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YUCCA MOUNTAIN

YUCCA MOUNTAIN SITE CHARACTERIZATION PROJECT

STUDY 8.3.1.3.4.1
STUDY 8.3.1.3.4.3

BATCH SORPTION STUDIES AND DEVELOPMENT OF SORPTION MODELS

PREPARED BY

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STUDY PLAN FOR BATCH SORPTION STUDIES AND DEVELOPMENT OF SORPTION MODELS

Los Alamos National Laboratory

ABSTRACT

This investigation is focused on the quantification of potential chemical interactions between key radionuclides (i.e., elements) dissolved in ground waters and the solid surfaces present in the rock units between the disturbed zone and the accessible environment of the potential repository at Yucca Mountain. The study consists of 6 activities. Three of the activities are concerned with the determination of sorption coefficients on whole-rock samples for each of the key elements in emplaced waste, involving each of the hydrologic units and all of the conditions addressed in the scenarios to be considered by the performance assessment task as found in Section 8.3.5.13 of the Site Characterization Plan [SCP]: Yucca Mountain Site (DOE, 1988). The first activity will determine minimum K_ds for elements that have high affinities for Yucca Mountain rock/mineral surfaces. The second activity will determine isotherm parameters for elements with low- to intermediate-affinities for these surfaces. The third activity will determine the influence of key ground-water compositional parameters on sorption coefficients for the low- to intermediate-affinity elements. The fourth activity is concerned with sorption of the key elements on colloids that may be present in the Yucca Mountain ground-water flow system. The fifth activity will concentrate on the sorption behavior of the key elements on pure separates of mineral phases identified in Yucca Mountain rock units. The data obtained in this activity will be used in the first activity to identify the least-sorptive major mineral phases and in the second and third activities to rank the mineral phases in Yucca Mountain according to their affinity for a given element. The pure-mineral data could also be used in the derivation of K_as for fracture-lining minerals. The last activity will involve evaluation and modeling of the sorption behavior of the key elements. This will include (1) derivation of minimum K_ds for high-affinity elements, (2) derivation of probability distributions for sorption coefficients for the low- to intermediate-affinity elements, (3) isotherm modeling of whole-rock sorption data, (4) derivation of pure-mineral K_as for fracture-lining minerals and (5) derivation of a capability for the prediction of sorption coefficients for key elements under water/rock conditions not addressed in the experimental program. This investigation will require experimental and modeling data from the mineralogy of transport pathways investigation (SCP 8.3.1.3.2), the ground water characterization and modeling investigation (SCP 8.3.1.3.1), and the solubility investigation

(SCP 8.3.1.3.5). It will provide data to the dynamic transport investigation (SCP 8.3.1.3.6), the reactive tracer field test activities (SCP 8.3.1.3.7.2), and the retardation sensitivity investigation (SCP 8.3.1.3.7). The sorption coefficients obtained in this investigation are intended for the evaluation of whether or not the site meets the geochemical requirements set forth in 10 CFR 60.112,113,122 and to address issues 1.1, 1.2, 1.3, 1.8, 1.9, and 1.10 as discussed in the SCP.

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STUDY PLAN FOR BATCH SORPTION STUDIES AND DEVELOPMENT OF SORPTION MODELS

