

12/14/87

DEVELOPMENT OF A METHODOLOGY OF GEOCHEMICAL SENSITIVITY  
ANALYSIS FOR PERFORMANCE ASSESSMENT

SAND87-1133C

Malcolm D. Siegel  
Waste Management Systems Division  
Sandia National Laboratories  
Albuquerque, New Mexico

Sidney L. Phillips  
Information and Computing Sciences Division  
Lawrence Berkeley Laboratory  
University of California  
Berkeley, California

James O. Leckie  
Environmental Engineering and Science Division  
Department of Civil Engineering  
Stanford University  
Stanford, California

Walton R. Kelly  
Department of Environmental Sciences  
University of Virginia  
Charlottesville, Virginia

ABSTRACT

The objective of this geochemical sensitivity analysis is the formulation of criteria for valid simplification of radionuclide transport models used in performance assessment. In the past, limitations in available models, data and computer codes have necessitated the use of simplified representations of radionuclide chemistry and water/rock interactions in analyses of high level waste repositories. The validity of these simplifying approximations is a crucial element in the design of performance assessment methods and must be assessed relative to the appropriate performance measure and experimental frame.

In this paper, we illustrate the complementary roles played by (1) simple transport models designed to bound the

8712140171 871109  
PDR WMRES EXISANL  
A-1756 PDR

88131221  
WM Project: WM-10, 11, 16  
PDR yes  
(Return to WM, 623-55)

WM Record Files: A-1756  
LPDR yes

H

radionuclide discharge over wide ranges of physicochemical conditions, (2) detailed geochemical models that provide a structured method to obtain reliable information about solute/rock/water interactions, and (3) sensitivity and uncertainty analysis techniques used to assess the significance of errors in both data and models. In this multi-year project, progress has been made in the following areas: (1) compilation of computerized data bases of critically evaluated thermodynamic data and empirical sorption (batch  $K_d$ ) data for waste elements, (2) assessment of the potential use of surface complexation models in existing performance assessment methodologies, and (3) simulation of radionuclide discharge for generic and site-specific systems over 10,000 year periods. The development of the methodology will be illustrated with examples describing behavior of neptunium and uranium at hypothetical HLW repository.

-----  
This work was supported by the United States Nuclear Regulatory Commission and performed at Sandia National Laboratories, operated for the U. S. Department of Energy under contract number DE-AC04-76DP00789; at Stanford University, and at Lawrence Berkeley Laboratory.

Sensitivity analyses and performance assessment calculations of radionuclide transport from high-level waste (HLW) repositories rely on simplified representations of complex chemical behaviors of aqueous radionuclides and hydrologic flow fields. The structure of these calculations is strongly influenced by: 1. current theories describing the transport and reaction of chemical species in natural systems, 2. the availability of data from both empirical and mechanistic studies of solute/rock/water interactions in the specific geochemical environments of interest and 3. the costs associated with computer simulations of large systems. Limitations in these three areas prevent the inclusion of all possible phenomena in any single analysis. A crucial element in the design of the models to be used in these studies is the validity of the simplifying assumptions that are used.

Sandia National Laboratories (SNLA) is assisting the Nuclear Regulatory Commission (NRC) in the development of a performance assessment methodology for HLW repositories. For the past several years, an effort has been made to develop a method of geochemical sensitivity analysis. This work has been a collaborative effort among staff at SNLA, Lawrence Berkeley Laboratory (LBL) and the Nuclear Regulatory Commission. The objective of this analysis is to assess the significance of errors in calculations of radionuclide discharge due to various approximations used to describe geochemical processes. The purpose of this paper is to describe the approach of this work by evaluating some questionable assumptions inherent in performance assessment models and associated sensitivity analyses.

## MODEL VALIDITY AND SIMPLIFICATION

### General Principles

Zeigler (1) provides a useful framework for defining criteria for valid model simplification. He identifies the following five distinct elements of a model/simulation:

1. the real system, which is the source of observations,
2. experimental frames or subsets of observations,
3. the base model, a hypothetical model that is valid in all experimental frames,
4. lumped models, which are simple models designed for particular experimental frames, and
5. the computer codes which carry out the simulations.

Various methods of simplification have been discussed by Henize (2). He suggests that a weakness in many sensitivity studies of large systems is the failure to include all significant feedback mechanisms between the individual components (ie. submodels) of the system. A common error in simulations and sensitivity analyses is to make invalid ceteris paribus assumptions. This practice involves holding the values of one or more variables constant during a parametric analysis of the system behavior. If significant interactions are ignored in model simulations then the results of the analysis can be misleading.

Henize also notes that another common error in sensitivity analyses and simulations is failure to direct the calculations toward the appropriate performance measure. The number of independent and dependent variables that could be used to describe even a simple system is potentially very large. If the most useful subset of parameters is not identified early in the analysis, then the simulations and sensitivity analyses can be inefficient or irrelevant.

Criteria for valid simplification of models used in performance assessment should be defined in light of these basic concepts. The appropriate experimental frame must be defined and the significance of potential interactions must be assessed relative to the correct performance measure. The application of the general concepts outlined above are applied to specific aspects of performance assessment models in the following section.

#### Simplification of Geochemical Models for Performance Assessment Calculations and Sensitivity Analysis

In the performance assessment methodology developed by SNLA for the NRC, the Latin Hypercube sampling (LHS) procedure (3) is used to create combinations of values of input parameters for large numbers of calculations in sensitivity analyses. As illustrated in Figure 1, ranges and distributions are assigned to each input variable, values of each variable are selected and combinations of parameter values are used for calculations with the NEFTRAN (4) or SWIFT (5) codes. The results of many such calculations produce a distribution of values of the performance measure which can be used in sensitivity analyses or to assess compliance of a site with the EPA Standard 40CFR191 (6,7). If the results of these calculations are to be valid, then the following must be shown: 1. it is possible to assign realistic distributions of the input parameters using available data and 2. the

correlations between the input variables as represented by the Latin Hypercube sampling procedure reflect the true relationships in nature. When these assumptions are not valid, then the analysis may suffer from the corresponding two errors: 1. use of an inappropriate experimental frame and 2. invalid ceteris paribus assumptions or incorrect interactions among system variables.

The Latin Hypercube sampling procedure allows for the assignment of simple correlations between variables. Generally, however, the nature of the relationships among variables is not known and many parameters are assumed to be uncorrelated. For example, the radionuclide distribution coefficient  $K_d$ , matrix porosity and ground-water velocity are commonly assumed to independent. In a later section of this paper, the adequacy of this assumption will be examined.

Figure 2 illustrates the general structure of radionuclide transport calculations carried out by the NEFTRAN and SWIFT-2 computer codes in performance assessment studies (4,5). Interactions among radionuclides, water and rock are represented by retardation factors whose values are determined using a number of simplifying assumptions. These are:

1. A single chemical species exists for each radionuclide.
2. The composition of the ground water is constant in each transport leg.
3. The rock composition is constant in each transport leg.
4. Reversible, equilibrium sorption that can be described by a linear or Freundlich isotherm is the only chemical process occurring.
5. Chemical exchange between fractures and rock matrix can be described by a bulk retardation factor, a linear-driving-force (mass transfer) approximation or an effective diffusion coefficient.
6. Radionuclide transport by colloids or organic complexes is negligible.

# LAMN HYPERCUBE SAMPLE

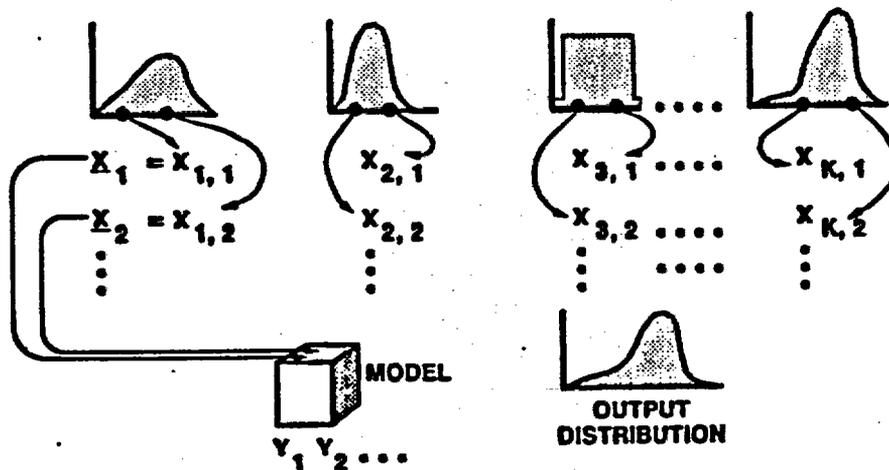


Figure 1.

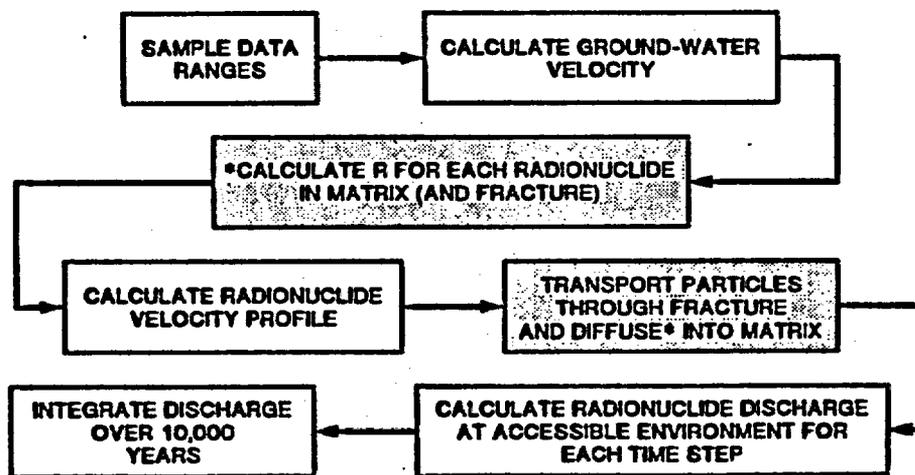


Figure 2.

Figure 3 contrasts the lumped model of chemical interactions (3a) used in these performance assessment models with a hypothetical base model for the real system (3b). The lumped model includes only reversible sorption and diffusion of radionuclides into dead-end pores of the rock matrix. The base model includes a number of other processes such as organic complexation, oxidation-reduction, inorganic complexation, irreversible sorption, ion filtration and colloid formation. It is generally accepted that the base model depicted in Figure 3b is more predictively valid than the lumped model in Figure 3a. It has been suggested that more sophisticated computer codes that include all of these phenomena be used in performance assessment calculations (8). In later sections of this paper, however, it will be shown that limitations in available data and computer codes currently prevent the use of such comprehensive models in a performance assessment methodology.



One alternative to the use of either the inadequate lumped model described in Figure 3a or the impractical base model in Figure 3b is to give no credit to geochemical retardation in assessments of compliance with the EPA Standard. In a later section of this paper, it will be shown that uncertainties in hydrologic data for potential sites preclude reliance solely on hydrologic barriers to radionuclide release.

