (1981) took a sample of Z-1-A contaminated sediment from 9 m below the crib bottom (^{239}Pu = 0.107 µCi/g, ^{241}Am = 0.100 µCi/g, saturated paste pH = 3.9). Both batch and column desorption tests were performed. Both synthetic groundwater (ionic strength = 4.5×10^{-3} M) and 0.01 M $CaCl_2$ solution (ionic strength = 3×10^{-2} M) were used as leachants in the column tests. In the batch tests numerous solutions: distilled water, 0.001 M to 1 M $CaCl_2$, 0.01 M to 0.3 M $Al(NO_3)_3$, 0.01 M to 0.1 M NaF, and synthetic groundwater were used at solids-to-solution ratios of 0.3 to 4 g/mL and contact times from 2 min to 3 weeks.

Batch test leachates showed Pu concentrations were always below the concentration predicted to be in equilibrium with excess PuO_2 solid. As the leachant ionic strength increased more Pu was extracted from the sediment suggesting ion exchange desorption as the dominant process. No specific Pu data were presented to allow quantification of the Rd desorption. The batch test results for Am agree fairly closely with an empirical solubility expression determined on a similar contaminated soil sample (see Rai et al. 1981).

At all contact times, solid-to-solution ratios, and types of leachants, the solution Am concentration remained within 0.4 log units of the empirical predictor line. The leached Am was in true solution (did not filter out onto 0.003-pm membranes) and was cationic.

The column leachates showed relatively high concentrations of Am, H^+, Na', K^+, Mg^{2+}, Ca^{2+}, Al^{3+}, NO_3^-, and F in the first few pore volumes. Plutonium and americium had similar elution patterns, but Pu activity in solution was two orders of magnitude lower than Am despite being present in the sediment at equal activities.

More than 80% of the americium leached in 210 pore volumes was removed in the first pore volume (with pH = 3.5). The observed Am concentration in solution exceeded the empirical solubility equation (see Rai et al. 1981) by one order of magnitude for the first two pore volumes. From pore volume 3 through 210, the Am concentrations were lower than the empirical solubility. Delegard, Gallagher and Kasper (1981) speculate that complexants in the original waste enhanced Am solubility for the first two pore volumes and then were completely flushed. After 210 pore volumes of leaching with simulated groundwater, less than 1% and about 30% of the Pu and Am, respectively, were removed from the contaminated sediments. Almost all the mass leached out in the first few pore volumes.

Rai et al. (1981) studied Am leaching from Z-9 crib sediments into low ionic strength (0.0015 M $CaCl_2$) solutions at pH values between 3.5 and 8. The data suggest that Am release is solubility controlled and not desorption (R_d) controlled. The liquid wastes disposed to the Z-9 crib were high salt acidic and similar to the waste disposed in Z-1-A. Two sediments used had a saturated paste pH between 3.5 and 4.3. In batch tests, 2 g of contaminated sediment were contacted with 20 ml of 0.0015 M $CaCl_2$ solution with pH adjusted to between 3.5 and 8 up to 700 days. The resultant solutions contained ~30 mg/L Al, 13 mg/L Fe, 70 mg/L Zn, 10 mg/L F, 4 mg/L NO_3, and variable amounts of phosphate, all apparently leached from the sediments. The leachate Am activities reached steady-state values within a few days and were highly correlated to the solution pH but no other measured variables.

The Am concentrations in solutions contacting contaminated sediments at Hanford (and in laboratory sorption tests on generic rocks, soils, and minerals) appear to be predictable using the following empirical equation:

$$\log \mathrm{Am}(M) = -(3.76 \pm 0.24) - (1.07 \pm 0.04)\mathrm{pH} \qquad (10)$$

The empirical equation is akin to an empirical solubility relationship for an unknown compound, dubbed Am (soil), reacting with hydronium (H^+) to form a monovalent Am aqueous complex:

$$Am_{(soil)} + H^{+} \overset{H_2O}{\rightleftharpoons} Am(OH)_2^{+} ; \quad \log K = -4.12 \tag{11}$$

In summary, the actual data base on desorption Rd values and empirical solubility relationships that could be directly used in performance assessment codes is quite limited (see Table 22). Field data on waste migration from actual Hanford LLW sites in the vadose sediments are very sparse or not readily available. There are data on the activity of some radionuclides from contaminated cribs, trenches, and reverse wells. Much of the data are gamma-ray scintillation logs taken in cased boreholes within or around the site. Scintillation logs yield a qualitative to semiquantitative estimate of the extent of migration of gamma emitting nuclides only. Direct calculation of R_d values is generally not possible because the disposal history (quantity of each isotope, chemical composition of liquid waste, and infiltration

TABLE 22. Available Data Base for Contaminated Soils

In Situ R_d Values (activity on solid/pore water activity)

^{90}Sr	0.8 to 2.7	Crib 216-A-10	High salt/acidic
	0.25 to 2.75	Crib 216-U-12	High salt/acidic
^{137}Cs	300	Crib 216-S-1, S-2	High salt/acidic

Desorption R_d Values (lab leach test)

^{90}Sr	17	Crib 216-A-10	High salt/acidic
^{90}Sr	5.7	Crib 216-A-36B	High salt/basic
^{137}Cs	64	Crib 216-A-36B	High salt/basic

Empirical Solubility

$\log Am(M) = -3.76 - 1.07$ pH High salt/acidic attributes) is not known accurately to allow an R_d from the soil column data. Some monitoring wells intercept the unconfined aquifer and yield groundwater samples that can be used to measure chemicals and radionuclides that have reached the water table. The diverse nature of the liquid waste streams (low ionic strength, high salt, acidic, basic, organic contents, high suspended solids, etc.) makes it likely that numerous sequestration processes remove contaminants from the liquid waste. Suspended solids are likely physically filtered in the porous media, especially in the small pores of fine sand and silt. The percolation rates into the porous sediments in the cribs, etc., is much slower than the gravity feed or pumped velocities maintained in the distribution pipes such that suspended solids would settle even in large media such as coarse sand and gravel.

The Hanford sediments are alkaline and typically contain from 0.5 to 2.0% calcium carbonate by weight. Acidic liquid waste on contacting these sediments will react and be buffered to pH values 4 to 8. Transuranic elements such as Pu and Am, fission products such as Eu, Ce, Zr, and Nb, and activation products such as Co, Ni, and Fe have solubilities that are very sensitive to pH. All are relatively soluble in acid but insoluble at neutral to basic pH values. Thus, the likely process that removes most of these radionuclides from acid waste streams is sediment neutralization that promotes precipitation of insoluble hydroxides, oxides, or nondescript scavenging into hydrous oxide films.

The other process most often invoked to explain sediment removal of contaminants is adsorption. Soils and sediments contain particles such as clays that contain a fixed negative surface charge caused by substitution of lesser charged cations into lattice sites generally reserved for Al^{3+} or Si^{4+}. When an Fe^{2+} or Fe^{3+} or Mg^{2+} or Ca^{2+} replaces the Al^{3+} or Si^{4+}, there is a net loss of +1 to +2. Thus the particle seeks or attracts cations toward its surface and adsorbs these cations from the pore waters. Other soil particles (hydrous iron, manganese and aluminum oxides, and organic matter) have variable surface charges that depend on the pH of the pore waters. At low pH all these particles exhibit a net positive surface charge, while at neutral to basic pH values these particles exhibit a net negative charge. Under normal Hanford sediment conditions, these particles exhibit a negative charge and thus adsorb cation species. Therefore, it is quite common for cationic forms of contaminants to travel through porous sediments at velocities much slower than the transporting water molecules.

The release model used in the HDWEIS for contaminated soil sites for all but a few selected radionuclides was the R_d desorption concept, in which clean water will desorb a portion of the contaminant bound on the soil to reestablish the equilibrium ratio, R_d. (For a few selected radionuclides, an empirical constant solubility release model was used.) This R_d approach is simplistic and ignores the fact that much of the inventory in the soils may not be chemically adsorbed but instead is likely physically bound as filtered suspended solids or pH-sensitive insoluble precipitates. Physically bound contaminants are remobilized differently than adsorbed species. Further, the R_d concept is strictly empirical and must rely on measurements typically performed in the laboratory. The R_d is sensitive to the nature of the adsorbent (contaminated soil), the adsorbate (contaminant speciation and concentration), and type of water present (pH, Eh, and chemical composition). Very few desorption experiments of a contaminated Hanford soil have been documented (Delegard et al. 1981; Smith and Kasper 1983). The HDWEIS used R_d values that represent adsorption studies of contaminated liquids onto clean sediments or in other instances educated guesses. There have been several reports that suggest that the R_d measured in the adsorption direction differs from the R_d measured in the desorption direction (Barney 1981; Serne and Relyea 1983). Table 22 shows a similar trend for ^{90}Sr where the desorption R_d was 17 mL/g while in situ R_d values are only 0.8 to 2.7 mL/g.

We will defer the discussion of recommended R_d values to use in contaminated soil release calculations to the discussion on adsorption data (Section 3.3).

2.3.4 Solid-Waste Burial Grounds

We could not find any studies or data that address the release of contaminants from solid wastes buried at Hanford. The approach currently used that considers solid-waste release and subsequent leachate migration as similar to these processes for contaminated soil sites is reasonable until some data can be obtained to corroborate or conflict with the assumption.

3.0 SEDIMENT INTERACTION

3.1 GENERAL DESCRIPTION

Solute (including contaminants) transport in the subsurface is controlled by advection, hydrodynamic dispersion, molecular diffusion, and geochemical interaction. Advection and hydrodynamic dispersion refer to movement of solute at a rate dependent on the various water pathways and velocities. Molecular diffusion refers to the gradual mixing of molecules of two or more substances as a result of random motion and/or a chemical concentration gradient. Diffusion flux spreads solute via the concentration gradient (i.e., Fick's law). Diffusion is a dominant transport mechanism when advection is insignificant, and is usually a negligible transport mechanism when water is being advected in response to various forces. Variability in the advection process gives rise to the transport process called hydrodynamic dispersion. Hydrodynamic dispersion is a result of variability in travel paths, that is, velocities, taken by the advected solute. Geochemical interactions cover all reactions that are driven by chemical and biochemical forces.

Once contaminants are leached from the buried wastes they may chemically interact with the soils and sediments. The major processes affecting transport include the following: dissolution/precipitation, adsorption/desorption, filtration of colloids and small suspended particles, and diffusion into micropores within mineral grains. The former two processes are considered more important. Further, for the Hanford Site low-level waste (LLW) disposal application, precipitation is likely a key only for cases where significant pH and/or redox changes occur when leachates migrate away from the wastes. In most Hanford Site LLW situations, we speculate that adsorption processes are the key to contaminant migration, especially outside areas where the waste has dramatically altered the sediment's natural chemical environment.

Adsorption reactions have been acknowledged as the most important contaminant retardation process in far-field transport analyses for hazardous waste disposal options. Adsorption processes are known to increase the travel times for some contaminants by 10^3 to 10^6 times relative to the groundwater. Such long travel times allow nuclides to decay to lower concentrations and less hazardous nuclides before reaching the accessible environment (i.e., the biosphere). Furthermore, some adsorption process are effectively irreversible and permanently prevent contaminants from reaching the groundwater, thus preventing their release to the biosphere.

3.1.1 Constant Distribution Coefficient

To predict the effects of retardation using computer safety assessment codes, adsorption processes must be described in quantitative terms. An empirical parameter, the distribution coefficient (often called R_d or K_d), is readily measured by laboratory experimentation and allows such a quantitative estimate of nuclide migration. Knowledge of the R_d and of media bulk density and porosity (for porous flow), or of media fracture surface area, aperture width, and matrix diffusion attributes (for fracture flow), allows calculation of the retardation factor, R of R_f. The retardation factor is defined as $R = \frac{V_w}{V_n}$ where Vw is the velocity of water through a control volume and V_n is the velocity of the contaminant.

For one-dimensional advection-dispersion flow with chemical reaction, the transport equation can be written as

$$\frac{\partial C_i}{\partial t} = \frac{\left[D_x \frac{\partial^2 C_i}{\partial x^2} - \nu_x \frac{\partial C_i}{\partial x} \right]}{R_i} \qquad (12)$$

where C_i = concentration of a particular radioactive species (i) in solution (mass/length^3)

D_x = dispersion coefficient of species (i) (length^2/time)

ν_x = pore velocity of groundwater (length/time)

R_i = retardation factor for species i.

(For simplicity, radioactive decay has been left out.)

The retardation factor is a function of all contaminant retardation mechanisms: 1) chemical precipitation/dissolution of bulk solid phases, 2) chemical substitution of one element for another in a solid phase, 3) exchange of stable isotope of an element with a radioactive isotope in solution, 4) physical filtration of colloids, 5) cation and anion exchange, and 6) adsorption (Muller, Langmuir and Duda 1983). Typically, all these mechanisms are folded into a single empirical distribution coefficient that implicitly assumes that the reactions go to equilibrium and are reversible, and that the chemical environment along a solute flow path does not vary in either space or time. The limitations associated with this assumption are well known to investigators, but the paucity of Hanford Site-specific geochemical data precludes a more rigorous conceptual model. Geochemical processes may also be irreversible or at least directionally dependent (e.g., adsorption and desorption may be represented by different model parameters), and yet the assumption of reversibility and single-valued model parameters are generally employed, with the justification that the approach builds conservatism into the analysis.

In the constant R_d model, the distribution of the contaminant of interest between the solid adsorbent and solution is assumed to be a constant value. There is no explicit accommodation of dependence on characteristics of the sediments, groundwater, or contaminant concentration. Typically, an R_d value for a given contaminant is determined in the laboratory using sediment from the study area and actual or simulated groundwater to which a radionuclide tracer is added at some trace concentration. Then,

$$R_d = \frac{\text{amount of radionuclide adsorbed on solid per gram}}{\text{amount of radionuclide in solution per milliliter}} \tag{13}$$

The term trace typically denotes that a low mass is added, but the mass or activity must be sufficient to facilitate good counting statistics. The experiments are often equilibrated by contacting the solid with several aliquots of the water before adding the radiotracer, to attempt to approach the condition expected in the field. Several standardized laboratory techniques (ASTM 1984; Serne and Relyea 1983) are commonly used to determine this ratio.

Most of the laboratory experiments performed to measure distribution coefficients do not systematically investigate the effect of important parameters and do not attempt to identify the processes causing the observed adsorption. Because it is an empirical measurement, the R_d value does not necessarily denote an equilibrium value or require some of the other assumptions inherent in the more rigorous use of the term "K_d". The term "R_d" will be used as simply the observed distribution ratio of nuclide between the solid and solution. We reserve the term "K_d" for true equilibrium reactions that show reversibility and further do not yield a distribution ratio that is dependent upon the tracer concentration in solution.

Furthermore, it is customary with the constant R_d model to measure the total concentration or radioactivity of the tracer and thus to treat the tracer as being one species. This assumption is not an inherent requirement, but it is generally applied for convenience. If one knows that the tracer distributes among several species and one can measure or predict the distribution, separate R_d values can be and should be calculated for each species.

This conceptual model, which depends on experimental determination of the distribution coefficient, R_d, is quite simple, but it is also limited in that it does not address sensitivity to changing conditions. If the groundwater properties (e.g., pH, dissolved solids content) change, a new experiment must be performed.

The constant R_d model is mathematically very simple and readily incorporated into transport models and codes via the retardation factor term. That is, for porous flow

$$R = 1 + \frac{\rho_b}{\phi_\epsilon} R_d \tag{14}$$

or

$$R = 1 + \frac{1-\phi_\epsilon}{\phi_\epsilon} \rho_p R_d \tag{15}$$

where R = the retardation factor $\nu_w w/\nu_n$

ρ_b = porous media bulk density (mass/length^3)

ϕ_ϵ = effective porosity at saturation of media

R_d = distribution coefficient

ρ_p = particle density (mass/length^3).

For the constant R_d model, the retardation factor (R) is a constant for each layer of geologic media (each layer is assumed to have a constant bulk density and saturated effective porosity). Thus, this transport equation does not require knowledge of any other parameters such as pH or surface area, and it is easily solved to determine the solution concentration as a function of time and at any given point. It is the use of the constant R_d conceptualization in the retardation factor that has caused most of the criticism: Few natural groundwater pathways are spatially or geochemically homogeneous to the extent that the retardation factor for a species remains constant.

3.1.2 Parametric R_d Model

There is little incentive for a researcher using the constant R_d conceptual adsorption model to characterize or measure in detail the basic chemical and physical parameters of the sediment and groundwater, because no dependency is explicitly accommodated. On the other hand, researchers will soon realize that the need to perform a new experiment to collect the R_d value for each different condition becomes burdensome and uneconomical. For this reason, and to satisfy their curiosity as to what mechanisms control adsorption, sorption experimenters often characterize their experimental systems by measuring selected parameters. Unfortunately, as there is no physicochemically based conceptual model, the experimenter has little guidance as to which parameters are more important and worthy of measurement.

A second practical conceptual model for adsorption is called the parametric R_d model. Parameters such as the amount and type of minerals (or more generally surface adsorption sites) present in the adsorbent, amount and types of ions in the groundwater (especially competing ions and complex-forming ligands), pH, Eh, temperature, and experimental procedures (e.g., solid/liquid separation techniques and contact times) can affect the observed distribution coefficient. Systematic empirical studies have often been performed to investigate the effects of many of these variables on the adsorption of contaminants on soils, sediments, or rocks. The most common approach is to vary one or more parameters systematically, measure the resultant distribution coefficient, and then, using available statistical analyses schemes, to develop some predictor relationship.

Because the distribution coefficient is a function of so many variables, it is common to systematically vary several parameters simultaneously in one experimental study. Factorial design strategies are most often invoked to determine the systematics in varying the independent variables and the dependent variables (Yates 1958; Cochran and Cox 1957; Davies 1954; Plackett and Burman 1946; Box and Behnken 1960). (The dependent variables are typically the distribution coefficient.) Statistical methods commonly used to derive quantitative predictor equations include standard linear or nonlinear regression (e.g., Snedecor and Cochran 1967), stepwise regression (e.g., Hollander and Wolfe 1973), and adaptive learning networks (e.g., Mucciardi et al. 1979, 1980).

All these techniques have been used successfully to develop empirical relationships that describe the distribution coefficient in terms of other variables (e.g., Routson and Serne 1972; Routson et al. 1981; Delegard and Barney 1983; Serne, Routson and Cochran 1973).

The empirical predictor equations commonly take the form of a nonlinear multinomial expression. For example, an expression for strontium-90 adsorption might take the form:

$$\begin{aligned} R_d(\mathrm{Sr}) = {} & a(\mathrm{Ca}^{2+}) + b(\mathrm{Na}^{+}) + c(\mathrm{K}^{+}) + d(\mathrm{Ca}^{2+})(\mathrm{Na}^{+}) + e(\mathrm{Ca}^{2+})(\mathrm{K}^{+}) \\ & + f(\mathrm{Na}^{+})(\mathrm{K}^{+}) + g(\mathrm{Ca}^{2+})(\mathrm{Na}^{+})(\mathrm{K}^{+}) + h \end{aligned} \qquad (16)$$

where a, b, ..., h are regression coefficients and (Ca^{2+}), (Na^{+}), and (K^{+}) represent molar solution concentrations of competing macro cations. In this system, the independent variables were (Ca^{2+}), (Na^{+}), and (K^{+}), and the dependent variable was the distribution coefficient for strontium. For this example, squared terms such as $(\mathrm{Ca}^{2+})^2$ or $(\mathrm{K}^{+})^2$ were not found to increase the predictive equation's "goodness-of-fit" for the data significantly; therefore, these quadratic terms were ignored. For other empirical models, other powered, exponential, or logarithmic terms may be useful.

Although the empirical relationships generated from these types of statistical analyses are more powerful than knowledge of individual distribution coefficients, they should not be used to predict R_d values for conditions beyond the range studied. Furthermore, the statistical relationships delineate only the apparent effect that the chosen independent variables have on the distribution coefficients; they do not identify conclusively the cause or process controlling adsorption. That is, the statistical analyses may suggest a very strong relationship between one variable, for instance, pH, and the distribution coefficient, when the actual adsorption process is controlled by hydrous iron oxide scavenging. Because the stability and surface charge of iron oxide are a function of pH, a statistical relationship could be calculated suggesting the adsorption is solely caused by pH.

Empirical and purely statistical approaches are useful in assessing contaminant adsorption tendencies, but they do not lead to a general understanding of the physicochemical processes controlling the interactions among sediments, groundwaters, and solutes. Therefore, more rigorous, mechanistic studies that rely on thermodynamic constructs have been and are currently proposed to increase our knowledge of trace constituent adsorption processes. Systematic studies to determine the effects of competing ions and of pH (another way of referring to competing H^+ ions) can be related to thermodynamic models.

The parametric R_d conceptual model requires characterization of solid phase (soils, sediments, etc.) and solution phase (groundwater and dissolved contaminant content) parameters. The statistical model does not provide an a priori ranking of which parameters should be measured, but by using physicochemical knowledge of possible adsorption processes and experience, the more important parameters can be identified.

The parametric R_d conceptual model can be used in the retardation factor term [see Equations (14) and (15)] and the transport equation [see Equation (12)]. When used in the transport equation, the code must also keep track of the current value of the independent variables [such as Ca^{2+}, Na^+, and K^+; see Equation (16)] at each point in space and at each time to continually update the value of R_d. Thus the code must track many more parameters, and some numerical solving techniques (such as closed-form analytical solutions) can no longer be used to perform the integration necessary to solve for concentration. Generally, computer codes that can accommodate the parametric R_d model use a chemical subroutine to update R_d or R when called by the main transport code. The added complexity in solving the transport equation with the parametric R_d adsorption model and its empirical nature may be the reasons this technique has been used sparingly for waste disposal safety assessment exercises. The TRANSS code used to date for most Hanford PA activities currently cannot accept parametric R_d values.

3.1.3 Other Adsorption Conceptual Models

Three well-established adsorption conceptual models are discussed in Appendix C. These models explicitly accommodate the dependency of R_d on contaminant concentration, competing ion concentration, variable surface charge on the adsorbent, and solute species solution distribution. The description of these conceptual models is presented as an appendix because we judge them of little practical use in near-term performance assessment activities at Hanford. The complexity of installing these models into existing transport codes that are favored for complete disposal system performance assessment and the diversity of Hanford waste leachate/sediment/contaminant combinations of interest would require a data collection effort more intense and costly than is likely to be available. Other technical limitations are also discussed for each model in Appendix C. The appendix is included to familiarize the performance assessment community with all available adsorption model choices so they can gain a complete perspective. The discussions also can act as a primer for adsorption models that are considered more sophisticated and mechanistically sound than the R_d models just discussed.

3.1.4 Acid/Base-Mediated Precipitation

Several acidic waste streams were disposed to Hanford Site sediments in the past. Many transition metals, lanthanides, and actinides are more soluble in acid solutions than in neutral or mildly basic ($pH \leq 10$) solutions. When contacting Hanford Site sediments, acidic solutions become buffered to more neutral pH values. Important reactions include acid reacting with carbonates and dissolving amorphous and crystalline oxides and hydroxides of iron, aluminum, manganese, and silicon. Transition metals, lanthanides, and actinides soluble in acid will precipitate as amorphous and crystalline hydroxides and oxides when the acidic waste is neutralized. Before precipitation the free cations of these metals will tend to hydrolyze and form soluble complexes of the form $M(OH)_x^{(n-x)}$. These species are readily adsorbed by hydrous oxides of iron, aluminum, manganese, and silicon.

Thus, as pH increases most metals and radionuclides will react either by adsorption reactions onto hydrous oxides (best modeled using the surface complexation conceptual models described in Appendix C) or as insoluble precipitates (best modeled using the thermodynamic construct, K_{sp}, the solubility product described in Section 2.1.1). Geochemical computer codes such as PHREEQE, MINEQL, and MINTEQ have algorithms to solve both adsorption and solubility simultaneously. A key point is that the migration potential of transition metals, lanthanides, and actinides is greatly diminished as pH increases. The percent removal from solution for metals usually dramatically increases over a very short span of pH values, which gives rise to the concept of adsorption pH edge (see Leckie et al. 1980). For some metals adsorption becomes essentially complete (100%) as pH increases from 2 or 3 up to 4 or 5. Remobilization requires that additional acid be disposed to drive the soil pore water to acidic conditions (pH 4 4). This is the probable cause of the recent mobilization of uranium at the U1/U2 Crib Sites discussed in Delegard et al. (1986) and Baker et al. (1988).

3.1.5 Redox-Mediated Precipitation

A few radionuclides and regulated chemicals show large differences in mobility in groundwaters depending upon which of their valence states are present (e.g., Cr, Tc, Sn, U, Np, and Pu). In general each of these elements is much less mobile in geologic environments when present in the reduced state. If liquid waste streams are quite oxidizing (e.g., reactor cooling pipe decontamination solutions enriched in sodium dichromate), disposal in certain sediments promote changes in oxidation state and dramatic changes in element mobility. For example, Rai et al. (1984) report that many soils are capable of reducing mobile Cr(VI) to immobile Cr(III). Rai et al. (1980a) and Meyer et al. (1983, 1984) report that several common minerals and rocks can promote the reduction and precipitation/adsorption of plutonium and technetium.

Presently, there are some indications that the Hanford Site sediments are not immobilizing all these redox-sensitive elements in every instance. The Hanford Site-Wide Ground Water Monitoring Program has documented several CrO_4^- plumes and isolated ^{99}Tc (likely as TcO_4^-) plumes in Hanford groundwater (e.g., Evans et al. 1988). It is not clear whether these observations are the result of disposal of large volumes of oxidized solutions such that the reducing capacity of the sediments has been exhausted or an indication that the Hanford sediments have very little inherent reducing capacity.

