# Determination of Radionuclide Sorption for Assessment of High-Level Waste Isolation

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DETERMINATION OF RADIONUCLIDE SORPTION FOR ASSESSMENT OF HIGH-LEVEL WASTE ISOLATION NRC TECHNICAL POSITION

## 1.0 INTRODUCTION

# 1.1 Purpose

The purpose of this document is to present a general approach for determining radionuclide sorption on solids anticipated in a nuclear repository in support of high-level waste site characterization, repository construction authorization and licensing decisions. It is not intraded to prescribe methods for radionuclide sorption determinations. Instead, the Department of Energy (DOE) should use this guidance to prepare detailed plans for radionuclide sorption determinations and should submit appropriate documentation early in the site characterization review process.

## 1.2 Definition of Sorption

Sorption is defined in this technical position as one or more physicochemical processes, excluding precipitation of stoichiometric (fixed composition) solid phases, in which solute is removed from a liquid phase by interaction with a solid phase. These processes can include ion exchange, adsorption, chemisorption, and precipitation of radionuclide solid solutions. When a liquid is flowing through permeable solid media, sorption processes act to retard the migration of the solute relative to the groundwater flow.

1.3 Use of Sorption

Radionuclide sorption experimentation can be used to quantify three facets of site characterization and performance. First, sorption experiments can be used to help screen for "key" radionuclides which are defined here as those radionuclides that are highly toxic, mobile, and occur in significant quantities in the nuclear repository. The mobility of radionuclides depends on groundwater flux and radionuclide concentrations in groundwater. Radionuclide concentrations, in turn, depend on the solubilities of radionuclide-bearing solid phases and the sorptive characteristics of repository solids.

Radionuclides which are strongly sorbed on solid media could be eliminated from extensive testing if it could be shown that they will never exceed the release rates or significantly contribute to the integrated radionuclide flux in accordance with the NRC regulations. Second, sorption studies can be used to determine the quality of engineered barriers to isolate radionuclides. Parameters such as sorption or desorption ratios (defined as the ratio of the amount of radionuclide sorbed on the solid versus the amount dissolved in the liquid, R<sub>c</sub>) derived from these experiments can be used to quantify the ability of the engineered barriers to retard radionuclide migration. The sorptive capacity of solid material (defined as the maximum quantity of radionuclide sorbed on unit mass of the solid) comprising the engineered barrier system can be determined in sorption experiments. This parameter can be used in performance assessment calculations. Third, the sorption studies can be used to determine the ability of the host rock in the far field to retard radionuclide migration. This use of sorption studies is similar to that described above except that host rock is used as a starting material instead of engineered barrier material and the physicochemical conditions simulate far-field instead of near-field conditions.

#### 1.4 Regulatory Framework

The Nuclear Waste Policy Act of 1982 (P.L. 97-425) defines the role of Federal agencies in the national program for disposal of civilian (commercial) nuclear waste. For high-level radioactive wastes, the Environmental Protection Agency (EPA) is responsible for developing "...generally applicable standards for protection of the general environment from offsite releases from radioactive materials in repositories." The NRC implements the EPA standard and develops and issues "...technical requirements and criteria that it will apply in approving or disapproving (i) applications for authorization to construct repositories; (ii) applications for licenses to receive and possess spent nuclear fuel and high-level radioactive waste in such repositories; and (iii) applications for closure and decommissioning such repositories." The DOE is responsible for collecting the data needed for site characterization and for constructing and operating a waste disposal facility in accordance with NRC regulations.

Prior to approving construction authorization, the NRC must have "...reasonable assurance that the types and amount of radioactive materials described in the application can be received, possessed, and disposed of in a geologic repository operations area of the design proposed without unreasonable risk to the health and safety of the public...," (NRC, 1984). NRC criteria require information on the near-field behavior of the repository resulting from waste package/water/rock interactions. EPA criteria are evaluated on the basis of far-field performance assessment. Each assessment requires information on the release of radionuclides to the accessible environment which depends on groundwater flux, radionuclide concentrations in groundwater, sorptive characteristics of t'e solids present, radionuclide-bearing colloids and particulates.

## 2.0 BACKGROUND

A geologic repository achieves isolation and controls the rate of radionuclide release to the accessible environment by means of two major subsystems: (1) the geologic setting and (2) the engineered system. The site is selected for geologic, hydrologic and geochemical attributes of the underground setting which can enhance isolation. Because licensing of a high-level waste repository ultimately will involve performance assessment modeling of radionuclide release to the accessible environment, input of radionuclide sorption parameters to performance assessment models is necessary. Radionuclide sorption parameters applicable to portions of the nuclear repository system may be very difficult to determine precisely when future geochemical conditions will not be known with complete certainty. However, a conservative estimate for the sorption parameters can be defined through experimental determination of sorption of radionuclides on site-specific solids under anticipated repository conditions.