1.0 PURPOSE AND OBJECTIVES OF STUDIES

1.1 Objectives of Study

The rock units in Yucca Mountain contain mineral and other solid phases known to have significant sorption affinities for most of the radionuclides likely to be emplaced in the potential repository (Daniels et al., 1982). These phases make up one of the multiple barriers to radionuclide migration in the potential repository block. The purpose of this study is to obtain data on the sorption behavior of key radionuclides under the physical and chemical conditions anticipated in the rock volume between the disturbed zone and the accessible environment. In this study plan, key radionuclides are those radionuclides for which a sorption barrier could provide a significant contribution to the regulatory compliance strategy. For experimental purposes, the term key radionuclides is equivalent to the term "key elements" because all isotopes of a given element chemically behave essentially the same way. The key elements to be studied in this investigation include Am, C, Cm, Cs, I, Nb, Ni, Np, Pu, Ra, Se, Sn, Tc, Th, U and Zr. Data will be obtained that will provide input to the evaluation of alternative models for transport (e.g., matrix versus fracture flow). Alternative models for sorption behavior will be investigated through studies on pure mineral separates. Key radionuclides that sorb dominantly by surface complexation mechanisms will be studied in addition to radionuclides that sorb dominantly by ion exchange. Alternative models for transport will be addressed by studies of minerals that are found as fracture linings in Yucca Mountain and by studies on the sorptive potential of natural colloids in Yucca Mountain. Investigation of the sorption behavior of fracture-lining minerals will provide data on the impact of these minerals on the retardation of the important radionuclides/elements during fracture flow. The potential for the transport of radionuclides/elements adsorbed onto colloidal materials will be investigated by studying the degree to which the important radionuclides/elements sorb to natural colloids found in the Yucca Mountain ground waters. Experimental investigation of the dynamic coupling of sorptive behavior with flow parameters is addressed in the dynamic transport investigation (SCP 8.3.1.3.6).

1.2 Regulatory Rationale and Justification

The sorption data and models generated in this study will be one of the elements considered in evaluating whether or not the site meets the requirements of 10 CFR 60.112, Overall System Performance Objective for the Geologic Repository After

Permanent Closure. This section states that the "geologic setting shall be selected...to assure that releases of radioactive materials to the accessible environment following permanent closure conform to such generally acceptable environmental standards for radioactivity as may have been established by the Environmental Protection Agency...". Sorption is one of the mechanisms that might significantly affect the rate at which radionuclides are released to the accessible environment. 10CFR 60.113(b) notes that the "geochemical characteristics of the host rock, surrounding strata, and groundwater" are one of the factors that the Nuclear Regulatory Commission might take into account in approving or specifying other radionuclide release rates, designed containment periods, or pre-waste-emplacement groundwater travel times that may be used in meeting the overall performance objective." The results of these studies will also be used in evaluating the favorable conditions of 10 CFR 60.122(b) "Geochemical Conditions that-(i) Promote Precipitation or Sorption of Radionuclides; (ii) Inhibit the Formation of Particulates, Colloids, and Inorganic and Organic Complexes that Increase the Mobility of Radionuclides; or (iii) Inhibit the Transport of Radionuclides by Particulates, Colloids, and Complexes." Similarly, the results of these studies will be used in evaluating the potentially adverse conditions of 10 CFR 60.122(c): "Geochemical Processes that Would Reduce Sorption of Radionuclides, Result in Degradation of Rock Strength, or Adversely Affect the Performance of the Engineered Barrier System."

The sorption data and models generated in this study will be used in the resolution of the following issues described in the SCP (DOE, 1988):

Issue	SCP Section
1.1	8.3.5.13
1.2	8.3.5.14
1.3	8.3.5.15
1.8	8.3.5.17
1.9	8.3.5.18
1.10	8.3.4.2

One of the supporting parameters needed in evaluating Issue 1.1 (SCP Table 8.3.5.13-17) is the distribution coefficient (K_d) in the rock matrix for the following chemical elements: Am, C, Cm, Cs, I, Np, Pu, Sr, Tc, U, and Zr. This list has been expanded in this study plan because preliminary performance assessment calculations indicated the need for sorption coefficients for other elements. These coefficients are to be provided for all hydrologic units in the controlled area. The performance assessment (i.e., total system) calculations that are to be carried out for the resolution of Issue 1.1 are to include all credible scenarios for future events and processes at the Yucca Mountain site. For this reason, the resolution strategy for this issue, as it relates to sorption processes, can also be used in the resolution of the sorption-related questions in most of the other issues. However, for Issues 1.8 and 1.9, the resolution strategies call for expert professional judgment and other calculations in addition to the total system calculations. The resolution strategy for Issue 1.5 (Waste Package and Engineered Barrier Performance Evaluation, SCP 8.3.5.10) calls for a set of hydrothermal sorption experiments independent of this task. Near-field sorption is not addressed in this study plan.