The disposal of highly reducing liquid or solid wastes in the vadose zone sediments could also lead to redox changes over time. The partially saturated sediments allow influx of air (oxygen), which could oxidize redox-sensitive elements and perhaps enhance their mobility.

Redox-mediated reactions are incorporated into most geochemical codes and can conceptually be modeled. The resultant speciation distribution calculated by such a code is used to determine potential solubility controls and adsorption potential. Many redox reactions have been found to be kinetically slow in natural groundwaters, and several elements may never reach redox equilibrium between their various oxidation states. Thus it is more difficult to predict with accuracy the migration potential of redox-sensitive species.

3.1.6 Effects of Unsaturated Conditions on Chemical Reactions and Transport

Almost all studies on waste-form leaching and leachate-sediment adsorption are performed at water-saturated conditions. The water flow regime at Hanford at the disposal sites is unsaturated. The average moisture content of Hanford vadose zone sediments ranges from 4% to 7% by volume, which is equivalent to 10% to 20% saturation (e.g., Gee and Heller 1985; Schalla et al. 1988). Under separate funding, a literature review and critical synthesis of available information on whether the saturation state of the system can affect leaching and adsorption will be performed in the last quarter of FY 1989. Later, a letter report will be prepared that documents the findings.

3.2 RETARDATION MODELS CURRENTLY USED IN HANFORD PERFORMANCE ASSESSMENT ACTIVITIES

This section discusses details on the retardation (e.g., adsorption) models used in past efforts [the Hanford Defense Waste Environmental Impact Statement (HDWEIS)] and when available, current performance assessment activities for each specific waste form (single-shell tanks, grout, contaminated soils, and solid-waste burial grounds). We reiterate that the HDWEIS was clearly a bounding analysis as opposed to the most realistic analyses possible. The HDWEIS modeled contaminant transport from the waste to either a drinking-water well 5 kilometers (km) downgradient in the upper unconfined aquifer or to the Columbia River. Contaminants were assumed to either diffuse vertically to the water table or to diffuse and advect in a vertically dominated fashion to the water table. The contaminants and recharge water then mix with the upper 5 m of the unconfined aquifer and travel horizontally to the well or Columbia River. The steamtube approach (defined by two adjacent streamlines) is used in both the unsaturated sediments and the unconfined aquifer, as shown in Figure 3 (Appendix O of HDWEIS; DOE 1987b).

The transport code TRANSS was used to calculate the migration of contaminants from the waste form and through the unsaturated sediments and aquifer to the well or Columbia River. The streamtubes allow no lateral spreading or dispersion, but through variations in streamline travel times and pathlengths do allow aquifer-scale longitudinal dispersion to be included. In all scenarios for all waste forms, contaminant migration is calculated using the constant distribution coefficient conceptual retardation model. The user

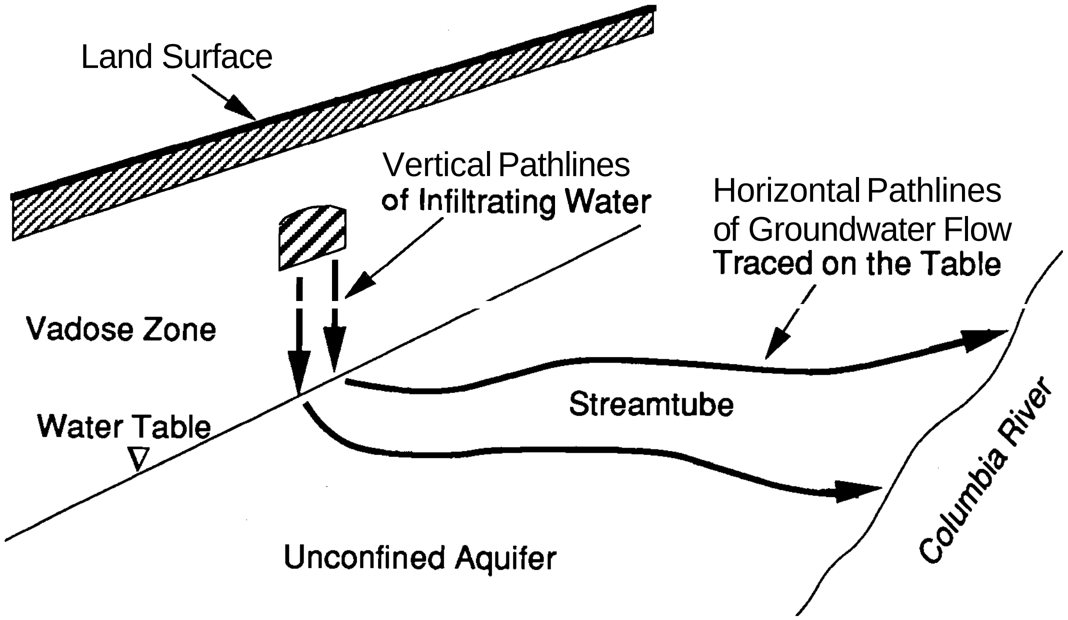

FIGURE 3. Depiction of the Streamtube Approach to Transport in the Vadose Zone and the Unconfined Aquifer

must supply TRANSS with the travel time of water through the vadose zone sediments, access to the aquifer streamline files [generated by the code VTT (Reisenauer 1979a-c; Kipp et al. 1976) for HDWEIS work] to the 5-km well and Columbia River, and the R_d values for contaminants.

3.2.1 Single-Shell Tanks

The HDWEIS calculated the transport of selected radionuclides using the constant distribution coefficient retardation model. TRANSS transport calculations assumed the distribution coefficient would vary as a function of the chemical composition of the pore solution. For the diffusion-controlled region of the vadose zone sediments (see Figure 2), the pore water would be very concentrated (i.e., tank liquor). For the advection-controlled region of the vadose zone sediments and the saturated zone in the unconfined aquifer, the water chemistry would be more dilute and thus the competition among solutes for the adsorption sites would be lessened (i.e., more adsorption of trace contaminants could occur). Table 23 lists the R_d values used in the HDWEIS to calculate the transport of important radionuclides from single-shell tanks. The data are conservative estimates based on experiments by Delegard and Barney (1983) on simulated tank liquors or on expert judgment. Transport calculations were also performed for selected regulated chemicals (Cr, Cd, Hg, NO_3^-, NO_2^-, and F^-) but all were considered nonsorbing ($R_d = 0$).

Recently Droppo and co-workers at PNL performed additional performance assessment calculations with the code MEPAS. The transport portion also relied on the constant distribution coefficient conceptual retardation model. Table 24 reports the values chosen for radionuclides and chemicals that were modeled.

The source of the R_d values used by Droppo and his co-workers is not explicitly documented. The MEPAS protocol calls for site-specific R_d values when available but defaults to a master table of R_d values when the user can not provide actual values. The master table (shell) requires the user to input leachate pH, leachate total dissolved solids content, weight percent clay-sized particles, sediment organic matter, and the sum of the sediment iron and aluminum oxyhydroxide content. The shell has look-up tables to provide R_d values for each contaminant based on the category (the five parameters) of the leachate-sediment.

TABLE 23. R_d Values for Single-Shell Tank Leachates (mL/g) Used in HDWEIS

Radionuclide	Diffusion Zone	Advection Zone
^{14}C	0	0
^{79}Se	3.3	3.3
^{90}Sr (a)	0.022	0.39
^{99}Tc	0	0
^{129}I	0	0
^{137}Cs	26	26
^{151}Sm (b)	5.6	5.6
^{237}Np (a)	3.9	8.7
^{239}Pu (a)	0.63	21
^{241}Am (a)	5.6	5.6

(a) Conservative interpretations taken from Delegard and Barney (1983).
(b) Similar to Am by chemical analogy.

Both transport codes (TRANSS and MEPAS) use Equation (14) to determine the retardation factor for each contaminant. The R_d values used in each performance assessment activity are shown in Tables 23 and 24. The values for bulk density and effective porosity used in the HDWEIS were fixed at 1.8 g/cm^3 and 0.33, respectively. Droppo used paired values (bulk density-porosity) that ranged from 1.39 g/cm^3 and 0.475 to 1.64 g/cm^3 and 0.380, depending on the lithologic strata underneath the various tank farms. These values lead to generalized retardation factor equations of $R = 1 + 5.45\ R_d$ for the HDWEIS and the range $R = 1 + 2.93\ R_d$ to $R = 1 + 4.32\ R_d$.

Table 25 compares the retardation factors that can be calculated from the stated R_d values, bulk densities, and porosities. The retardation factor for ^{90}Sr used in the HDWEIS is much lower than that used by Droppo et al. and the retardation factor for Np in the HDWEIS is two to five times larger than Droppo's. It would thus not be surprising if the HDWEIS found ^{90}Sr from single-shell tanks to be more mobile than the newer assessment. Conversely the HDWEIS would predict Np migration to be less mobile than Droppo's predictions. There is general agreement in the values for the other radionuclides.

TABLE 24. R_d Values for Single-Shell Tank Leachates (mL/g) Used by Droppo

Element	R_d	Chemical	R_d
Ac	8.2	Ag	0.40
Am	8.2	Al	353.
C	0.0	Ba	530.
Cm	8.2	Cl	0.0
Cs	51.0	Cr	1.0
I	0.0	EDTA	0.0
Nb	1.2	F^-	0.0
Ni	1.2	Fe	1.5
Np	3.0	CN	0.0
Pa	3.0	Mn	16.5
Pb	234.0	NO_2^-	0.0
Po	3.0	NO_3^-	0.0
Pu	10.0	Na	0.0
Ra	24.3	Ni	1.2
Ru	27.0	Pb	234.0
Se	5.9	SO_4^{2-}	0.0
Sm	8.2	Zr	5.0
Sn	25.0		
Sr	24.3		
Tc	0.0		
Th	40.0		
U	0.0		
Y	5.0		

TABLE 25. Comparison of Retardation Factors

Radionuclide	HDWEIS	Droppo et al.
^{14}C	1	1
^{79}Se	19	18.3 to 26.5
^{90}Sr	1.1 to 3.1	72.2 to 106
^{99}Tc	1	1
^{129}I	1	1
^{137}Cs	143	150 to 221
^{151}Sm	31.5	25 to 36
^{237}Np	22 to 48	9.8 to 14
^{239}Pu	4.4 to 115	30.3 to 44.2
^{241}Am	31.5	25 to 36.4

3.2.2 Grout

The HDWEIS calculated the transport of selected radionuclides in grout leachates using the constant distribution coefficient retardation model and the TRANSS code. Two sets of distribution coefficients were selected, based on whether organic complexants in the original tank wastes were destroyed or not destroyed before processing into glass and grout. The values selected are based on conservative interpretations of experiments by Delegard and Barney (1983) on adsorption of nuclides from simulated tank waste. Table 26 lists the values chosen for the two situations.

In the phosphate/sulfate waste (PSW) grout performance assessment performed by Sewart et al. (1987), the transport of leachate through Hanford sediments was modeled with TRANSS using the constant R_d conceptual adsorption model. The R_d values and retardation factors are reported in Table 27. The Sewart et al. (1987) analysis is very similar to the HDWEIS complexed leachate, the only difference being the use of an experimentally determined R_d for Sr that was obtained by Serne et al. (1987) on PSW grout leachate and Hanford sediment from the grout vault site and inclusion of U and deletion of Np analyses. Again the R_d values for contaminants were considered constant for all soil layers, water chemistry, and flow rates. Sewart et al. (1987) also calculated the transport of regulated chemicals to the 5-km well and Columbia River but

TABLE 26. R_d Values (mL/g) Chosen to Describe Grout Leachate Migration Through Sediment (HDWEIS)

Radionuclide	Complexed	Noncomplexed
^{14}C	0	0
^{79}Se	3.3	3.3
^{90}Sr (a)	0.39	0.64
^{99}Tc	0	0
^{129}I	0	0
^{137}Ca	26	26
^{151}Sm (b)	5.6	76
^{237}Np (a)	8.7	16
^{239}Pu (a)	21	71
^{241}Am (a)	5.6	76

(a) Conservative interpretations taken from Delegard and Barney (1983).
(b) Similar to Am by chemical analogy.

assumed no retardation occurred. Contaminants were limited by a constant concentration release from the grout monolith but once removed they were considered mobile. Elements considered were As, Ba, Cd, Cl, Cr, Cu, F, Fe, Pb, Hg, Mn, N as NO_3^-, Ag, and Zn.

TABLE 27. R_d Values (mL/g) and Retardation Factors Used for PSW Grout Performance Assessment (Sewart et al. 1987)

Radionuclides	Rd	R(a)
^{14}C	0	1
^{90}Sr	31	170
^{99}Tc	0	1
^{129}I	0	1
^{238}U	0	1
^{239}Pu	21	115
^{241}Am	5.6	31.5

(a) Assumes bulk density = 1.8 g/cm^3 and saturated porosity = 0.33 (same values as HDWEIS).

Other unpublished grout performance assessment calculations were performed for the Criteria and Standards program. These efforts used the same methodology as the HDWEIS and Sewart et al. (1987), but added analyses for ^3H ($R_d = 0$, $R = 1$), rounded off the plutonium retardation factor to 110, and reverted to the HDWEIS R_d value for Sr.

The current performance assessment (PA) analyses of grouted double-shell tank waste also use the constant distribution coefficient conceptual model to describe contaminant retardation. The values for R_d used are based on specific laboratory tests using Hanford grout leachates, groundwaters, and sediments for selected radionuclides and regulated chemicals or expert judgement when data are not available. Exact details will be available in late 1989.

3.2.3 Contaminated Soil Sites

Performance assessment analyses that include release and transport calculations for the contaminated soil sites at Hanford are limited to activities reported in the HDWEIS. As mentioned the HDWEIS considered only transuranic (TRU) waste-contaminated soils. The retardation calculations for TRU-contaminated soils also relied on the constant distribution coefficient model. Because there were very few actual data available when the HDWEIS was being written, the R_d values selected were conservative estimates based on the laboratory studies of Delegard and Barney (1983) on adsorption of radionuclides from simulated tank liquors. The values used in the HDWEIS (Table 28) are based on assumptions that contaminated soil leachates are akin to dilute tank solutions with low organic complexant concentrations.

3.2.4 Solid-Waste Burial Grounds

Performance assessment analyses that include release and transport calculations for solid-waste burial grounds at Hanford are limited to those presented in the HDWEIS. The retardation of radionuclides was modeled using the constant distribution coefficient approach. The values of R_d chosen are the same as those for TRU-contaminated soils shown in Table 28.

3.3 CURRENT ESTIMATES OF ADSORPTION CONSTANTS

The purpose of this section is to document any available Hanford Site-specific data that could be used to develop adsorption conceptual models or

TABLE 28. R_d Values (mL/g) Used to Describe TRU-Contaminated Soils in HDWEIS

Radionuclide	R_d
^{14}C	0
^{90}Sr	0.64
^{137}Cs	26
^{237}Np	16
^{239}Pu	71
^{241}Am	76

data that provide actual values for input parameters to available adsorption models.

Because the data base is small and the currently used adsorption model, constant R_d, is simplistic, we do not discuss the adsorption potential of each waste form's leachates separately. All available data are discussed together and then categorized into eight generic types (Table 29).

Current understanding of Hanford LLW and TRU waste leachates suggests the following classification in each category (Table 30). Existing conditions at Hanford suggest that most leachates will fall in categories 8, 2, and 1. At increasing distances from the disposal facility (tank, crib, trench, grout vault), the chemical nature of leachates, pore waters, or adulterated groundwater should tend toward category 8 (low salt, low organic content, and neutral pH).

It is quite common to divide the flow path from the disposal facility to the receptor (e.g., domestic well or Columbia River) into two zones, the waste-influenced or -affected, and the unaffected zones. For instance, some of the data presented in Section 2.3 on the release of contaminants from cribs that received acidic waste show soil-paste pH values are quite low immediately below the crib but rise to background values (pH = 7.5 to 8) several meters or a few tens of meters deeper in the sediment profile. The volume of sediment where acid attack is evident would be designated the affected zone. Constant R_d values for this zone should likely be different than values for the more distant unaffected zone.

TABLE 29. Generic Leachate Waste Streams

High Salt - High Organic - Acidic
High Salt - High Organic - Basic
High Salt - Low Organic - Acidic
High Salt - Low Organic - Neutral or Basic
Low Salt - High Organic - Acidic
Low Salt - High Organic - Neutral or Basic
Low Salt - Low Organic - Acidic
Low Salt - Low Organic - Neutral or Basic

High Salt: Wastes that are more than 0.3 M in specific salts such as $NaNO_3$ or have an ionic strength greater than 0.5 M

High Organic: Refers to leachates with significant quantities of dissolved organic matter, especially chelating/complexing agents. Solutions with dissolved organic contents greater than 0.2 g/L (200 mg/L) are considered high organic.

Acidic: Solutions with pH values ≤ 4
Basic: Solutions with pH values 210.5
Neutral or Basic: Solutions with pH values >4

Performance assessment exercises often use default R_d values of 0 for affected zones when knowledge of the chemical reactions is lacking but then use normal background R_d values for the unaffected zone. We recommend that future performance assessment activities on Hanford LLW consider at a minimum this two-valued retardation approach with values for the affected and unaffected zones.

At present the available data base for radionuclide adsorption onto Hanford soils includes laboratory-derived R_d values for Co, Sr, Np, Pu, Am, Cs, Ru, and Sb for high-level tank leak solutions [Knoll 1966, 1969; Delegard and Barney

TABLE 30. Existing Leachates Classified by Category

Category 1	High Salt - High Organic - Acidic Several contaminated soil sites (e.g., 216-A-10, 216-Z-1A)
Category 2	High Salt - High Organic - Basic Most single-shell tanks and some cribs (e.g., 216-A-36B)
Category 3	High Salt - Low Organic - Acid Some contaminated soil sites might qualify (e.g., 216-U-12, 216-S-1,S-2)
Category 4	High Salt - Low Organic - Neutral or Basic Some contaminated soil sites might qualify Some single-shell tanks
Category 5	Low Salt - High Organic - Acid Some contaminated soil sites might qualify
Category 6	Low Salt - High Organic - Neutral or Basic None identified at Hanford
Category 7	Low Salt - Low Organic - Acid Some contaminated soil sites might qualify
Category 8	Low Salt - Low Organic - Neutral or Basic Hanford groundwater Many contaminated soil sites Grout

1983; HDWEIS[(a)]; Sr, Zr, Tc, Ru, I, Cs, Ce, Eu, Co, Np, Pu, Am, and Cm for selected sediments and solutions similar to diluted Hanford wastes and groundwaters [Ames and Rai 1978; Rhodes 1957; Benson 1960; Serne and Rai 1976; Sheppard, Kittrick and Hardt 1976; Hajek 1966; Routson and Serne 1972; Serne et al. 1973; Routson et al. 1976, 1978, 1980, 1981; Gee et al. 1981; HDWEIS[(a)]; and for Mn, Co, Sr, Cs, Tc, and I for grout leachates contacting a typical 200-East Area sediment [Serne et al. 1987].

For many other elements, R_d values can be estimated by analogy to other similar elements [see, for example, HDWEIS[(a)]. The available data are discussed by element in greater detail in the following subsections.

3.3.1 Strontium Data

Strontium is the most extensively studied radioisotope in the Hanford Site soil environment. Thermodynamic data summarized by Ames and Rai (1978) indicate that strontium exists as a divalent cation throughout the potential range of groundwater pH in the absence of complexing anions and organic ligands. It is generally accepted that strontium sorbs by ion exchange as a cation. The degree of sorption in Hanford soil is dependent on the types and concentrations of other cations in solution that can compete successfully for sorption sites. A large data base exists that includes measurements of the effects of different cations and their concentrations on strontium sorption. The data indicate that all common cations (e.g., hydrogen, potassium, sodium, calcium, and magnesium) can influence strontium sorption depending on their concentrations. The majority of experiments were done with Hanford Site soil, which has the general features of being high in sand content (-70 to 80 wt%), moderate in silt content (-10 to 20 wt%), and low in clay content (<1 to 10 wt%). Predominant minerals include quartz, feldspar, and pyroxene with small amounts of micas, smectite clays, oxides, and apatites.

To investigate the effect of hydrogen, Rhodes (1957b) measured strontium R_d at variable pH. Sorption R_d of 5, 30, and 120 mL/g were observed at pH values of 6, 8, and 10, respectively. McHenry (1958) investigated the effects of varying concentrations of potassium, lithium, sodium, and ammonium. Initial

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(a) See page 0.39 in volume 3 of DOE (1987b) for references to specific unpublished citations.

strontium concentrations of 10^{-4} to 10^{-7} M with equal amounts of one or two other cations in solution at approximately neutral pH resulted in sorption R_d in the range 20 to 80 mL/g. These data indicate that these cations do not compete successfully at these concentrations for sorption sites with strontium. Routson et al. (1981) investigated the effects of a wider range of sodium concentrations (10^{-3} to 3 M) and observed a drop in strontium R_d from 39 to 5.6 to 0.6 mL/g at 1.5×10^{-2}, 1.5×10^{-1}, and 1.5 M sodium, respectively. In the presence of potassium, the Sr R_d dropped from 23 at 1×10^{-2} M to 7.9 at 5×10^{-2} M potassium.

Experiments performed to measure the effect of the divalent cations calcium and magnesium on strontium sorption indicate that these cations are the more successful competitors for sorption sites. Rhodes (1956) and Brandt (1957) measured strontium R_d in the range of <1 to 10 mL/g at calcium concentrations between 1×10^{-3} and 1×10^{-2} M and pH values of -6 to 12. Similarly, Routson et al. (1981) showed strontium R_d drop from 10 to 0.3 mL/g when calcium concentrations increase from 5×10^{-3} to 2×10^{-1} M. Nelson (1959) found strontium R_d to drop from 19 to 2 mL/g as magnesium concentrations increased from 1×10^{-3} to 1×10^{-1} M.

Experimental data indicate that common inorganic anions at concentrations observed in the environment do not form significant complexes with strontium, and subsequently do not form anionic aqueous species that would not sorb. McHenry (1958) measured strontium R_d as a function of nitrate, chloride, oxalate, sulfate, and phosphate at concentrations of ~10^{-7} to 1×10^{-4} M and neutral pH. Only phosphate and oxalate influenced Sr sorption and only at their highest concentrations. These anions actually enhanced the measured sorption values. Work by Ames et al. (1958) demonstrated that a calcium phospate mineral, apatite, will form in the soil system containing phosphate and calcite. The calcium dissolved from calcite combines with the phosphate to form the apatite. If strontium is available, it will behave similarly to calcium and coprecipitate in the newly formed phosphate mineral. Consequently, the observed increase in strontium "sorption" is probably due to coprecipitation reactions. It is hypothesized that a similar type of reaction occurs with oxalate.

Little quantitative work has been done to measure R_d values of strontium in the presence of organic anions. Work that has been done indicates that a definite interaction between strontium and some organics does occur, which reduces the sorption of strontium. Knoll (1969) showed that a mixture of 0.4 M d-(2-ethyl hexyl) phosphoric acid (d-2-EHPA) and 0.2 M tributyl phosphate (TBP) in normal paraffin hydrocarbons (NPH) would completely desorb strontium from a soil column. Ames et al. (1958) indicated that cyanide (CN^-) would also complex with strontium. Other experimental data not related to the Hanford soil environment (Fuller and L'Annunziata 1969) show that N-(2-hydroxyethyl) ethylenediaminetetraacetic acid (HEEDTA), ethylenediaminetetraacetic acid (EDTA), ethyleneglycoltetraacetic acid (EGTA), and diethylenetriaminepentaacetic acid (DTPA) will form anionic complexes with strontium and reduce sorption.

Given this data base, sorption R_d for strontium in Hanford Site soil will fall between 0 and 100 mL/g, except in the presence of phosphate or oxalate in which case "sorption R_d" are of the order of 200 to 500 mL/g. Strontium sorption is sufficiently sensitive to groundwater cation concentrations and its own initial concentration that narrowing the R_d range is dependent on the individual situation. It is recommended that a value of 5 to 10 mL/g be used to be conservative, recognizing that in some cases sorption values may be much higher. The use of low values is based on the unconfined aquifer groundwater compositions, which contain $\sim 10^{-3}$ M of calcium. Relatively speaking, calcium should be the dominant factor affecting strontium sorption under most conditions in ambient Hanford soil. Under acidic conditions, a recommended sorption range is 3 to 5 mL/g. Given the much higher salt concentrations in single-shell tank wastes, the recommended R_d for Sr in the presence of solutions similar to those given in Table 9 is 1 mL/g. Limited data on strontium interactions with organic constituents (cyanide, TBP) in Hanford soil suggests that anionic species could form which would further reduce the sorption of strontium.

3.3.2 Cesium Data

A moderate number of investigations of cesium behavior in Hanford soil have been completed. Thermodynamic data summarized by Ames and Rai (1978) indicate that cesium will exist as a monovalent cation throughout the potential range of groundwater pH at Hanford. Cesium has shown no tendency to complex with inorganic or organic ligands, to polymerize, or to form colloids.

Consequently, Cs is expected to sorb primarily by ion exchange. The degree of sorption in Hanford soil is dependent on the types and concentrations of other cations in solution that can compete with cesium for sorption sites. The data indicate that all common cations (e.g., hydrogen, potassium, sodium, calcium, and magnesium) can influence cesium sorption depending on their concentrations. The majority of experiments were done with Hanford soil, which has the general features of being high in sand content (-70 to 80 wt%), moderate in silt content (-10 to 20 wt%), and low in clay content (<1 to 10 wt%). Predominant minerals include quartz, feldspar, and pyroxene with small amounts of micas, smectite clays, oxides, and apatites.