## DEVELOPMENT OF A METHOD FOR GEOCHEMICAL SENSITIVITY ANALYSIS

### Role of Geochemical Sensitivity Analysis in Performance Assessment

Although it is anticipated that advances in geochemistry, hydrology and computer science will allow for comprehensive descriptions of radionuclide transport at the repository sites at some future time, it is prudent to design an interim approach to address the aforementioned weaknesses in the transport models currently used in performance assessment. Such a approach should identify site-specific conditions under which the approximations used in the current performance assessment models significantly hinder our ability to assess compliance with respect to the EPA Standard. Another objective of this analysis would be to determine if the available solubility and sorption data are adequate to define the experimental frame for performance assessment models.

The components of the analysis are identified in Figure 4. The probabilistic risk assessment (PRA) codes NEFTRAN, CCDPLT and LHS are being used to assess the amount of geochemical retardation needed to ensure compliance with the EPA Standard 40CFR191 at a hypothetical basalt repository site. The Sandia Sorption Data Management System (SSDMS) and the Aqueous Solutions Database (ASD) are being developed to store and facilitate retrieval of  $K_d$  values and thermodynamic property values, respectively. These parameter values are used either in the PRA codes or in speciation codes such as PHREEQE (9) and MINEQL (10). Coupled reaction/transport codes such as TRANQL (11) do not use a retardation factor to approximate chemical behavior of the radionuclides. With the proper modifications, it is hoped that codes like these can be used to carry out simulations in which many of the assumptions associated with retardation factors can be relaxed. In the sections that follow, examples of the use of each of the components with site-specific data are given.

Performance Assessment Calculations for a Hypothetical Basalt Site.

The radionuclide flow path assumed in these calculations is shown schematically in Figure 5. The flow path is similar to that assumed in performance assessment studies of the proposed repository site at the Hanford Reservation in Washington state (12,13,14). The repository is located in the interior of a basalt flow. Radionuclides flow vertically from the repository through the dense interior to a porous flow top and then horizontally five kilometers to the accessible environment. Data from several sources were used to calculate cumulative distribution functions for ground-water travel times in the horizontal leg of this flow path (15,16,17). Curves 1 to 3 in Figure 6 were calculated from hydraulic head and conductivity data assuming 1-dimensional Darcian flow. These curves illustrate the large uncertainty associated with

the current estimates for ground-water travel time at the basalt site.

Curve 4 in Figure 6 shows a distribution in which 15% of the ground-water travel times are less than 1000 years and 99.9% of the travel times are less than 10,000 years. In a recent draft technical position paper (18), the Nuclear Regulatory Commission suggested that a travel time distribution similar to this might satisfy the pre-closure ground-water travel time requirement of NRC regulation for HLW disposal 10CFR60 (19). In the analysis that follows, it was assumed that the ground-water travel time in the vertical leg of the flow path (L2 within the dense interior) was negligible and that the post-closure travel time within the horizontal leg was equal to the pre-closure ground-water travel time. It should be noted that Figure 6 shows that one interpretation of available hydrologic data along the proposed path yields a

# REFERENCE BASALT SITE

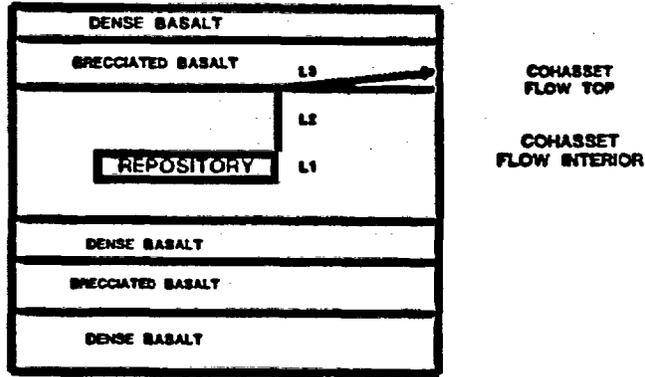


Figure 5.

## GROUND-WATER TRAVEL TIME COMPARISON

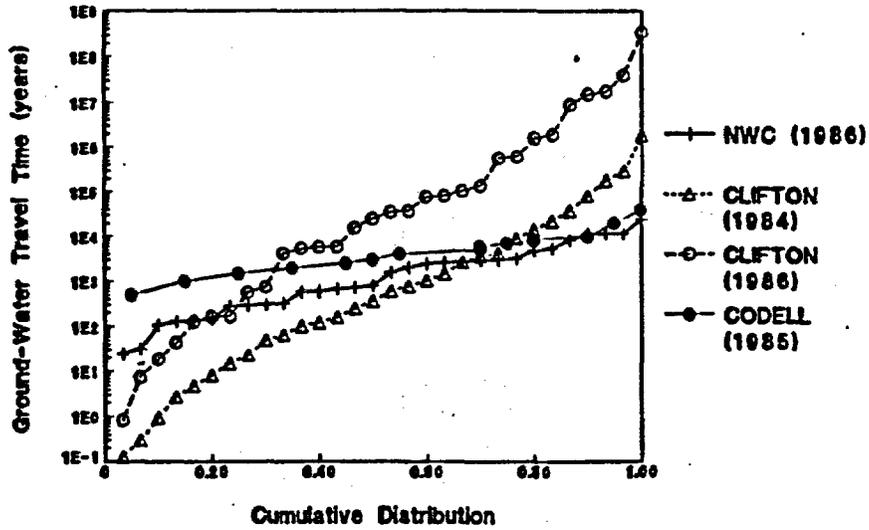


Figure 6.

ground-water travel time distribution (Curve 1) that is more conservative than the NRC requirement.

Curve 4 in Figure 6 gives a reasonable approximation of the most conservative (worst-case) hydrologic scenario that could be accepted by the NRC for a licensable HLW site. This distribution was used in conjunction with nominal values for other NRC HLW performance criteria (ie. release period of 100,000 years and isolation period of 300 years) to calculate integrated radionuclide discharges for a repository inventory of 10-year-old spent fuel rods (Table 3 in 20). The 10,000 year integrated discharges are compared to the EPA Standard 40CFR191 in Figure 7 for conservative geochemical conditions (ie.  $K_d = 0$ ). The distribution curve lies above the EPA limit indicating that this scenario would lead to violations of the EPA Standard. The construction of complementary cumulative distribution functions and their use in assessing compliance

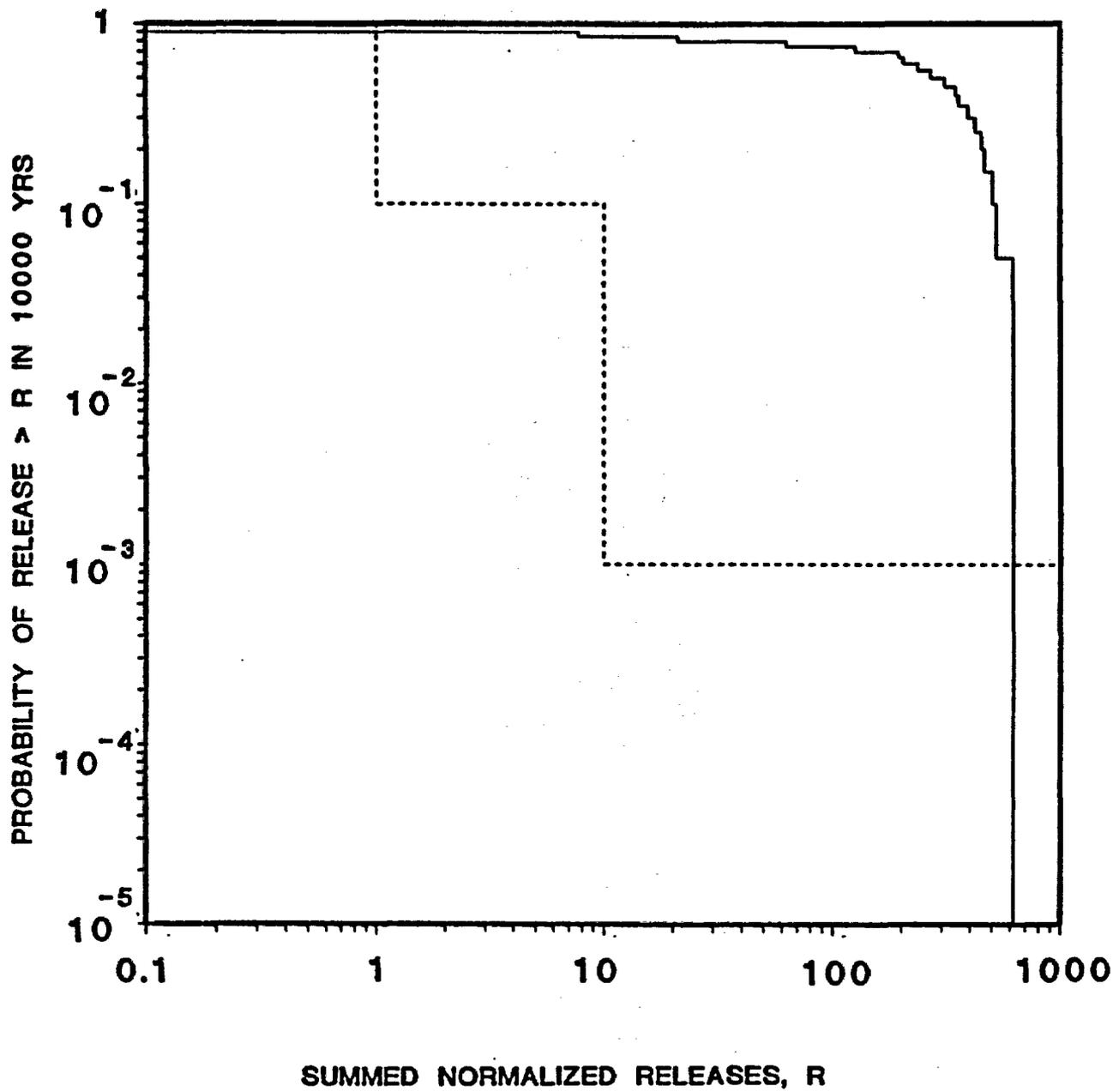


Figure 7.

of a repository with the EPA Standard is discussed elsewhere (21). These calculations show that even if a repository site meets the three numerical performance criteria of the NRC HLW Regulation 10CFR60, the site will violate the EPA Standard 40CFR191 if no geochemical processes retard radionuclide migration.

#### Review of Available Sorption Data Relevant to a Basalt Repository Site

An estimate of the radionuclide retardation due to geochemical processes is required to determine if the basalt site described above will comply with the EPA Standard. A first step in this process is to choose conservative values of retardation factors and sorption ratios ( $K_d$ 's or  $R_d$ 's) which can be used to calculate realistic upper bounds to radionuclide discharges. Before this can be done, however, it

was necessary to critically evaluate the available data to determine if such conservative values could be selected in a technically defensible way.