The Nuclear Regulatory Commission (NRC), in its "Generic Technical Position on Sorption" (1987), has drawn attention to a number of potential problems in the interpretation and application of batch sorption data. These problems concern aspects of the experimental technique and application of the results to real-world situations. Data obtained in this task will be combined with data obtained in the dynamic transport investigation (SCP 8.3.1.3.6) to address NRC's concerns (Meijer, 1990).

2.0 RATIONALE

2.1 Technical Rationale and Justification

2.1.1 Approach

The derivation of sorption ratios appropriate to the entire range of scenarios to be considered for postclosure performance assessments would require experiments that address all the values of the dominant physical and chemical variables involved in the scenarios. The number of separate experiments required to address directly all the variables over their estimated ranges would be unrealistically large. Further, this approach would provide little in the way of predictive capability to address scenarios not included in the experimental matrix. With an eye towards a more pragmatic approach, a sorption strategy has been developed (Meijer, 1992) that is based on sound chemical principles, requires a smaller number of experiments, and provides a basis for prediction of the sorption behavior of the key radionuclides.

In this strategy (Figure 1), the key radionuclides are divided into three groups on the basis of what is known about their affinity for the types of solid surfaces available in rocks from Yucca Mountain. The groups are (1) high-affinity, (2) low- to intermediate-affinity, and (3) "no-affinity." Radionuclides in the high-affinity group should have sufficiently large sorption coefficients (e.g., > 100 ml/g), even in the worst case flow scenarios, so that regulatory constraints

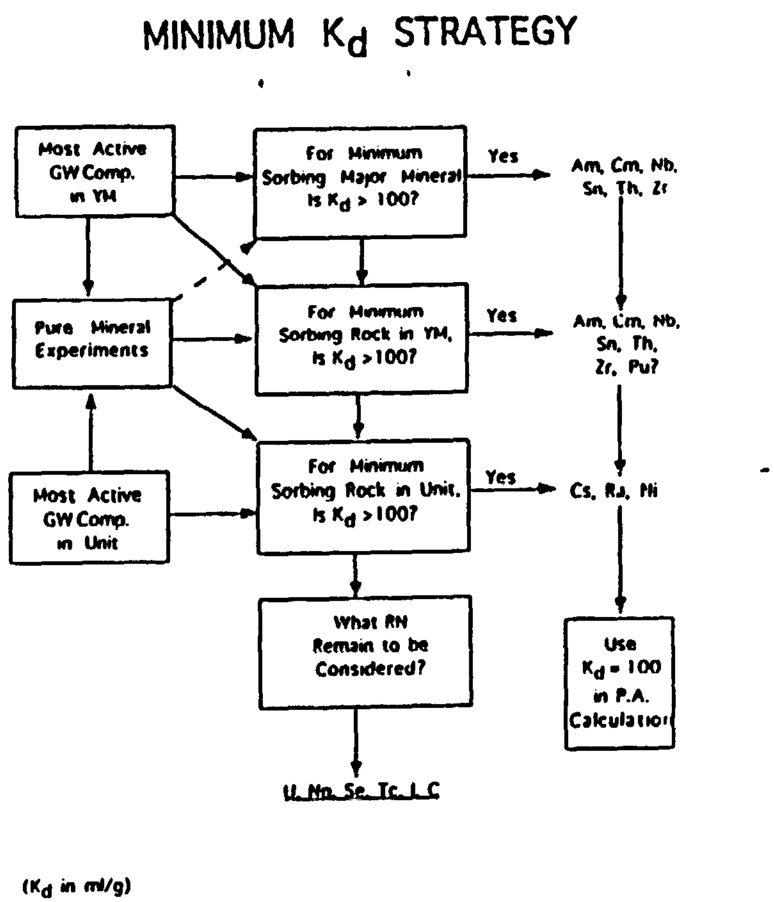

Figure 1a. Minimum K_d strategy for high affinity radionuclides/elements. Symbols are defined as follows: YM = Yucca Mountain
GW = ground water
RN = radionuclide
P.A. = Performance Assessment