In general, sorption experiments can be subdivided into two types: those involving closed systems and those involving open systems. A closed system is one in which the amount of material remains constant during the experiment. An open system, on the other hand, is one in which material is introduced and/or removed from the reaction vessel during the experiment. The two types of experiments model different possible radionuclide release scenarios. Thus,

both approaches have been used to describe repository performance. For characterizing sorption phenomena, closed-system experiments, such as batch tests, involve contacting radionuclide-free solids with a radionuclide-bearing solution for the duration of the experiment followed by analytical determination of the sorption ratio. Batch desorption experiments; on the other hand, involve contacting radionuclide-free liquid with radionuclide-bearing solids, followed by measurement of the quantity of radionuclide leached. Open-system experiments, such as flow-through column tests, involve the introduction of fluid at one end of a reaction vessel containing solid and the removal of the fluid at the other end. The solid material sorbs solute and, as a result, retards the flow rate of the solute relative to that of the liquid. The ratio of the liquid velocity to the velocity of the solute of interest is defined as the retardation factor,  $R_f$ .

There are advantages and disadvantages to both experimental approaches. For example, closed-system experiments are relatively simple to carry out and the residence time of the solution in contact with the solid can be greater than in an open-system experiment. The longer residence times in closed-system tests may more closely simulate residence times in a nuclear repository. However, open-system experiments may better model sorption processes in flowing systems and may reveal the presence of multiple speciation, colloids or particulates the closed-system experiment (batch test) might miss. Multiple species, colloids, or particulates can lead to nonconservative sorption ratios calculated from closed-system experiments.

## 3.0 STATEMENT OF POSITION

It is the position of the NRC that sorption parameters used in radionuclide release rate calculations should be derived experimentally. Those sites determining sorption parameters should:

 Develop a matrix of experiments that involves key radionuclides and starting materials based on the anticipated range of proportions and compositions of phases under the various physicochemical conditions expected in a nuclear waste repository;

- 2) Characterize solid and liquid reactants and products;
- For closed-system experiments, develop sorption isotherms in which radionuclide concentrations are varied up to the apparent concentration limit when all other physical and chemical parameters are held constant;
- 4) Verify the applicability of sorption parameters to repository performance by using various experimental approaches including both open and closed laboratory systems and in situ field tests;
- 5) Determine the effects of flow rates and flow regimes on retardation factors;
- Document the magnitudes of experimental and conceptual uncertainties from all anticipated sources;
- 7) Use geochemical modeling only for interpreting experimental results and for planning experiments;

The NRC staff considers that this experimental approach should result in reasonable estimates of sorption parameters applicable to repository conditions. If carefully planned, sorption experiments could yield valuable information concerning some aspects of repository performance. The amount of . experimental work necessary for determination of radionuclide sorption on engineered barrier material and host rock in order to support waste isolation can be limited if it is restricted to site-specific conditions.

#### 4.0 DISCUSSION

Determining release rates of radionuclides requires information on both radionuclide concentrations and groundwater fluxes. Radionuclide concentrations, in turn, are strongly dependent on the radionuclide sorption properties of the solid-liquid systems to be encountered in the repository. In determining release rates, consideration should be given to the physicochemical characteristics of the waste and other solids, groundwater chemistry, flow

rates, flow regimes, retardation factors, sorptive capacity of solids, repository temperature and pressure, and kinetics of reactions. Acquiring and confirming this information will be an ongoing, long-term goal to be achieved prior to repository closure. However, the NRC staff considers that it is possible to reduce the level of effort needed to obtain a release rate by making a bounding estimate of radionuclide concentration and coupling this with groundwater flux.

#### 4.1 Matrix Development

A matrix of experiments can be used to determine which tests are required to characterize the sorption of radionuclides on solids anticipated in the various physicochemical environments of a nuclear waste repository. Variables which should be included in the matrix are solid compositions, liquid compositions, proportions of phases, temperature, pressure, grain size, flow rate and regime, time and ionizing radiation. Prior to experimentation, the total range in compositions and proportions of phases that occur anywhere and at any time in the repository should be considered.

For solid materials, emphasis should be placed on the identification and characterization of solids which can include waste form, canister, backfill, seals, packing, and host rock primary and secondary minerals occurring along likely groundwater flow paths . These are the solids most likely to react with groundwater and affect radionuclide concentrations and release rates. Analysis of the solids should include chemical, mineralogical, textural, and grain size determinations. Concerns about the applicability of ground solids in sorption experiments to repository conditions should be addressed. It is possible that the surfaces of ground material are significantly different from the surfaces of intact material, both porous and fractured. Grinding may expose the surfaces of minerals different from those groundwater would contact in a repository or may change the reactivity of the same mineral surfaces with dissolved radionuclides. In designing sorption experiments, selection of solid reactants should be based on this characterization.