Rhodes and Nelson (1957) measured cesium R_d at variable pH. The hydrogen ion competed successfully for sorption sites at pH values of 0.4 and 1.8 with Cs R_d values of 37 and 138 mL/g, respectively. For pH values from 3 to 10, the measured Cs R_d values exceeded 200 mL/g. Routson et al. (1981) investigated the effects of varying the concentrations of potassium, sodium, and calcium on cesium sorption. Of these, potassium was the most successful competitor, followed by sodium and calcium. Cesium R_d values dropped from 280 to 5.8 mL/g as potassium concentrations increased from 10^{-3} to 2×10^{-1} M, respectively. In the presence of sodium, Cs R_d values were measured at >1200 mL/g for 1×10^{-3} M sodium and then dropped to 570 mL/g at 1×10^{-2} M Na and to 26 mL/g at 3 M Na concentration. Calcium was the least influential competing cation with R_d values decreasing only slightly (2200 to 790 mL/g) when Ca increased from 2×10^{-3} to 2×10^{-1} M. Similarly, Barney (1978) measured cesium R_d in mixed cation systems composed of sodium and potassium with small amounts of humic acid (17 and 33 mg/L); the maximum potassium and sodium concentrations used were 10^{-2} and 1×10^{-1} M, respectively. All measured Cs R_d values exceeded 200 mL/g. Rhodes and Nelson (1957) also measured cesium R_d at much higher sodium concentrations (-1 to 6 M) and observed significant decreases in Cs R_d (from 100 to 18 mL/g) as sodium concentrations increased. Ames and Rai (1978) report work on cesium sorption in simulated tank waste with competing cations (sodium, potassium, calcium, and ammonium) at combined concentrations of >2 M; they reported Cs R_d values from <1 to 14 mL/g.

Relatively little work has been completed to investigate the potential for cesium complexation with anionic ligands. However, data indicate that cesium does not interact with any common inorganic anions and has little interaction with most organic anions. Knoll (1969) observed that a small amount of sorbed cesium on a Hanford Site soil column (-12% after 70 column volumes) could be desorbed when exposed to a flushing solution containing 0.4 M d-2-EHPA - 0.2 M TBP.

Given these data, sorption R_d for cesium in Hanford soil will fall between 0 and >1000 mL/g. Under ambient conditions [i.e., near neutral in pH, relatively low ionic strength (-1 x 10^{-3} M for competing cations), and low concentrations of aqueous organic species], a minimum value of 200 mL/g is a reasonable Cs R_d for use in release and transport analyses. For high-salt wastes and acid wastes, a Cs R_d range of <1 to 200 mL/g is recommended, depending on the ionic strength and relative abundances of competing cations. As the relative potassium concentration increases and the overall ionic strength increases, the appropriate Cs R_d value will decrease to the lower part of the range. The available data base indicates that cesium sorption is relatively insensitive to organic constituents. Therefore, at this time no changes in recommended cesium sorption values are proposed as a function of organic constituents present in a given waste stream.

3.3.3 Plutonium Data

A moderate number of investigations of plutonium behavior in Hanford Site soil have been completed. Thermodynamic data summarized by Ames and Rai (1978) indicate that plutonium may form anionic or cationic aqueous species depending on solution pH and Eh. For oxidizing conditions expected at the Hanford Site, cationic plutonium species should predominate up to a pH value of approximately 6 while plutonium carbonate and plutonium hydroxyl-carbonate complexes with negative charges are expected to occur in the pH range of 6 to 12. The potential for plutonium sorption should, therefore, decrease with increasing pH. However, clear evidence exists (Rhodes 1957c) that plutonium tends to hydrolyze above a pH value of 2. Hydrolysis leads to the formation of finely dispersed precipitates, which can be removed from solution by physical sorption processes and reduce plutonium mobility.

Plutonium sorption has been investigated as a function of pH, salt content, and organic complexants. Rhodes (1957c) showed that plutonium sorption onto Hanford soils is very sensitive to pH. Minimum Pu sorption occurs in the pH range of -1 to 3 (R_d of -30 mL/g). Maximum Pu sorption occurs in the pH range of -4 to 8.5 (R_d, >1980 mL/g) and moderate Pu sorption occurs in the pH range of -10 to 12 (R_d, 380 to 80 mL/g). It is likely that physical sorption of precipitates is a significant process in the maximum sorption range. Limited investigation of cation competition effects on plutonium sorption indicates neglible competition in the neutral pH range. Rhodes (1957c) measured a Pu R_d of 275 in a 4 M solution of sodium nitrate at pH of -7. He also indicated negligible effects on sorption in the presence of 4 M ammonium. Cation exchange competition may influence plutonium sorption at extremely acid pH conditions. Hajek and Knoll (1966) measured R_d values of <1 mL/g at pH values of -1 to 3 and combined calcium, sodium, and magnesium concentrations of -2.5 M. An alternate explanation of Hajek and Knoll's data would be that Pu precipitation is minimized at low pH values and thus the apparent R_d is small.

Investigation of the effects of inorganic anions on plutonium sorption has been limited to nitrate. Evidence indicates that nitrate has little effect on plutonium sorption (Rhodes 1957b). Numerous organic anions have been shown to react with plutonium, forming soluble organic complexes that reduce the sorption of plutonium; these include DBBP, TBP, d-2-EHPA, and hydroxyacetic acid (Knoll 1969). The data show that different plutonium mobilities result from the order in which plutonium and the organics are introduced to a soil column. The least influence occurs when plutonium is first sorbed onto the soil column without organics, followed by flushing of the column with organic constitutents. The greatest reduction in sorption occurs when plutonium and the organic complexants are both present in the infiltrating solution. The data are insufficient to predict R_d values for plutonium in the presence of these species.

Based on the available data, the recommended range of R_d values for plutonium under ambient Hanford soil conditions is -100 to 1000 mL/g. Under acid conditions (pH of -1 to 3), the recommended Pu sorption R_d is <1 mL/g. A wide range of Pu R_d values is possible in neutral to basic pH systems containing appreciable organic compounds, and further data must be collected before a reasonable range can be recommended.

3.3.4 Americium Data

A systematic investigation of americium behavior has not been completed for the Hanford Site soil environment. Thermodynamic data (summarized by Ames and Rai 1978) suggest that sorption of americium is favored because the predicted ionic state of americium is cationic through the pH range of interest. Conversely, there is evidence suggesting the formation of americium hydroxide polymers with increasing pH, which effectively reduces the positive charge of americium aqueous species (Polzer and Miner 1977). Given this understanding it is predicted that americium sorption would be dominated by ion exchange and cation competition at acid pH values and a mixture of ion exchange and physical sorption (polymerization and precipitation) at neutral to basic pH values.

Under acid pH conditions (pH values of -1 to 3), available data indicate that americium sorption R_d are <1 (Hajek and Knoll 1966). Under neutral to moderately alkaline conditions (pH values of -7 to 8) a large range of R_d values (-50 to >1000) have been measured (Routson et al. 1976; Glover et al. 1977).

Investigation of the effects of inorganic anions on americium sorption has been limited to nitrate. Evidence indicates that nitrate has little effect on americium sorption; Routson et al. (1976) observed americium R_d values of >1200 mL/g at nitrate concentrations to 3 M. Numerous organic anions have been shown to react with americium forming soluble organic complexes that reduce americium sorption: these include DBBP, TBP, d-2-EHPA, and hydroxyacetic acid (Knoll 1969). The data show that different americium mobilities result from the order in which americium and the organics are introduced to a soil column. The least influence occurs when americium is first sorbed onto the soil column without organics, followed by flushing of the column with organic constitutents. The greatest reduction in sorption occurs when americium and the organic complexants are both present in the infiltrating solution. The data are insufficient to predict R_d values for americium in the presence of these species.

Based on the available data, the recommended range of R_d values for americium under ambient Hanford soil conditions is -100 to 1000 mL/g. Under acid conditions (pH of ~1 to 3), the recommended Am sorption R_d is <1 mL/g. A wide range of R_d values is possible in neutral to basic pH systems containing appreciable organics, and further data need to be collected before a reasonable range can be recommended. It is expected that the appropriate R_d value may be very sensitive to the type and concentration of organic species of concern.

3.3.5 Neptunium Data

Thermodynamic data summarized by Ames and Rai (1978) suggest that neptunium exists as a monovalent cation, NpO_2^+, under oxidizing conditions except above a pH of approximately 9 where it forms a neutral species with bicarbonate ($NpO_2HCO_3^0$). The data also indicate that neptunium is also capable of complexing with other common anions (chloride, sulfate, fluoride, and nitrate). However, complexed species should not occur at significant concentrations under ambient low ionic strength Hanford groundwater conditions. Assuming that NpO_2^+ is the dominant aqueous species, neptunium should sorb via cation exchange. Work by Routson et al. (1976) and Benson (1961) indicates that neptunium does not compete successfully with common cations for sorption sites. Routson et al. (1976) observed a range of Np R_d of 2.37 and 0.36 mL/g for Burbank sand at calcium concentrations of 2 x 10^{-3} to 2 x 10^{-1} M, respectively. Neptunium sorption in the presence of sodium was also very low (R_d values of 3.9 to 3.2 mL/g at 1.5 x 10^{-2} to 3 M sodium).

Based on these data, the recommended range of sorption R_d for neptunium in ambient Hanford soil conditons is <1 to 5 mL/g. No recommendation for values can be given for any high-salt, high-organic and/or -acid conditions because of the lack of data.

3.3.6 Cobalt Data

Thermodynamic data summarized by Ames and Rai (1978) indicate that aqueous cobalt exists primarily as Co^{2+} up to a pH of approximately 9.5 and then as a neutral hydroxide species $Co(OH)_2^0$ at pH >9. Thermodynamic data also predict that cobalt will complex with common anions (chloride, nitrate, hydroxide, and sulfate) to form mostly neutral or anionic species. These species will not occur at significant concentrations under ambient Hanford groundwater conditions. At a pH value of 9 or less, cobalt should sorb via cation exchange if it does not react with other anions to form anionic or neutral species. Routson et al. (1981) investigated the influence of calcium, sodium, and potassium on cobalt sorption in the presence of a variety of Hanford sediments taken from different boreholes. Of the three cations, calcium was the most successful competitor with cobalt for sorption sites. Sorption R_d for cobalt decreased from 3400 to 200 mL/g as calcium concentrations increased from 2×10^{-3} to 2×10^{-1} M. On the other hand, cobalt R_d increased with increasing sodium and potassium concentrations (from 2100 to 4700 mL/g as Na increased from 1×10^{-3} to 3 M, and from 500 to 3400 mL/g as potassium increased from 2×10^{-3} to 2×10^{-1} M). These data clearly indicate that the cation exchange process is not the only process affecting cobalt sorption. The authors suggested that colloid formation and physical sorption were occurring. Conversely, Barney (1978) observed that the sorption of cobalt on Hanford soil was reduced in the presence of potassium. Specific R_d values were not reported.

Some field studies and laboratory studies on Hanford soil indicate that cobalt readily reacts with organic and inorganic anions when they are present at high concentrations. These observations are supported by other studies on soils similar to Hanford soil. Haney (1967) reported the occurrence of cobalt in groundwater under the 216-BY crib. He proposed that the apparent high mobility of cobalt in the soil column was due to the formation of anionic cobalt phosphate complexes resulting from the high phosphate content in the waste stream. Barney (1978) observed that the sorption of cobalt on Hanford soil was reduced in the presence of nitrite (NO_2^-) and humic acid, presumably because of the formation of anionic or neutral complexes with cobalt. Wilding and Rhodes (1963) demonstrated that the addition of EDTA to a soil water system would reduce the cobalt R_d by a factor of 100.

Based on the foregoing information, the recommended range of sorption R_d for cobalt is 500 to 2000 mL/g for ambient Hanford soil conditions (neutral to slightly basic pH, low ionic strength, and low organic content). A recommended range for high-salt, high-organic, and/or -acid condtions cannot be specified with any confidence because of the lack of data. General indications are that R_d values will be much lower under these conditions.

3.3.7 Uranium Data

Under oxidizing conditions (typical for Hanford), dissolved uranium is predicted to exist as a cation (UO_2^+) up to a pH of approximately 6, as a neutral hydroxide species $UO_2(OH_2)^0$ from a pH of approximately 6 to 8, and as an anionic carbonate $UO_2(CO_3)_3^{4-}$ above a pH value of 8. Uranium may also complex with other anions (e.g., fluoride, chloride, and phosphate) to form neutral or anionic species, but such complexes should not exist in significant concentrations under ambient Hanford groundwater conditions. These estimated species distributions suggest that uranium would sorb via cation exchange under acid conditions and sorb very poorly under neutral and basic conditions.

No laboratory studies have been published describing uranium sorption in Hanford soil, but unpublished work (Wayne Martin at PNL) and U1/U2 pond experience (Delegard et al. 1986) suggest uranium is not adsorbed under ambient Hanford groundwater conditions and slightly acidic conditions, respectively. Characterization of 300 Area soil underneath the 316-4 crib by Ames and Phillips (1979) indicates that uranium is rather immobile because of solubility constraints rather than sorption. Strong evidence is presented that a uranium phosphate has precipitated because of the high phosphate content in the waste stream. Leaching experiments were completed as part of the study and showed that 0.1 N HNO_3 acid was very successful at removing uranium from the contaminated soil column while distilled water and a methyl isobutyl ketone solution did not remove uranium from the soil. The data indicate that nitric acid dissolves the uranium phosphate phase.

General indications are that uranium sorption values will be low under most circumstances because uranium tends to form neutral or anionic species at neutral or basic pH values and is a poorly adsorbing cation at acid pH values. We recommend more data be collected on U adsorption from waste leachates and groundwater onto Hanford sediments.

3.3.8 Ruthenium Data

Thermodynamic data that predict aqueous speciation of ruthenium are largely unknown. Available data indicate that ruthenium exists primarily in the +3 and +4 oxidation states and is rarely, if ever, a simple cation. Ruthenium readily complexes with common anions (hydroxide, nitrate, nitrite, chloride) and may form a variety of anions or cations depending on the given chemical system. Consequently, ruthenium sorption is highly variable and predictions of expected sorption ranges are quite sensitive to a particular waste stream. Rhodes (1957a) investigated ruthenium sorption on Hanford soil as a function of pH. Ruthenium was introduced into solution as ruthenium chloride ($RuCl_3$). Maximum sorption occurred in the pH range 4.7 to 8.5 (R_d 101 to 274 mL/g) and at pH values of 13 and 14 (R_d 101 and 752 mL/g). Intermediate Ru R_d values (~20 to 100 mL/g) occurred at other pH values except at extremely acid values (pH $\leq$ 1.3) where no sorption occurred. These high sorption values are invalid in the presence of nitrate/nitrite-bearing solutions. Ames and Rai (1978) report work on ruthenium sorption from simulated tank solutions with >1 M nitrate and observed Ru R_d values of <2 ml/g. Barney (1978) observed that the sorption of ruthenium on Hanford soil was reduced in the presence of nitrite (NO_2^-), presumably because of the formation of anionic or neutral complexes. Conversely, the presence of humic acid tends to enhance ruthenium sorption.

Based on available data, a recommended range of sorption values can only be provided for the condition where ruthenium-bearing waste also contains nitrate. In this case, the R_d sorption range is <1 to 5 mL/g.

3.3.9 Technetium and Iodine Data

Little work has been done on Hanford Site soil to measure the sorption of technetium or iodine. Routson et al. (1976) measured technetium sorption on Hanford soil and measured R_d values 0 to <1 mL/g. No work has been completed for iodine sorption. However, other experimental work on similar soils indicates that both iodine and technetium exist as negative anions (TcO_4^-, I^-, IO_3^-) in oxidizing soil environments and do not readily complex with other chemical species. Consequently, these elements are considered to be relatively nonadsorbing in almost every soil environment. Sorption may occur in soils that contain considerable organic matter which tends to sorb anionic species, and in the case of technetium may reduce its valence to the +4 state causing precipitation or sorption. Because these types of soils are nonexistent at Hanford, the recommended sorption R_d range for Tc and I for all types of waste conditions is 0 to <1 mL/g.

4.0 GEOCHEMICAL DATA NEEDS AND STRATEGY FOR IMPROVING CONTAMINANT RELEASE AND TRANSPORT

4.1 STRATEGY

The process proposed to define and constrain the proposed geochemical data collection program is illustrated in Figure 1. The initial phase is subdivided into four parts that comprise baseline data collection. Radionuclides and contaminants are identified from historical records, existing analyses of waste site materials, and computer projections of inventories (e.g., TRAC; see Adams, Jensen and Schulz 1986).

Geochemical parameters are chemical and physical properties of the waste disposal environment that influence geochemical reactions between the radionuclides and hazardous wastes and the pore water and sediments. The reactions of interest are those affecting radionuclide and contaminant mobility, including solubility, sorption, desorption, and release rates from solid-waste forms. The important parameters include pore water and recharge water composition, sediment composition, and waste-form composition. Other important parameters influencing contaminant transport by groundwater are sediment porosity, permeability, moisture content, and groundwater recharge characteristics.

Hydrologic parameters used in performance assessment analyses are generally derived from properties measured at the specific site of interest. Geochemical reaction values for radionuclides or hazardous chemicals (e.g., sorption, solubility) are generally derived from laboratory studies that evaluate the effects of chemical parameters for the ranges of values that are pertinent to the site. Solubility data are sometimes derived from thermodynamic calculations that use site-relevant chemical conditions. As part of this report, a baseline data base that is specific to Hanford Site defense waste has been assembled from available information.

Having established a data base, an iterative loop process is needed to delimit completion of data collection. Additional data needs are identified on the basis of performance assessment modeling (i.e., pathways analysis) or generally acknowledged lack of information. If the pathways analysis, which is done on an element-by-element basis, indicates an unacceptable degree of uncertainty for the reaction values used as input to the models, additional data are required. Additional data may also be required to quantify parameter values that affect geochemical reaction values. For example, the effect of moisture content on sorption distribution coefficients (R_d) can be theoretically calculated, but such calculations are supported by few test data.

Once data have been collected and appropriate analyses have been used to generate model input data, the adequacy of available data is evaluated by using the input data in a computer code that predicts transport and release of contaminant to the environment. To address uncertainty, a range of input values is generally used. The model results are compared to acceptable release values to determine if predicted releases are acceptable. If the range of values used results in a range of predicted release values that is ambiguous (e.g., releases are unacceptable or acceptable, depending on which specific value within the range of values is used), then additional data on the waste form or engineered system may be required (see Figure 1) to reduce (or at least better define) the range of uncertainty.

4.2 DATA NEEDS FOR IMPROVED RELEASE MODELS

Additional data are required to quantify the release of contaminants from the various Hanford Site wastes. These needs are a function of the particular type of waste to be buried because each type of waste has unique characteristics that influence the type of data that need to be collected. To focus data collection, the major uncertainties or issues relating to the release of radionuclides or hazardous elements from each waste form must also be identified in the context of available information on release characteristics and modeling assumptions used to date.

A data collection approach is then identified that addresses the uncertainties. The principal emphasis for this report is on laboratory or bench-scale methods; however, other methods are also discussed. The emphasis of the testing approach should be empirical; the expected environment is simulated, and geochemical reactions between radionuclides or hazardous chemicals and the simulated environment are observed. This approach is recommended for two reasons. First, in many cases, numerous kinds of reactions are possible such that mechanistic studies could never be completed, given the time or resources available. Second, the empirically derived data can easily be used by computer codes that generate estimates of radionuclide or hazardous chemical release.

A mechanistic approach could be used where feasible (e.g., solubility calculations). For each test method, the data to be collected are identified and their use in a performance assessment is described. The advantages and disadvantages of the proposed test method and the proposed scope of the test matrix are also described. To the extent possible, the decision points to be used to judge completion of the testing will also be identified.

In addition to empirical data collection, associated tasks are identified that either provide information on the environment the tests are to simulate or provide corroborative data for comparing with empirically derived data. In the following section the status of associated tasks and their potential constraints on completion of collection of empirical data are discussed.

4.2.1 Single-Shell Tanks

The ultimate fate of the wastes currently stored in 149 single-shell tanks is not yet determined. Several options discussed in the HDWEIS include in-place stabilization and isolation under protective barriers and retrieval of wastes and subsequent treatment, with some waste components processed by a glass vitrification plant and others disposed as grout in concrete-limited vaults.

It is likely that small amounts of waste will remain in the tanks even if the bulk of their contents are retrieved. Murthy et al. (1983) discuss the 26 tanks that have been confirmed to have leaked and suggest that 31 additional tanks may have lost integrity. At least 5 x 10^5 gallons of waste that has leaked into vadose sediments adjacent to the tanks also need to be considered.

The most defensible concept of contaminant releases from the single-shell tanks consider recharge water or water vapor entering breaches in the tanks, leaching wastes, mixing with existing drainable liquors, and subsequently escaping from the tanks.

Empirically determined solubility values (constant concentrations), as given in Table 15, are recommended as model input parameters for simulating release. Where no data exist, the estimated inventories of constituents and percentage soluble in water (see Table 4) should be used with congruent leach concepts to generate estimates. For example, Table 15 lists no estimate for Ag. If we assume that the Ag ratio to the nitrate inventory is 1 x 10^{-4}, then a congruent release model would suggest is 0.1 mg Ag is released for every gram of nitrate. If this assumption is combined with the observation that on average only 4% of the silver in tank waste dissolves in water (100% of nitrate dissolves), then 4 μg of Ag would be released per gram of nitrate. The recommended value for a constant empirical solubility limit for NO_3 (see Table 15) is 360 g/L. Consequently, a value of $(4 \times 10^{-6} \cdot 360)$ 1.44 x 10^{-3} g/L of Ag is calculated.

Additional coring and chemical analysis of cores of single-shell tank wastes are planned to begin in 1990. Additional chemical analyses of drainable liquors and water-leachable percentages, analogous to data prevously reported (Weiss 1986; Weiss and Schull 1988a-i), will also be collected. Attempts will be made to identify additional radionuclides and hazardous chemicals that may be present in the drainable liquors and water leachates. These future data will be valuable to Hanford Site performance assessment activities. Constituents that merit particular attention include F, NO_3, Be, CN, Cr, Am, Pu, Np, U, ^{137}Cs, ^{129}I, ^{126}Sn, ^{99}Tc, ^{90}Sr, ^{63}Ni, and ^{14}C, and organic chemicals such as carbon tetrachloride, methylene chloride, and trichloromethane. This list is based on estimated tank inventories, presence in Hanford Site groundwaters, and existing dose and health effects calculations.

4.2.1.1 Description and Purpose of Proposed Experimental Testing

It will likely be prohibitively expensive to analyze actual drainable liquor and water leachates to empirically determine solubility limits for all potentially important regulated constituents of single-shell tank wastes. Consequently, synthetic tank liquors (without radionuclides and "exotic" trace constituents) should be prepared and used for empirical solubility tests. In such tests, the constituent of interest should be added until a maximum solution concentration is reached. For tests on synthetic drainable liquors, the use of radiotracers would be ideal because direct chemical analyses are difficult for high ionic strength brines.

Besides performing empirical solubility experiments on tank waste constituents that are important to performance assessment but not routinely (and successfully) measured in characterizing single-shell tank wastes (see

Weiss and Schull 1988a-i), the effects on solubility of organic chemicals present in the wastes merit study. As shown in Tables 7 and 9, drainable liquors and water leachates contain significant quantities of organic chemicals. Characterization of organic chemicals in actual tank solutions (e.g., double-shell tank) has been attempted once (Toste et al. 1987). Generic experiments using known double-shell tank organic compounds (e.g., Toste et al. 1987), known process reagents (e.g., Delegard and Gallagher 1983), or archetypical complexing agents could obtain data on the general effects of organic chemicals on the solubility of important contaminants in leachates of single-shell tank wastes.

Collection of thermodynamic data necessary to accommodate high ionic strength calculations is recommended as salt content (ionic strength) of drainable liquors and water leachates from single-shell tank wastes is large (>3 M). Thermodynamically based activity corrections, necessary to properly calculate solubilities, are very important for such solutions. The ion association approach common to most geochemical computer codes is not adequate for the solutions in single-shell tanks, and an alternate approach, ion interaction (e.g., Felmy and Weare 1986; Harvie et al. 1984; Pitzer 1973, 1979), is recommended. The ion interaction approach requires empirical virial coefficients to describe binary and ternary interactions between cations and anions. Such coefficients are available for only a few tank waste constituents and rarely for trace constituents such as radionuclides and transition-group metals with environmental hazard potentials. Felmy et al. (1989) have predicted actinide solubilities in brines by assuming that their interaction parameters are similar to those of known lanthanide elements.

4.2.1.2 Status and Estimated Resource Requirements

From the perspective of performance assessment, the greatest short-term need is to coordinate the tank characterization (e.g., Weiss and Schull 1988a-i) and performance assessment activities (recent internal PNL activities by Salter and co-workers and Droppo and co-workers) to optimize use of available resources. Currently, single-shell tank waste characterization is focused on sampling tank waste and determining its composition. To date, performance assessment has used simplistic release and transport models (e.g., RAPS/MEPAS) to generate guidance on constituents of the waste that might be most detrimental to the environment. Data are currently available to create a more technically defen-sible release model that could provide better guidance. However, additional empirical solubility data are needed for potentially important contaminants, the effects of organic chemicals, and appropriate methods for determining chemical activities in the high-salt liquors. Estimated resources to address the performance assessment needs identified for single-shell tank wastes are given in Table 31.