The Sandia Sorption Data Management System (SSDMS) has been developed to store and organize data obtained from batch and column radionuclide sorption experiments (22). All available batch ( $K_d$ ) data relevant to the BWIP site have been compiled in the data base (23). These data have been collected for rock-water combinations that are considered representative for the proposed repository site. Extensive descriptions of experimental conditions and procedures are included in the data base to allow examination of the correlations between experimental parameters and  $K_d$  values. Statistical and graphical utilities are available to facilitate these analyses. Based on this evaluation, each datum is assigned a quality index which facilitates subsetting and manipulation of the data. Detailed description of the data fields, programs and scope of the available data can be found in (22,23).

A major concern emerged from our critical evaluation of the available batch sorption data. In general, the data have been acquired without an understanding of the properties of the substrates or identification of the species present in solution. The potential for the introduction of spurious effects is large in these experiments. Many of the  $K_d$  values obtained may include the effects of processes other than reversible sorption (cf. Figure 3b) and cannot be used to calculate valid retardation factors for use in solute transport equations. Without a prior model for the chemical system, critical evaluation of these data has proceeded in an empirical manner. In the past, incorrect laboratory procedures and faulty data often have been identified by trial and error (see 23 and cited works). Observations of the effects of experimental procedures on the measured  $K_d$  values have been used to determine if the data are conservative. The data can be accepted on only a provisional basis until they are shown to be flawed. There is no way to show that the data are valid due to the incomplete descriptions of solutions, solids and experimental procedures.

These specific areas of uncertainty were identified during our review of the sorption data:

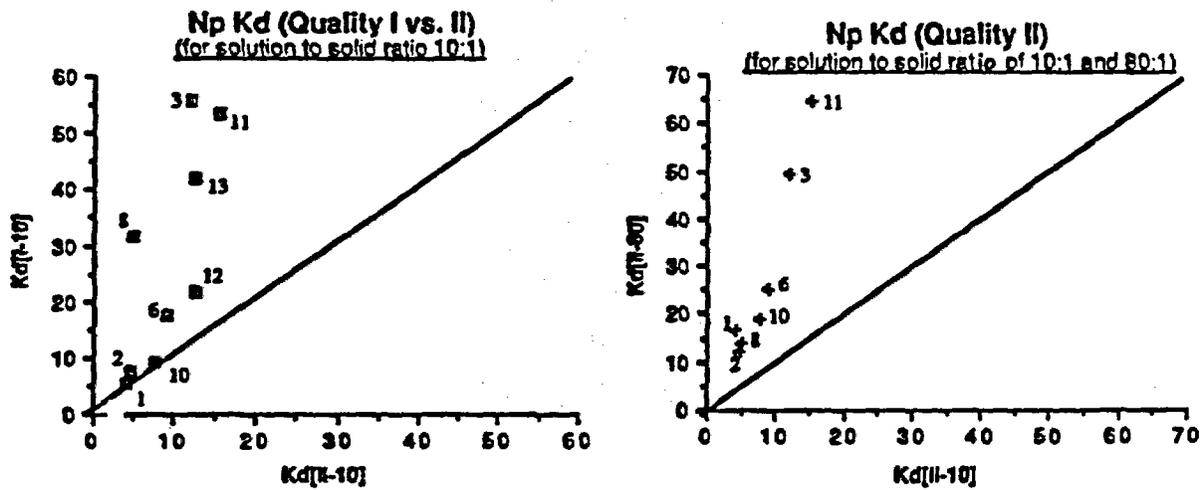
1. At best, data are valid only for the specific physicochemical conditions of a particular

experiment. Since the effects of changes of solution and substrate composition on the  $K_d$  values are not understood, the data should not be extrapolated to other conditions. As shown in the next section, attempts to bound the range of  $K_d$  values by carry out experiments under the extrema of field conditions may produce misleading results.

2. It is not known if the substrate surfaces in contact with solution during the experiments are representative of in-situ mineral surfaces. Methods used to prepare samples for batch experiments often include grinding the samples. This procedure may create new sites which bind radionuclides by processes other than sorption (eg. electron transfer and co-precipitation). Such processes would give non-conservative (high)  $K_d$  values.
3. The nature and rates of chemical reactions which may control the speciation of sorbed and aqueous species are not known. Although an apparent steady state is reached in many batch experiments, it is not known if true equilibrium has been achieved. In many cases the observation of a sorption/desorption hysteresis suggests that the binding process is not reversible under the conditions of the experiment.

Figure 8 summarizes the results of the review of available  $K_d$  data for neptunium in basalt/water systems (23). In this figure, average  $K_d$  values for several rock/water combinations are plotted. It can be seen that the  $K_d$  values depend on parameters that can be related to field conditions such as rock type, ground-water type and temperature. In addition, a significant dependence upon experimental parameters that are not easily related to in-situ conditions is observed. These include the solution:solid ratio and redox conditions of the experiment and a variety of sample preparation techniques that are lumped together under the 'Quality' index indicated in the figure.

These data can be sorted by type and quality and distributions of  $K_d$  values can be obtained as shown in Figure 9. The setting of ranges for valid sensitivity analyses, however, is complicated by the lack of an underlying model for



Key	Sorption Interval	Ground Water	Redox	Temp. (°C)	Sorption Category
1	McCoy Canyon	GR-1	Oxic	25	basalt
2	Pomona	GR-1	Oxic	25	basalt
3	Pomona	GR-1	Oxic	25	smectite
4	Pomona	GR-2	Oxic	25	basalt
5	Pomona	GR-2	Oxic	25	smectite
6	Umtanum	GR-1	Oxic	25	basalt
7	Umtanum	GR-2	Oxic	25	basalt
8	McCoy Canyon	GR-1	Oxic	60	basalt
9	McCoy Canyon	GR-2	Reducing	60	basalt
10	Pomona	GR-1	Oxic	60	basalt
11	Pomona	GR-1	Oxic	60	smectite
12	Umtanum	GR-1	Oxic	60	basalt
13	Umtanum	GR-2	Oxic	60	basalt

Figure 8.

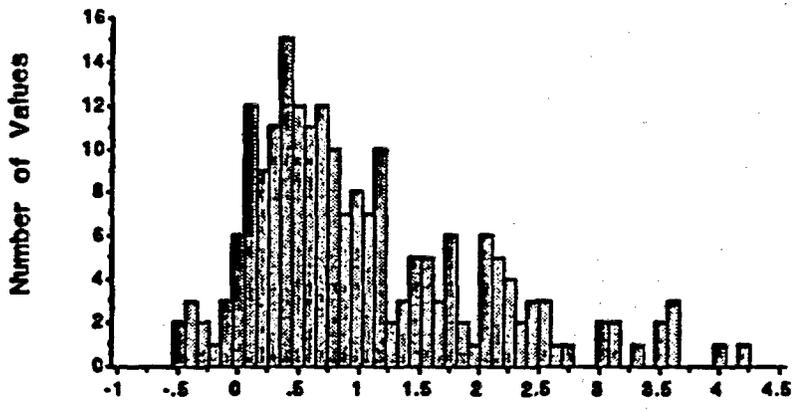
radionuclide behavior. Such a model would enable us to determine what part of the range of  $K_d$  values is due to spurious effects that are not relevant to field conditions. In Figure 9, it is clear that subsetting the data on the basis of solution and solid composition produces a narrow distribution compared to the range for all data. However, the limits of the range can only be set by subjective judgement based on these empirical, 'process-blind' observations.

#### Use of Detailed Chemical Models to Predict Radionuclide Behavior

An alternative and more robust method to describe radionuclide/solid reactions is provided by surface complexation models such as the triple-layer model or the constant capacitance model (24, 25). These approaches allow for a complete accounting for all species in solution, solids

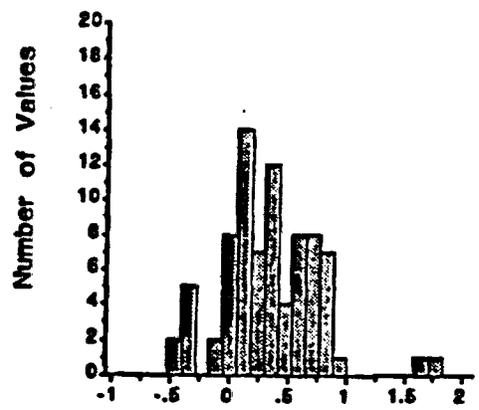
or sorbed onto solid/solution interfaces. They are based on electrostatic models for the structure of the solid/solution interface. Surface reaction sites compete with aqueous ligands in complexation reactions involving free cations or anions.

Calculations of the speciation of neptunium under oxidizing conditions in water with major solute compositions similar to those reported at the BWIP site have been carried out with the MINEQL code. Figures 10 to 12 present the results of these calculations and illustrate the power of the surface complexation models. Figure 10 is a distribution diagram for neptunium in a model system which illustrates features common to many of the systems that were studied. The system parameters are described in the figure and figure caption. It can be seen that at low pH values, most of the neptunium is present as the aqueous neptunyl ion  $\text{NpO}_2^+$ . At pH values above 6.5, most of the neptunium is sorbed onto the amorphous iron oxyhydroxide substrate (indicated as  $\text{SOHNpO}_2\text{OH}$ ). These calculations suggest that under oxic conditions at pH values similar to those measured at the BWIP site (pH = 8 to 11), neptunium will sorb strongly onto iron oxyhydroxide present in water-bearing fractures.



log Kd of Np

All Np Data



log Kd of Np

Ground Water: GR-2  
 Sorption Type: basalt  
 Atmosphere: oxic  
 Quality Index: g/vg

Figure 9.

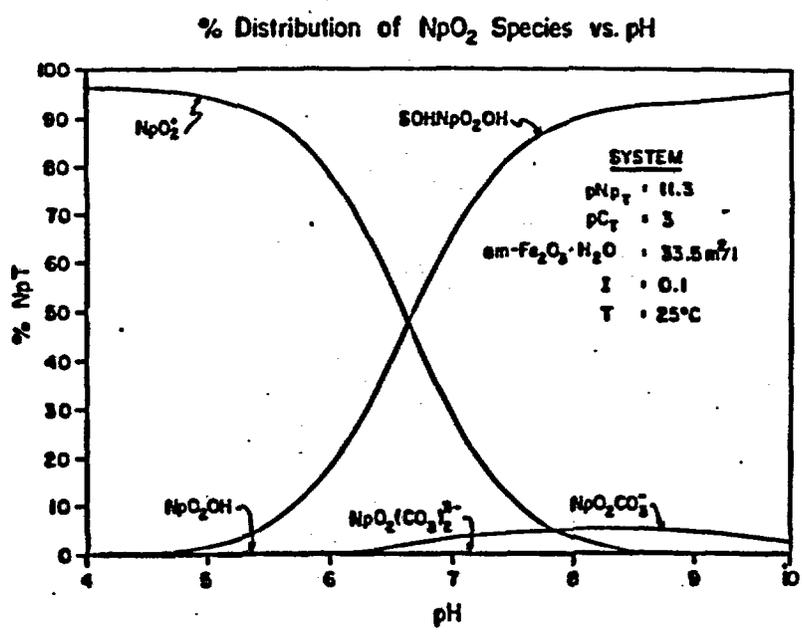


Figure 10.