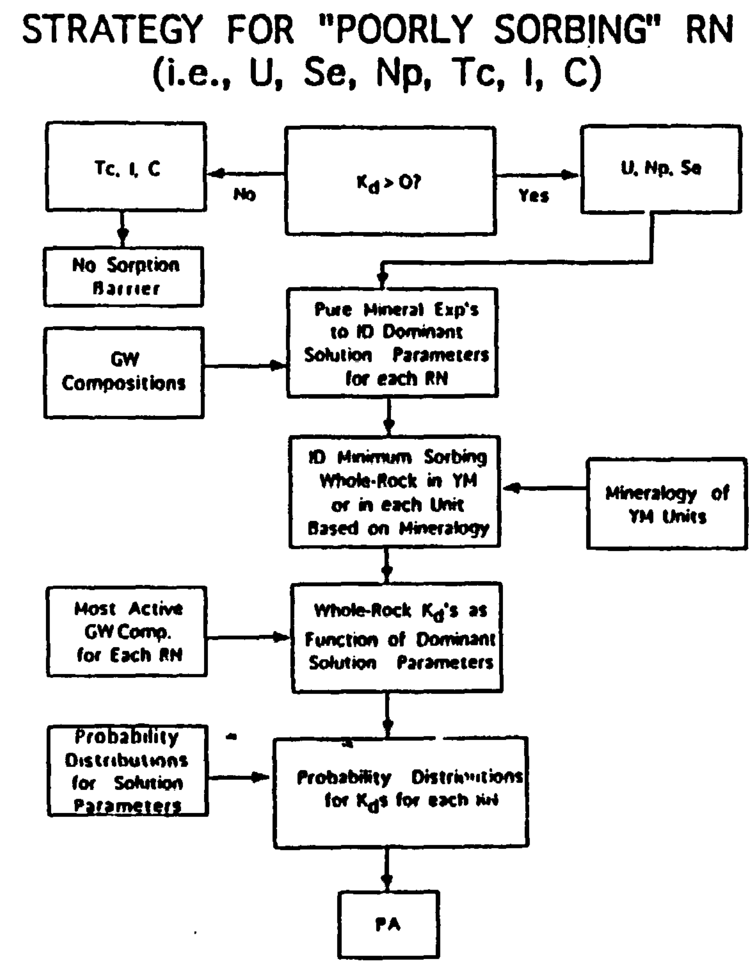

Figure 1b. Strategy for no-, low-, and intermediate-affinity radionuclides/elements. Symbol ID = identification.

can be met in any case (Barnard et al., 1992). Therefore, knowledge of the exact value of the sorption coefficient for each of these radionuclides at any point in the flow system will not be critical and a minimum K_d value should suffice. Which of the key radionuclides are in this group will be determined through experiments involving the most reactive water composition identified in Yucca Mountain for each of the key radionuclides, and the least-sorptive rock composition as identified on the basis of the pure mineral studies discussed below. Out of the range of compositions expected in Yucca Mountain, the most reactive water composition is that which yields the highest concentration of the radionuclide in solution. Those radionuclides having no affinity for the solid surfaces in rocks from Yucca Mountain will not have a sorption barrier. These radionuclides will also be identified on the basis of whole-rock and pure mineral experiments.

The radionuclides with low to intermediate affinities for the rock surfaces in Yucca Mountain will require the most detailed evaluation. They will initially be identified by failing to fall into either the high- or no-affinity groups. Once identified, their sorption behavior will be investigated through additional experiments on pure-mineral separates in which the major solution (e.g., ground water) compositional parameters (e.g., pH) are varied over the ranges of values anticipated in the Yucca Mountain flow systems. These experiments and any pertinent information that may be available in the literature will be used to identify those solution parameters that most affect the sorption behavior of each of the low- to intermediate-affinity radionuclides. Once these "controlling" solution parameters have been identified, a series of whole-rock experiments will be performed involving representative samples from each of the hydrologic units identified at Yucca Mountain and representative ground waters in which the controlling solution parameters for each radionuclide are varied over the ranges expected within Yucca Mountain. The term "representative" refers to samples with compositions within the range seen in the field. Attention will also be given to parameters that have a large effect in sorption as determined by experiments and calculations. By combining the results of these experiments with probability distributions for the controlling ground-water compositional parameters, probability distributions for the sorption coefficients for these radionuclides will be derived for each of the hydrologic units.