4.2.2 Grout

The current conceptual release model for contaminants from grout is based on diffusion theory. The model is generally accepted in the technical community because cement and cementitious mixtures commonly used to encapsulate many low- and intermediate-level nuclear wastes and numerous hazardous wastes throughout the world appear to release contaminants by diffusion-like processes. Also, the available generic and Hanford Site-specific data base is large relative to that for other waste forms. Several yet-to-be-resolved issues being studied include the effects of curing temperature and aging on leaching of contaminants from grout.

Because the Hanford Grout Technology Program has incorporated project-specific performance assessment capabilities, work in support of the geochemical aspects of assessing system performance is adequately covered and not discussed

TABLE 31. Proposed Activities and Resource Estimates for Single-Shell Tank (SST) Release

Activity	Time Frame (yr)	Resource Estimate (man-yearlyr)
Near-term coordination	1990	0.33
Long-range coordination and planning Planning, future SST conceptual model development	1991-1995	0.33
Empirical solubility testing (emphasize simulated SST)	1990-1993	0.50
Effects of organics on solubility/sorption	1991-1994	1.0
Improve thermodynamic codes/data base	1990-1991	0.25
	1992-1996	0.5 to 1.0

further in this document.

4.2.3 Contaminated Soils

Suprabasalt sediments of the Hanford Site have been contaminated by the disposal of waste solutions from processing facilities and service operations. Consequently, these sediments are a potential source for migration of contaminants to the water table. These soils are partially saturated and contain contaminant residues physically or chemically attached to soil particle surfaces. Over time, rainwater, or in some cases additional process solutions, will flow through the contaminated soils and potentially flush contaminants to the water table.

Two key questions that must be answered for a given site are 1) What is the extent of the contaminated volume of soil and the distribution of radionuclides or contaminants within that volume in terms of types and concentrations? and 2) how will radionuclides or contaminants be released from the contaminated soil and be transported to a receptor? To answer the first question, site characterization must determine the actual volumes of contaminated soil and the types and concentrations of contaminants. This report concentrates on the need to develop data to answer the second question. To do so, transport analyses must be completed using site characterization data and laboratory data that quantify the hydrologic, geologic, and geochemical interactions controlling contaminant release and transport. The distribution of contaminants at active and inactive sites is under the purview of RCRA and CERCLA activities, respectively. This report addresses only the needs for data on the release of radionuclides or hazardous chemicals from the waste source.

As described in Sections 2.2.3, 2.3.3 and 3.2.3, only a generic analysis has been completed to describe release and transport of contaminants from existing contaminated soil sites. Both solubility and desorption concepts have been used to define the source-term for a few radionuclides. These source-terms, combined with assumed flow characteristics, were used to predict eventual maximum contaminant concentrations at a receptor well. Consequently, several gaps exist in conceptual models and contaminant data. With regard to geochemical reactions and data input needs of performance assessment computer codes, several environmental characteristics have not yet been considered.

These include 1) the effects of partial saturation and intermittent flow on contaminant release rates; 2) the effects of differing soil characteristics (e.g., mineralogy, porosity); and 3) the effects of other contaminants (e.g., aqueous complexants or competitors for sorption sites) that may have been present in a waste stream on sorption/desorption distribution coefficients or solubilities. These factors are potentially capable of significantly influencing the mobility and transport of radionuclides or contaminants along the groundwater pathway.

The test methods discussed in the following sections are recommended for investigating and quantification of radionuclide and/or chemical contaminant reactions (i.e., determination of solubility, sorption/desorption coefficients, and retardation factors). as a function of these environmental factors.

To estimate the amounts and rates of contaminant releases from waste sources to a receptor, the concentrations in solution, solution volumes, and rates of transport must be estimated. Typically, the concentration in solution is controlled by 1) a solid phase that incorporates a radionuclide and/or chemical with an associated solubility; or 2) an equilibrium or steady-state distribution of contaminant between adsorbent surfaces (sediment) and solution. A transport model typically defines the source term either as the empirically determined solubility (constant concentration) or the solution concentration resulting from the distribution coefficient between soil and water. All other factors considered equal, an increase in the assumed concentration of the source results in a prediction of greater maximum concentration at the receptor. By comparing maximum predicted concentrations with maximum allowable concentrations, a decision can be made between no action and a remedial action such as removal of some portion of the source and treatment or in situ treatment to reduce release rates from the source.

The ultimate behavior of a given radionuclide or contaminant is dependent on the physical and chemical environment in which it resides. This environment includes the sediment characteristics (phase mineralogy, grain size, porosity, permeability, and moisture content), the transporting liquid characteristics (Eh, pH, and organic components), and the chemical characteristics of the radionuclide or contaminant of interest. To a certain extent each site is unique. However, common features exist from site to site that largely control radionuclide or contaminant mobility. The most immediate concerns relative to specific waste disposal sites at Hanford have generally been identified. The Hanford Site Performance Assessment program focuses on the features common to the sites and predicts their effects on contaminant mobility. Particular emphasis will be placed on specific contaminants identified as potentially harmful to the environment. As needs arise or more specific information becomes available, additional information needs can be identified as required.

The available sources of information are primarily records of materials and waste processing, waste disposal (e.g., Stenner et al. 1988), and soils characterization data. From these information sources, a list of radionuclides and contaminants that have been disposed at specific disposal sites can be compiled and the chemistry of disposal liquids can be identified (Table 32). From this list, a matrix of tests could be derived to quantify contaminant releases for the combinations of radionuclides, contaminants, disposal liquids, and soil types known to exist. The focus should be on those combinations of contaminants, disposal liquids, and sediment types that are considered most harmful and mobile in the sediments and unconfined aquifer.

4.2.3.1 Description and Purpose of Batch Experiments

Batch tests for sorption are commonly used to measure the distribution of an element between a solid (e.g., soil) and a liquid (e.g., groundwater). The test is conducted by spiking a solution with the element of interest, mixing the solution with the solid for a specified period of time, separating the solution from the solid, and measuring the concentration of the spiked element in the solution or solid. The ratio between the two phases (solid over liquid) is commonly referred to as a distribution coefficient or R_d (see Section 3.1.1).

A primary advantage of such data is that they are easily inserted into hydrologic transport codes to quantify reduction in the rate of transport of the contaminant relative to groundwater, either by advection or diffusion. A second advantage is that such experiments can be completed quickly for a wide variety of elements and chemical environments.

The primary disadvantage is that the batch experiment does not necessarily reproduce the chemical reactions that take place in the real environment,

TABLE 32. list of Identified Radionuclides, Hazardous Metals, and Organic Constituents in Liquid Effluents

100 Area

Radionuclides + Metals	Major Constituents	Waste Stream
U	Sodium dichromate	Sulfuric acid + sodium dichromate
Pu	Sodium oxalate	
Cd	Sulfuric acid	Chromic acid + oxalic acid + sulfuric acid + soda ash
Hg	Sulfamic acid	
Pu	Potassium borate	
^{3}H	Copper sulfate	Sulfuric acid + NaOH
Co	Sodium sulfamate	Nitric acid + hydrofluoric acid
Sr	NaOH	
Eu		Cs ± base
Ni		

200 Area

Radionuclides + Metals	Major Constituents	Waste Stream
^{3}H	Dibutyl butyl phosphonate	Nitric acid
Sr	Nitric acid	
Cs	Kerosene	Sodium salts + fluoride + nitrate + sulfate + phosphate + aluminate
Pu	Phosphates	
Co	Sulfuric acid	
Ru	Fluoride	
U	Sodium aluminate	Sodium salts + fluoride + oxalate + nitrate + sulfate + phosphate + ammonium nitrate
	Methylisobutyl ketone	
	Aluminum fluoride nitrate	
	Calcium nitrate	
	Magnesium nitrate	
	Tributyl phosphate (TBP)	TBP + kerosene
	Sodium dichromate	
	Ammonium carbonate	Ammonium nitrate
	Sodium oxalate	
	Ferrocyanide	Na-dichromate, Na-aluminate, Na-nitrate, and Na-hydroxide
	Sodium silicate	
	Sodium nitrite	
	Ferrous sulfamate	Nitric acid + sulfuric acid + sodium dichromate ± NaOH
	Carbon tetrachloride	
	Aluminum nitrate	
	Ferric nitrate	Sodium nitrate + fluoride
		Sodium salts + nitrate + sulfate + aluminum fluoride nitrate + Mg nitrate + Ca nitrate ± (carbon tetrachloride + TBP + dibutyl butyl phosphonate)

TABLE 32. (contd)

200 Area

Radionuclides + Metals	Major Constituents	Waste Stream
		NaOH
		Butyl phosphates + kerosene + ammonium carbonate
		Methyl isobutyl ketone + sodium nitrate + sodium dichromate
		Na nitrate + Na phosphate

300 Area

Radionuclides + Metals	Major Constituents	Waste Stream
Cr (VI)	NaOH	Trichloroethylene + methyl isoketone + nitric acid + nitrite
Cd	Nitrate	Methyl isoketone
Pb	Nitrite	
Hg	Nitric acid	
U	Trichloroethylene	
Zn	TBP	
Be		
Co		
Pm		
Pu		
Sr		
Cs		

where the solution is passing through the soil column at a finite rate because both reaction time and the degree of mixing between solid and solution can be much less in the flow-through situation. Consequently, distribution coefficients from batch experiments can be high relative to reality, resulting in nonconservative estimates of release using transport codes with these data as input (e.g., Coles and Ramspott 1982). A second disadvantage relative to the Hanford Site vadose zone environment is that batch experiments are done under saturated conditions so that the effects of partial saturation on sorption processes cannot be investigated. A third disadvantage is that the sorption experiment does not really simulate release of radionuclides or contaminants from a contaminated soil waste source because that reaction is basically a desorption reaction. However, sorption values are frequently used based on

1) the assumption that sorption and desorption reactions are reversible; and 2) the observation that elements tend to desorb at a slower rate or be irreversibly sorbed to some extent. Thus, use of sorption values in release and transport models is considered to provide conservative or high release estimates.

Limited batch adsorption experiments therefore will be used to identify the potential for high mobility of radionuclides or hazardous chemicals under chemical conditions in the soil column altered by discharge of liquid waste with significantly different chemical characteristics relative to natural pore waters, groundwater, and rainwater. Data describing interactions of radionuclides and organic complexants in soils that have been flushed with highly acidic or nitrate-rich solutions are sparse. Short-term batch experiments for potential radionuclide, complexant, and liquid composition combinations will be performed and compared with an existing data base for radionuclides sorption characteristics under normal soil/groundwater conditions. Those combinations that behave very differently from the normal will require more sophisticated flow-through testing to quantify mobility. The batch sorption R_d values could also be used in scoping release calculations to estimate radionuclide or complexant release. Four parameters to be considered in the test matrix for batch sorption experiments include sediment types, contaminants and their concentrations, potential organic and inorganic complexants and their concentrations, and solute composition (pore water, waste solution, or mixtures of both). The rationale for the selection of each component and the proposed list are provided next.

Soil types are chosen on the basis of information gathered on sediments collected from boreholes and geologic investigations. Information is available on physical properties (grain-size distribution) and gross chemical properties (carbonate content) for numerous boreholes in the ROCKSAN data base (Michele Chamness, PNL, personal communication). The chemical properties of the soils are pertinent for understanding chemical reactions between radionuclides, complexants, percolating solutions, and soils. Although more precise mineralogic information is desirable, these gross descriptions should be sufficient to establish a representative testing matrix. Generally observed relationships for radionuclide-mineral interactions indicate that mixtures including quartz sand, basalt sand, smectite clay, organic matter, and calcium carbonate should be sufficient to determine a range of sorption behavior that will bracket radionuclide and contaminant mobility at the Hanford Site. As a starting point, it is recommended that five types of soil be used in experiments: pure or nearly pure quartz sand (≥90%), pure or nearly pure basalt sand (≥90%), intermediate clay-sand mixes (~40-60% each), nearly pure clay materials (≥90%), and an organically rich (by Hanford Site standards) clay-sand mix. It is likely that soil samples collected from Hanford Site boreholes would be readily placed into these broad categories. Actual samples used will depend on the amount and type of samples collected. Samples could also be collected from the sides of deep pits or trenches at representative depths. The solutions used to contact the sediments will be generic waste leachates (see Table 29). Most contaminated soil sites are in categories 1, 3, 4, 7, and 8 (Table 29).

Identified radionuclides, organic complexants, hazardous materials (mostly metals), and types of effluent solutions as a function of the Hanford Areas are listed in Table 32. As can be seen from these lists, derived from the National Priority List (NPL) investigations and draft work plans for the top priority CERCLA operational units, several waste site components are universal. Further information is likely to change the list of components. Not all combinations can or need to be included in a batch sorption test matrix, and existing chemical principles and experimental data allow reducing the list of component combinations to consider. Combinations found in larger quantities at waste sites high on the cleanup priority list [as ranked by Stenner et al. (1988)] will be considered first.

4.2.3.2 Task Status and Estimated Resource Requirements

Some sorption experiments have been completed with Hanford Site soils (see Section 3.3) and interactions between radionuclides and some potential organic complexants have been investigated. However, more data are needed. An initial scoping study (i.e., approximately 1 to 2 man-years total effort) would generate a data base allowing more objective detailed planning. More time might be required if sample availability must depend upon CERCLA site characterization schedules. Noncollection of scoping data will result in either using highly conservative sorption data in performance assessment models (i.e., higher release rate estimates) or increasing the amount sophisticated testing (i.e., flow-through column leach/adsorption tests) to quantify contaminant release.

The following activities are required to complete or support the batch sorption scoping activity:

Uncontaminated Soil Sample Collection -- Collect representative clean sediment samples from the site as a function of depth and type. Collect samples from boreholes, archived samples, and sides of new trenches and pits. Analyze soil for phase mineralogy and percentages of phases. The objectives are 1) to provide representative soil for experiments and 2) to ensure that a representative group of "soil chemistry environments" can be defined for which a range of sorption values can be established and used in performance assessment analyses. The present data base suggests that a few representative Hanford Site soil types can be selected that cover the expected range in sorptive behavior.

Sample collection and analysis will likely be a limited task. Soil samples could be coupled with well drilling efforts in conjunction with the RCRA/CERCLA groundwater monitoring well installation programs. Analyses of soil samples are estimated to require 0.5 man-year/yr of effort. Completion of this task will be determined by professional judgment supported by statistical analysis. Failure to complete this task will result in continued use of conservative (low) sorption values in performance assessment analyses and higher estimates of release.

Literature Review -- Perform literature review to identify combinations of radionuclides, contaminants, soil types, and effluent solutions that require further data to quantify sorption behavior or that can be eliminated from the test matrix on the basis that sufficient information is already available. Partial completion of this task is reported here. Interaction between radionuclides and organic complexants requires more study. It is likely that relatively little information is available, and thus only ~6 man-months are required to finish this task. Failure to conduct the literature review could result in collecting unnecessary data or duplicating existing information.

Contaminated Soil Sample Collection -- Collect, analyze, and preserve contaminated soil samples to identify potential test matrix constituents. Few such samples have been collected, and none have been completely characterized to date. Characterization is a key component of CERCLA investigations that will continue indefinitely. We will obtain samples of contaminated soils from CERCLA projects for additional study.

4.2.3.3 Description and Purpose of Solubility Experiments

The solubility of some contaminants of interest may be sufficiently low that release from the contaminated soil zone is limited by an solid phase that has precipitated in the contaminated zone. If so, the maximum solution concentration is time invariant (assuming chemical conditions remain constant in the contaminated zone) and determined by the equilibrium reaction between the phase and recharge water; the equilibrium solution concentration can then be used as the source-term for release from the contaminated zone.

Estimates of solubilities are necessary for all radionuclides or contaminants so that a decision on the appropriate source-term can be made. To perform sorption experiments unambiguously, it is also necessary to ensure initial radionuclide or contaminant concentrations do not exceed solubility. If concentrations exceed solubility, sorption effects cannot be distinguished from precipitation effects when the element is distributed between solid and liquid phases.

We recommend only a few solubility-type experiments be done because solubility values from literature sources can likely be used for most radionuclides and contaminants of interest. A solubility experiment may be completed in a fashion similar to the sorption tests: a solution could be spiked with the contaminant or radionuclide at varying initial concentrations and placed in contact with the soil of interest. The empirical solubility value can be determined by observing the relationship between the initial and final solution compositions. When the final solution concentration cannot be increased as the initial concentration continues to be increased, that concentration value will be taken as the solubility value. A similar experime can also be completed without the soil. Alternatively, excess suspected precipitate can be placed in simulated groundwater and the final steady state solution concentration measured. When all these three tests yield similar results, one can be fairly certain that an accurate solubility value has been determined for the given conditions.

As with sorption values, empirical solubility concentrations can easily be placed in transport codes as the source-term and provide conservative estimates of release unless environmental conditions change such that solubility is increased. This points out the importance of justifying the likely range of chemical conditions over time in the contaminated soil column. A disadvantage of the empirical solubility experiment is that other factors such as colloid formation may artificially increase the observed concentration thereby increasing release estimates and possibly leading to unnecessary and costly remedial action.

The parameter types to be considered in solubility experiments are essentially identical to those for batch adsorption tests: soil types, choice of radionuclide or contaminant, and types of effluent solutions. Establishment of the test matrix will depend on the same rationale used in the selection of batch sorption experiments (see discussion of sorption).

4.2.3.4 Task Status and Estimated Resource Requirements

The need to perform solubility experiments has not been clearly established. In most cases it is unlikely that solubility experiments will be necessary, either because solubility controls are unlikely to control release or solubility values are sufficiently known from indirect means. For a given element in a given situation, confirmatory solubility tests may be considered useful to support performance assessment validation efforts. Two issues that may warrant further study in contaminated soils are the effects of high ionic strength and organic complexants on radionuclide and trace metal solubility. The effort required to complete this task is estimated at 2 to 3 man-years. Failure to generate the data may cause the use of a higher solubility value in performance assessment analyses resulting in higher release estimates.

The following tasks are required to support completion of the solubility activity:

Perform Literature Review -- Perform literature review to identify empirical solubility values for radionuclides and contaminants over the range of environmental conditions likely to occur in Hanford Site soil. Identify those combinations of elements and environment for which solubility constraints do not apply (e.g., iodine). Partial completion of this task is reported here.

Interaction between radionuclides and organic complexants and solubility at high ionic strength require further study. It is expected that relatively little additional information is available, and that ~4 man-months should be sufficient to finish this task. Failure to collect this information could result in the design of tests that are not necessary or duplicate existing information.

Perform Thermodynamic Calculations -- Solubility estimates can in many cases be derived from available thermodynaniic data that are applicable to the Hanford Site soil environment. These estimates, when used alone or with empirical data, can provide a justifiable range of solution concentrations for use as source terms in a performance assessment analysis. Thermodynamic calculations have been completed for many nuclides and some hazardous constituents and computer codes (e.g., MINTEQ and EQ3/6) are well developed. Consequently, little further effort is required; approximately 1 to 3 man-months on an as-needed basis should be sufficient. This estimate might be exceeded if thermochemical data for organic complexes with radionnuclides and hazardous metals must be added to the code data bases or if high ionic strength conditions require ion interaction theory to be invoked (see discussion on single-shell tanks in Section 4.2.1.1).

4.2.3.5 Description and Purpose of Proposed Flow-Through (Column) Experiments

Flow-through column experiments are intended to provide a more realistic simulation of the soil column environment and to quantify the movement of contaminants relative to groundwater flow. The basic experiment is completed by flushing liquid through a column of soil with the contaminant of interest, either spiked in the solution or previously adsorbed onto the soil column. Two situations must be considered to evaluate contaminant release from contaminated soil sites. First, it may be necessary to simulate the original waste disposal activity and to characterize the initial distribution of contaminants in the soil column by flushing a solution that mimics the waste liquid in composition through the soil column. Characterization of the soil and effluent solution will provide characteristics of the source-term. The second need is to pass rainwater through the contaminated soil column to simulate release and transport of contaminants from the source. By measuring changes in concentration of contaminants or radionuclides in the soil column and rainwater, estimates of retardation factors, sorption coefficients, and release rates versus time can be quantified. This step could also be accomplished by flushing simulated rainwater through a column of actual contaminated soil.

Sorption or desorption processes can be studied in this manner. The column experiment combines the chemical effects of sorption and the hydrologic effects of groundwater flow through a porous medium to provide an estimate of retarded movement of the contaminant of interest. The retardation factor is measured directly from the experimental data, rather than a sorption coefficient, as in the case of the batch sorption experiments. A sorption distribution coefficient can be back calculated from the retardation factor. It is frequently useful to compare the back-calculated sorption coefficient from these experiments with those derived directly from the batch experiments to evaluate the influence of limited interaction between solid and solution imposed by the flow-through system.

As with batch sorption data, the retardation factor can be inserted easily into a hydrologic transport code, quantifying the reduction in the rate of transport of the element relative to groundwater by either advection or diffusion. A second advantage is that the column experiment provides a much closer approximation of the real environment than a batch sorption experiment, and affords greater confidence in the application of the data to transport models. Not only the influence of limited interaction (by either time or physical contact) between water and solid on sorption reactions, but also the influence of partial saturation and partially saturated flow, can be investigated. A potential disadvantage is that techniques that accurately simulate partially saturated flow probably need further development. A second disadvantage is that some soil properties cannot be accommodated by laboratory-size equipment because of the large particle size of some typical soils (e.g., cobbles and boulders). A third disadvantage is that sorption or desorption reactions can occur by numerous mechanisms that cannot be distinguished by these types of experiments. Consequently, caution must be used when generalizing the results from one set of experimental conditions to field conditions. Care must be taken to justify the assumption that environmental changes between laboratory and field situations have no significant effect on contaminant distributions between soil and water.

The types of parameters to be considered as a matrix for column tests are quite similar to those for both sorption tests. These include soil types, contaminants and their concentrations, potential organic and inorganic complexants and their concentrations, and waste liquid, groundwater, and rainwater compositions. However, both physical and chemical soil characteristics are needed for column experiments, particularly ranges of porosity, permeability, and grain-size distribution. Physical properties dictate the flow of contaminants through a column while chemical properties influence chemical reactions that retard or reduce contaminant transport relative to groundwater. Also, while batch sorption experiments would use only one soil type at a time, it is probable that certain column tests would use multiple soil types to provide a better simulation of the real system. The list of contaminants (radionuclides and chemicals) and waste liquid compositions to be tested with column experiments will be reduced relative to the combinations tested in the batch sorption experiments because many contaminants lack the potential for release above regulatory limits, as demonstrated by the batch sorption tests and conservative transport modeling results. Additional potentially influential parameters include the degree of saturation and flow characteristics. The most important zone of transport for contaminated soil sites that needs quantification is likely the vadose zone, which is variably saturated depending on the depth below surface, the intermittent and seasonal variability of recharge from precipitation, and particle size distribution. At present, these variations have not been rigorously examined experimentally. Similarly, current mathematical representations of transport through the vadose zone are extremely simplified.

4.2.3.6 Task Status and Estimated Resource Requirements

At present, no test data are available to address release from a waste source under vadose zone conditions. A test matrix will be defined that includes the factors, soil type, contaminant concentration (radionuclides and chemicals), moisture content, chemical composition of leachant, and flow characteristics (e.g., steady versus intermittent). Assuming that test procedures and appropriate equipment can be developed (see associated task), approximately 3 to 5 man-years of effort over a 2- to 3-year period (in addition to site-specific CERCLA efforts) are estimated to complete this task. Failure to complete this task will prevent collection of release data as a function of some potentially significant environmental factors, particularly transient flow conditions. This may result in the use of very high release rate values in performance assessment analyses leading to proportionately high release estimates at the receptor location. A decision to complete the task will be based on the following considerations:

- If the measured release rates from the waste source using this experimental approach are not substantially lower than those currently used in performance assessment, this task will be terminated.
- If the experimental equipment cannot be designed to simulate and measure vadose zone environmental processes, the task will be terminated.
- If the experimental process is successful and demonstrates significant reduction in measured release rates, the task will be terminated when the test matrix is completed.

The following activities are required to support or complete these column tests.

<u>Perform literature survey</u> -- Perform literature survey to identify available techniques for conducting flow-through experiments under partially saturated conditions. The objective of this task is to establish the amount of work that will be required to initiate the experiments. We estimate that a 0.5 man-year effort is required to complete this task.

<u>Develop test methodology</u> -- Define and complete a test program to develop or refine partially saturated flow-through experiments. The objective of this task is to identify equipment that can simulate and monitor the environmental conditions of interest. Some equipment available at PNL that may be useful is being investigated this year. It is estimated that an additional man-year of effort is required to complete this task. Failure to complete this task will prevent collection of release data as a function of some potentially significant environmental factors, particularly transient flow conditions. This may result in the use of very high release rate values in performance assessment analyses leading to proportionately high release estimates at the receptor location.

Characterize contaminated soil samples -- Collect and characterize contaminated soil samples for experimental work. The objective of this task is to simulate environmental conditions as closely as possible by providing real samples for testing. Characterization provides initial conditions relative to contaminant distribution and moisture content in the soil profile. These can then be compared to final distributions following flow-through experiments. This data base can then be used in comparison with modeling results to determine our ability to predict transport through the vadose zone. Ability to proceed with this task is very much dependent on the schedule for soil sample collection at CERCLA field sites. Also, the availability of storage space for contaminated soil samples has not been addressed. The task would necessarily be completed on a case-by-case basis. It is estimated that 1 to 3 man-months of effort would be required for characterization for each case. The primary advantage of this task will be to increase confidence in laboratory data derived from simulated contaminated soil columns and modeling analyses that predict release from the contaminated soil profile.