Calculations like those illustrated in Figure 10 can be used to evaluate the validity of some of the assumptions commonly made in sensitivity analyses. For example, Figure 11 shows the effect of surface area on the amount of sorption. In this figure, a  $K_d$  value has been calculated from the ratio of amounts of sorbed and free neptunium from data like those in Figure 10. The amount of surface area of the substrate is directly related to the concentration of available sorption sites and also may be related to the effective porosity of the rock matrix. Figure 11 shows that  $K_d$  is directly related to available surface area of the substrate and suggests that the use of uncorrelated  $K_d$  and effective matrix porosity distributions in the Latin Hypercube sample is not realistic.

Figure 12 shows that in some chemical systems the actual range of  $K_d$  values cannot be predicted from a few 'extreme' ground-water compositions. In the presence of low

concentrations of the complexing agent, EDTA, a maxima is present in the  $K_d$ -pH curve. If  $K_d$  values had been obtained only from measurements at pH values of 6 and 8, an overly conservative  $K_d$  range would probably be selected for sensitivity analyses.

#### Uncertainties in Speciation and Sorption Calculations

Figures 10 to 12 do not consider the uncertainties in the thermochemical data used to calculate the  $K_d$  values. These uncertainties may be significant and should be addressed in a method of geochemical sensitivity analysis. Two main types of uncertainty should be considered. These are 1. questions of the existence of certain species and 2. numerical uncertainties in the values of complexation constants ( $\log K$ ).

An example of the first type of uncertainty is the controversy concerning the existence of the  $U(OH)_5$  species. In their model for the hydrolysis of tetravalent uranium, Baes

Log Kd vs. pH for a Neptunyl System

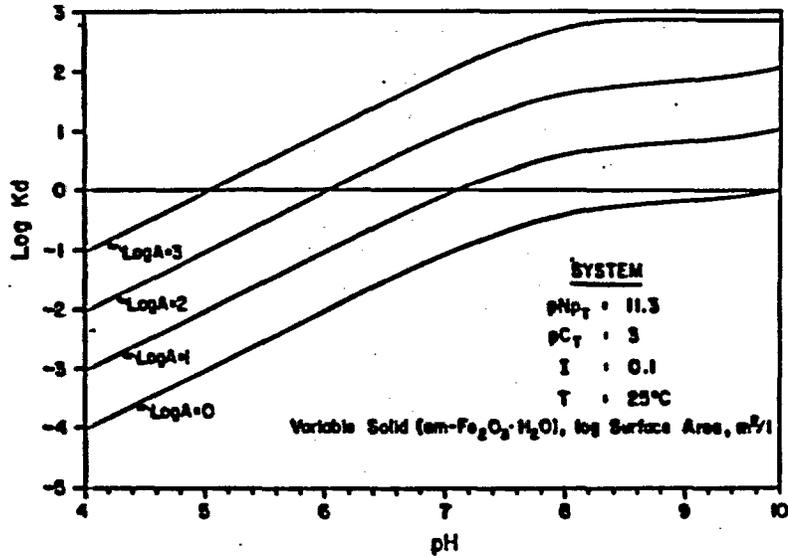


Figure 11.

EFFECT OF EDTA ON ADSORPTION

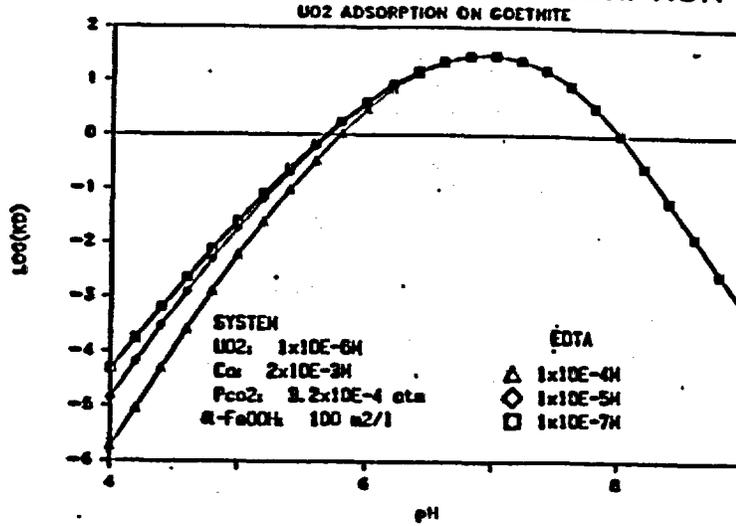


Figure 12.

and Mesmer (26) assumed that the  $U(OH)_5^-$  species was a dominant species in alkaline solutions in contact with the solid  $UO_2$ . Based on this assumption and assuming a regular progression of hydrolysis constants, they calculated formation constants for  $U(OH)_2^{2+}$ ,  $U(OH)_3^+$  and  $U(OH)_4$ . Recently, however, Ryan and Rai (27) and Bruno (28) have challenged the evidence supporting the existence of the  $U(OH)_5^-$  species and thereby the values of the other hydrolysis constants. The controversy over the aqueous model for uranium is a source of uncertainty that should be included in speciation and solubility calculations.

Numerical uncertainties in the values of equilibrium constants can be significant even in systems for which there is general agreement on the aqueous model. For example, estimates for the value of the formation constant of  $PuCO_3^{2+}$  range from  $10^{13}$  (29) to  $10^{47}$  (30). The calculated solubility and identity of the dominant species depend on the value of the constant that is used in speciation calculations.

The Aqueous Solutions Database (ASD) has been developed to store and process thermodynamic property values and associated uncertainties for sensitivity analysis. The data base contains a well-documented, critically-evaluated, internally-consistent set of values for  $DG^\circ$ ,  $DH^\circ$ ,  $S^\circ$ , and  $C^\circ$  for elements of interest in HLW disposal. The features of the data base are described in Figure 13; the procedure used to critically evaluate the data are discussed in detail in Phillips and others (31,32). The data base is accessible over telecommunication networks such as MILNET to any interested researchers.

The ASD has been designed to facilitate examination of the sensitivity of calculated solubility limits and speciation on uncertainties in the thermodynamic data. One kind of analysis, illustrated in Figure 14, involves randomized sampling of log K values from user-defined distributions. The extrema and shape of the distributions can be determined from actual experimental uncertainties or can be calculated from the free energies and propagated uncertainties stored in the ASD. By sampling repeatedly from log K distributions and carrying out replicate speciation calculations, uncertainties could be calculated for the estimated concentrations of aqueous species. Examination of the resulting response surface by a variety of statistical techniques could identify the

## **THERMODYNAMIC DATABASE FOR GSA**

- **ASD FORMAT 1:** GHS and Cp data
- **ASD FORMAT 2:** log K for specific reaction
- **ADDREACT:** add new reaction to FORMAT 2
- **COMPLOGK:** compute log K  $\pm$   $\sigma$  for reaction
- **BRIDGE:** produce new MINEQL database from ASD data with log K  $\pm$   $\sigma$  and  $\Delta H, \pm \sigma$
- **LHSMIN:** prepare file for multiple runs of MINEQL for different log K
- **MNOLMLT:** carry out multiple MINEQL runs and write specified results to a file for post-processing

Figure 13.

### **FUNCTIONS OF ASD PREPROCESSOR BY SPECIATION SENSITIVITY ANALYSIS**

1. Reads  $\Delta G$  values and  $\sigma$  from ASD for basis species
2. Calculates log K's and uncertainties for input to LHS
3. Uses LHS to produce nxm array of log K values
- 4.1 Reads vector of log K's input for a single calculation
- 4.2 Performs speciation calculation and writes results to a file
- 4.3 Chooses important species and writes their concentrations or other parameters to a file
- 4.4 Repeats for each vector
5. Prepares input for sensitivity analysis on results by graphical or other methods

Figure 14.

particular constants that dominate the uncertainty in the calculated solubility, speciation, and sorption.

#### Use of Detailed Geochemical Models in Performance Assessment Calculations

The inclusion of chemical phenomena described in Figure 3b in performance assessment calculations will require computer codes that couple chemical speciation calculations like those carried out by the MINEQL code with equations for advective/diffusive transport. Several such codes have been described in the literature recently (11,33,34). The potential use of the TRANQL code (11) in performance assessment studies has been evaluated as part of this study. The evaluation has considered both the availability of data needed by the code as well as the computer resources required for multiple, 10,000 year, five kilometer simulations. As discussed above, large numbers of simulations are needed to construct the CCDF's used to assess compliance of HLW sites with the EPA Standard 40CFR191.

A critical evaluation of radionuclide sorption data was carried out to identify data sets that could be processed with the triple-layer model (TLM) (25). Figure 15 summarizes the chemical systems for which high-quality data were found. The criteria used in the review are discussed in (25). It can be seen that only data for simple hydrous oxides in simple electrolyte systems are available. Present formulations of the triple-layer model are not applicable to carbonates, salts or materials with fixed charges such as clays. In addition, the model can not be applied rigorously in solutions more concentrated than an ionic strength of 0.1 molal. These limitations mean that at present, the TLM can not be applied directly to many of the substrates or solutions that must be modeled in HLW performance assessment.

Examination of the TRANQL code (11) revealed that the available version of the code was not useful for performance assessment calculations. The code cannot simulate many important chemical phenomena such as oxidation/reduction, radioactive production, or precipitation of a sorbing species. The code is inefficient; estimates of the cost of running a single simulation of transport of a single element over a five kilometer distance for a 10,000 year time period range from \$10,000 to \$40,000 (14,35).

Based on the information discussed above, it has been concluded that without major improvements in both data bases

and computer codes, detailed chemical models cannot be used in place of codes such as NEFTRAN or SWIFT-2 to assess the compliance of a repository site with the EPA Standard 40CFR191. At present, detailed chemical speciation and chemical transport models are best used to provide insights into the nature of significant interactions and correlations among system variables. The codes should be used to assess the validity of simplifying assumptions used in performance assessment tools and to extend sensitivity and uncertainty analysis of system behavior to detailed geochemical processes.