The pure mineral experiments used to derive the high-, low-intermediate-, and no-affinity groupings can also be used in estimating sorption coefficients for fracture linings as a function of the surface area and fracture water compositions, assuming these data are available. If the dominant sorption mechanisms can be determined in the pure mineral experiments with each radionuclide, a basis for the prediction of sorption behavior would be developed that would aid in the evaluation of scenarios that are not under consideration at the present time but may become significant in the future.

2.1.2 Types of Measurements to be Made

The measurements to be made in this study (SCP 8.3.1.4.1 and SCP 8.3.1.4.3) make up the following activities:

- batch sorption measurements as a function of solid phase composition (SCP 8.3.1.3.4.1.1),

- batch sorption measurements as a function of sorbing element concentrations (isotherms) (SCP 8.3.1.3.4.1.2),

- batch sorption measurements as a function of ground water composition (SCP 8.3.1.3.4.1.3)

- batch sorption measurements on particulates and colloids (SCP 8.3.1.3.4.1.4)

2.1.3 Rationale for Types of Measurements

2.1.3.1 Rationale for the Selection of Techniques

The basic technique selected for the four activities listed above is the batch sorption experiment in which the distribution of a radionuclide between a solution phase (e.g., ground water) and a crushed or powdered sample is measured as a function of any number of variables. This technique is valuable because it is simple and a large number of samples can be processed in a relatively short time. By varying the solid composition, the solution composition, the atmospheric composition, the radionuclide concentration, or the physical conditions (e.g., temperature) at which the experiment is conducted, sorption ratios can be determined for the various scenarios anticipated for the proposed repository in Yucca Mountain.

Alternative techniques for the derivation of sorption coefficients include the batch wafer technique, column migration experiments, field migration experiments, and natural analog studies. The batch wafer technique and column migration studies are described in the Study Plan for the Dynamic Transport Investigation (SCP 8.3.1.3.6). The batch wafer technique provides the same sort of data as the crushed-rock method. However, because of slow diffusion kinetics, particularly for the actinide elements, this technique requires considerably more time to achieve sorption equilibrium. Although column migration experiments can also yield sorption coefficients under ideal conditions, they involve a greater number of variables (e.g., flow rate, dispersion, diffusion) than batch experiments. For this reason, batch experiments are often required to interpret column experiments. Field migration experiments are described in the Reactive Tracer Field Test Activities Study Plan (SCP 8.3.1.3.7.2). In terms of the derivation of sorption coefficients, field migration experiments suffer from similar problems as the column migration experiments only to a greater degree. Unique values for sorption coefficients are very difficult to derive from field migration studies. Natural analog studies can potentially provide information on the sorption behavior of a given radionuclide in the natural environment. However, because a sufficiently detailed data base on the spatial and temporal variations in critical environmental parameters (e.g., pH, Eh, ground water composition) that determined the migration behavior of a given radionuclide at an analog site are rarely available, sorption coefficients derived from such studies are of qualitative value at best.

There are several new state-of-the-art experimental techniques that are being used in the surface science community to investigate the detailed chemical and physical nature of sorption reactions. These include extended X-ray absorption fine-structure analysis (EXAFS), photoacoustic spectroscopy (PAS), and scanning tunneling/atomic force microscopy (STM/AFM). In addition, there are other more established techniques that are used to study the composition and reactivity of surfaces including time-of-flight secondary ion mass spectroscopy, ion beam analysis, and microcalorimetry. Some or all of these techniques may be of use in the development of a basic understanding of the adsorption behavior of the key radionuclides on Yucca Mountain rock/mineral surfaces. Such understanding could be important to the development of robust predictive models for the sorption behavior of these radionuclides under conditions not addressed directly in the experimental program outlined below.