Similarly, the range of groundwater compositions expected in a repository system should be considered in selecting liquid reactants. Generally, in the

rock-dominated environments of a HLW repository, groundwater compositions will be controlled by reactions with solids at various temperatures and pressures. Considerations of the range in water compositions used in experimentation should be based on the range of compositions of analyzed groundwaters at ambient conditions and the range of groundwater compositions experimentally determined at elevated temperatures and pressures.

The flow regime anticipated in the repository should be considered in the design of sorption experiments. Porous media flow may be adequately simulated by using ground solids if the solids are site specific and their surfaces are not unlike those antic pated in the repository. However, for appropriate simulation of fractured media flow, experimental designs may require the use of intact solid material containing fractures. Additionally, consideration of the degree of saturation of the nuclear repository may affect the experimental design. Normally, sorption experiments are carried out under saturated conditions so that the liquid can be recovered easily and analyzed. However, unsaturated conditions can exist in some repositories and the effect of these conditions on retardation should be addressed.

Following consideration of the complete range of compositions and proportions of phases and flow regimes in a repository, the size of the matrix may be reduced by first considering the dependence or interrelation of phases and conditions upon each other and then deleting incompatible combinations. The matrix developed prior to experimentation can be modified continuously as information from experiments is obtained. Knowledge of liquid and solid compositions gained from the results of preliminary experiments can be used as input into subsequent tests. From the standpoint of concentrations, key radionuclides can be identified experimentally as those which are weakly sorbed while radionuclides which are strongly sorbed may be eliminated from the testing plan.

4.2 Characterization of Reactants and Products

A number of analytical methods are available for determining the concentration of major, minor, and trace elements in water samples. Since the utility, detection limits, and reliability of the various methods differ for different

elements, no single method can be recommended for a complete chemical analysis of a water sample. The choice of methods usually depends on the instruments that are available, the concentrations of the components to be measured, and the level of precision needed. In addition to analyzing for major, minor, and trace elements, characterization of the aqueous phase should include measurements of the pH and, if possible, redox conditions.

The extent of sorption of dissolved radionuclides on engineered barrier materials and host rock is strongly dependent on the redox potential (Eh) and acidity (pH) of the groundwater. These parameters affect the concentrations of the various radionuclide-bearing species. The degree to which solutes are sorbed depends on the species (complex) and the mechanism(s) of sorption involving those species. For example, Benjamin and Leckie (1981a) show that the sorption of Cd, Cu, Zn, and Pb on amorphous iron oxyhydroxide is strongly dependent on pH. The percentage of cation sorbed varies from approximately zero to one hundred with a change in pH of two units. Likewise, Kelmers et al., (1984) has shown that sorption ratios for neptunium and technetium are dependent on the redox condition of the system.

The NRC recognizes that characterization of some solids from experiments may be extremely difficult to perform due to the small quantities of these phases as run products. However, the characterization of solid run products from sorption experiments using analytical techniques including state-of-the-art methods is important. For example, under the same physicochemical conditions, different solid phases can have drastically different sorptive capacities for the same radionuclide. Characterization of the solids is important in determining which reactions took place and how these reactions depend on experimental technique. In addition to determination of the composition of solid phases, characterization should include surface area or grain size measurements. Inasmuch as sorption is predominantly a surface phenomenon, the surface area of the solid may strongly affect the experimentally determined sorption parameters. For example, neptunium sorption ratios varied inversely as a function of particle size (Kelmers et al., 1984).

## 4.3 Isotherm Development for Closed-System Experimentation

# 4.3.1 Theoretical Considerations

In this technical position, reactions or processes in heterogeneous systems involving solid and liquid phases are divided into two major categories: sorption/desorption and precipitation/dissolution processes. The sorption process can be subdivided into physical adsorption, electrostatic adsorption (ion exchange), specific adsorption, and chemical substitution (coprecipitation or solid solution) (NEA Sorption Workshop, 1983). The distinction between the two major categories of reactions, as defi ed in this technical position, is that in the precipitation/dissolution reaction, the concentration of radionuclide-bearing component, i, is fixed at constant temperature, pressure, and mole fractions of all other components,  $X_j$ , in the solid phase, (s). Under the same conditions, in sorption/desorption processes, the concentration of i in the solid can vary as a result of changes in the concentration of i in the liquid, (1). In addition, the chemical potential\* ( $\mu$ ) and the activity\* (a) of i in the solid is fixed in precipitation/dissolution reactions and can vary in sorption/desorption processes at constant temperature, pressure, and X; in the solid.