Comparison of Data with Model Predictions -- Compare contaminated soil characteristics with transport models that simulate contaminant movement with time. The objective of this task is to gauge the reliability of the modeling codes and to define the point at which sufficient data have been collected to make a waste management decision. Modeling activities are tied to CERCLA tasks for performing risk assessment studies and can be expected to continue for a long time on a site-by-site basis. However, for this purpose it is expected that the development of the modeling concepts and benchmarking and verification of the computer codes will be essentially completed by HSPA in the next 3 to 4 years. Failure to develop more realistic data bases and compatible modeling codes will result in the use of simpler, more indirect analytical methods and supporting data base; higher estimates of release will likely result with accompanying increase in remediation costs.

4.2.3.7 Description and Purpose of Proposed Diffusion Experiments

Diffusion is likely to be a dominant process in some parts of the vadose zone because of the sporadic nature of recharge over contaminated soil sites and the likely construction of RCRA-type caps or intrusion barriers over these sites; the latter will effectively limit infiltration into and immediately surrounding the contaminated soil zone. Diffusional transport is quantified through the measurement of diffusion coefficients whose values are dependent on several factors such as the type of radionuclide or contaminant, physical (e.g., moisture content, tortuosity, pore size, porosity) and chemical properties of the soil, and water composition. Coefficients can then be inserted into codes that predict diffusional transport.

Diffusion coefficients can be measured in half-cell or column experimental devices. Soils must have sufficiently low permeability to limit advective flow to the point that diffusional transport is much greater or the hydraulic gradients must be very low to discourage significant advective flow. In the half-cell experiment, two cylinders of soil are made up; one cylinder contains water that is spiked with the contaminant or radionuclide of interest and the other contains unspiked water. The two cylinders are joined and the contaminant allowed to redistribute by diffusion across the interface. By measuring the concentration-versus-distance profile through a cross section of the two cylinders, a diffusion coefficient can be calculated. A column diffusion experiment is set up very much like flow-through sorption experiments with a column of clean soil and radionuclide or contaminant spiked water pushed through the column at a rate slow enough that diffusion dominates over advection. By measuring concentration versus distance from the influx point or concentration in the effluent as a function of pore volumes, a diffusion coefficient can be calculated.

The types of parameters to be considered as a matrix for diffusion tests are quite similar to that for flow-through sorption tests. These include soil types, contaminants (radionuclides and chemicals) and their concentrations, effluent liquid, groundwater and rainwater compositions, and moisture content. Particular attention will be paid to mobile elements (e.g., Tc and I) under partially saturated conditions because the greatest potential benefit in reducing the conservatism in release estimates appears to exist where partial saturation and diffusion dominated transport could limit the movement of mobile contaminants that exist within the waste source. Similarly, soil types that make up the contaminated and adjacent soil will be considered.

4.2.3.8 Task Status and Resource Requirements Estimate

Techniques for completing static diffusion experiments are well developed from fully saturated experiments and have been attempted for partially saturated conditions (Buckley 1978). This, plus the fact that the experiments are fairly simple, indicate that diffusion experiments could be started rather quickly. Some start-up time may be required to manufacture the half-cell equipment. A general test matrix, which has been established in this report, needs to be finalized before the beginning of testing. It is estimated that 1 to 2 man-years of effort are required to complete a test matrix for diffusion controlled release. Failure to complete these tests will result in uncertainty in the performance assessment results because currently the empirical diffusion coefficients used in the codes are not obtained with Hanford-specific materials. The decision to conclude this task will be made by comparing laboratory-derived diffusion data with the predictions using generic data and currently available transport codes. If the agreement is good (e.g., within an order of magnitude), then the task can be terminated. Column diffusion experiments are unlikely to be relevant to most, if not all, nonbarriered release scenarios because of the sandy soil that surrounds emplaced waste at the Hanford Site. Any naturally created flow-through condition occurring in sandy soil will result in advection-dominated contaminant transport.

Soil Sample Collection -- Collect and analyze a representative suite of soil samples through which diffusional release may occur (needs covered in sorption section on contaminated soil).

4.2.4 Solid Wastes

Low-level solid wastes have been disposed in unlined shallow land trenches, primarily in the 200 Area plateau, for several decades. These wastes have been generated during processing operations that manufacture weapons materials. Materials are contaminated with a variety of radionuclides and, in some cases, with hazardous constituents. Contaminated materials include scrap metal, wood, plastic, rags, etc., and typically have been packaged in cardboard, fiberboard, or wood boxes and in steel drums. The new DOE Order 5820.2A is requiring an examination of these practices and a recommendation for future disposal practices that are justified on the basis of performance assessment. Performance assessment provides an estimate of radionuclide release from a low-level waste disposal facility and compares that estimate with acceptable limits set by regulatory criteria. Various possibilities for future disposal that could be recommended include continuation of present practices, development of engineered barriers systems such as the grout facility (e.g., grout vaults, multilayer caps, and asphalt-coated gravel diffusion barriers), or some combination of facility types. An evaluation of current practices is also being required by CERCLA legislation in terms of the risk assessment activity required by the remedial investigation process. Risk assessment in CERCLA is essentially the same as performance assessment for DOE Order 5820.2A.

At present, release has not been directly observed from currently buried solid waste. In the rare instance where release from these sites has been inferred, it appears that codisposal of liquids (organic solvents) is the cause. The lack of migration from solid wastes is expected for two reasons. First, solid wastes are generally contained in some type of package that provides some measure of protection from water interaction. Second, the potential for contact with water is sporadic because of the intermittent recharge provided by rainfall. Thus, it is expected that radionuclide or contaminant release from solid waste in burial grounds at Hanford is currently minimal and difficult to detect. Although this situation is desirable from the perspective of near-term safety, it is more difficult to predict long-term events because of the lack of data with which to predict release. Therefore, a key question that needs to be answered is "What is the appropriate quantitative description of the release of contaminants from solid waste?"

Release of radionuclides or contaminants from solid waste has been modeled as contaminated soil sites or by assuming a leach rate that is generally derived from cement or grout leaching experiments done under fully saturated conditions according to a standard leaching procedure. Alternatively, some information on leaching of actual solids under saturated or largely saturated conditions from other sites (e.g., Stone et al. 1985; McIntyre 1986) has been used as source-term release data. These approaches could be considered as conservative or nonconservative. On the one hand, it is intuitively apparent that leaching under fully saturated conditions will occur at a greater rate than under partially saturated conditions. On the other hand, use of leach rates from cemented waste forms to represent ungrouted solid waste could underestimate leach rates because of the physical, diffusional barrier provided by the grout material. Grout provides a tortuous path for elemental transport because it has a poorly connected pore structure, whereas leaching from solid waste would transfer elements directly to the soil column. To improve release rate predictions for solid-waste burial grounds and subsequent transport, experimental data are needed to generate release data under conditions which more accurately reflect the real environmental conditions.

4.2.4.1 Description and Purpose of Proposed Release Rate Tests

The purpose of release rate tests is to measure the rate of dissolution/desorption of radionuclides and contaminants from contaminated material in the presence of water or water plus other solid components that are part of the waste environment. A standard experimental protocol has been developed (ANSI 16.1; see ANS 1986) to measure the rate of release of a given element in the system, water plus the contaminated material. The material is brought into contact with a series of volumes of fresh leachant, and the concentration of the contaminant within each volume of leachate is measured. The test is essentially the same as a series of batch desorption tests. A diffusion coefficient is calculated to describe the cumulative fraction released versus volumes of liquid or time.

This term is easily inserted into a release code as the source-term and describes the rate of release from the source. This term can also be used to calculate the length of time required to deplete the source of the contaminant. A second advantage of this type of experiment is that it can be completed quickly for a wide variety of elements and chemical environments. A third advantage is that radionuclide or contaminant types initially present in the waste material can be identified. The primary disadvantage is that this experiment and the data produced depend on a number of experimental assumptions that may not hold true in the real environment for very long times. Typical uncertainties are that a specific surface-to-volume ratio is assumed in the diffusion coefficient calculation, the water composition is essentially invariant, and the material is a cylindrical shape. In the case of contaminated material, extrapolation of surface-area-to-volume relationships from laboratory sample size to real size is difficult to demonstrate, and correlation to cylindrical size is unlikely. Another disadvantage relative to the Hanford Site vadose zone environment is that batch leach experiments are done under saturated conditions so that the effects of partial saturation on dissolution cannot be investigated. A final disadvantage is that solid waste may not satisfy the ANS 16.1 waste-form requirements because the waste is unlikely to be cylindrical and contaminants are unlikely to be distributed uniformly throughout the waste material. If this is the case, release may occur as intermittent "instantaneous" slug release such that a diffusion coefficient cannot be used to model release from solid waste.

For these reasons, batch leach experiments will be used in a limited fashion to identify radionuclide and contaminants present in the material, the change in rainwater chemistry as a function of interaction with the solid waste, and a baseline leach rate to compare with those derived from other conceptual model predictions.

The types of parameters to be considered in a test matrix include soil type, water composition, radionuclides, contaminants, and waste forms. The only soil types to be considered are those near the surface in which the wastes are buried. These soils are largely made up of quartz-rich or basaltic sands. The only water composition of interest is that of rainwater which would infiltrate the burial trenches. A list of contaminants potentially of interest is given in Table 33. The list is based primarily on calculations of processing waste stream radionuclide inventories with which contaminated materials (i.e., the solid waste) came in contact. Actual direct chemical analyses of contaminated solid materials are minimal to nonexistent. Also, the identity of hazardous constituents existing in solid waste is limited. A group of toxic metals is considered to be part of solid waste. Hazardous organic constituents are not known. Given the ever-increasing restrictions on disposal of hazardous components, however, it is likely that future solid waste will contain little or no hazardous organic components. Because of the lack of hard data on the exact nature of contamination from both radionuclide and hazardous constituents and their concentrations, the initial test matrix needs to be developed using the waste forms as a parameter that is varied. Waste forms to consider are either the contaminated materials (e.g., metal, wood, plastic, rags) or solidified materials. A primary candidate for solidifing solid material is grout, which is being investigated by the Hanford Grout Technology program.

TABLE 33. List of Potential Radionuclides, Hazardous Compounds, and Solid-Waste Materials in Present Solid-Waste Burial Grounds and Future Disposal Facilities

Radionuclides	Hazardous Contaminants	Solid-Waste Materials
Sr	Aluminum nitrate	Wood
Zr	Calcium nitrate	Ferrous metals
Tc	Cerium nitrate	Plastic
Ru	Gadolinium nitrate	Rags
Pd	Yttrium nitrate	Paper
I	Cadmium sulfate	
Cs	Chromic sulfate	
Ce	Cupric sulfate	
Pn	Sodium fluoride	
Sm	Sodium hydroxide	
H-3	Zirconium	
C	Ammonium fluoride	
Co	Barium	
Cr	Cadmium	
Eu	Chromium	
Am	Mercury	
Np	Silver	
Pu	Lead	
Th	Asbestos	
V		
Nb		
Sn		
Sb		

The initial test matrix will include 1) the solid waste plus water and 2) the waste material plus soil plus water. The standard ANS 16.1 leach test will be run, and a longer term static leach test to identify the steady-state water composition. In both tests, useful data will be the identification of specific radionuclides and other constituents leached from the waste material. The leach tests will provide a release rate term to be used in transport models. Steady-state concentrations from the longer term tests can be used to determine if solubility limits are being achieved on an element-specific basis. If so, a solubility concentration can be used in conjunction with water flow-rate characteristics to estimate release from the waste source.

4.2.4.2 Task Status and Estimated Resource Requirements

At present, no release rate tests have been performed on Hanford solid wastes. A general test matrix has been defined in this report as a starting point. Definition of a specific test matrix and collection of actual materials for testing must be performed before testing. It is expected that this will not be trivial because of potential difficulties in identifying and procuring representative samples. An option to consider is to simulate solid waste by contaminating typical waste materials with radionuclides and chemicals of interest and then using the simulated materials in leaching tests. Collection of actual materials or simulating solid wastes is estimated to require 6 to 12 man-months of effort. The leach tests will depend on the final matrix, but are likely to require 3 to 5 man-years of effort during 3 years. Failure to complete this task eliminates the most elementary understanding of contaminant release from solid waste. The task will be complete when the test matrix has been exhausted or when test results allow a better understanding of probable release mechanisms.

The following tasks are required to support or complete these tests:

Thermodynamic Calculations -- A geochemical code (e.g., MINTEQ) will be used to predict solubilities of radionuclides and other constituents in steady-state solutions from long-term experiments. The objective of this task is to estimate the solubilities of elements under environmental conditions imposed by the contribution of the waste form to the chemical conditions (e.g., change in pH). It is expected that this task will be limited because many of these calculations are already available and incorporated in data bases that support performance assessment analyses. Approximately 1 to 3 man-months of effort on an as-needed basis are required to complete this task.

Solid-Waste Characterization -- Given the lack of direct characterization of solid waste and the tendency to characterize the radionuclide inventories of many wastes as coming from the same waste source in terms of radionuclide ratios, there is a recognized need to improve the solid-waste characterization data base. A significant effort is underway to increase the data base through the collection of all available data from the generator (based on records) and potentially through direct characterization of sample waste. The initial step in the testing process of selecting representative solid waste materials to test directly or simulate for testing is highly dependent on this activity.

4.2.4.3 Description and Purpose of Proposed Column Experiments

The method for completing a flow-through leach test is described in the section for contaminated soil sites. The purpose of the tests is to provide a better simulation of real conditions under which radionuclides or contaminants might be leached from the solid-waste material. The primary differences between these tests and contaminated soils tests will be that the waste material will be embedded in the soil column so that radionuclides or other contaminants will be concentrated at the source rather than evenly disseminated throughout the soil column or initially present in the infiltrating fluid.

Parameters are the same as in the batch release rate tests with the addition of water characteristics in the soil and environment, including moisture content, water flow rate, and soil density. These are described in greater detail in the section on flow-through experiments for contaminated soils.

4.2.4.4 Task Status and Estimated Resource Requirements

At present, no column leach experiments have been completed for Hanford Site solid wastes. Supporting activities for these tests are essentially the same as for the batch release rate tests including definition of matrix, collection of actual materials, or simulation of actual materials for testing. In addition, development of experimental equipment may be required (see Subsection 4.2.3.5 for discussion). Approximately 2 to 4 man-years during a 2- to 3-year period is estimated to complete this task. Failure to complete this task will prevent collection of release data as a function of some potentially significant environmental factors, particularly transient flow conditions. This may result in the use of very high release rate values in performance assessment analyses leading to proportionately high concentration estimates at the receptor location. Highly engineered and expensive facilities could then be required to be in compliance with DOE Order 5820.2A.

Associated tasks include a literature survey of appropriate test methods, development of test methodology, and comparison of data with model predictions (see Subsection 4.2.3.5 for discussion).

4.2.4.5 Description and Purpose of Proposed Diffusion Experiments

The method for completing a diffusion test is described in the section on diffusion tests for contaminated soil sites (Subsection 4.2.3.7). In this case, only a static experiment is realistic because shallow soils at the Hanford Site do not contain enough clay to naturally allow diffusion to dominate transport in a flow-through experiment. The only reason diffusion is a possible means of transport is because of intermittent recharge from precipitation and possibility of emplacement of water barriers. The experiment would be completed by embedding solid waste in partially to fully saturated soil, allowing the diffusion to occur, and then measuring the concentration profile in the soil away from the source. From these data, a diffusion coefficient can be calculated.

Parameters are the same as in the batch release rate tests with the addition of water and soil characteristics in the environment, including moisture content and soil density.

4.2.4.6 Task Status and Estimated Resource Requirements

Diffusion experiments have not been initiated. Test methodology is fairly well developed, and it is expected that tests could be initiated quickly (see Subsection 4.2.3.7 for further discussion). A potential problem is the size of the waste material that must be used to represent solid waste. If waste material is a large volume relative to available standard half-cells, larger cells may have to be manufactured. A general test matrix that has been established in this report needs to be finalized before testing begins. It is estimated that 2 to 4 man-years of effort are required to complete a test matrix. Failure to complete these tests will result in uncertainty in the accuracy of empirical diffusion coefficient descriptions used in assessment codes that currently are not demonstrated with Hanford Site-specific data. The decision to conclude the task will be made by comparing laboratory data with the predictions from simplified computer modeling. If the agreement is good (e.g., within an order of magnitude), then the task can be terminated or alternatively the task can be stopped if the overall predicted impact on receptors is negligible.

Soil Sample Collection -- Collect and analyze a representative suite of soil samples through which diffusional release may occur (see sorption section on contaminated soil for further discussion of this task).

4.3 DATA NEEDS FOR IMPROVED TRANSPORT MODELS

Additional data are required to quantify leachate transport for the various wastes that are or may be buried in Hanford Site soil. These needs are discussed as a function of the particular type of buried waste to be consistent with the discussion of waste source release. To focus recommendations for further data collection, the major uncertainties or issues relating to transport of radionuclides or other contaminants from each waste are identified in the context of available information about transport characteristics and modeling assumptions used to date.

A data collection approach is then identified to address the concern. As with the release discussion in Section 4.2, the primary emphasis is on laboratory- or bench-scale methods that are largely empirical. The same kinds of testing methods used for release testing are applicable to measurement of transport properties. Consequently, the reader is referred to the appropriate discussion in Section 4.2 for estimates of task status, work scope, and associated tasks.

4.3.1 Single-Shell Tanks

Transport away from single-shell tanks occurs as drainable liquor or water-soluble leachate that percolates through vadose zone sediments and ultimately mingles with the upper unconfined aquifer. The waste-affected zone could conceivably include the entire unsaturated sediment plume because of the high dissolved salt and organic content of the leachate. The high pH will likely be readily moderated by interactions with the vadose zone sediments.

Empirical R_d values would thus need to consider the high salt and perhaps high dissolved organic content and a neutral to slightly basic pH.

4.3.1.1 Description and Purpose of Proposed Experimental Testing

Very little actual retardation data exist for single-shell tank leachates contacting Hanford site sediment. Simulated tank liquors (with and without organic chelates) have been used in a few tests (Ames and Rai 1978; Delegard and Barney 1983; Delegard, Barney and Gallagher 1984). For radionuclides studied (Sr, Am, Np, and Pu), the presence of organic chelators had a much more dramatic effect than did the high salt content in lowering R_d values in comparison to commonly observed values in dilute groundwater-sediment tests. The presence of high salt might deleteriously affect ^{137}Cs adsorption, but most other radionuclides and hazardous inorganic chemicals might not exhibit significantly lower R_d values from solute competition. It would be quite difficult to simulate the organic content of single-shell tank leachates without actual study; thus, generic adsorption tests in the presence of organics such as Delegard and Barney (1983) should be viewed with caution.

Our recommendation is to study the retardation of contaminants within actual water leachable effluents from single-shell tank core characterization (see Tables 8 and 10). Studies with drainable liquor would be useful, but Weiss and Schull (1988a-i) report that the quantities of drainable liquor available are quite small.

The first tests we recommend would be small column adsorption tests with water leachates of actual single-shell tank core. Solutions could be obtained from future single-shell tank characterization studies in quantities (50 to >100 mL) to flow through small columns of Hanford sediments. Column pore volumes should be kept about 10 mL to allow breakthrough curves to be developed. Effluent samples after passing through the sediment column would be analyzed by the same procedures used by Weiss and Schull (1988a-i) to determine which constituents were not removed from the leachates.

Additional desorption tests in which rainwater is percolated through the loaded sediment column (in both saturated and partially saturated conditions) would be used to evaluate which contaminants are slightly mobile. Once a data base is developed for constituents that are readily measured in the water leachates, additional tests using tracers (of performance assessment important constituents) would be performed. The tracers would be added to actual water leachates to increase the chances of quantifying their retardation. Should analytical challenges remain large or costly, the effluents from one soil column test might be respiked with important tracers and recontacted with a second soil column. (This assumes that the first soil test removes much of the difficulty in measuring trace contaminants but leaves intact soluble and potentially mobilizing constituents such as dissolved organics.) Finally, column adsorption tests in which simulated drainable liquors or water leachates are spiked with important waste contaminants could be used to develop an R_d data base. (This option could be performed with and without possible organic constituents and other interfering components from the analytical measurement standpoint, to optimize analytical conditions and explore the effect of organics on adsorption.) The sediment types discussed in Subsection 4.2.3 should be used to ascertain the variation in R_d with sediment attributes.

The purpose of these adsorption tests is to enhance the empirical R_d data base for single-shell tank leachate solutions contacting Hanford sediments. Actual data might show that past work with simulated solutions replete with high concentrations of organic chelators significantly under predict adsorption. Further, the available data base is limited to a handful of radionuclides and does not include any regulated stable chemicals.

4.3.1.2 Task Status and Estimated Resource Requirements

As mentioned no adsorption tests with actual single-shell tank solutions have ever been performed in the laboratory. The proposed tests should be performed sequentially over a 2- to 3-year period in conjunction with renewed tank characterization efforts. The experimental and manpower requirements to perform the column tests are modest (0.5 to 1.0 man-year/yr), but analytical costs could triple the needed budget. Advice on analytical protocol and costs should be sought from Weiss and Schull, at Westinghouse Hanford Company.

4.3.2 Grout

Transport away from grout requires leachate to travel through vadose zone sediments and mix with water in the upper unconfined aquifer. The chemical nature of Hanford grout leachate is fairly well known from numerous laboratory leaching studies. The leachates are alkaline (pH 9 to 12), low in alkaline earth cations, and enriched in sodium and potassium compared to Hanford Site groundwaters. Depending on the waste stream grouted, the leachates also contain elevated levels of nitrate, nitrite, fluoride, and sulfate.

Past adsorption studies on grout leachates suggest the they can be categorized as similar to studies using Hanford groundwater. That is, the R_d values obtained upon contacting Hanford Site sediments with grout leachate fall in the same range as those found for spiked groundwater. Interestingly, the constituents that leach fastest from grout (NO;, NO;, ^{129}I, ^{99}Tc, and F^-) also show very little tendency to adsorb on Hanford Site sediments.

Additional adsorption work needed for grout leachates will be identified by performance assessments. As shown in Figure 1, further data collection is suggested when a constituent appears to generate an unacceptable consequence. If adsorption tendencies are unknown or were previously discounted by conservative assumptions, specific testing is performed. Currently, the Hanford Grout Technology Project allocates funds to support specific work when performance assessment activities identify problematic constituents. Thus, no generic adsorption studies for grout waste forms are proposed herein.

4.3.3 Contaminated Soils

Transport away from contaminated soil sites can be considered to occur in two zones, the vadose zone outside and adjacent to the contaminated zone, and some portion of the unconfined aquifer along the groundwater pathway leading to the receptor location. The importance of each zone relative to transport is somewhat dependent on the site characteristics. Transport estimates in areas with a deep vadose zone (i.e., the 200 Areas) will be dominated by the effects of vadose zone characteristics on chemical and physical properties. In either zone, the dominant type of chemical reaction to be investigated will be the adsorption quantified by the distribution coefficient. Even though this measurement is highly empirical and can represent a variety of reactions, it is considered at this time to be a viable means of characterizing the chemical effects of contaminant movement in groundwater. It is assumed that the environmental conditions fall within a manageable range and can be simulated well enough to allow useful measurement of distribution coefficients. It is also assumed that uncertainties in the ranges of sorption coefficient values for particular elements are within uncertainties for other environmental characteristics used as code inputs, especially hydrogeologic variability of permeability, hydraulic conductivity etc.

4.3.3.1 Proposed Experimental Testing - Description and Purpose

Data generated from three of the test methods described in Section 4.2 will be used as input in the transport analyses. These include the batch sorption/desorption experiments (Subsection 4.2.3.1), the column experiments (Subsection 4.2.3.5), and the diffusion experiments (Subsection 4.2.3.7). The batch experiments will provide sorption data that can be used in the transport analyses for the saturated unconfined aquifer. Additional resource requirements beyond those identified under release tasks should be small (~ 0.5 man-year/yr). If it is determined that different soil types exist in the unconfined aquifer that could significantly affect sorption behavior, then further batch experiments should be planned. Additional resource requirements may be required to conduct column tests under partially saturated conditions if the use of generic distribution coefficients measured under saturated water conditions is not considered sufficient.

4.3.3.2 Task Status and Estimated Resource Requirements

Transport data for use in vadose zone transport calculations will be generated by all three test methods (batch, column, and diffusion cell). Additional resource requirements beyond those identified under release tasks should be minimal or not required because sufficient funding should be provided under the scope of work envisioned in Section 4.2. If it is determined that ambient groundwater chemistry is not adequately represented or significantly different soil types exist in the vadose zone outside the contaminated soil zone along the groundwater path, then additional sorption data must be collected.

4.3.4 Solid Waste

Three potential zones can be defined along the groundwater pathway between solid waste and the point of compliance. These include 1) a portion of the vadose zone adjacent to the waste source that has been physically or chemically disturbed by the waste so that chemical transport is significantly affected; 2) the ambient vadose zone, which is not significantly affected by waste emplacement, but through which radionuclides and other contaminants are transported; and 3) the unconfined aquifer. Given the general nature of solid waste, it is unlikely that the first type of zone really exists because of low moisture content in the waste zone and the slow dissolution of waste that is largely nonreactive or unable to contribute aqueous components to the groundwater which influence sorption reactions. Zones 2 and 3 are essentially the same as those described for contaminated soil, and the same discussion applies concerning additional data to be collected and required resources. An exception would occur if chemicals released from solid waste are different from those observed in contaminated soil and significantly influence chemical reactions. If both of these conditions occur, then the test matrix to collect distribution coefficients would necessarily be expanded.