2.1.3.2 Rationale for the Selection of Tests

The tests and analyses to be carried out in this investigation include the following:

- sorption measurements as a function of rock composition and sorption measurements on pure mineral phases (SCP Activity 8.3.1.3.4.1.1),

- sorption measurements as a function of sorbing element concentrations (isotherms) (SCP Activity 8.3.1.3.4.1.2)

- sorption measurements as a function of ground water composition (SCP Activity 8.3.1.3.4.1.3)

- sorption measurements on particulates and colloids (SCP Activity 8.3.1.3.4.1.4)

As noted above, the strategy developed to obtain sorption coefficients for performance assessment calculations (Meijer, 1992) assigns the important radionuclides into one of three groups according to the affinity of each radionuclide for the mineral and other solid surfaces present in the hydrologic units delineated within Yucca Mountain. In the first activity listed above, experiments will be conducted to allow assignment of each of the important radionuclides into one of the three groups. For radionuclides with high affinities for the rock surfaces, these experiments will provide the basis for the assignment of minimum K_d values to be used in performance assessment calculations. These values will reflect conservative assumptions concerning water compositions (i.e., the most reactive water compositions) and the sorption potential (i.e., least sorptive) of various solid surfaces in Yucca Mountain. The most reactive water compositions will be identified on the basis of all pertinent data available in the literature concerning the radionuclides of interest and a limited number of experiments with different water compositions as discussed further below. The least sorptive mineral/rock surfaces will be identified in the pure mineral experiments. For many of the high-affinity radionuclides (e.g., Am, Cm, Nb, Ra, Sn, Th, and Zr), the experiments will involve solution concentrations near the solubility limit as these elements have low to very low solubilities in near-neutral waters. This means isotherms will not be required for these elements.

Those radionuclides for which no reliable (positive) sorption coefficient can be demonstrated in whole-rock experiments, using the least reactive ground water and the lowest reasonable solution concentrations, will not be investigated further by this study.

The second and third activities listed above will concentrate on those elements which have relatively high solubilities and low to high sorption potentials in Yucca Mountain ground waters. The experiments will be divided into two groups; one for high-affinity/high-solubility radionuclides and the other for low-affinity/high-solubility radionuclides. The high-affinity/high-solubility group will likely include the element Cs and possibly the element Ni. Isotherm experiments with these elements will involve a minimum-sorbing rock type from each of the hydrologic units, the ground-water composition with the highest ionic strength, and concentrations up to the maximum values expected to be released from the engineered barrier system. If the minimum K_d measured in these experiments is sufficiently large, as evaluated by transport calculations in the retardation sensitivity investigation (SCP 8.3.1.3.7), no further experiments will be carried out with these elements. On the other hand, if the measured K_d is not sufficiently large for either of these elements, the element will be assigned to the low-affinity/high-solubility group.

The low-affinity/high-solubility group is the most challenging in terms of the characterization of sorption behavior in a complex system such as the Yucca Mountain hydrologic flow system. The elements in this group will likely include U, Np, Se, and possibly Pu and Ni. Addressing the sorption behavior of this group will require the evaluation of couplings between three of the four activities listed above. First, the (aqueous) solution parameters that have the greatest influence on the sorption behavior of each element will be identified through experiments with pure mineral separates of the major and some of the minor phases identified in Yucca Mountain rocks (SCP Activity 8.3.1.3.4.1.1). The identities and ranges of the solution parameters to be considered will be obtained from literature reviews and from the ground water characterization and modeling investigation (SCP 8.3.1.3.1). Second, experiments will be performed for each of the low-affinity elements involving representative rock samples from each of the hydrologic units identified at Yucca Mountain and several ground waters representing each of the major ground water types identified at Yucca Mountain. The values of those solution parameters (e.g, pH) that were identified as having a significant influence on the sorption behavior of a given element will be varied in each ground water over the ranges anticipated in Yucca Mountain. Third, isotherms will be obtained on a subset of the previous experiments. Finally, the resulting database will be used in conjunction with probability distributions for each of the dominant ground water compositional parameters and radionuclide source term concentrations to obtain probability distributions for the K_ds for each of the low-affinity/high-solubility elements in each hydrologic unit within Yucca Mountain. This activity will be part of the sorption modeling activity (SCP 8.3.1.3.4.3).