In a heterogeneous system involving a solid and liquid phase, component i will be transferred from the solid to the liquid in a dissolution/desorption reaction as the system approaches equilibrium if  $\mu_{i,s} \ge \mu_{i,l}$ . Component i will pass from the liquid to the solid in a precipitation/sorption reaction if  $\mu_{i,l} \ge \mu_{i,s}$ . When equilibrium exists between the solid and liquid phases,  $\mu_{i,s} = \mu_{i,l}$  and no net transfer of component i occurs between the phases.

For the chemical equation,  $ij_s = i_1 + j_1$ , where i is the radionuclide-bearing component and j are all other components common to both phases, the equilibrium constant is

$$K = \frac{a_{i,1}a_{j,1}}{a_{ij,s}}$$
 (1)

If the solid is pure ij, then a<sub>ii</sub> equals one and the equation becomes

$$\zeta_{\rm sp} = a_{\rm i,l}a_{\rm j,l} \tag{2}$$

where  $K_{sp}$  is the solubility product constant. For nonequilibrium conditions, if the right side of (2) is less than the left side, the liquid is undersaturated with respect to the radionuclide-bearing solid. If, on the other hand, the right side is greater than the left side, then the liquid is oversaturated with respect to the solid.

## 4.3.2 Experimental Considerations

The theoretical considerations concerning solid-liquid reactions can be used as a basis for determining experimental protocol in radionuclide sorption studies. These experimental procedures should yield radionuclide sorption parameters that are demonstrably conservative.

From the definition of sorption used in this technical position, the radionuclide-bearing solid phase controlling the solid-liquid reaction should be a nonstoichiometric phase. The chemical potential of i in this type of solid is less than that in a pure phase or radionuclide-rich end member of a solid solution under the same physicochemical conditions. As a result, at equilibrium the radionuclide concentration in the liquid is greatest when the composition of the solid controlling the reaction is fixed.

Experimentally, it may be possible to determine when the composition of the solid controlling the solid-liquid reaction is fixed. For example, at the same temperature, pressure, and  $X_j$  in the liquid, two sorption experiments  $(\mu_{i,1} \ge \mu_{i,s})$  with different radionuclide concentrations in the liquid starting material should yield the same radionuclide concentrations in the liquid run products. At the apparent concentration limit, using the same method, the radionuclide concentrations in the two liquids would be the same.

In sorption experiments, equilibrium conditions may not be obtained in a reasonable length of time. However, equilibrium radionuclide concentrations can be estimated by determining concentrations under steady-state conditions.

Steady state is defined as the condition where measurable changes in concentrations are not occurring over practical experimental times. It should be noted, however, that this technique can lead to uncertainties in the estimated equilibrium concentration if metastable phases are involved in the sorption/desorption reactions.

Probable release scenarios call for radionuclide concentration gradients in the repository system. Under equilibrium conditions, the concentrations of radionuclides in the repository can range from zero to an apparent concentration limit where the amount of dissolved radionuclide is controlled by the solubility of some stoichiometric radionuclide-bearing solid phase. In fact, under nonequilibrium conditions, groundwaters can be supersaturated with respect to some solids, resulting in higher radionuclide concentrations than expected under equilibrium conditions. Below the apparent concentration limit, sorption processes predominate. Inasmuch as radionuclide concentrations are expected to vary in the repository, it is reasonable to design experiments to determine the effect of concentration on sorption ratios.

It has long been known that sorption ratios are dependent on solute concentration. Figure 1, a generic sorption isotherm, illustrates the relationship between concentration on the solid versus concentration in the liquid when all other parameters are held constant. Analysis of the liquid run product can assure the constancy of the other parameters. Although this figure shows a linear sorption region, many sorbed species, including radionuclides show nonlinear relationships between the quantity sorbed and the solution concentration. Different methods of plotting sorption isotherms so as to linearize the relationship between the quantity sorbed and the quantity dissolved have been developed by Freundlich, Langmuir, and Dubinin and Raduskevich. These plots may allow for easier interpolation but have limited theoretical justification when applied to solute/solid systems.

4.4 Verification of Sorption Parameters by Multiple Experimental Approaches

Simulation of all anticipated repository conditions in sorption experimentation can be difficult and/or impractical. Some experimental parameters can be varied over a large enough range as to bound the conditions anticipated in the

repository. These parameters include SA/V ratio, temperature, pressure, and composition. Other parameters that often are not duplicated in the laboratory are scale, residence time, flow rate, water/rock ratio, and flow regime. Experiments are designed so that measureable effects of physicochemical reactions can be monitored in a reasonable time. At the relatively low temperatures (less than 300°C) anticipated in the repository, chemical reactions involving geologic materials can be extremely slow. In order to accelerate these reactions so that changes are measureable in experimental time, conditions other than those anticipated in the nuclear waste repository are imposed on the experimental system. For example, experiments can employ fine-ground solid material, high concentrations of solutes, agitation, catalysts, and rapid flow rates.