The complementary roles of several modeling approaches and computer codes in this kind of sensitivity analysis are illustrated in Figure 16. Computer codes such as PHREEQE (9) or MINEQL (10) can be used to define possible ranges in ground-water compositions and corresponding radionuclide speciation under site-specific conditions. Such information can be used to assess if available sorption data (Kd's or retardation factors) can be used to bound radionuclide sorption behavior at the HLW sites and to examine the nature

of interactions among geochemical parameters. The performance assessment codes NEFTRAN (4) and SWIFT (5) represent radionuclide/rock interactions in terms of retardation factors and mass transfer (exchange) coefficients. Site-specific hydrologic data for fractured and porous media, experimental sorption data and the results of the speciation calculations could be used to estimate ranges for these parameters and to assign meaningful correlations among system variables. Coupled reaction/transport codes like TRANQL (11) could be used to carry out transport simulations for a limited number of conditions in order to determine the range of discharge rates that result when interactions between solution composition and sorption behavior are included in the model. The results of these calculations could be compared to simulations carried out with the SWIFT and NEFTRAN codes to determine if the simple geochemical approximations in those codes provide conservative results (ie. overestimates of radionuclide discharge).

## RESULTS OF STANFORD REVIEW OF AVAILABLE TLM DATA

<u>Substrate</u>	<u>Electrolyte</u>	<u>Metals</u>
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	NaCl	-
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	KCl	-
$\alpha$ -FeOOH	KNO <sub>3</sub> , NaCl, Na <sub>2</sub> SO <sub>4</sub> , KCl, MgCl <sub>2</sub> , CaCl <sub>2</sub> , CaCO <sub>3</sub>	UO <sub>2</sub> <sup>2+</sup>
am-Fe <sub>2</sub> O <sub>3</sub> ·H <sub>2</sub> O	NaNO <sub>3</sub> , K <sub>2</sub> SO <sub>4</sub> , NaHCO <sub>3</sub>	UO <sub>2</sub> <sup>2+</sup> , Cd <sup>2+</sup> NpO <sub>2</sub> <sup>2+</sup> , SeO <sub>4</sub> <sup>2-</sup>
$\delta$ MnO <sub>2</sub>	NaNO <sub>3</sub> , NaCl	-
am-SiO <sub>2</sub>	NaCl, KCl	-

Figure 15.

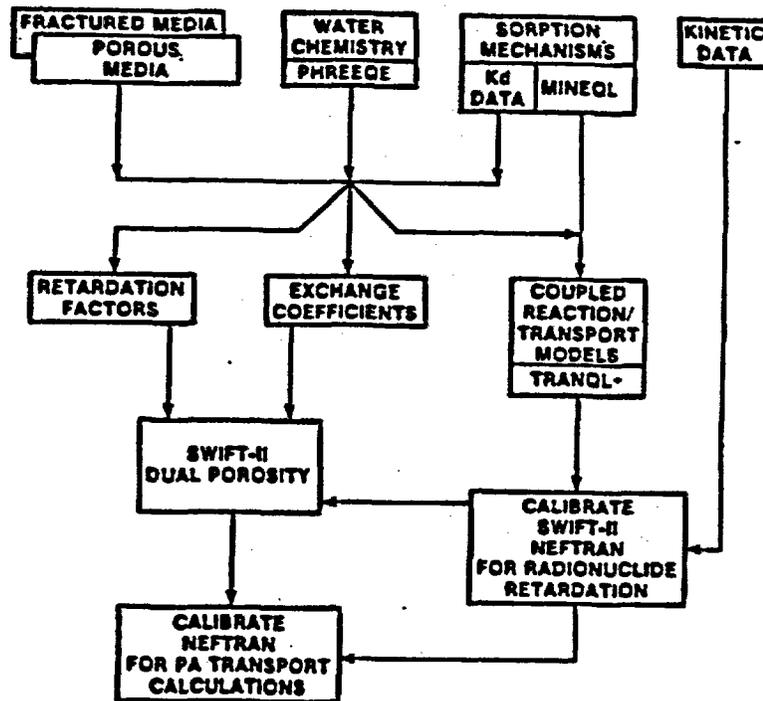


Figure 16.

## Kinetic Effects

The assumptions of homogeneous and heterogeneous chemical equilibrium are implicit in chemical speciation codes such as MINEQL, MICROQL and PHREEQE and in transport codes such as SWIFT and NEFTRAN. Previously (36), criteria for the validity of three approximate methods to calculate radionuclide discharges in fractured porous rock were derived. The three methods are: 1. an equivalent-porous-medium approximation in which the bulk rock matrix is in equilibrium with the fracture fluid, 2. a linear-driving-force approximation in which local chemical equilibrium exists between the pore fluids and the rock matrix and radionuclide diffusion rates are proportional to the difference in average radionuclide concentrations in the rock matrix and fracture fluids; and 3. an approximation where radionuclide diffusion into the matrix is calculated assuming a semi-infinite matrix.

The first of the above approximations is implicit both in the use of a bulk retardation factor to calculate radionuclide travel times or in the coupled reaction/transport code TRANQL. The second approximation is used by the NEFTRAN code to model matrix diffusion. Analytical solutions based on the third assumption appear commonly in the literature and in texts.

These criteria can be seen as a subset of a set of more general criteria for the validity of the assumption of local chemical equilibrium (LEA). Criteria for the validity of this assumption are based on the identification of conditions that allow for chemical reaction rates to proceed to equilibrium at rates substantially greater than the advective flow of ground water. Additional theoretical and experimental work is required to obtain the data needed to define criteria for the LEA for radionuclides under conditions relevant to HLW disposal.

## SUMMARY AND CONCLUSION

The need for and form of a method of geochemical sensitivity analysis can be seen to emerge from the above discussion. The objective of this analysis is to define criteria for the valid simplification of transport models to be used in performance assessment. An underlying principle of the work is that the validity must be assessed relative to the proper performance measure, in the relevant experimental frame, and considering all significant interactions among system variables. The performance measures of interest are the 10,000 year integrated discharges of each radionuclide at the

boundary of the accessible environment as defined by the EPA Standard. The experimental frames are the ranges of physicochemical parameters expected at the candidate repository sites.

In this analysis the probabilistic risk assessment (PRA) codes NEFTRAN, CCDPLT and LHS are being used to assess the amount of geochemical retardation needed to ensure compliance with the EPA Standard 40CFR191 at a hypothetical basalt repository site. The Sandia Sorption Data Management System (SSDMS) and the Aqueous Solutions Database (ASD) are being developed to store and facilitate retrieval of  $K_d$  values and thermodynamic property values, respectively. These parameter values are used either in the PRA codes or in speciation codes such as PHREEQE (7) and MINEQL (8). Coupled reaction/transport codes such as TRANQL (9) do not use a  $K_d$  value to approximate chemical behavior of the radionuclides. With the proper modifications, it is hoped that codes like these can be used to carry out simulations in which many of the assumptions associated with  $K_d$ 's and retardation factors can be relaxed.

Commonly-used techniques in batch sorption experiments do not allow for an explicit accounting of the fate of all of the radionuclide introduced into the solution. In general, the available  $K_d$  data are inadequate to show that the sorption of radionuclides is the process responsible for the observed  $K_d$  value. With the available data, it cannot be shown that a  $K_d$  value of zero would not be realistic under in-situ conditions.

A critical review of data for use in the more robust triple-layer sorption model was carried out. In addition, an evaluation of the suitability of the TRANQL code for use in performance assessment was made based on code flexibility and computing efficiency. Based on these reviews, it was concluded that without major improvements in both data bases and computer codes, detailed chemical models cannot be used in place of codes such as NEFTRAN or SWIFT-2 to assess the compliance of a repository site with the EPA Standard 40CFR191. At present, detailed chemical speciation and chemical transport models are best used to provide insights into the nature of significant interactions and correlations among system variables. The codes can be used to assess the validity of simplifying assumptions used in performance assessment tools and to extend sensitivity and uncertainty analysis of system behavior to detailed geochemical processes.

### LITERATURE CITED

1. Zeigler, B.P., Theory of Modeling and Simulation, Wiley-Interscience, New York (1976).
2. Henize, John, Large Scale Systems, 1, 89 (1980).
3. Iman, R.L., J.M. Davenport, and K. Ziegler, "Latin Hypercube Sampling (Program User's Guide)," SAND79-1473, Sandia National Laboratories, Albuquerque, NM (1980).
4. Longsine, Dennis E., Evaristo J. Bonano, and Charlene P. Harlan, "User's Manual for the Neftran Computer Code," NUREG/CR-4766, (SAND86-2405), Sandia National Laboratories, Albuquerque, NM (1987).
5. Reeves, Mark, D.S. Ward, N.D. Johns, and R.M. Cranwell, "Theory and Implementation for SWIFT II, The Sandia Waste-Isolation Flow and Transport Model for Fractured Media," NUREG/CR-3328, (SAND83-1159), Sandia National Laboratories, Albuquerque, NM (1986).
6. Siegel, M.D., M.S. Chu, and R.E. Pepping, "Compliance assessments of hypothetical geological nuclear waste isolation systems with the Draft EPA Standard," in Scientific Basis for Waste Management VI, Brookins, D.G. (Ed.), Mat. Res. Soc. Symp. Proc., 15, Elsevier Science Publishing Co., Inc., Amsterdam (1983).
7. US Environmental Protection Agency, "Environmental Standard for the Management and Disposal of Spent Nuclear Fuel, High Level and Transuranic Radioactive Waste; Final Rule, 40CFR191," Federal Register, 50, 38066.
8. Muller, A.B., D. Langmuir, and L.E. Duda, "The formulation of an integrated physicochemical-hydrologic model for predicting waste nuclide retardation in geologic media," in Scientific Basis for Waste Management VI, Brookins, D.G. (Ed.), Mat. Res. Soc. Symp. Proc., 15, Elsevier Science Publishing Co., Inc., Amsterdam (1983).
9. Parkhurst, D.L., D.C. Thornstenson, and L.N. Plummer, "PHREEQE-a Computer Program for Geochemical Calculations," U.S. Geological Survey, Reston, VA. (1980).
10. Westall, J.C., J.L. Zachary, and F.M.M. Morel, "MINEQL: A Computer Program for the Calculation of Aqueous Systems,"

Tech Note 18, Water Control Laboratory, Mass. Inst. of Technol. Boston (1976).