5.0 CONCLUSIONS AND RECOMMENDATIONS

Regulations dealing with waste disposal require performance assessment analyses before licensing or remedial cleanups. Performance assessment analyses predict transport of radionuclides/contaminants from the waste source to a receptor via pathways that are considered credible. The groundwater pathway is generally most significant when considering long-term effects. Geochemical reactions of contaminants within waste forms with the groundwater pathway and hydrologic characteristics largely control release and transport to the receptor. Consequently, data that quantify the geochemical reactions are required to adequately complete a performance assessment. This report documents the currently available geochemical data base for release and retardation that employs actual Hanford Site materials (wastes and/or sediments). The review also provides recommendations for specific laboratory tests and rationale as to why the tests are deemed high priority.

The release of contaminants from Hanford Site waste forms must be described quantitatively and becomes the source-term in the overall performance assessment analyses. After characterizing the physical and chemical attributes of each waste form, one must determine what will occur when recharge waters percolate into the waste. Currently available leach models can be categorized as either empirical or being solubility, diffusion, or desorption controlled. Each conceptual leach model requires that one or more parameters be quantified (e.g., a solubility limit or diffusion coefficient). In general, this requires some laboratory testing to produce appropriate values. Different contaminants within the same waste form often are modeled using different conceptual leach models, and thus different leaching parameters are often needed for one waste form. For example, the release of one contaminant from contaminated soil sites could be quantified by a solubility limit while a second contaminant could be quantified by a desorption distribution coefficient. Although rarely practiced, different species of the same contaminant within one waste form can be described using distinct conceptual release models. For example, ^{60}Co adsorbed onto lab waste might be modeled by desorption while ^{60}Co within activated metal parts might be modeled by diffusion. Both forms could conceivably be placed in one solid-waste burial ground.

We assume that the release of contaminants from single-shell tanks occurs either by existing liquors draining through cracks in tank walls or bottoms or from dissolution of tank salt cake and sludge into recharge waters that invade the tanks and then drain through existing cracks. On the basis of this release scenario, we conclude that release of contaminants from single-shell tanks is best modeled using the solubility-based conceptual model. Further, the available data base and theoretical understanding of thermodynamics of high ionic strength solutions precludes a rigorous use of thermodynamic solubility constraints. Rather, the available data suggest that empirical solubility constraints (e.g., constant concentration limits based on empirical observations) are most appropriate.

Data collected by Schulz (1978), Weiss (1986), and Weiss and Schull (1988a-i) on the chemical composition of drainable liquors provide values (upper-limit constant concentrations) for many radionuclides and stable constituents. Thirty analyses of drainable liquors from 19 tanks are available for about 30 stable chemicals and about 10 radionuclides. Based on the available data (the chemical composition of drainable liquors, percentage of single-shell tank core material that readily dissolves in water, projected tank inventories, and probable adsorption (retardation) potential of single-shell tank leachates in Hanford Site sediments), contaminants can be placed into four categories: 1) known to be mobile and likely to cause environmental impact; 2) slightly mobile and of some environmental concern; 3) known to be relatively immobile and thus not likely to cause environmental impact; and 4) contaminants for which data are lacking. In the fourth category can be further subdivided to where the uncertainty lies (i.e., no inventory data, no water leachability data, or no adsorption data).

Table 34 summarizes our appraisal of the current status. For those species for which data are lacking, the tests specified in Subsections 4.2.1.1 and 4.3.1.1 are recommended to collect pertinent information on leaching and adsorption tendencies. Those constituents classified in category 1 are potentially the key contaminants that would reach the receptor at concentrations significantly above natural background, but estimates of environmental impact are beyond the scope of our review. A few contaminants [^{14}C, F, ^{129}I, and

TABLE 34. Categories for Contaminants in Single-Shell Tanks

Contaminant	Category[(a)]					
	1	2	3	4		
				Inventory	Leaching	Adsorption
^{14}C	?				X	X
NO_2	X					
NO_3	X					
F	?				X	
Na	X					
PO_4			X			
SO_4		X				
Cl		X				
Ca			X			
Cr						X
Mn			X			
Fe			X			
Co						X
Ni		X				
Cu		X				
Zn			X			
As				X	X	X
Se				X	X	X
Sr			X			
Zr			X			
Nb					X	X
Mo				X	X	
Tc	X					
Ag				X		X
Cd				X		
Sn					X	X
I	?				X	
Cs		X				
Ba			X			
Lanthanides			X			
Hg				X	X	X
Pb			X			
Bi		X				
Th			X			
U						X
Np					X	X
Pu						X
Am, Cm						X
TOC	?					X

(a) Category 1. Known to be mobile and present in significant quantities in single-shell tanks;
Category 2. Known to be somewhat mobile in single-shell tank environment;
Category 3. Known to be rather immobile in single-shell tank environment;
Category 4. Data lacking.

TOC (total organic carbon)], were designated as possible category 1 contaminants if the required information under category 4 data uncertainties is found to be unfavorable. Of particular interest is the nature of the high total dissolved organic content in the tanks and its effect on the solubility and adsorption of trace contaminants such as actinides.

In terms of prioritization by waste form, single-shell tanks likely should not be ranked number one because their fate is rather uncertain. Should the contents of a single-shell tank be removed and processed to form glass and grout waste forms, single-shell tank environmental impacts at Hanford may change dramatically. In the event that most of the single-shell tanks are disposed in place, the priority for obtaining the additional data required for performance assessment analyses would rise.

Hanford Site grouts are formed by mixing liquid low-level nuclear waste with dry solids that harden in a manner similar to cement. During curing the permeability of the grout decreases significantly. The permeability decrease physically isolates waste inside the grout from ready access to recharge water. Furthermore, some of the waste constituents chemically react with the solids during hydration and curing and become strongly bound in the grout matrix.

The low permeability exhibited by the grout makes it reasonable to assume that any recharge water that reaches the monoliths (grout plus concrete retaining vault) will advect around the waste forms. The pore water entrapped within the grout and the water impinging on the grout vault surface will act as a diffusion conduit for contaminants to reach the waste-form surface. Thus a release model based on diffusion has been chosen for the purpose of projecting the long-term impacts. An effective diffusion model (in which each contaminant has its own empirically derived coefficient, D_e, the effective diffusion coefficient) was selected because it is simple yet satisfactorily describes most laboratory leach data collected to date. The leach rate is related to the square root of the effective diffusion coefficient.

To date, leach tests on grouts prepared with three types of tank wastes have been performed by the Grout Technology Program. The effective diffusion coefficients for about 30 radionuclides and stable chemicals have been determined on at least one grout type. The effective diffusion coefficients vary over seven orders of magnitude (10^{-8} to 10^{-15} cm^2/s). Much of the variation is likely caused by chemical reaction (e.g., solubility reactions) between contaminants and grout-forming materials. For certain constituents thought to be unreactive (e.g., NO_3) there appears to be one to almost two orders of magnitude variation between grout types, perhaps an indication of differences in physical attributes such as porosity and tortuosity.

All the grout leach tests show that leaching slows down with time, at least over the first 3 years. If the trend continues in longer time frames, the predictions based upon measured D_e values should result in conservative performance assessment analyses. Currently, none of the data on leaching of grout or cement waste forms available in the literature suggest that the D_e values calculated on small test specimens vary significantly from large (210-L specimens) samples. Thus, the scaleup from lab specimens to large monoliths appears to be technically defensible.

Based on projected inventories of contaminants in grout, available leaching, and retardation data, a prioritization of future work has been prepared (Table 35). For consistency we use the same four categories as introduced for single-shell tanks.

As found for single-shell tanks, nitrite, nitrate, ^{99}Tc, and ^{129}I appear to be mobile in the groundwater pathway considered for grout. Numerous other anions, the nuclide ^{137}Cs, and some metals (Se, Mo, and Cr) might be mobile enough to elicit concern in a system performance assessment. To date the organic content of the liquid wastes solidified in grout has not caused any significant increases in metal leaching or decreases in adsorption properties.

The existing leach data base, knowledge of the inventory, and leachate-sediment adsorption data base are more complete for grout than other Hanford Site waste forms. From general chemical principles and the available data, it appears that the "problem" constituents have already been identified. Should the Hanford Grout Technology Program continue to support leaching and adsorption work at the current level of effort (-2 man-years/yr), the data base should become adequate for technically defensible performance assessment analyses.

Because the Hanford Grout Technology Program funds its own performance assessment efforts, the iterative looping strategy shown in Figure 1 and

TABLE 35. Categories for Contaminants in Grout

Contaminant	Category[(a)] 1	2	3	4		
				Inventory	Leaching	Adsorption
^{14}C			X			
NO_2	X					
NO_3	X					
F		X				
Na		X				
PO_4			X			
SO_4		X				
Cl		X				
Ca			X			
Cr		?				X
Mn			X			
Fe			X			
Co			X			
Ni					X	
Cu					X	
Zn					X	
As			X			
Se		?				X
Sr			X			
Zr			X			
Nb					X	X
Mo		X				
Tc	X					
Ag			X			
Cd			X			
Sn					X	X
I	X					
Cs		X				
Ba			X			
Lanthanides			X			
Hg						X
Pb			X			
Bi					X	X
Th			X			
U			X			
Np					X	X
Pu			X			
Am, Cm			X			
TOC		?				X

(a) Category 1. Known to be mobile and present in significant quantities in grout;
Category 2. Known to be somewhat mobile in grout environment;
Category 3. Known to be rather immobile in grout environment;
Category 4. Data lacking.

discussed in the introduction is ongoing. The data collection is driven by the results of past performance assessments such that data gaps and priorities are being addressed in logical fashion.

Contaminated soil sites consist of injection wells, covered French drains, cribs (covered drain fields), trenches, and ponds. Currently, contaminants within contaminated soil exist as precipitated radionuclides and/or hazardous constituents that are bound in the soil column after discharged waste solutions have drained. The types of liquid wastes that were or are currently being disposed range from very low ionic strength cooling waters and condensates to high-salt process wastes with pH values ranging from less than 1 to greater than 12. Many of the basic waste streams contain suspended particles of insoluble compounds. Some waste streams contained significant concentrations of organic solvents and complexing agents. Geochemical conditions (ambient water characteristics, soil exchange capacities, and buffering capacities) in the soil columns may vary widely as a function of discharge fluid chemistry and spatial proximity to the source of discharge.

Conceptual leaching models for contaminated soils have not been well established. It appears that two conceptual models, desorption and solubility, will be needed dependent on the contaminant of interest. To characterize and predict release and transport of radionuclides and/or hazardous constituents, solubility and sorption values as a function of these various environments are needed. The available experimental and theoretical data base varies with these environments. The best data base is that which corresponds to the moderately alkaline, low ionic strength, organic complexant-free groundwater contacting sandy soil, an environment typical of much of the Hanford Site vadose zone and unconfined aquifer. Although the actual data base (radionuclide sorption and solubility measurements using Hanford Site soil and groundwater) is moderate, sufficient experimental work has been reported in the literature to propose a range of sorption and solubility values for many radionuclides and regulated chemicals of interest. These values can be used in preliminary transport analyses. Only a minimal amount of corroborative data collection with actual Hanford soils is recommended for the ambient case. In addition to the ambient conditions prevalent at many sites and in the vadose zone surrounding contaminated soil columns outside the zone of contamination, numerous "affected zones" exist that may be characterized chemically as highly acidic, highly basic, organic-rich, or salt-rich. Under these conditions, the data base to quantify solubility or sorption values for radionuclides and/or hazardous constituents is generally inadequate to propose a range of values which can be used in transport modeling. This problem is compounded by the lack of specific data that quantify concentrations of radionuclides, hazardous constituents, and organic and inorganic complexants existing at a given contaminated soil site.

To generate a useful data base given the lack of site-specific information, a list of potential conditions and important chemical constituents has been identified from records and existing site-specific investigations. It is recommended that a series of sorption and empirical solubility tests (see Subsections 4.2.3.1, 4.2.3.3, 4.2.3.5, and 4.3.3.7) be run on the basis of the information using Hanford Site soils to provide ranges of sorption and solubility values for use in transport modeling. Based on the lack of available information, emphasis needs to be placed on radionuclide interactions with complexing organic compounds and the extent of acid influence at sites where acid solutions were disposed. Also, actual data that describe the effects of partial saturation on radionuclide or contaminant transport in Hanford soil are very sparse. The primary tests to be completed include 1) batch sorption/desorption tests to develop distribution coefficients or empirical solubility values, and 2) flow-through column tests to quantify retardation factors under the combined influences of hydrologic flow and chemical/reactivity. The parameters to be varied in the test matrix in addition to chemical components include soil types, moisture content, and flow characteristics (e.g., advection flow rates and diffusion fluxes as a function of moisture content).

Stenner et al. (1988) concluded that many of the contaminated soil sites at the Hanford Site have released radionuclides, regulated chemicals, and organic constituents into the upper unconfined aquifer. From a performance assessment standpoint, we conclude that contaminated soil sites warrant top priority in need for geochemical data collection.

In the spirit of the previous two tables on single-shell tank and grout, we offer a summary table (Table 36) on selected contaminants in contaminated soil sites. The categories differ somewhat because actual data are lacking;

TABLE 36. Priority Needs for Contaminants in Contaminated Soil and Solid-Waste Burial Grounds

Contaminant	Category[a]			
	1	2	3	
			Leaching	Adsorption
^{14}C			X	X
NO_2	X			
NO_3	X			
F			X	
Na	X			
PO_4		X		
SO_4			X	
Cl		X		
Ca		X		
Cr	?		X	X
Mn		X		
Fe		X		
Co			X	X
Ni			X	
Cu			X	
Zn			X	
As			X	X
Se			X	X
^{90}Sr	?		X	
Zr		X		
Nb			X	X
Mo			X	
Tc	?		X	
Ag			X	X
Cd			X	
Sn			X	X
^{129}I	?		X	
^{137}Cs	?		X	
Ba		X		
Lanthanides		X		
Hg			X	X
Pb		X		
Bi			X	X
Th		X		
U			X	X
Np	?		X	X
Pu	?		X	X
Am, Cm	?		X	X
TOC			X	X

(a) Category 1. Likely are mobile or deserve high priority study;
Category 2. Likely immobile and deserve lower priority study;
Category 3. Area where data are lacking.

knowledge of general soil chemistry was used to identify probable constituents of most concern. Category 1 contains contaminants that merit early study while category 2 is contaminants that are of least interest. Category 3 are contaminants that cannot be assigned because of the lack of general chemical knowledge. After establishing a baseline inventory of contaminants in Hanford Site contaminated soil sites, a second prioritization could be performed to emphasize contaminants with suspected high inventories.

A data base that quantifies the chemical reactivity of solid wastes and their radioactive/hazardous constituents with the Hanford Site soil environment is essentially nonexistent. Therefore, the mechanism for release of radionuclides and/or hazardous constituents is not known. To provide estimates of release and transport of these elements or compounds along a groundwater pathway, assumptions must be used with data from other sources. For example, the HDWEIS analysis assumed that solid waste was analogous to an equivalent volume of soil with radionuclides distributed uniformly throughout the soil. Release was controlled by desorption- or solubility-controlled dissolution. This analogy is not realistic but is justified as being conservative relative to actual solid-waste leaching.

A major unknown at this point is the potential for complexing agents to dissolve from solid-waste materials along with radionuclides or other hazardous constituents, thereby enhancing mobility significantly (e.g., by an order of magnitude or more). If this were the case, previous estimates of release would not be conservative. The primary recommendation, then, is to perform a set of laboratory leaching tests with real or simulated solid waste to derive an empirical leach rate or solubility that can be compared with the assumed desorption- or solubility-controlled release rates from contaminated soils. Particular attention should be place on identifying other components, particularly organics, which might enhance radionuclide mobility. It should be acknowledged that Stenner et al. (1988) concluded that there is no evidence that any contaminants from Hanford solid waste in designated burial grounds have reached the water table.

Other studies that are not strongly recommended at this time but may require evaluation at a later date are the quantification of hazardous organic constituent dissolution rates from solid waste and transport through the groundwater pathway. At present, it is assumed that land disposal restrictions will prohibit disposal of materials containing significant quantities of hazardous organic compounds.

Once contaminants are leached from the various Hanford Site waste forms they may chemically interact with the soils and sediments. The major processes affecting transport include the following: dissolution/precipitation, adsorption/desorption, filtration of colloids and small suspended particles, and diffusion into micropores within mineral grains. The former two processes are considered more important. Further, for the Hanford Site low-level waste disposal application, precipitation is likely a key factor only if significant pH and/or redox changes occur when leachates migrate away from the wastes. In most Hanford Site low-level waste situations, we speculate that adsorption processes are the key to contaminant migration, especially outside the zone where the waste has dramatically altered the natural chemical environment of the sediment.

To predict the effects of retardation using performance assessment codes, adsorption processes must be described in quantitative terms. An empirical parameter, the distribution coefficient (often called R_d or K_d), is readily measured by laboratory experimentation and allows a quantitative estimate of nuclide migration.

In the constant R_d model, the distribution of the contaminant of interest between the solid adsorbent and solution is assumed to be a constant value. There is no explicit accommodation of dependence on characteristics of the sediments, groundwater, or contaminant concentration. Possible retardation mechanisms include 1) chemical precipitation of bulk solid phases, 2) chemical substitution of one element for another in a solid phase, 3) exchange of stable isotope of an element with a radioactive isotope in solution, 4) physical filtration of colloids, 5) cation and anion exchange, 6) chemisorption, and 7) physical adsorption. All these mechanisms are folded into the empirical distribution coefficient. The limitations associated with this approach are well known to investigators, but the paucity of Hanford Site-specific geochemical data precludes justifying a more rigorous conceptual retardation model at this time. The constant R_d model is mathematically very simple and readily incorporated into transport models and codes.

A second practical conceptual model for adsorption is called the parametric R_d model. Numerous statistical strategies have been used to develop empirical relationships that describe R_d as a function of other variables such as the amount and types of minerals present in the sediment, amounts and types of dissolved species in the groundwater, pH, and Eh. Parametric R_d relationships delineate apparent effects of key variables but do not conclusively identify controlling processes. These statistical approaches have been demonstrated to yield accurate predictions for conditions within the range of conditions studied. When the parametric R_d retardation model is used the performance assessment code must keep track of the current values of all independent variables that determine the value of R_d. Because of the added complexity in solving the transport equation explicit use of the parametric R_d model has been infrequent. On the other hand, the parametric R_d approach can be used to objectively develop a suite of time- or space-dependent constant R_d values to be used in a given performance assessment analysis. This latter approach is the philosophy recommended for future Hanford performance assessment activities.

Because the data base is small and the currently used adsorption model, constant R_d, is simplistic, we did not discuss the adsorption potential of each waste form's leachates separately. Instead all available data were lumped into generic categories based on pH, total dissolved salt, and organic content of the waste leachate. Existing conditions at Hanford suggest that most leachates will fall into one of three categories. As the leachates move further from the disposal facility, the chemical nature of the solution should tend toward one category -- low salt, low organic content, and neutral to slightly basic pH.

It is quite common to divide the flow path from the disposal facility to the receptor into two zones: the waste influenced or affected, and the unaffected zones. Performance assessment exercises often use default R_d values of 0 for affected zones when knowledge of the chemical reactions is lacking but then use normal background R_d values for the unaffected zone. We recommend that future performance assessment activities on Hanford Site low-level waste consider at least this two-valued retardation approach with values for the affected and unaffected zones.

A data collection approach that relies on feedback from performance assessment analyses to ascertain when adequate amounts of data have been collected was described. The data collection scheme emphasizes laboratory testing. The emphasis in the laboratory testing approach is empirical; the expected environment is simulated, and geochemical reactions between radionuclides or contaminants and the simulated environment are quantified.

The proposed laboratory waste-form leach studies rely on standard intermittent solution-exchange batch leach tests and once-through flow column leach tests, static solubility tests, and static diffusion tests. Laboratory retardation tests use leachates from the waste form release tests and Hanford Site sediments. Both static (batch) R_d and column adsorption tests are recommended. Batch tests are used to delineate the mobile contaminants that should be studied in more detailed column studies. The effects of partially saturated conditions on contaminant retardation processes should be addressed using flow-through column tests.

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APPENDIX A

PREFERRED SOURCE-TERM VALUES

APPENDIX A

PREFERRED SOURCE-TERM VALUES

This appendix consists of three tables that list release values for radionuclides and selected regulated chemicals.

Table A.l lists constant concentration release values for constituents in single-shell tanks.

Table A.2 lists effective diffusion coefficients for the release of radionuclides and selected regulated chemicals for Hanford Site grout. The values are for a generic grout. Values of specific grouts are shown in Table 18 in the text of this document.

Table A.3 lists desorption R_d values or constant concentration release values to be used for scoping performance assessment analyses for contaminated soil sites. Because no data exist for release of constitutents from solid wastes, Table A.3 should be used for preliminary analyses. The values in Table A.3 are generally conservative estimates based on experience and expert judgment because actual data are not available.

A reference for each value is given when appropriate. When no actual citable document is available and we supply an estimated value, a brief explanation/rationale is provided. For some constituents it is difficult to estimate a source-term value without performing experiments. We use the designation "unknown" on each table for those constituents for which no release estimates are currently provided because the chemical behavior of the constituent either is complicated or has not been studied in the environment.

TABLE A.1. Constant Concentration Release Values for Single-Shell Tank Constituents

Constituent	Constant Concentration	Reference/Rationale
^{3}H	Unknown	
Be	Unknown	
^{14}C	3 μCi/L	Weiss and Schull 1988a-i
CN	Unknown	
NO_2	60. g/L	Schulz 1978
NO_3	360. g/L	Weiss 1986
F	0.5 g/L	Weiss 1986
Na	300. g/L	Weiss and Schull 1988a-i
PO_4	15. g/L	Weiss 1986
SO_4	15. g/L	Schulz 1978
C1	5. g/L	Weiss 1986
Ca	0.2 g/L	Weiss and Schull 1988a-i
Cr	10 g/L	Schulz 1978
Mn	0.2 g/L	Weiss and Schull 1988a-i
Fe	2.0 g/L	Weiss and Schull 1988a-i
^{60}Co	3 x 10^{3} μCi/L	Schulz 1978
Ni	0.2 g/L	Weiss and Schull 1988a-i
^{59}Ni	Unknown	
Cu	0.2 g/L	Weiss and Schull 1988a-i
Zn	0.01 g/L	Weiss and Schull 1988a-i
As	Unknown	
Se	Unknown	
^{90}Sr	1.5 x 10^{5} μCi/L	Schulz 1978
^{95}Zr	35 μCi/L	Schulz 1978
^{94}Nb	Unknown	
Mo	Unknown	
^{99}Tc	300 μCi/L	Weiss and Schull 1988a-i
Ag	0.02 g/L	Weiss and Schull 1988a-i
Cd	0.02 g/L	Weiss and Schull 1988a-i
Sn	Unknown	
^{129}I	0.3 μCi/L	Weiss and Schull 1988a-i

TABLE A.1. (contd)

Constituent	Constant Concentration	Reference/Rationale
^{137}Cs	5 x 10^5 μCi/L	Schulz 1978
Ba	0.06 g/L	Weiss and Schull 1988a-i
Lanthanides	1 x 10^4 μCi/L	Schulz 1978
Hg	Unknown	
Pb	0.1 g/L	Weiss and Schull 1988a-i
Bi	0.2 g/L	Weiss and Schull 1988a-i
Ra	Unknown	
Th	Unknown	
U	2.6 g/L	Weiss and Schull 1988a-i
Np	140 μCi/L	Delegard and Gallagher 1983
Pu	100 μCi/L	Weiss and Schull 1988a-i
^{241}Am	1500 μCi/L	Schulz 1978
^{244}Cm	Unknown	

TABLE A.2. Effective Diffusion Coefficients For Release from Grout (cm^2/s)

Constituent	Diffusion Coefficients	Reference/Rationale
^{3}H	5×10^{-8}	Analogous to Cl, NO_3, I
Be	Unknown(e)	
^{14}C	1×10^{-12}	Serne et al. 1989(a)
CN	Unknown(e)	
NO_2	5×10^{-8}	Serne 1989(b)
NO_3	5×10^{-8}	Serne 1989(b)
F	1×10^{-10}	Serne et al. 1989(c)
Na	5×10^{-8}	Serne 1989(b)
PO_4	1×10^{-12}	Serne et al. 1989(d)
SO_4	1×10^{-8}	Serne et al. 1989(a)
Cl	5×10^{-8}	Serne 1989(b)
Ca	5×10^{-11}	Analogous to Sr
Cr	1×10^{-10}	Serne 1989(b)
Mn	5×10^{-11}	Serne et al. 1987
Fe	5×10^{-11}	Serne et al. 1987
^{60}Co	5×10^{-11}	Serne et al. 1987
Ni	5×10^{-10}	Serne et al. 1989(c)
^{59}Ni	5×10^{-10}	Serne et al. 1989(c)
Cu	5×10^{-10}	Analogous to Ni
Zn	5×10^{-10}	Analogous to Ni
As	5×10^{-10}	Serne et al. 1989(d)
Se	2×10^{-10}	Serne 1989(b)
^{90}Sr	5×10^{-11}	Serne et al. 1989(a)
^{95}Zr	1×10^{-12}	Serne et al. 1989(a)
^{94}Nb	Unknown(e)	
Mo	2×10^{-8}	Serne 1989(b)
^{99}Tc	1×10^{-8}	Serne 1989(b)
Ag	5×10^{-11}	Serne et al. 1989(d)
Cd	5×10^{-10}	Serne et al. 1989(d)
Sn	Unknown(e)	
^{129}I	5×10^{-8}	Serne 1989(b)

TABLE A.2. (contd)

Constituent	Diffusion Coefficients	Reference/Rationale
^{137}Cs	5×10^{-10}	Serne et al. 1989(c)
Ba	5×10^{-11}	Analogous to Sr
Lanthanides	5×10^{-11}	Analogous to Sr
Hg	5×10^{-11}	Serne et al. 1989(d)
Pb	1×10^{-11}	Serne et al. 1989(d)
Bi	Unknown(e)	
Ra	5×10^{-11}	Analogous to Sr
Th	1×10^{-12}	Analogous to U
U	1×10^{-12}	Serne et al. 1989(d)
Np	1×10^{-11}	Estimate
Pu	5×10^{-13}	Serne et al. 1989(a)
Am, Cm	5×10^{-13}	Serne et al. 1989(a)

(a) Serne, R. J., W. J. Martin, S. B. McLaurine, and V. L. LeGore. 1989. Leach Tests of Cladding Removal Waste Grout and Combined Tests Using Hanford Sediment. PNL Draft, Pacific Northwest Laboratory, Richland, Washington.