Besides accelerating reaction rates, laboratory experiments are designed so that the amount of material can be handled reasonably. By scaling down systems of interest (repository size) to laboratory size, certain physical conditions. must be altered. For example, the water/rock ratio in most repository systems is less than one. However, in order to obtain enough water for analysis in laboratory experiments, the W/R ratio is ordinarily increased significantly. This technique makes the bulk chemistry of the experimental system different from that in the repository. The effect of this technique on sorption parameters is unknown and should be considered. One can argue that in a fractured media, with little porosity, most of the rock will not be in contact with the groundwater. Consequently, following this line of reasoning, water/rock ratios used in experimentation should be lower than those that take into account all the rock in a repository system. If this argument is used, however, it follows that the solid reactants should be predominantly fracture material and not bulk rock. Sorption experiments involving crushed bulk rock might have little applicability to sorption phenomena in fractured media.

Although some studies such as Siegfried (1988) have shown that the water/rock ratio has little effect on water-rock equilibria, the surface area of the solid to the volume of the liquid ratio, SA/V, might have a strong effect on the sorption parameters (EXAMPLE). Theoretically, if the number of sorption sites is proportional to the surface area of the solid in contact with the liquid, the sorption ratio should vary directly with the SA/V ratio as predicted by the

law of mass action (Leckie'). The SA/V ratio of natural systems can vary several orders of magnitude depending on the type of void space - fracture or pores, the fracture aperture or pore size, and the degree of saturation. Due to the uncertainty of SA/V ratios in repository systems, these ratios should be varied in the sorption experiments to such an extent as to bound the ratios anticipated in the repository. In this way, when all other variables are held constant, the measured sorption parameters should bound the anticipated sorption parameters of the repository.

The fact that some parameters or conditions cannot be bounded requires the extrapolation of these conditions to those expected in the repository. This extrapolation introduces uncertainty into the determination of sorption parameters. Due to the possibility that sorption of radionuclides may involve numerous solute/solid interactions, the laboratory experiments take on an empirical nature. As a result, although the tests are simple, without a basis for understanding the various sorption mechanisms, extrapolation becomes extremely risky.

In order to verify the applicability of experimentally determined sorption parameters to a repository system, the site should use multiple experimental approaches. In so doing, sorption parameters can be analyzed and compared. For example, the sorption ratio,  $R_s$ , obtained from batch experiments has often been used to calculate a retardation factor,  $R_f$ . The relationship between  $R_s$ and  $R_f$  is

$$R_{f} = 1 + \rho R_{s} (1 - \phi_{e})/\phi_{e}$$

where  $\rho$  is the bulk density of the rock, and  $\phi_e$  is the effective porosity. This relationship is based on ion exchange theory as applied to porous media flow. Since ion exchange is only one of the possible processes involved in sorption, the calculated  $R_f$  value may not equal the measured  $R_f$  value. Furthermore, factors such as multiple speciation, colloid and particulate migration, hydrodynamic dispersion, ultrafiltration, and matrix diffusion can affect radionuclide migration. Batch experiments are adequate for determining many individual sorption ratios with a minimum of time and effort. These tests are well-suited to the early stages of experimentation where many scoping experiments are required involving various radionuclide/groundwater/solid combinations. Key radionuclides and site-specific parameters can be identified easily.

Sorption isotherms can be developed using monomineralic or multiphase solids. Using single phase solids, it may be possible to extrapolate sorption parameters to multiphase systems by some combinatorial formula. Although it may be relatively simple to characterize the solids, a disadvantage to this method is that the bulk chemistry of the system is probably different from that of the repository system. Thus, the results may be totally irrelevant. Experiments involving multiphase solids may produce more reasonable R<sub>s</sub> values because the proportions of solid phases and the compositions of the solids and the liquid are closer to those expected in the repository. By varying the amount of one solid phase, while holding constant and at site-specific conditions the proportions of all other solid phases, it may be possible to determine the sorptive characteristics of individual phases at site-specific bulk compositions (Blencoe, J.G., 1985, personal communication). This technique could be useful in determining sorption parameters for systems which have solid phases with drastically different sorptive characteristics.

Desorption phenomena and reversibility should be studied. Irreversible chemisorption mechanisms may play an important role in explaining radionuclide migration and, thus, desorption parameters may be necessary for accurately describing site performance. Slow desorption rates can only benefit the performance of the repository to isolate radionuclides as chromatographic elution peaks are retarded and broadened.