11. Cederberg, G., "TRANQL: A Ground-Water Mass-Transport and Equilibrium Chemistry Model for Multicomponent Systems," PhD Dissertation, Stanford University, Stanford, California (1985).
12. US Department of Energy, "Environmental Assessment, Reference Repository Location, Hanford Site, Washington," DOE/RW-0070 (1986).
13. Bonano, E.J., M.S.Y. Chu, R.M. Cranwell, and P.A. Davis, "Development of Performance Assessment Methodology for Nuclear Waste Isolation in Geologic Media," in The Symposium on Groundwater Flow and Transport Modeling for Performance Assessment of Deep Geologic Disposal of Radioactive Waste: A Critical Evaluation of the State of the Art, NUREG/CP-0079, (PNL-SA-13796, CONF-8505180), Pacific Northwest Laboratory, Richmond, Washington (1986).
14. Siegel, M.D. (Ed.), "Geochemical Sensitivity Analysis, Interim Progress Report, FY86-FY87," SAND87-2633, Sandia National Laboratories, Albuquerque, NM. (1987).
15. Clifton, P.M., and R.C. Arnett, "Preliminary Uncertainty Analysis of Pre-Waste-Emplacement Groundwater Travel Times for a Proposed Repository in Basalt," SD-BWI-TA-013, Rockwell Hanford Operations, Richland, Washington (1984).
16. Clifton, P.M., "Groundwater Travel Time Analysis for the Reference Repository Location at the Hanford Site," SD-BWI-7I-303, Rockwell Hanford Operations, Richland, Washington (1986).
17. Nuclear Waste Consultants, "Review of 'Groundwater Travel Time Analysis for Reference Repository Location at the Hanford Site', SD-BWI-TI-303", letter report to the Nuclear Regulatory Commission (June 13, 1986).
18. Codell, R., "Draft Generic Technical Position on Ground-Water Travel Time (GWTT), Nuclear Regulatory Commission, Washington, D.C. (1985).
19. Nuclear Regulatory Commission, "Disposal of High-Level Radioactive Wastes in Geologic Repositories: Technical Criteria," 10 CFR Part 60, Washington, D.C. (June 30, 1983).
20. Siegel, M.D., and M.S. Chu, "Technical Assistance for Regulatory Development: Review and Evaluation of the Draft EPA Standard 40CFR191 for Disposal of High-Level Waste, Volume 3: A Simplified Analysis of a Hypothetical Repository in a Tuff Formation," NUREG/CR-3235, Sandia

- National Laboratories, Albuquerque, NM. (1983).
21. Ortiz, N.R., and R.M. Cranwell, "Risk Assessment Methodology for High Level Waste: Assessing Compliance with the EPA Draft Standard Including Uncertainties," SAND82-0596, Sandia National Laboratories, NM. (1982).
  22. Faith, Stuart, Malcolm Moore, and Malcolm Siegel, "Sandia Sorption Data Management System (SSDMS): Volume 1. User's Guide," SAND87-2634, Sandia National Laboratories, Albuquerque, NM. (1987).
  23. Siegel, Malcolm D., and Stuart Faith, "Sandia Sorption Data Management System (SSDMS): Volume 2. Evaluation of Sorption Data for a Repository in Basalt," SAND87-2635, Sandia National Laboratories, Albuquerque, NM. (1987).
  24. Westall, John, and Herbert Hohl, Advances in Colloid and Interface Science (Amsterdam) 12, 265 (1980).
  25. Kent, Douglas B., V.S. Tripathi, N.B. Ball, and J.O. Leckie, "Surface-Complexation Modeling of Radionuclide Adsorption in Sub-Surface Environments," NUREG/CR-4807, (SAND86-7175), Sandia National Laboratories, Albuquerque, NM. (1987).
  26. Baes, C.F., and R.E. Mesmer, The Hydrolysis of Cations, John Wiley and Sons, Inc., New York (1976).
  27. Ryan, J.L., and D. Rai, Polyhedron, 2, 947, (1983).
  28. Bruno, J., D. Ferri, I. Grenthe, Acta. Chem. Scand., A40, 428, (1986).
  29. Silva, R.J., "Carbonate Complexation of Pu(IV) in Aqueous Solutions," Paper No. 44, Div. of Nucl. Chem. and Tech., 189th Amer. Chem. Soc. Mtg., Miami Beach, FL (1985).
  30. Moskvina, A.I., and A.D. Gel'man, Jour. Inorg. Chem. (USSR) 3, 198 (1958).
  31. Phillips, S.L., F. Hale and M.D. Siegel, "A Thermodynamic Data Management System for Nuclear Waste Isolation Performance Assessment", presented at the International Conference on Thermodynamics of Aqueous Systems with Industrial Applications, Airlie House, Warrenton, VA. (May 10-14, 1987).
  32. Phillips, S.L., M.D. Siegel, F.V. Hale, and L.F. Silvester, "Thermodynamic Tables for Nuclear Waste Isolation: Volume 1. Aqueous Solutions Database," NUREG/CR-4864, (LBL-22860, SAND87-0323), Sandia National Laboratories, Albuquerque, NM. (1987).

33. Miller, C.W., "Toward a Comprehensive Model of Chemical Transport in Porous Media," in Scientific Basis for Waste Management VI, Brookins, D.G. (Ed.), Mat. Res. Soc. Symp. Proc., 15, 481 (1983).
34. Yeh, G.T. and V.S. Tripathi, HYDROGEOCHEM- A Coupled Model of HYDROlogical Transport and GEOCHEMical Equilibria in Multicomponent Systems, ORNL-6371, Oak Ridge National Laboratories, Oak Ridge, TN (1987).
35. Siegel, M.D. (Ed.) "Geochemical Sensitivity Analysis, Progress Report FY84 to FY85", SAND85-1644, Sandia National Laboratory, Albuquerque, NM. (1985).
36. Erickson, K.L., M.S.Y. Chu, M.D. Siegel, and W. Beyeler, "Approximate Methods to Calculate Radionuclide Discharges for Performance Assessment of HLW Repositories in Fractured Rock," in Waste Management 86, 2, 337, Post, R. G. (Ed.), University of Arizona, Tucson, AZ. (1986).

- Figure 1. Use of the Latin Hypercube sampling procedure in sensitivity analysis. Distributions and correlations are assigned to each variable  $X$ ; values  $X_{n,k}$  of the variables are sampled and combined into data sets  $X_k$  for model input. Multiple calculations produce a distribution of output values  $Y_k$ .
- Figure 2. Outline of radionuclide transport calculations as carried out by the NEFTRAN computer code.
- Figure 3. Comparison of 'model' system as represented in transport codes that use a  $K_d$  or retardation factor with a 'real' system containing many potentially important chemical processes. The processes illustrated in the figure are described in the text.
- Figure 4. Components of a method of geochemical sensitivity analysis. The method described in the text involves complementary use of probabilistic risk assessment (PRA) codes, data bases of sorption and thermochemical data, and computer codes which can model chemical speciation and transport.
- Figure 5. Hypothetical reference basalt site used in geochemical sensitivity analysis. Data from the BWIP site in Washington State is used for many of the system variables, however, it is not claimed that the reference site accurately represents any real site. The flow path used in the radionuclide discharge calculations is indicated along L1, L2, and L3.
- Figure 6. Comparison of cumulative distribution functions of ground-water travel times for basalt repository site. See text for discussion of method and assumptions used to calculate each curve. Curve identified as Codell (1985) was used in radionuclide discharge calculations.
- Figure 7. Complementary cumulative distribution function (CCDF) for discharge of radionuclides from repository complying with numerical criteria of 10CFR60 as described in the text. Results are

given for case in which no credit is given for retardation ( $K_d = 0$ ).

- Figure 8. Summary of  $K_d$  values for neptunium in different combinations of rocks and waters found at the BWIP site. After evaluation of experimental method used to obtain  $K_d$  value, a quality index of I is assigned to 'good' data, an index of II is assigned to 'less reliable' data.
- Figure 9. Histograms of  $K_d$  values for neptunium. (a) All available sorption data for basaltic environments. (b) Highest quality data for unaltered basalt in GR-2 synthetic water, under oxic conditions.
- Figure 10. Distribution diagram for neptunium species under oxic conditions.
- Figure 11. Relationship between  $K_d$  and surface area (A) for a model system for neptunium.
- Figure 12. Relationship between  $K_d$  for uranium and pH in the presence of a complexing ligand, EDTA.
- Figure 13. Components of the Aqueous Solutions Database for use in sensitivity analysis.
- Figure 14. Example of use of the Aqueous Solutions Database in geochemical sensitivity analysis.
- Figure 15. Summary of chemical systems for which high-quality data is available for the Triple-layer model.
- Figure 16. Complementary roles of different models discussed in this paper in transport sensitivity analysis.

# LAMIN HYPERCUBE SAMPLE

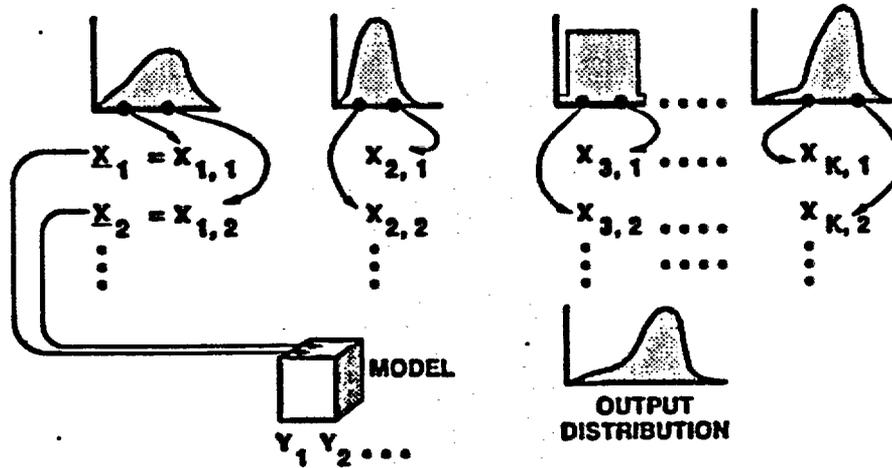


Figure 1.

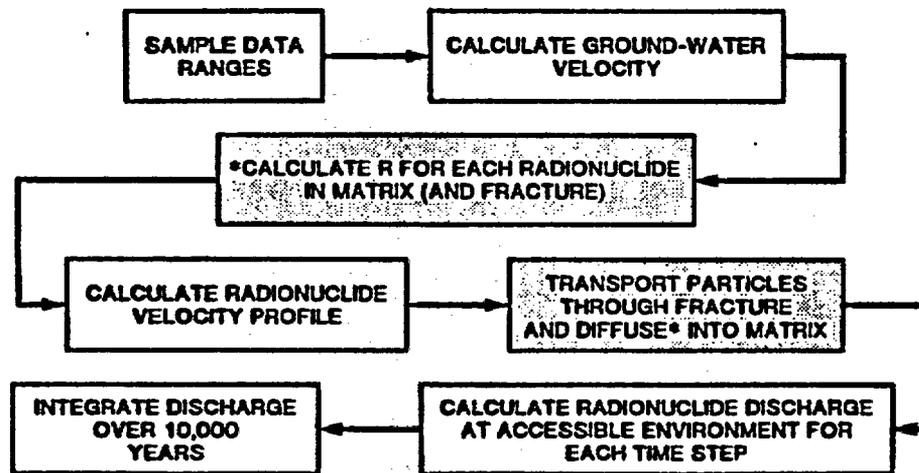


Figure 2.