(b) Serne, R. J. 1989. Grouted Waste Leach Tests: Pursuit of Mechanisms and Data For Long-term Performance Assessment. PNL-SA-17600. Pacific Northwest Laboratory, Richland, Washington.

(c) Serne, R. J., W. J. Martin, R. O. Lokken, V. L. LeGore, C. W. Lindenmeier, and P. F. C. Martin. 1989. Leach and EP Toxicity Test on Grouted 106-AN Tank Waste. PNL-6960, Pacific Northwest Laboratory, Richland, Washington.

(d) Serne, R. J., W. J. Martin, V. L. LeGore, C. W. Lindenmeier, S. B. McLaurine, P. F. C. Martin, and R. O. Lokken. 1989. Leach Test on Grouts Made with Actual and Trace Metal-Spiked Synthetic Phosphate/Sulfate Waste. PNL-7121, Pacific Northwest Laboratory, Richland, Washington.

For preliminary calculations, use $D_e = 5 \times 10^{-8} cm^2/s$. The release rate will likely be lower than this value. Thus, performance assessment results should be conservative. Actual experimentation is warranted only if the bounding calculations (using $5 \times 10^{-8} cm^2/s$) show a potential problem.

TABLE A.3. Qualitative Discussion of Solubility and Estimated Desorption R_d Values for Release from Contaminated Soils/Solid Wastes

Constituent	Solubility[a] Acid/Organic	Neutral/Basic	Desorption R_d (mL/g) Acid/Organic	Neutral/Basic	Reference/Rationale
^{3}H	S[b]	VS	0	0	Assume present as H_2O
Be	Unknown	Unknown	Unknown	Unknown	
^{14}C	VS	VS	0	0	Assume present as HCO_3^-
CN	Unknown	Unknown	0	8	Assume anionic
NO_2	VS	VS	0	8	(c)
NO_3	VS	VS	0	0	(c)
F	VS	VS	0	0	(c)
Na	VS	VS	0	5	Estimate[d]
PO_4	MS	LS	0	20	Estimate
SO_4	VS	MS	0	0	Anionic, soluble
Cl	VS	VS	0	0	Anionic, soluble
Ca	VS	MS	2	10	Estimate
Cr	VS	MS	0	0	Assume CrO_4^{2-}
Mn	MS	LS	0	50	Estimate
Fe	MS	LS	0	50	Estimate
^{60}Co	VS	MS	0	20	Estimate
Ni	VS	MS	0	28	Estimate
Cu	VS	MS	0	20	Estimate
Zn	VS	MS	0	28	Estimate
As	VS	VS	0	0	Assume AsO_4^{3-}
Se	VS	VS	0	0	Assume SeO_4^{2-}
^{90}Sr	VS	MS	2	10	Smith and Kasper (1983)
^{95}Zr	MS	LS	5	50	Estimate
^{94}Nb	MS	Unknown	Unknown	Unknown	
Mo	VS	VS	0	0	Assume MoO_4^{2-}

TABLE A.3. (contd)

	Solubility		Desorption R_d (mL/g)		
Constituent	Acid/Organic[a]	Neutral/Basic	Acid/Organic	Neutral/Basic	Reference/Rationale
^{99}Tc	VS	VS	0	0	(c)
Ag	VS	MS	0	10	Estimate
Cd	VS	MS	0	20	Estimate
Sn	VS	Unknown	Unknown	Unknown	
^{129}I	VS	VS	0	0	(c)
^{137}Cs	VS	VS	5	30	Smith and Kasper (1983)
Ba	MS	LS	5	50	Estimate
Lanthanides	MS	LS	5	50	Estimate
Hg	Unknown	Unknown	Unknown	Unknown	
Pb	MS	LS	5	50	Estimate
Bi	MS	LS	5	50	Estimate
Ra	VS	MS	2	30	Estimate
Th	MS	LS	5	50	Estimate
U	VS	MS	0	10	Estimate
Np	VS	MS	0	10	Estimate
Pu	MS	LS	5	100	Estimate
Am	-3.76 -1.07 pH = Am(M)[e]		5	100	Estimate
Cm	MS	LS	5	100	Estimate

(a) Acid environments are Hanford sediments with pH values <4.5. Neutral/basic environments are Hanford sediments with pH values >4.5 and <12.5. Organic environments are those where the codisposal of strong chelating and complexing agents could bind radionuclides and regulated metals forming mobile species.

(b) qualitative estimates of solubility:

VS = very soluble; common controlling solids would allow more than 1 g/L in solution

MS = moderately soluble; common controlling solids would allow more than 1 mg/L in solution

LS = low solubility; common controlling solids would allow less than 1 mg/L in solution.

(c) Unpublished adsorption tests on cladding removal waste grout leachates onto Hanford sediments.

(d) The rationale 'estimate' is our expert opinion based on general knowledge of adsorption of contaminants onto sand soils. The values given are biased low to add conservatism. If these low R_d values lead in no deleterious environmental impacts in performance assessment calculations, it is probable that detailed studies to gather actual values are not necessary.

(e) See Rai et al. (1981) for empirical solubility of Am from contaminated soils.

APPENDIX B

PREFERRED CONSTANT R_d VALUES

APPENDIX B

PREFERRED CONSTANT R_d VALUES

This appendix consists of three tables that list adsorption coefficients, R_d values, for radionuclides and selected regulated chemicals. Three generic types of solution environments are considered (one per table): 1) high salt content and/or dissoved organics with acidic pH; 2) high salt content and/or dissolved organics with neutral or basic pH; and 3) low salt content and low dissolved organics with neutral or basic pH. Several contaminated soil sites (e.g., 216-A-10 and 216-Z-1A) are representative of type 1. Most single-shell tanks and a few contaminated soil sites (e.g., 216-A-36B) are representative of type 2. Many contaminated soil sites, grout leachate and ambient Hanford groundwater are representative of type 3. No data are available on the chemical composition of leachates leaving solid-waste burial grounds but we speculate that many would fall into type 3.

The values presented (often a range and a "conservative average" value) can be used for scoping performance assessment activities. As discussed in the text, adsorption values are very site- and situation specific. We encourage actual measurement using solutions and sediments from the specific environment.

When the available data were quite variable, we used expert judgment to choose a "conservative average" value. References are given when available, with emphasis on identifying the source of the "conservative average." Conservative average means choosing an R_d value on the low side to minimize the chances of overpredicting retardation. When no citable reference was found we supply an estimated value and brief rationale. We use the designation "unknown" on each table for those constituents for which no adsorption estimates are available, either because the chemical behavior of the constituent in the type of solution being considered is very complicated or because it has not been studied.

TABLE B.1. R_d for High Salt or Organic Solutions with Acidic pH

Constituent	R_d Range	"Average" R_d (mL/g)	Reference/Rationale
^3H	0	0	Present as water
Be	Unknown	Unknown	
^{14}C	0	0	In acid $CO_2(g)$, $H_2CO_3^0$
CN	Unknown	0	Soluble anion → HCN gas
NO_2	0 to <1	0	Soluble anion
NO_3	0 to <1	0	Soluble anion
F	0 to <1	0	Soluble anion
Na	<1 to 10	1	Weak exchanger
PO_4	Variable	3	Somewhat insoluble in soils
SO_4	0 to <1	0	Soluble anion
Cl	0	0	Soluble anion
Ca	<1 to 10	3	Some adsorption vs. acid
Cr	Variable	3	Estimate, soluble in acid
Mn	Variable	3	Estimate, soluble in acid
Fe	Variable	3	
Co	Variable	0	Soluble in acid, readily complexed
Ni	Variable	1	Soluble in acid, somewhat complexed
Cu	Variable	0	Soluble in acid, readily complexed
Zn	Variable	1	Soluble in acid, somewhat complexed
As	Unknown	Unknown	
Se	Unknown	Unknown	
Sr	0 - 10	3	Knoll 1969
Zr	Variable	5	Readily hydrolyzes
Nb	Unknown	Unknown	
Mo	Unknown	0	Soluble anion
Tc	0 to 1	0	Soluble anion
Ag	Unknown	3	Soluble in acid, no complexing
Cd	Unknown	1	Soluble in acid, some complexing
Sn	Unknown	Unknown	
I	0 to 1	0	Soluble anion
Cs	<1 to 200	5	Knoll 1969
Ba	Unknown	3	Analogous to Ca
Lanthanides	Unknown	5	Forms many insoluble compounds; good adsorber
Hg	Unknown	Unknown	
Pb	Unknown	5	Analogous to La
Bi	Unknown	Unknown	
Ra	Unknown	3	Analogous to Ca
Th	Unknown	5	Analogous to Zr
U	Unknown	0	Estimate
Np	Unknown	Unknown	
Pu	Unknown	0.5	Knoll 1969
Am, Cm	Unknown	0.5	Knoll 1969

TABLE 6.2. R_d for High Salt or Organic Solutions with Neutral pH

Constituent	R_d Range	"Average" R_d (mL/g)	Reference/Rationale
^3H	0	0	Present as water
Be	Unknown	Unknown	
^{14}C	0 to >1	0	HCO_3^- or CO_3^{2-} anion
CN	Unknown	0	Soluble anion
NO_2	0 to <1	0	Soluble anion
NO_3	0 to <1	0	Soluble anion
F	0 to <1	0	Soluble anion
Na	Variable	1	Weak exchanger
PO_4	Variable	5	Insoluble in soils
SO_4	Variable	0	Soluble anion
Cl	0 to <1	0	Soluble anion
Ca	Variable	5	Moderate exchanger
Cr	Unknown	0	Assume CrO_4^-
Mn	Variable	10	Rather insoluble
Fe	Variable	10	Rather insoluble
Co	Variable	0	Complex former
Ni	Variable	3	Moderate complex former
Cu	Variable	1	Complex former
Zn	Variable	3	Moderate complex former
As	Unknown	Unknown	
Se	Unknown	0	Assume arsenite anion
Sr	0 to 200	7	Rhodes 1956; Routson et al. 1981
Zr	20 to 200	20	Strong adsorber
Nb	Unknown	Unknown	
Mo	Unknown	0	Assume anion
Tc	0 to <3	0	Assume anion
Ag	Unknown	10	Guess
Cd	Unknown	5	Moderate complex former
Sn	Unknown	Unknown	
I	0 to <1	0	Soluble anion
Cs	<1 to 200	10	Good adsorber, no complexes
Ba	Unknown	10	Good adsorber; insoluble
Lanthanides	Unknown	10	Good adsorber; insoluble
Hg	Unknown	5	Guess
Pb	Unknown	10	Good adsorber; insoluble
Bi	Unknown	5	Guess
Ra	Unknown	10	Analogous to Ba
Th	Unknown	20	Analogous to Zr
U	Unknown	0	Carbonate complexes are anionic
Np	Unknown	Unknown	
Pu	10 to 1000	10	Conservative choice
Am, Cm	10 to 1000	10	Conservative choice

TABLE 8.3. R_d for Low Salt and Organic Solutions with Neutral to Basic pH

Constituent	R_d Range	"Average" R_d (mL/g)	References/Rationale
^3H	0	0	Present as water
Be	Unknown	Unknown	
^{14}C	0 to <5	0	HCO_3^- or CO_3^{2-}
CN	Unknown	0	Soluble anion
NO_2	0 to <1	0	Soluble anion
NO_3	0 to <1	0	Soluble anion
F	0 to <1	0	Soluble anion
Na	Variable	3	Eestimate
PO_4	Variable	10	Estimate
SO_4	Variable	0	Soluble anion
Cl	0 to <1	0	Soluble anion
Ca	Variable	10	Estimate
Cr	Vvariable	0	Assume CrO_4^-
Mn	Variable	20	Estimate
Fe	Variable	20	Estimate
Co	500 to 2000	10	Routson et al. 1981
Ni	Variable	15	Estimate
Cu	Variable	15	Estimate
Zn	Variable	15	Estimate
As	Variable	0	Assume AsO_4^{3-}
Se	Variable	0	SeO_3^{2-} or SeO_4^{2-}
Sr	5 to 100	10	Rhodes 1956; Routson et al. 1981
Zr	Variable	30	Estimate
Nb	Unknown	Unknown	
Mo	Unknown	0	Assume MoO_4^-
Tc	0 to <1	0	Routson et al. 1977; (a)
Ag	Unknown	20	Estimate
Cd	Unknown	15	Estimate
Sn	Unknown	Unknown	
I	0 to	0	(a)
Cs	6 to >1000	50	Routson et al. 1981
Ba	Unknown	50	Estimate
Lanthanides	Unknown	50	Estimate
Hg	Unknown	Unknown	
Pb	Unknown	30	Estimate
Bi	Unknown	20	Estimate
Ra	Unknown	20	Estimate
Th	Unknown	50	Estimate
U	0 to <10	0	(b)
Np	<1 to 5	3	Routson et al. 1977
Pu	80 to >2000	100	Rhodes 1957c
Am, Cm	100 to >2000	100	Routson et al. 1977

(a) As yet unpublished adsorption tests on Cladding Removal Waste Grout Leachates.

(b) Letter, W. J. Martin (PNL) to P. E. Bramson (PNL), "Equilibrium Distribution Coefficients (K_d) for Uranium in Sandy Hanford Sediments," March 12, 1987.

APPENDIX C

ADDITIONAL ADSORPTION CONCEPTUAL MODELS

APPENDIX C

ADDITIONAL ADSORPTION CONCEPTUAL MODELS

As mentioned in Section 3.1.3, the following discussion describes three adsorption conceptual models that are well established and more mechanistically based than the constant and parametric R_d models described in the main text. For various reasons, the three models discussed will likely not be of direct practical use in the foreseeable future for Hanford waste disposal system performance assessment.

C.1 ISOTHERM ADSORPTION MODELS

The results of a suite of experiments evaluating the effect of nuclide concentration on adsorption while other parameters are held constant are called an "adsorption isotherm." Three adsorption isotherm models used frequently are the Langmuir, Freundlich, and Dubinin-Radushkevich models.

The Langmuir model has been used to describe adsorption of gas molecules onto homogeneous solid surfaces (crystalline materials) that exhibit one type of adsorption site (Langmuir 1918). Many investigators have tacitly extended the Langmuir adsorption model to describe adsorption of solution studies onto solid adsorbates including heterogeneous solids. The Langmuir model for adsorption is

$$X = \frac{bX_mC}{1 + bC} \tag{C.1}$$

where X = amount of solute adsorbed per unit weight of solid
b = a constant related to the energy of adsorption
X_m = maximum adsorption concentration of the adsorbate
C = equilibrium solution concentration of the adsorbate.

Substituting $1/B$ for b, we obtain

$$X = \frac{X_mC}{B + C} \tag{C.2}$$

A plot of values of X (y-axis) versus values of C (x-axis) passes through the origin and is nearly linear at low values of C. As C increases, X should approach X, One can rearrange Equation (C.2) by taking its reciprocal and multiplying both sides by $X \bullet X_m$, to yield $X = -B(X/C) + X_m$. Then by plotting X on the y-axis and (X/C) on the x-axis, we can determine the value for -B from the slope of the best-fit line and the value of X_m from the intercept. For radionuclide adsorption onto heterogeneous soils and sediments, the Langmuir model is typically a weak predictor of actual adsorption events, although Salter, Ames and McGarrah (1981a) cite several instances where the Langmuir isotherm has successfully fit trace adsorption by natural substrates. Further, Salter, Ames and McGarrah (1981b) discuss recent modifications of the Langmuir model to accommodate two distinct sites and competition of two adsorbates (the nuclide and the ion it replaces on the adsorbent), which should further extend this conceptual model's usefulness on natural substrates.

The Freundlich isotherm model (Freundlich 1926) is defined as

$$X = KC^N \qquad (C.3)$$

where X = amount of solute adsorbed per unit weight of solid
C = equilibrium solute solution concentration
K, N = constants.

The Freundlich model does not account for finite adsorption capacity at high concentrations of solute, but when considering trace constituent adsorption, ignoring such physical constraints is usually not critical. The Freundlich isotherm can be transformed to a linear equation by taking the logarithms of both sides of Equation (C.3) :

$$\log X = \log K + N \log C \qquad (C.4)$$

When log X is plotted on the y-axis and log C on the x-axis, the best-fit straight line has a slope of N, and log K is its intercept. When N = 1, the Freundlich isotherm represented by Equation (C.4) reduces to a linear relationship, and because X/C is the ratio of the amount of solute adsorbed to the equilibrium solution concentration (the definition of R_d), the Freundlich K is equivalent to the value of the R_d.

Because adsorption isotherms at very low solute concentrations are often linear, either the Freudlich isotherm with N equaling 1 or the Langmuir isotherm with bC much greater than 1 fits the data. The value of N for the adsorption of many radionuclides is often significantly different from 1, such that nonlinear isotherms are observed. In such cases, the Freundlich model is a better predictor than the Langmuir model.

A third adsorption model that has been used recently in nuclide studies is the Dubinin-Radushkevich isotherm (Dubinin and Radushkevich 1947). This model is applicable for the adsorption of trace constituents. Should the adsorbent surface become saturated or the solute exceed its solubility product, the model is inappropriate. The Dubinin-Radushkevich model is more general than the Langmuir model because it does not require either homogeneous adsorption sites or constant adsorption potential. Its mathematical form is

$$X = X_m e^{-K\epsilon^2} \tag{C.5}$$

where X = observed amount of solute adsorbed per unit weight
X_m = sorption capacity of adsorbent per unit weight
K = constant
ϵ = $RT \ln (1 + 1/C)$
R = gas constant
T = temperature (Kelvin scale)
C = solute equilibrium solution concentration (in molarity).

The Dubinin-Radushkevich equation can be transformed to

$$\ln X = X_m - K\epsilon^2 \tag{C.6}$$

A plot of $\ln X$ (y-axis) versus c^2 (x-axis) allows the estimation of $\ln X_m$ as the intercept and $-K$ as the slope of the resultant straight line. Ames et al. (1982) successfully used this model to describe adsorption of uranium and cesium onto basalt and its weathering products.

All three isotherm models can be compared against data from experiments that systematically vary the mass of trace constituent or radionuclide while holding all other parameters as constant as possible. It is important to consider the total mass of the element present including all stable and other radioactive isotopes, when evaluating isotherms. It is incorrect to calculate isotherms based on only one isotope if the system includes several (both stable and radioactive) for a particular element. For convenience, isotherm experiments tend to consider only the total concentration or radioactivity content and thus lump all species for a given contaminant.

It can be argued that all three models, but especially the Langmuir and Dubinin-Radushkevich models, are based on physicochemical processes or mechanisms. If the experiments are performed and characterized rigorously to ensure equilibrium conditions and constancy of variables aside from the trace constituent concentration, the resultant constants undoubtedly have some relationship to adsorption capacities and to site adsorption energies, provided only one species predominates in solution for each contaminant. On the other hand, any suite of experiments that can be plotted as amount adsorbed versus amount in solution at the time of measurement can also be analyzed using these models to see whether predictive equations can be determined. The latter empirical approach is a step up in sophistication over the constant R_d model's distribution coefficient determinations.

It must be stressed that isotherm models as expressed by Equations (C.1), (C.3), and (C.5) explicitly consider dependency of the distribution coefficient on only the solution concentration of the contaminant of interest. Isotherm models do not consider dependence on other solid and solution parameters that can influence adsorption.

The incorporation of isotherm adsorption models into transport codes is relatively easy. Each of the aforementioned isotherm equations can be rearranged to calculate a distribution coefficient, R_d, that is a function of C, the solution concentration of the contaminant, and one or two constants. As the transport model solves for C, substitution of an equation that depends only upon C (and derivable constants) for the R_d in the retardation factor [see Equations (14) and (15) in the main text] should be straightforward. For simple cases, analytical closed-form solutions are possible, or numerous numerical approximation schemes can be used. Thus, with little additional work or increases in computer storage requirements, most transport codes can be formulated to predict radionuclide migration with an isotherm adsorption model. We restate that this approach accounts for the dependency of R_d on only one parameter, the concentration of the radionuclide.

C.2 MASS-ACTION ADSORPTION MODELS

Ion-exchange processes (e.g., electrostatic adsorption) use mass-action laws and equilibrium constant constructs to derive rigorous predictive equations for trace constituent adsorption. Ideal binary ion exchange is a simple case often used to illustrate this model. For ideal binary ion exchange we assume that the contaminant of interest is present in such trace concentrations that it does not appreciably affect either the concentration of the major constituent adsorbed on the solid or the activity coefficient ratio of the binary mass-action equation components. The thermodynamically rigorous mass-action equilibrium expression for a binary cation-exchange reaction, such as strontium or cesium adsorbing onto a calcium-saturated clay, is

$$aN^{b+} + b(MX) \rightleftharpoons a(NX) + bM^{a+} \qquad (C.7)$$

where a = valence of macro ion (e.g., calcium)
N = trace component
b = valence of trace ion (e.g., radionuclide)
M = macro component in binary system
X = solid adsorbent.

The equilibrium constant, K, can be expressed as

$$K = \frac{[NX]^a \, [M^{a+}]^b}{[MX]^b \, [N^{b+}]^a} \qquad (C.8)$$

where the brackets, [], indicate thermodynamic activities. If we assume that the exchange capacity, C, of the solid adsorbent is constant (equivalents per unit weight) and that N is present at low (trace) concentration, then the concentration of the trace constituent adsorbed (NX) is much smaller than C, and the concentration of macro ions adsorbed on exchange sites (MX) is approximately equal to C/a [i.e., $(MX) = C/a$] in terms of moles per unit of weight, because $C = (NX)b + (MX)a$. Then, by using the standard definition of the distribution coefficient, $R_d = (NX)/(N^{b+})$, where (N^{b+}) is the solution concentration of the trace constituent at equilibrium with the solid, and by substituting the relationship that activity is equal to the concentration times an activity coefficient, i.e., $[A] = \gamma_A(A)$, we can rewrite Equation C.8 as

$$K = \frac{(Kd)^a \ (M^{+a})^b}{(C/a)^b} \bullet \Gamma \qquad (C.9)$$

where Γ is the ratio of the activity coefficients:

$$\Gamma = \frac{\gamma^a_{\{NX\}} \ \gamma^b_{\{M^{a+}\}}}{\gamma^b_{\{MX\}} \ \gamma^a_{\{N^{b+}\}}} \qquad (C.10)$$

For ideal ion exchange of a trace constituent where the exchange capacity, C, is constant, the ratio of activity coefficients for the adsorbed ions γ_{NX}/γ_{MX} is constant. Further, for low ionic strength solutions the ratio $\gamma_{M^{a+}}/\gamma_{N^{b+}}$ is also a constant, and thus Γ becomes a constant. Using these conditions/assumptions and a logarithmic transform of Equation (C.9), the dependence of R_d (the trace constituent distribution coefficient) on the macro ion concentration, M, reduces to $-b/a$, the ratio of tracer ion charge to the macro ion charge.

A plot of log R_d (y-axis) versus log M^{a+} (x-axis) should yield a straight line with its slope equal to $-b/a$. Kraus and Nelson (1955), Kraus et al. (1958), Rafferty et al. (1981), Shiao and Meyer (1981), and Shiao, Egozy and Meyer (1981) discuss the use of this ion-exchange approach to model both cation and anion exchange of trace constituents on to hydrous oxides and clays. Theoretical and experimental efforts to model mixtures of solid adsorbents, e.g., clays plus oxides, are discussed by Triolo and Lietzke (1980) and by Palmer et al. (1981). The underlying principle used in dealing with mixtures is the assumption of additivity of the individual adsorption capacities of each solid adsorbent, based on the weight fraction of each solid present.

Routson and Serne (1972) and Langmuir and **Mahoney** (1984) present a slight variation of this ideal ion-exchange approach that also uses the mass-action equations and the equilibrium constant concept. In their derivation, the mass-action expression for binary ion-exchange reactions, Equation (C. 7), is expressed as an empirical equilibrium constant:

$$K^* = \frac{[M^{+a}]^b}{[N^{+b}]^a} \left(\frac{NX}{MX}\right)^P \qquad (C.11)$$

where the activity ratio of the ions N and M adsorbed to the solid is replaced by its concentration ratio or mole fraction of total sites raised to some empirical constant, P. The true equilibrium constant is replaced by a pseudo equilibrium constant, K^*.

For analysis of experimental data, the logarithmic transform of Equation (C.11), with the substitution of the solution concentration, C, multiplied by an activity coefficient, 7, is used for solutes activities. The activity coefficients of ions can be estimated from **Davies'** extension of the **Debye-Huckel** theory (Butler 1964), and the concentrations of ions in solution are determined by standard chemical analysis techniques. Alternately, a thermodynamic chemical code, such as EQ3 (Wolery 1979), MINTEQ (Felmy, Girvin and Jenne 1984) or PHREEQUE (Parkhurst, Thorstenson and Plummer 1980), can be used to calculate activities for M and N in solution. By plotting log $[M^{+a}]^b/[N^{+b}]^a$ on the y-axis and log $(NX)/(MX)$ on the x-axis, and then calculating the best-fit line, the slope (an estimate of the empirical constant P) and the intercept (an estimate of log K^*) can be calculated.