Comparison of the sorption and desorption ratios obtained from closed-system and open-system experiments is possible. Generally, the sorption ratios derived from batch experiments are equal to or greater than those derived from flow-through tests using the same solid material. As a result, batch tests may overestimate the effectiveness of a repository system to isolate radionuclides (Relyea, et al., 1980). The difference in sorption ratios may be due to particle abrasion in stirred closed-system experiments or the relatively short

residence times in open-system experiments. It has been found that stirring speed can change sorption ratios by over one order of magnitude (NEA Sorption Workshop, 1983). One method that could increase residence times in open-system experiments is called the discrete static step procedure (NEA Sorption Workshop, 1983). Here, solid material is sequentially contacted with solution in separate reaction vessels. This method has the advantage of simulating very slow flow rates while eliminating hydrodynamic dispersion. As an open-system procedure, the effects of multiple speciation can be observed. For multiple speciation to affect sorption ratios, it is necessary that the reaction rates for solute-solute interactions are slow relative to those for solute-solid interactions. Otherwise, no chromatographic peak separation will occur.

Batch experiments often contain a filtration step for effectively separating the liquid from the solid. However, filtration may also remove suspended material such as colloids or particulates which in open systems can migrate along with dissolved material. If the colloids or particulates are radionuclide-bearing, the retardation factors calculated from the closed-system tests will be greater than those measured in open-system tests.

The extrapolation of sorption parameters from laboratory experiments to the large-scale, long-term repository system can be highly uncertain, especially if the natural system is a fractured crystalline rock. One method of reducing (not eliminating) this uncertainty could be to perform in situ tests on site-specific solid material. The scale of these tests can be larger than that of the experimental tests and smaller than that of the repository. Time constraints, however, would still apply in these experiments. Comparison between the laboratory and field results can illustrate the usefulness of the different approaches.

4.5 Flow Rates and Regimes

The flow rates of experimental systems are often much greater than those anticipated in a repository. The effect of fast flow rates on retardation factors is unknown and should be considered in the experimental matrix. Generally, fast flow rates should favor the migration of radionuclides. As flow rates are increased, the time allowed for interaction between solute and

solid is decreased. Thus, based on flow rates, experimental systems should yield conservative retardation factors. It is possible, however, that under certain circumstances, fast flow rates may cause the formation of altered solids (Dibble and Tiller, 1981) with different sorptive characteristics.

The flow regime can have a drastic effect on the applicability of laboratory-derived sorption parameters to repository performance. Most experimental systems use crushed material as a solid medium because it is easy to handle, characterize, and accelerates solute-solid reactions. The application of crushed material to intact porous media may be adequate but not so for fractured media. For exc-sple, Sinnock et al., 1984 has compared the retardation factors calculated for porous media versus fractured media. They show that for  $R_s$  values of 1 and 100, retardation factors assuming porous media flow are 5 and 500, respectively; for fracture flow, on the other hand, an  $R_s$  of 500 is needed to retard the radionuclides by a factor of two. Thus, for performance assessment calculations, consideration of flow regime can be of the utmost importance.

## 4.6 Sources of Uncertainties

Uncertainties associated with sorption experiments stem from the inaccurate experimental representation of portions of a nuclear waste repository and imprecise analytical techniques. The choice of experimental conditions that simulate those in a nuclear repository requires consideration of certain paremeters which might affect radionuclide release. These parameters could include groundwater composition and pH, redox conditions, rock/water ratios, flow rates and flow regimes, kinetics and metastability, and radionuclide-bearing colloids and particulates. One approach for handling uncertainties associated with choosing appropriate chemical conditions would be to determine, through sensitivity analysis, the range of repository conditions that could affect radionuclide sorption. These conditions would then be used in the experimental studies.

#### 4.6.1 Groundwater Composition and pH

Variation in groundwater composition and pH can have a strong effect on solute sorption (Benjamin and Leckie, 1981). Increasing the concentration of certain groundwater components can either increase or decrease radionuclide sorption. For example, some groundwater components can act as ligands and react with the free ions of the radionuclide to form complexes. The sorption mechanisms and the corresponding equilibrium constants involving these complexes can be different (Benjamin and Leckie, 1981a). In order to determine the effect of groundwater composition on sorption experiments should encompass the range of compositions expected in the nuclear repository.