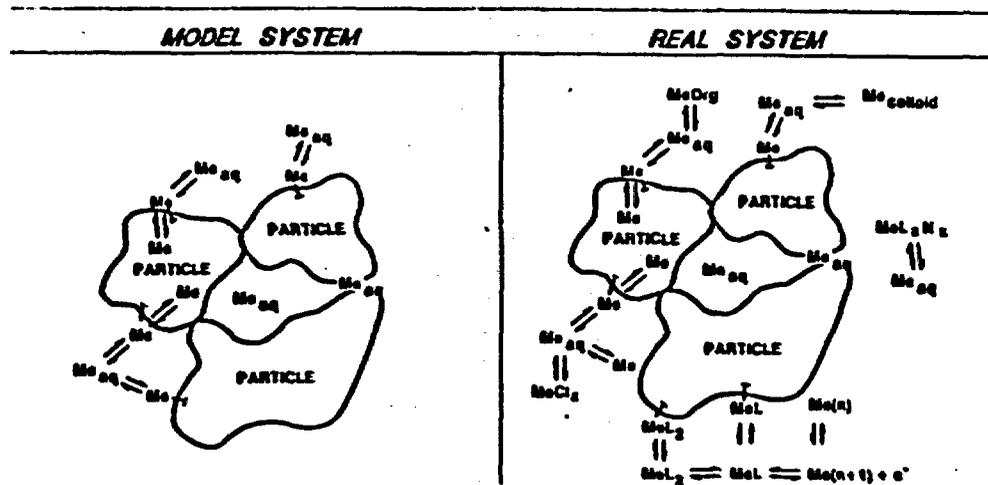


Figure 3.

## COMPONENTS OF ANALYSIS

### Data Bases

*SSDMS*

*ASD*

### PRA Codes

*NEFTRAN*

*LHS*

*CDFPLT*

### Speciation Codes

*MINEQL*

*PHRQPITZ*

### Coupled Codes

*TRANQL*

Figure 4.

# REFERENCE BASALT SITE

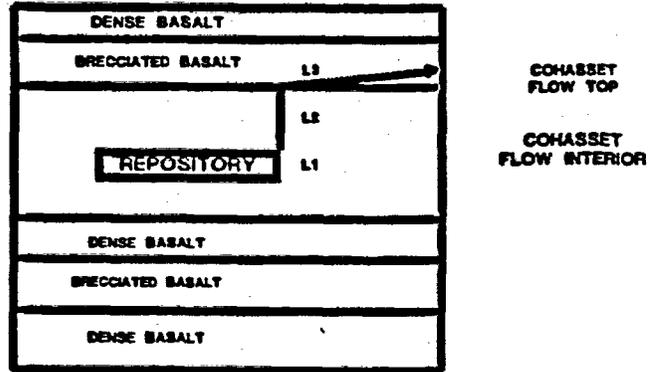


Figure 5.

## GROUND-WATER TRAVEL TIME COMPARISON

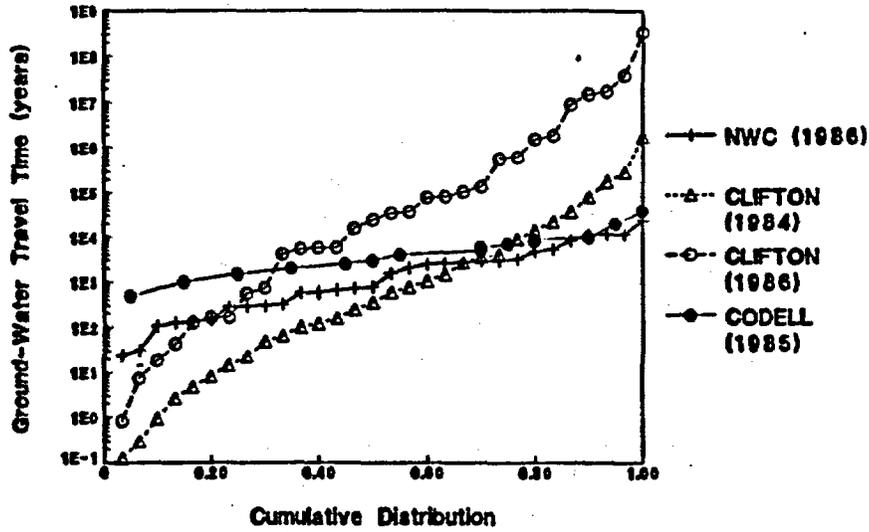


Figure 6.

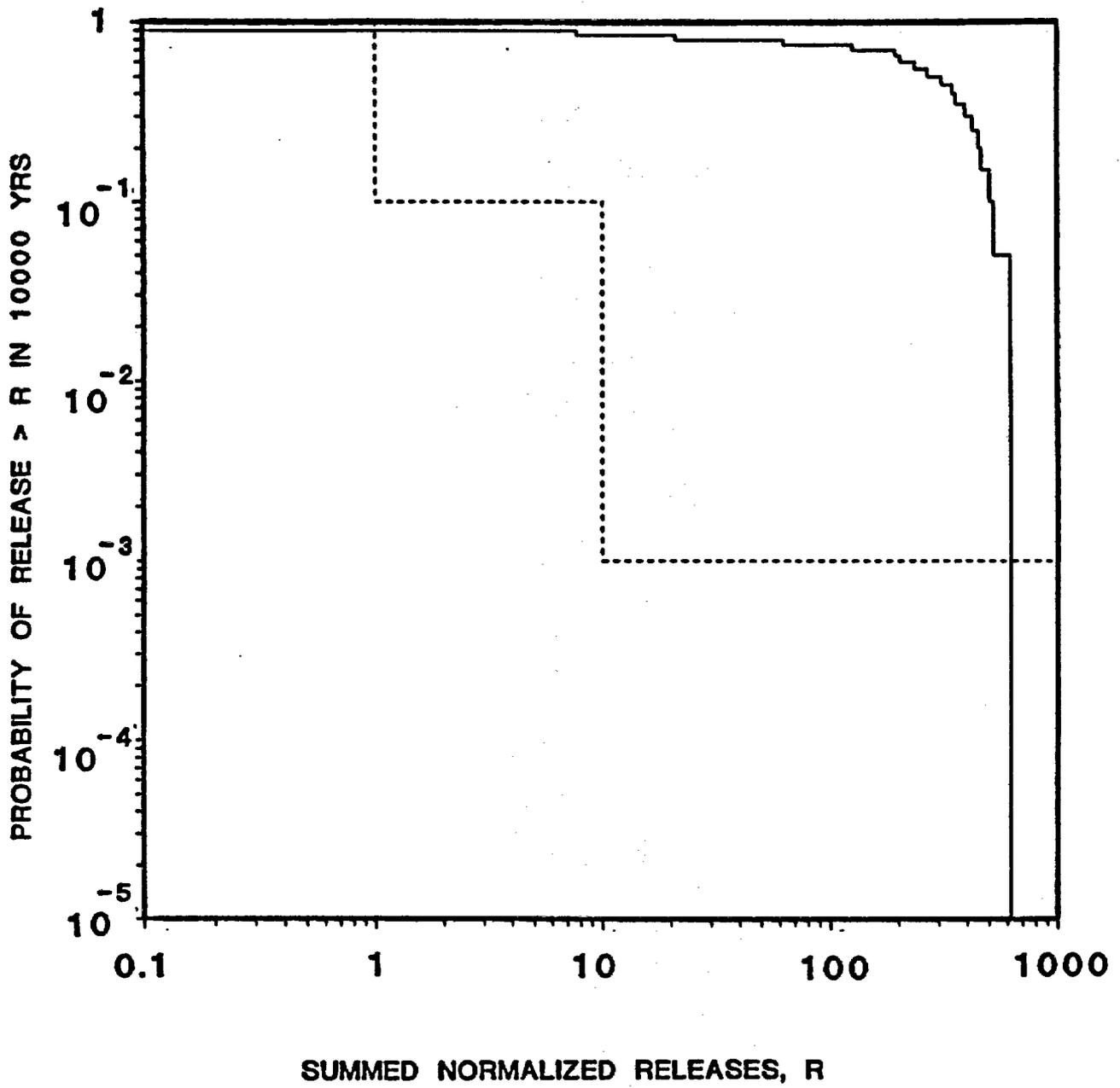
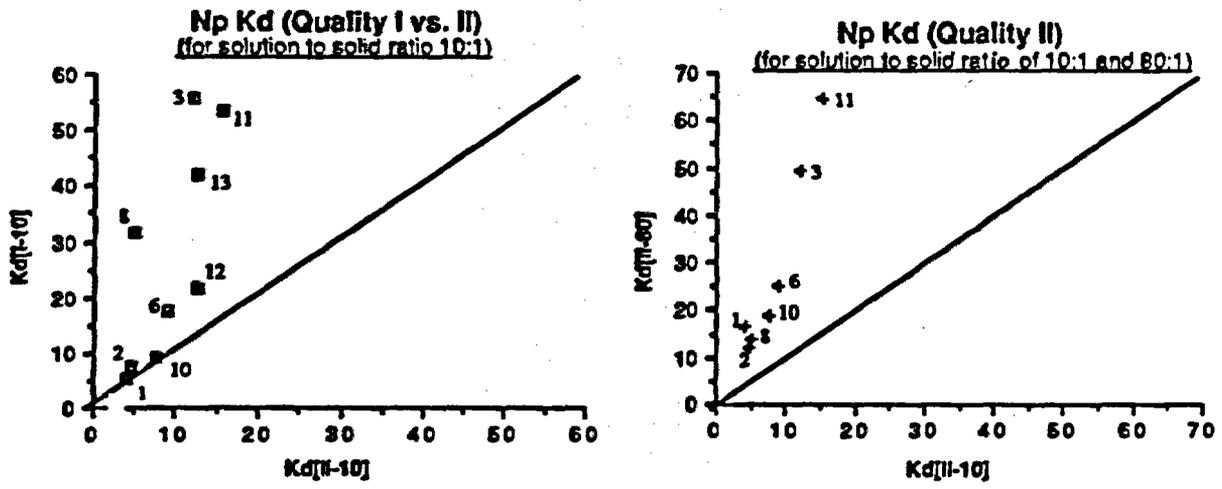
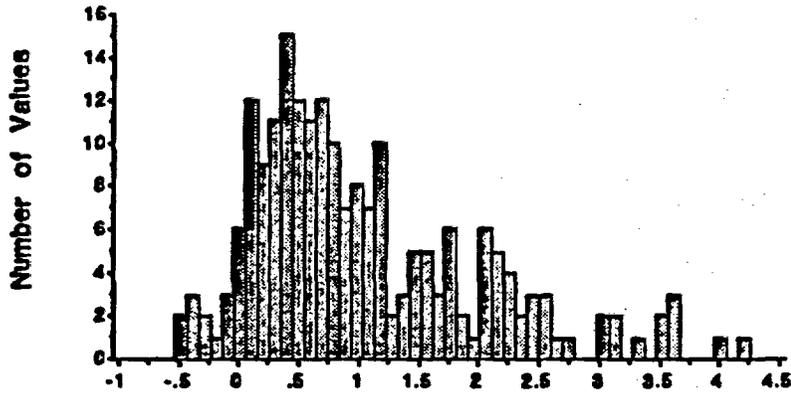


Figure 7.