Detailed discussions on the derivation and limitations of this empirical approach for both trace constituent adsorption and competition between two macro components are presented in Garrels and Christ (1965). Briefly, the approach relies on the same assumptions described for the ideal ion-exchange approach, that the number of bonding sites of the solid (-X) are constant and have essentially the same binding energy, and that the ions being adsorbed do not cause appreciable changes in the surface structure of the adsorbent. Walton (1949) and Serne, **Routson** and Cochran (1973) describe experiments in which Equation (C.II) was used to develop predictive models for exchange of one macro cation for another onto aluminosilicates and natural soils. The approach allows investigators to evaluate the dependence of the adsorption of one cation on the concentration of a second cation.

By developing computer algorithms based on Equation (C. 11), with laboratory-derived values for K* and P for sets of binary exchange reactions, Routson and Serne (1972) were able to model the simultaneous adsorption/exchange of Na^+, Ca^{+2}, Mg^{+2}, and K^+ in a synthetic Hanford waste water onto several sandy soils. The binary reaction sets (Na-Ca), (Mg-Ca), and (Na-K) were solved numerically on a computer by iterating through each equation until the change in predicted solution concentration for each species at the beginning and end of one complete pass was less than a specified value, such as 0.1%.

With a similar iteration technique, Robbins et al. (1980a,b) used a pseudothermodynamic mass-action equation variation of Equation (C. 11) to model the transport of alkali metals, specifically K^+ and Na^+, and alkaline earths, specifically Mg^{2+} and Ca^{2+}, through soils and clays. Robbins et al. used the mass-action equation

$$K = \frac{[M^{+a}]^b}{[N^{+b}]^a} \; \frac{X_{\frac{1}{b}}N}{X_{\frac{1}{a}}M} \qquad (C.\ 12)$$

where $X_{\frac{1}{b}}N$ and $X_{\frac{1}{a}}M$ are the equivalents of each cation adsorbed on the solid adsorbent, given in units of milliequivalents per 100 g.

For example, the pseudoequilibrium constant, frequently called the "selectivity coefficient" in soils literature, for sodium exchange on to a calcium-saturated soil for the exchange reaction

$$Na^+ + Ca_{\frac{1}{2}}X \rightleftharpoons \frac{1}{2}\, Ca^{2+} + NaX \qquad (C.\ 13)$$

is

$$K^* = \frac{[Ca^{2+}]^{1/2}}{[Na^+]} \; \frac{(NaX)}{(Ca_{\frac{1}{2}}X)} \qquad (C.\ 14)$$

This approach, like the true thermodynamic mass-action conceptual models for Equations (C.7) through (C.10), assumes that 1) only free cation species are adsorbed; 2) the adsorbent cation-exchange capacity is constant and independent of pH and solution composition or total ionic strength; 3) the solutes are a true solution (i.e., the species activities are not affected by the presence of the solids); and 4) the exchange is reversible, and there is no hysteresis between adsorption and desorption. Most derivations also consider only one type of adsorption site with a fixed adsorption energy.

Brouwer et al. (1983) give a detailed discussion of a mass-action adsorption model with several types of adsorption sites having different energies or selectivities for adsorption of ions. Brouwer et al. also treat several simplifying cases, such as allowing one type of site to be more selective than another. These cases show that the adsorption of cesium and rubidium onto illite clay originally saturated with calcium, strontium, barium, sodium, or potassium is best described by assuming that there are three types of sites. Likely, most natural adsorption substrates are best modeled as a mixture of sites with differing adsorption energies.

Langmuir (1981) reviews the use of the pseudothermodynamic mass action conceptual model for both exchange of macro constituents and adsorption of trace constituents. Because Equation (C.11) includes an exponent, P, on the ratio of adsorbed phases, Langmuir has called this conceptual model the Power Exchange Model. From reviewing numerous adsorption publications, Langmuir found that $P \approx 1$ when two competing cations, especially alkali and alkaline earths, are present at near equal molar concentrations. But when one of the competing ions is present at very low concentrations relative to the other, P does not equal 1. Most heavy metal elements in nature are present at concentrations much less than alkali and alkaline earths, and the best-fit power exchange equation typically requires P to be greater than 1. A P value greater than 1 means that the trace constituent is preferably adsorbed as its concentration decreases. In other words, the R_d value gets larger as the solution concentration of the trace constituents decreases. (This trend is often observed in radionuclide adsorption studies and corroborates Langmuir's findings.) Further, Langmuir found that a complete description of trace metal adsorption over a wide range in solution concentrations of the trace metal requires that several regions be designated where distinct K^* and P values are determined. Conceptually one might suggest that each distinct region describes a separate adsorption process or separate type of adsorption site but as the Power Exchange Model is strictly empirical there is no fundamental basis for such a suggestion. At any rate, Langmuir cites numerous studies in which this empirical mass action conceptual model readily describes the adsorption of cationic species onto clays, hydrous oxides, zeolites, and soils, provided that the user segments the data versus concentration in solution or studies systems with only small ranges (e.g., two orders of magnitude) of solution concentrations for the trace constituent.

Finally, Langmuir shows that the Power Exchange Model [(Equation (C.11)] where the NX and MX solid terms are expressed as mole fraction reduces to the Freundlich adsorption model when the minor component mole fraction, NX, is less than 0.05. As derived in Equation (C.3) the Freundlich equation exponent N would be less than 1 for most trace radionuclides as it is similar to the reciprocal of P in Equation (C.11), which Langmuir finds is typically greater than 1 for trace metal adsorption.

A potential limitation for the study of trace constituent adsorption using this pseudoequilibrium-constant approach is the difficulty of obtaining accurate values of the ratio (NX)/(MX) when the ratio is either less than 0.05 or more than 0.95. In the case of trace constituent adsorption, it is quite common for this ratio to be less than 0.1. The use of radiotracers often helps make measurements more precise, but there will always be a threshold concentration below which accurate results are impossible. Many real-world cases may fall in this region.

The mass-action approach requires the investigator to track the activities of the free cations or free anions in solution and the amounts adsorbed on the solid phase (in terms of either mole fractions, equivalents per gram, or moles per gram). This need to keep track of the distribution of elements other than the contaminant of interest increases significantly the storage requirements for transport codes. Probably of greater concern is the fact that numerical solution algorithms to solve equations like Equations (C.8), (C.9), (C. 11), (C. 12), and (C. 14) often have convergence problems because of their highly nonlinear nature. This is particularly a problem for the binary exchange reaction, when one exchanging ion is present in much smaller quantities than the other.

Probably for these reasons, few transport codes exist that accommodate the mass-action conceptual adsorption mode. Furthermore, the behavior of many trace contaminants appear to be only poorly modeled by the mass-action approach without segmenting the system and using distinct **K*** and P values in each segment. Classical soil problems, such as salt transport by irrigation of saline soils, have provided the impetus to build mass-action adsorption transport codes (e.g., Robbins et al. 1980a,b; Dutt and Doneen 1963; Dutt, Shaffer and Moore 1972). However, so far few of these codes have found any usage in the nuclear waste management community for predicting radionuclide transport.

C.3 SURFACE COMPLEXATION MODELS

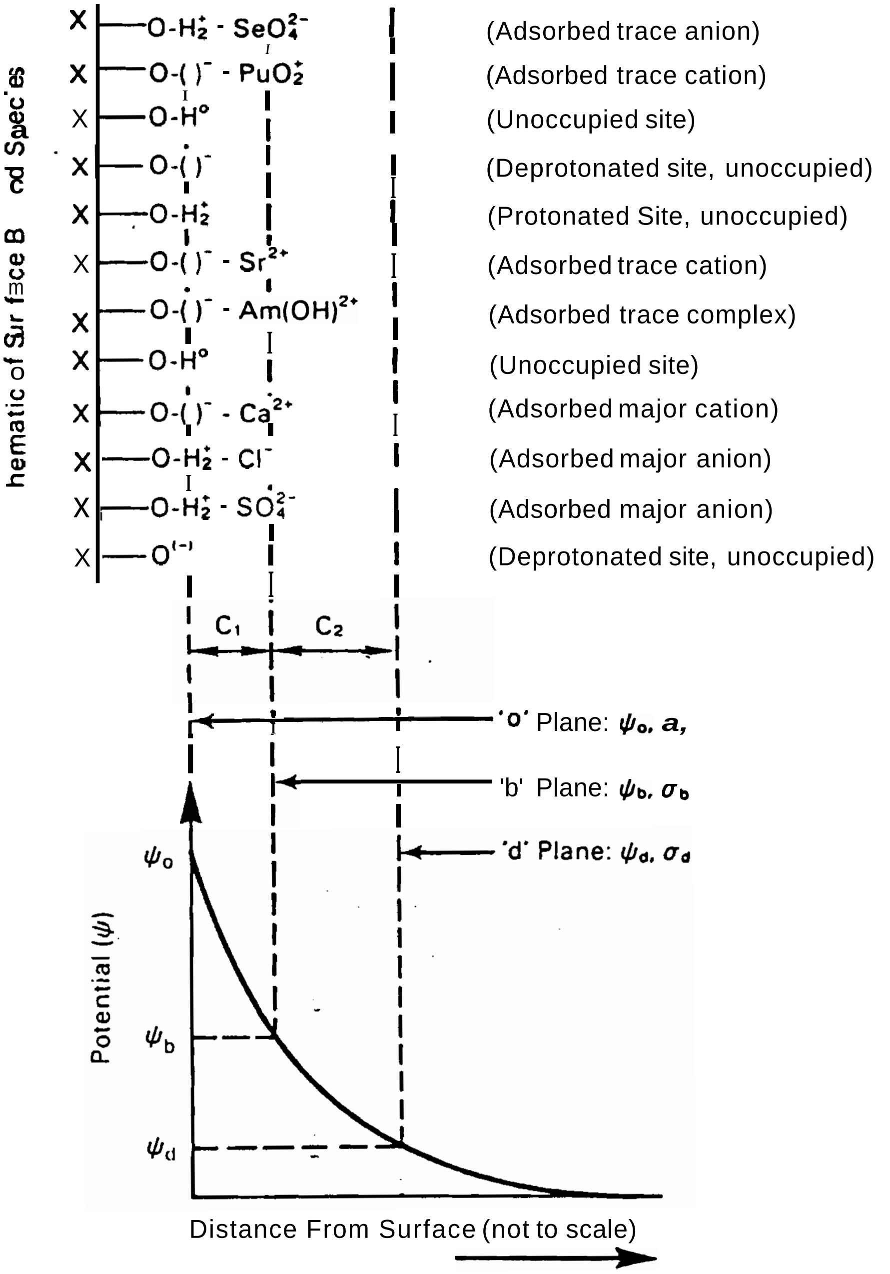
For many radionuclides and trace constituents, the literature states or implies that specific adsorption (i.e., adsorption occurring on to surfaces having the same net surface charge as the sorbing ion) is a major contributor to the adsorption at low solution concentrations (see, for example, Rai et al. 1984). Hydrous oxides of Fe, Mn, and Al, and amorphous aluminosilicates occurring either as discrete grains or surface coatings are assumed to be the prime adsorbents responsible for specific adsorption. These solid phases have variable surface charges and exhibit amphoteric behavior. The solids have a net positive charge at pH values below their point of zero charge (PZC) and a net negative charge at pH values above the PZC. James and Healy (1972) and Langmuir and Mahoney (1984) explain why specific adsorption occurs. Briefly, the free energy of adsorption is the sum of three terms: a coulombic term, a solution term, and a chemical reaction term. Mathematically the free energy of adsorption is

$$\Delta G^{\circ}_{ads} = \Delta G^{\circ}_{coul} + \Delta G^{\circ}_{solv} + \Delta G^{\circ}_{chem} \qquad (C.15)$$

For adsorption to occur, ΔG°_{ads} must be negative. The free energy of solvation, ΔG°_{solv}, represents the energy needed to dehydrate a species to bring it close enough to the adsorbent surface to attach. This quantity is always positive but is smaller for low valence state species, that is, $\Delta G^{\circ}_{solv} = f(\text{valence}^2)$. The coulombic term, ΔG°_{coul}, is positive for like charged entities (that is, if the adsorbent site is of the same charge as the adsorbing species, then ΔG°_{coul} is positive). Thus for specific adsorption, ΔG°_{coul} and ΔG°_{solv} are both positive; for ΔG°_{ads} to be negative, ΔG°_{chem} must be both negative and numerically larger than the sum of ΔG°_{coul} and ΔG°_{solv}. The ΔG°_{chem} represents the free energy of chemical bonding between the adsorbent and the adsorbate, and obviously it must be negative in charge and relatively large for species that specifically adsorb.

Surface complexation adsorption models treat the adsorbent surface as a plan of hydroxyl groups, X-OH, where X represents structural Al, Fe, Mn, Si, or other atoms. The adsorption sites, -OH, or hydroxyl groups are thought of as ligands that are acid/base sensitive and form complexes with solutes in solution. The model assumes that 1) adsorption occurs on the sites with neither chemical nor electrostatic interactions between adsorbed species; 2) all the adsorption sites have equal binding energies (i.e., each site is identical); 3) no matter how many sites are full, each remaining site has the same probability of adsorbing the next solute ion (i.e., the binding energy does not depend on sorption density); and 4) the maximum adsorption capacity allows only a single-layer coverage of each site. All four of these assumptions are also invoked for the Langmuir isotherm and ideal ion-exchange approaches described earlier.

In the surface complexation model, adsorption reactions are considered analogous to soluble complex reactions in solution, with one fundamental difference. The adsorption reaction includes an electrostatic energy term to account for the interaction of the charged adsorbing ion and the surface charge on the solid. The conceptual model is shown schematically in Figure C.1. For the surface complexation model, dubbed the "triple-layer model," originally suggested by James and Healy (1972, 1975), and applied by Davis, James and Leckie (1978), Davis and Leckie (1978, 1980) and Leckie et al. (1980), the space around the solid surface (usually represented as a semi-infinite planar surface) is arbitrarily broken into three layers or zones, separated by the 0 plane, the b plane, and the d plane, as shown in Figure C.1. The 0 plane represents the interface between the solid surface and solution. Only hydrogen and hydroxyl ions can enter the 0 layer to interact with the solid. Just



Electroneutrality requires $\sigma_o + \sigma_b + \sigma_d = 0$

Where **a,** = Surface charge at designated plane

Charge-potential relationships

$\psi_o - \psi_b = \sigma_o / C_1$

$\psi_b - \psi_d = -\sigma_d / C_2$

FIGURE C.1. **Schematic Representation of Triple-Layer Adsorption Model** beyond the O layer is the b layer, which extends out farther from the surface and ends at the boundary of the diffuse zone, the d plane. Solution ions, such as the macro cations and anions (Na^+, Ca^{2+}, Cl^-, SO_4^{2-}, etc.), and the trace constituents [Sr^{2+}, PuO_2^+, $Am(OH)^{2+}$], that are adsorbing onto the solid surface are found in the b layer. The third layer is the diffuse zone, where ions are not influenced strongly by electrostatic forces emanating from the solid surface. The ions in this region are considered to be counterions that neutralize any residual charge caused by the surface and specifically adsorbed ions in the b layer. The d layer blends into the bulk solution farther from the surface.

The electrostatic interactions modify the thermodynamic activities of ions as they move from the bulk solution into the various adsorption zones. The ion activity of species near the surface, $[Ion_S]$, is related to its activity in the bulk 'solution, $[Ion_B]$, by the relationship:

$$[Ion_S] = [Ion_B]\, e^{-ZF\Psi/RT} \qquad \text{(C. 16)}$$

where Z = charge of ion (e.g., Sr^{2+} = +2, SO_4^{2-} = -2)
F = Faraday constant
Ψ = electrostatic potential for the designated zone
R = gas constant
T = temperature (Kelvin scale).

Figure C.1 also shows the shape of the potential curve as an ion approaches the potentials (see James and Healy 1972) and equations like Equation (C.16) for each surface. The figure also defines two capacitance terms and three surface charges. Adsorption reaction onto oxide surfaces have been successfully described using the relationships between surface charges, capacitances, and species adsorbed onto the solid.

Adsorption dependence on acid/base reactions is explicitly accommodated by the following two reactions:

$$X\text{-}OH; \rightleftharpoons X\text{-}OH + H^+_{(s)}$$
$$X\text{-}OH \rightleftharpoons X\text{-}O^- + H^+_{(s)}$$

as

$$K_{a1}^{int} = \frac{[X\text{-}OH]\ [H_s^+]}{[X\text{-}OH_2^+]} = \frac{[X\text{-}OH]\ [H^+]e^{(-F\Psi_o/RT)}}{[X\text{-}OH_2^+]} \tag{C.17}$$

and

$$K_{a2}^{int} = \frac{[X\text{-}O^-]\ [H_s^+]}{[X\text{-}OH]} = \frac{[X\text{-}O^-]\ [H^+]e^{(-F\Psi_o/RT)}}{[X\text{-}OH]} \tag{C. 18}$$

where the equilibrium constants, $K_{a_1}^{int}$ and $K_{a_2}^{int}$, are similar to association constants for soluble complex formation and can be determined in the laboratory by systematic acid/base titrations (see Davis et al. 1978). The other variables in these equations are those defined for Equation (C.16).

Examples of cation and anion adsorption reactions for trace contaminants, such as radionuclides, are shown in Equations (C.19) and (C.20). Recall that these ions and the macro cations and anions are bound in the b layer not the O layer; therefore, the electrostatic terms differ from those in Equations (C.17) and (C.18). The first reaction shows the adsorption of the first hydrolysis species for americium:

$$X\text{-}OH + Am^{+3}_{(s)} + H_2O \rightleftharpoons [X\text{-}O^-\text{-}Am(OH)^{2+}] + 2H_s^+$$

$$K = \frac{[(X\text{-}O\text{-}AmOH)^{2+}]\ [H^+]^2\ e^{(-F\Psi_o/RT)}e^{(-F\Psi_b/RT)}}{[X\text{-}OH]\ [Am^{3+}]e^{-3F\Psi_b/RT}} \tag{C. 19}$$

The second reaction shows the adsorption of the selenate anion:

$$X\text{-}OH + H^+_{(s)} + SeO_4^{2-}{}_{(s)} \rightleftharpoons (X\text{-}OH_2^+\text{-}SeO_4^{2-})$$

$$K = \frac{[(X\text{-}OH_2\text{-}SeO_4^{2-})^-]}{[X\text{-}OH]\ \ [H^+]\ [SeO_4^{2-}]\ e^{-F\Psi_o/RT}\ e^{+2F\Psi_b/RT}} \tag{C. 20}$$

The triple-layer conceptual model explicitly accommodates variable surface charge, pH effects, ionic strength effects, speciation (that is, it allows for simultaneous adsorption of free cations or anions, and of hydrolyzed and complexed species), macro cation/anion competition [reactions similar to Equations (C. 19) and (C.20) for major constituents are included]. When incorporated into a thermodynamic code, this model can explicitly address oxidation/reduction effects on ion speciation and on the stability of solid adsorbents such as iron oxides. Serne, Peterson and Hostetler (1984) and Peterson, Martin and Serne (1986) have combined triple-layer adsorption algorithms with the MINTEQ thermodynamic code (Felmy et al. 1984) to describe uranium mill tailings waste leachate interactions with sediments. Their exercise modeled both solubility and adsorption (onto hydrous iron oxide) processes under variable pH, Eh, and solution ionic strength (Peterson, Martin and Serne 1986).

A second surface-complexation conceptual model is called the "constant-capacitance model" (Schindler et al. 1976; Schindler 1981; Hohl and Stumm 1976). In general, it is conceptually similar to the triple-layer model just discussed, but it considers only two planes for adsorption and assumes that all species adsorb in the inner zone, outside of which lies the diffuse layer of counterions that melds into the bulk solution. Morel, Westall and Yeasted (1981) and Westall and Hohl (1980) discuss the finer details of similarities and differences between these popular surface-complexation models, but in general both models can be used to explain observed adsorption onto hydrous oxide surfaces.

The use of the surface-complexation model requires detailed characterization of the adsorbent's adsorption capacity (i.e., number of sites or site density and surface area), of its dependency on pH (determined by acid/base titration), of its dependency on major cations/anions, and of the electrical properties of the surface (electrokinetic potential, specific conductivity, etc.), as well as detailed studies of the adsorption of trace constituents. Currently the model has been used successfully to predict adsorption of hydrolyzable trace metals (Zn, Cd, Cu, and others) and oxyanions (CrO_4^{2-}, SeO_4^{2-}, and others) onto oxide/hydroxide surfaces of Fe, Ti, Al, and Si. Several recent conferences have discussed the use of this approach to describe the adsorption of uranium onto hydrous iron oxides, of thorium and radium onto quartz and kaolinite, and of lead onto manganese oxide (Catts and Langmuir 1983; Hsi and Langmuir 1985; Langmuir and Riese 1982; Riese 1982; Riese and Langmuir 1981, 1983). The approach has also been used to model cesium adsorption onto montmorillonite (Silva, White and Yee 1981), neptunium

(V) adsorption onto hydrous iron oxide and alluvial sediments (Fruchter et al. 1985), and uranium(VI) species adsorption onto geothite, amorphous ferric oxyhydride, and hematite (Hsi and Langmuir 1985).

Leckie et al. (1980) discuss the extension of the triple-layer model to accommodate multiple and distinct types of sites. They suggest that highly accurate modeling of trace constituent adsorption on to hydrous oxides requires accommodations of variable binding energies on sites as a function of the amount of the species adsorbed. This adaptation would significantly increase the complexity of using the surface-complexation conceptual model.

Surface-complexation modeling requires detailed characterization of the solid adsorbent. Before surface-complexation conceptual models can gain wide acceptance in the nuclear waste management community, their application to natural rocks and sediments must be addressed. However, to date, only simple and pure oxide solids and kaolinite clays have been successfully characterized to obtain the necessary input values. Thus, solid substrates currently modeled are pure single-phase minerals or amorphous oxides/hydroxides. In principle, the conceptual model should work for natural adsorbents that are mixtures of pure minerals, sometimes mixed with amorphous coatings. One current approach is to treat the natural system as a linear combination of pure phases. That is, the natural solid is broken down into its primary components, and the individual properties of the primary components are weighted by the percentage of the whole mass that each component represents. The weighted values of such properties as surface area, site density, and so on, are then added to determine a value for the natural composite. Such a "weighted building block" approach has recently been explored by Honeyman (1984) and Altmann (1984). More work on various types of natural solids will be required to evaluate the applicability of the linear summation of primary components.

Use of the surface-complexation model also requires access to an ion speciation code such as PHREEQUE, MINTEQ, or EQ3. If the thermodynamic data for a particular contaminant is suspect or missing in the ion-speciation code, the activity of adsorbing species cannot be determined. In addition, systematic batch adsorption experiments that include complete solution analyses must be performed to determine the necessary adsorption constants corresponding to the K terms in Equations (C.19) and (C.20).

The need for detailed solids characterization appears to be another problematical aspect to be overcome before most experimenters involved in radionuclide adsorption studies will become interested in surface-complexation concepts because they generally are not experienced in solids characterization. With the increasing use of ion-speciation codes and with the elucidation of the applicability of the building block approach, then facile techniques to properly perform the detailed solids characterization will become the key to acceptance. Work is needed to evaluate the usefulness of current techniques to characterize pure mineral surfaces to characterizing natural solids. As a corollary, it is necessary to discover whether natural systems can be dissected into their individual pure minerals and amorphous coating components without significantly altering their adsorption properties.

Conceptually, the surface-complexation model is the most elegant and comprehensive adsorption theory available. Its explicit accommodation, based on theoretical principles, of solid characteristics (site density, electrostatics), and of the effects of pH and solution characteristics (ionic strength effects, speciation effects, redox effects, etc.) is a persuasive reason to endorse further study. The mathematical expressions are compatible with and readily included in thermodynamic geochemical computer codes (e.g., MINTEQ, MINEQL) referenced earlier so that the processes of speciation, complexation, solubility, redox, and sorption-desorption can be treated simultaneously as happens in the natural system.

At present only a few attempts have been made to incorporate surface-complexation adsorption models into transport codes. The same requirements discussed for the mass-action conceptual model apply. That is, the transport model must track other species and elements besides the contaminant of interest, and the solution algorithms must be very robust to accommodate the highly nonlinear nature of the adsorption equations. The surface-complexation conceptual model further exacerbates the convergence problem in that it requires that the charge electroneutrality and charge-potential constraints identified in Figure C.1 be satisfied as well as the various mass-action equations (with electrostatic terms) such as Equations (C.17) through (C.20). Murali and Aylmore (1981) discuss some convergence problems when modeling the adsorption of phosphate onto geothite. Murali and Alymore (1981) further imply that the simulation of transport is not easily performed using models that include electrostatic constraints.

Recent attempts at coupling a surface complexation adsorption model with transport codes have relied on simplifications such as setting the electrostatic terms as constants [e.g., Jennings, Kirkner and Theis (1982) and Miller and Benson (1983)] or relying on the constant capacitance model and a fixed system pH [e.g., Cederberg, Street and Leckie (1985)]. Further, these types of transport codes inevitably are illustrated on one-dimensional transport problems although the authors usually remark that there are no conceptual problems to converting to multiple dimensions. There may, in fact, be current practical problems such as computer storage limitations and excessive run times.

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