#### 4.6.2 Redox Conditions

The sorption of many radionuclides on solids can be markedly different in their different oxidation states (e.g., technetium and the actinides (Kelmers et al., 1983)). The oxidation state of multivalent radionuclides may be governed largely by redox reactions that occur as a result of rock/groundwater interactions. The redox potential (Eh) can be rigorously defined on a thermodynamic basis as the electrochemical potential of a system where all the reversible redox couples present are at equilibrium. Discussions of redox potential are presented by Hostettler (1984) and Garrels and Christ (1965). Natural systems usually contain more than one redox couple which should yield the same potential at equilibrium. However, redox reactions in natural systems are frequently irreversible (nonequilibrium), and the measured redox potential is often a mixed potential resulting from several redox reactions that may be coupled with each other. An unequivocal redox potential cannot be defined for such nonequilibrium systems (e.g., Lindberg and Runnells, 1984; Morris and Stumm, 1967; Whitfield, 1972).

#### 4.6.3 Rock/Water Ratio

The proportions of phases in experiments may affect radionuclide sorption parameters. Most experiments must be run under water-dominated conditions (mass of water  $\geq$  mass of rock), whereas a repository will typically be a rock-dominated (mass of rock  $\geq$  mass of water) system. Therefore, the effects

of varying the water/rock ratio should be considered in sorption determinations. At high water/rock ratios, certain solid phases may be totally consumed by dissolution. Sorption processes involving fracture material may be more representative in some cases (see section 4.10). As a result, liquid run products may not simulate groundwater anticipated in rock-dominated repositories.

## 4.6.4 Kinetics and Metastability

Uncertainties arise from experiments in which the phase assemblage does not reach equilibrium. Experiments that do not produce a unique steady-state concentration for a given set of physical and chemical conditions result in uncertainties in the sorption of the radionuclide. In this case, the size of the error is experimentally defined by the range in the sorption/desorption ratios under steady-state conditions. The inability to duplicate steady-state sorption/desorption ratios would require explanation. For example, irreversibility may indicate that an "unexpected" chemical reaction or experimental error had occurred. Consequently, the results could not be used. The inability to duplicate steady-state sorption/desorption ratios also may result from slow reaction rates which impede complete reversal. The sorption ratios, where the radionuclide concentration in the liquid decreases as the system approaches equilibrium, should be used because they are equal to or less than those at equilibrium.

A second type of uncertainty arises from experiments in which steady-state conditions involve equilibrium of a metastable phase assemblage. Steady-state concentration of the radionuclide involving a metastable phase assemblage can be greater than or less than steady-state concentrations involving a stable assemblage. In order to determine if the radionuclide concentrations in equilibrium with a metastable phase assemblage are greater than those in equilibrium with a stable assemblage, it is necessary to characterize the solids and use appropriate thermochemical data, <u>if it exists</u>, to calculate the stable phase assemblage and the radionuclide sorption characteristics.

#### 4.6.5 Other Sources of Uncertainty

Most studies of radionuclide migration in anticipated repository environments have focused on the transport of dissolved forms of the radionuclides by flowing groundwaters. Colloid formation, however, is not uncommon-in geologic systems, and colloidal and particulate forms of clays, ferric and aluminum hydroxide, and silicic acid polymers are frequently found suspended in groundwaters. It is possible that significant quantities of some radionuclides could be adsorbed on the surfaces of these particles in groundwaters (pseudocolloids) or, under the proper circumstances, the radionuclides themselves could form colloids (true colloids). Radionuclides in a colloidal form could conceivably migrate farther and faster than they would in a dissolved form involved in sorption/precipitation reactions (Apps et al., 1983).

Attempts to separate colloids from the liquid phase in sorption experiments can result in sorption on filters of dissolved radionuclide species resulting in . lower concentrations in the filtrate or incomplete filtration which results in higher concentrations than those under equilibrium or steady state conditions in the filtrate. If sorption on the filter is suspected, preconditioned (saturated) filters can be used. If incomplete filtration is suspected, finer filters or more rigorous centrifugation should be used. Comparison of results from open- and closed-system experiments may indicate the presence of colloids.

Most sorption experiments study the chemistry of only one radionuclide, in contrast to the repository system which will have numerous radionuclides. Sorption ratios obtained in studies of one radionuclide may be much greater than those in systems containing numerous radionuclides. For example, the sorption ratio of a single radionuclide would be greater than that if two or more radionuclides were present which competed for the same sorption sites. Sorption studies using multiple radionuclides can be used to address this uncertainty.

4.7 Geochemical Modeling and Sorption Calculations

Theoretical considerations of sorption processes are generally restricted to explaining simple systems involving simple mechanisms. Due to the many

possible mechanisms that might contribute to the sorption of radionuclides, calculations best explain systems in which one of the processes strongly dominates. Prediction of sorption ratios is necessarily uncertain. The results of these calculations may have limited validity for the following reasons:

A. <u>Equilibrium assumed.</u> Calculations of radionuclide sorption are based on the assumptions that both homogeneous (one-phase, groundwater) equilibrium and heterogeneous (multiphase, groundwater and solids) equilibrium are achieved. However, it is unrealistic to expect that reaction rates will be so rapid that both homogeneous and heterogeneous equilibria will continuously prevail under conditions of varying temperature, mineralogy, pH, and redox potential.