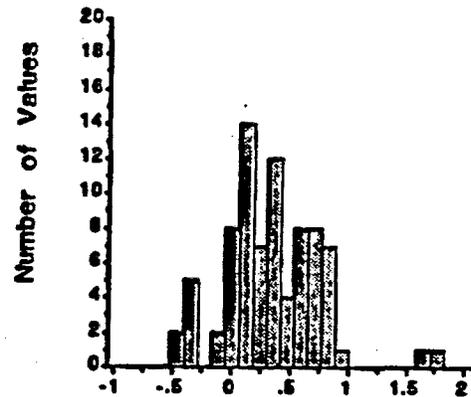
Key	Sorption Interval	Ground Water	Redox	Temp. (°C)	Sorption Category
1	McCoy Canyon	GR-1	Oxic	25	basalt
2	Pomona	GR-1	Oxic	25	basalt
3	Pomona	GR-1	Oxic	25	smectite
4	Pomona	GR-2	Oxic	25	basalt
5	Pomona	GR-2	Oxic	25	smectite
6	Umtanum	GR-1	Oxic	25	basalt
7	Umtanum	GR-2	Oxic	25	basalt
8	McCoy Canyon	GR-1	Oxic	60	basalt
9	McCoy Canyon	GR-2	Reducing	60	basalt
10	Pomona	GR-1	Oxic	60	basalt
11	Pomona	GR-1	Oxic	60	smectite
12	Umtanum	GR-1	Oxic	60	basalt
13	Umtanum	GR-2	Oxic	60	basalt

Figure 8.



log Kd of Np

All Np Data



log Kd of Np

Ground Water: GR-2  
 Sorption Type: basalt  
 Atmosphere: oxic  
 Quality Index: g/vg

Figure 9.

% Distribution of  $\text{NpO}_2$  Species vs. pH

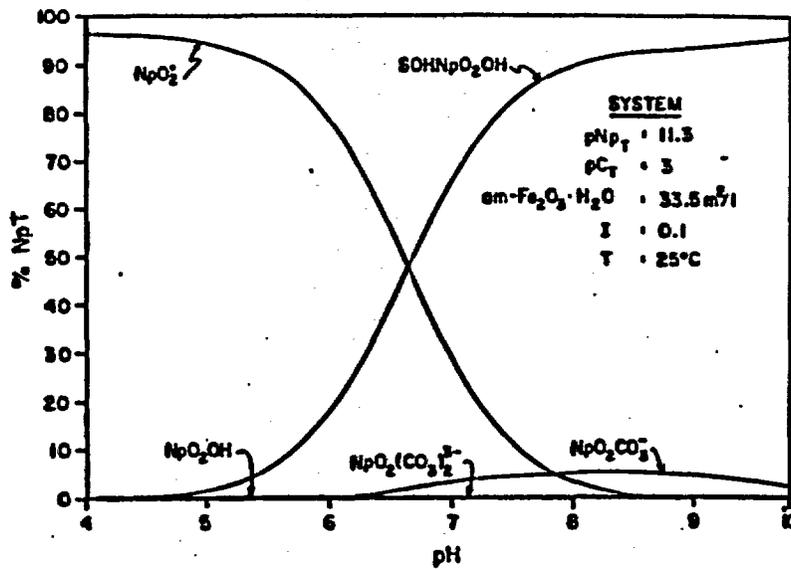


Figure 10.

Log Kd vs. pH for a Neptunyl System

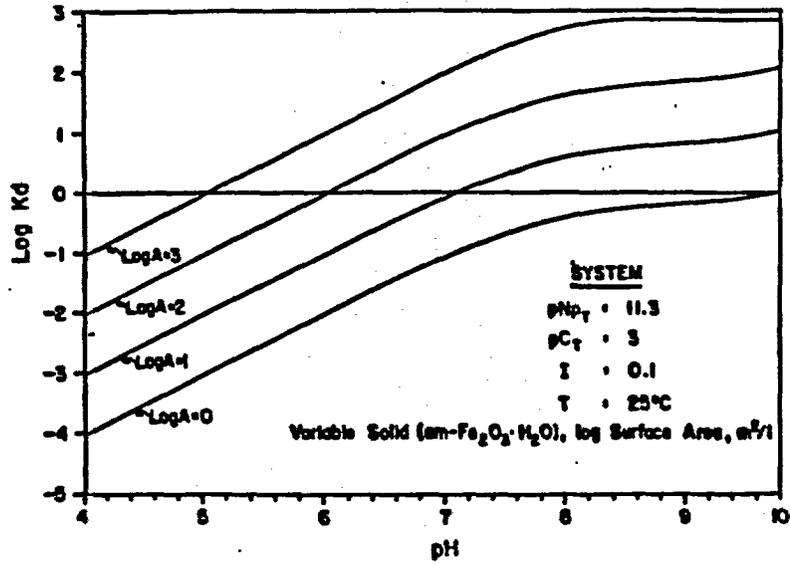


Figure 11.

EFFECT OF EDTA ON ADSORPTION  
 UO<sub>2</sub> ADSORPTION ON GOETHITE

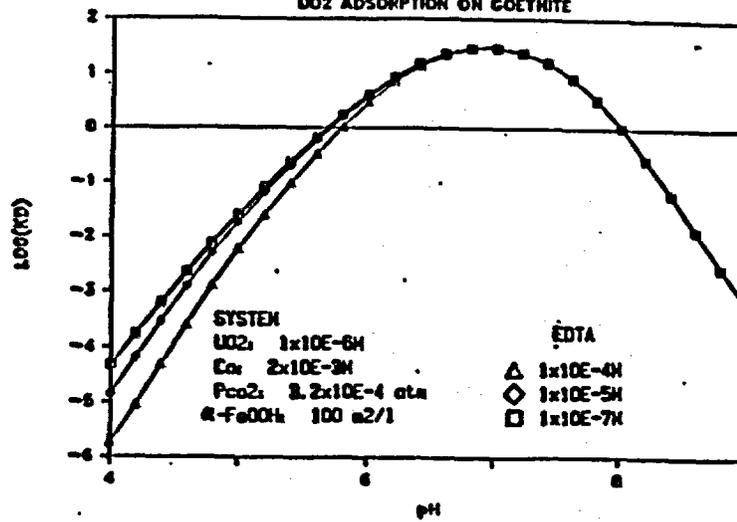


Figure 12.

## ***THERMODYNAMIC DATABASE FOR GSA***

- **ASD FORMAT 1:** GHS and Cp data
- **ASD FORMAT 2:** log K for specific reaction
- **ADDREACT:** add new reaction to FORMAT 2
- **COMPLOGK:** compute log K  $\pm$   $\sigma$  for reaction
- **BRIDGE:** produce new MINEQL database from ASD data with log K  $\pm$   $\sigma$  and  $\Delta H, \pm \sigma$
- **LHSMIN:** prepare file for multiple runs of MINEQL for different log K
- **MINEQLMLT:** carry out multiple MINEQL runs and write specified results to a file for post-processing

Figure 13.

### ***FUNCTIONS OF ASD PREPROCESSOR IN SPECIATION SENSITIVITY ANALYSIS***

1. Reads  $\Delta G$  values and  $\sigma$  from ASD for basis species
2. Calculates log K's and uncertainties for input to LHS
3. Uses LHS to produce nxm array of log K values
- 4.1 Reads vector of log K's input for a single calculation
- 4.2 Performs speciation calculation and writes results to a file
- 4.3 Chooses important species and writes their concentrations or other parameters to a file
- 4.4 Repeats for each vector
5. Prepares input for sensitivity analysis on results by graphical or other methods

Figure 14.

## RESULTS OF STANFORD REVIEW OF AVAILABLE TLM DATA

<u>Substrate</u>	<u>Electrolyte</u>	<u>Metals</u>
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	NaCl	-
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	KCl	-
$\alpha$ -FeOOH	KNO <sub>3</sub> , NaCl, Na <sub>2</sub> SO <sub>4</sub> , KCl, MgCl <sub>2</sub> , CaCl <sub>2</sub> , CaCO <sub>3</sub>	UO <sub>2</sub> <sup>2+</sup>
am-Fe <sub>2</sub> O <sub>3</sub> ·H <sub>2</sub> O	NaNO <sub>3</sub> , K <sub>2</sub> SO <sub>4</sub> , NaHCO <sub>3</sub>	UO <sub>2</sub> <sup>2+</sup> , Cd <sup>2+</sup> NpO <sub>2</sub> <sup>2+</sup> , SeO <sub>4</sub> <sup>2-</sup>
$\delta$ MnO <sub>2</sub>	NaNO <sub>3</sub> , NaCl	-
am-SiO <sub>2</sub>	NaCl, KCl	-

Figure 15.

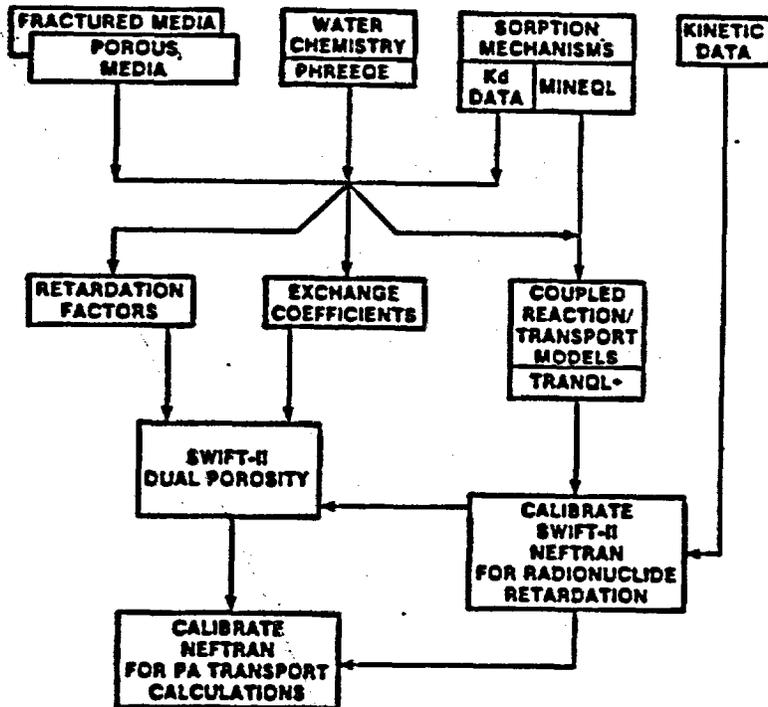


Figure 16.

PDR-1  
LPDR WM-10(2)  
WM-11(2)  
WM-16(2)

WM DOCKET CONTROL  
CENTER

'87 NOV -9 A9:55

*WM-RES*  
WM Record File  
HL 756  
*JNL*

WM Project 10, 11, 16  
Docket No. \_\_\_\_\_  
PDR   
XLPDR  (B, A, S)

Distribution:  
Bombia  
\_\_\_\_\_  
\_\_\_\_\_  
(Return to WM. 623-SS) *J.*