C. Data base limitations. It is well known that the data bases for radionuclides sorption parameters in computer codes are incomplete and also contain data of questionable validity. Numerous radionuclide complexes can form in groundwaters, but independent evidence that proves the existence of particular species is almost nonexistent. It is, therefore, likely that some complexes inferred to exist in significant concentrations under certain conditions may, in fact, not exist at all. Furthermore, it is likely that there are some important radionuclide complexes which have yet to be identified. Corresponding omissions also probably exist in the list of radionuclide-bearing solids that can form as a result of reactions between groundwaters and coexisting solid materials. Finally, the uncertainty (limits of error) of thermodynamic data, such as log K and  $\Delta H_f$  values for speciation reactions can be large.

D. <u>Experimental validation required</u>. As a result of the above considerations and the complexity of the repository system, any sorption calculations will require experimental validation before their results can be employed in repository performance assessments.

Thus, by themselves, the results of computer calculations are insufficient to establish the nature and significance of radionuclide sorption under repository conditions. However, geochemical models are useful for characterizing geochemical conditions (e.g., groundwater chemistry, redox, pH controls and

thermal stability), and for interpreting experimental data. These calculations could be used to guide experimental determinations and should only assume a supplementary and/or supporting role in the determination of sorption values unless they can be shown to be fully consistent with a substantial body of independent (experimental data) information.

## 5.0 REFERENCES

- Apps, J. A., Carnahan, C.L., Lichtner, P.C., Michael, M.C., Perry, D., Silva, R.J., Weres, O., and White, A.F., "Status of Geochemical Problems Relating to the Burial of High Level Radioactive Waste, 1982", NUREG/CR-3062, Lawrence Berkeley Laboratory, 1983.
- Benjamin, M. M. and J.O. Leckie, Conceptual Model for Metal-Ligand-Surface Interactions During Adsorption, <u>Environmental Science and Technology</u> vol. 15, p. 1050, 1981.
- Benjamin, M. M. and J. O. Leckie, Multiple-Site Adsorption of Cd, Cu, Zn, and Pb on Amorphous Iron Oxyhydroxide, Journal of Colloid and Interface Science, vol. 79, no. 1, p.209-221, 1981a.
- Denbigh, K., <u>The Principles of Chemical Equilibrium</u>, Cambridge University Press, London, 1971.
- Garrels, R.M. and C.L.Christ, <u>Solutions, Minerals, and Equilibria</u>, Harper and Row, New York, 1965.

Hostettler, J.D., "Electrode Electrons, Aqueous Electrons, and Redox Potentials in Natural Water", <u>Amer. Jour. Sci.</u>, (284), 734-759, 1984.

- Kelmers, A. D. et al., Evaluation of Radionuclide Geochemical Information Developed by DOE High-Level Nuclear Waste Repository Site Projects, NUREG/CR 3730, 1984.
- Lindberg, R.D. and D.D. Runnells, "Groundwater Redox Reactions: An Analysis of Equilibrium State Applied to Eh Measurements and Geochemical Modeling", <u>Science</u>, (225), p. 925-927, 1984.
- Moody, J.B., "Radionuclide Migration/Retardation: Reasearch and Development Technology Status Report", ONWI-321, Office of Nuclear Waste Isolation, Battelle Memorial Institute, Columbus, Ohio, 1982.
- Morris, J.Ç. and W.Stumm, "Redox Equilibrium and Measurements of Potentials in the Aquatic Environment", in <u>Equilibrium</u>, <u>Concepts in Natural Water</u> <u>Systems</u>, Advanced Chemistry Series, (67), p. 270-285, 1967.

- NEA (Nuclear Energy Agency), "Sorption, Modelling and Measurement for Nuclear Waste Disposal Studies", Summary of NEA Workshop held 6-7 June 1983 in Paris, 1983.
- NRC, "Nuclear Regulatory Commission, 10 CFR Part 60, Disposal of High-Level Radioactive Waste in Geologic Repositories", 1984.
- Relyea, J. F., R. J. Serne, and D. Silva, Methods for Determining Radionuclide retardation factors: Status Report, PNL-3349, Pacific Northwest Laboratory, Richland, Washington, 1980.
- Sinnock,S., Y. T. Lin, and J. P. Brannen, Preliminary Bounds on the Expected Posclosure Performance of the Yucca Mountain Repository Site, Southern Nevada, Sandia Report SAND 84-1492

Whitfield, M., "Eh as an Operational Parameter in Estuarine Studios", in Limnol. Oceanogr., (14), 547-558, 1969.

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