The data resulting from the experiments involving pure-mineral separates and ground waters from Yucca Mountain could also be used to estimate K_as (surface-area-based sorption coefficients) for fracture-lining minerals, assuming data are available on the distribution and accessibility of fracture coatings and on the composition of fracture waters.

If sorption of radionuclides occurs on colloids and/or other particulates and if those colloids and particulates could be transported by ground water to the accessible environment, then the use of sorption coefficients alone may not adequately predict the transport of the radionuclides. Transport could occur on naturally occurring colloids and particulates present in ground water (SCP 4.1.2.7), on material created by the degradation of components of the engineered barrier system (SCP 8.3.5.10), or by microbes (SCP 8.3.1.3.4.2) present in ground water or introduced into the repository during construction or operation. Experiments on the sorption of key radionuclides will be carried out in this investigation once the likelihood and the mechanisms of colloid and/or particulate transport in the repository environment have been demonstrated by the dynamic transport investigation (SCP 8.3.1.3.6).

2.2 Constraints

Constraints on these investigations include the availability of adequate information on (1) the ranges of water compositions, including pH and Eh and organics, expected in each hydrologic unit over the lifetime of the potential repository (SCP 8.3.1.3.1), (2) the identification and spatial distribution of major, minor, and trace minerals in each of the hydrologic units defined within the site (SCP 8.3.1.3.2), (3) the solubilities of each of the key radionuclides in Yucca Mountain ground waters (SCP 8.3.1.3.5), (4) the radionuclide source term from the engineered barrier system (SCP 8.3.5.10), and (5) the identity and thermodynamic characterization of the chemical species (e.g., complexes) of the key radionuclides in ground waters at Yucca Mountain (SCP 8.3.1.3.5.1.2). The availability of suitable solid samples and ground waters are another constraint.

Some data are available on each of these constraints at the present time and more will become available as the site characterization program goes forward. The experimental program in this investigation will start on the basis of the existing database and branch out as new information becomes available. For instance, once adequate data become available on the compositions of unsaturated zone waters at or below the potential repository level, experiments with this water composition will be initiated. This will eventually result in an understanding of sorption processes that can be used to support alternative conceptual models, including the multiple-barrier approach to containment.

2.2.1 Effect on the Site

Analyses necessary for this investigation should have minimal impact on the site because most of the necessary samples will be obtained from planned drill holes or existing core. The ground water samples will be obtained from either existing or planned wells in the area. Additional core samples and water samples from the unsaturated zone will be requested, if available, during construction of the exploratory studies facility. No sampling requirements or procedures are needed over and above those already in place.

2.2.2 Required Accuracy and Precision

The performance goals and confidence levels set for sorption coefficients for the key radionuclides in the Site Characterization Plan (i.e., SCP Table 8.3.5.13-17) are minimal and should be easy to meet given our current knowledge (e.g., Thomas, 1987; Meijer, 1990). Because new performance goals and confidence levels have not yet been defined, the accuracy and precision required to meet these goals and levels cannot be defined. In the interim, the accuracy and precision goals will be defined to be consistent with the strategy discussed in Section 2.1.3.2.

The accuracy and precision with which sorption coefficients for the key elements are to be measured are mainly a function of the group to which the element has been assigned. Those elements in the high-affinity group must have K_d values that exceed the minimum K_d when all associated errors (two standard deviations) are taken into account. For instance, if the measured K_d is 1000 ml/g and the desired minimum K_d value is 100 ml/g, the maximum error allowed in the measurement of the K_d would be +/- 900 ml/g at the 1.0 confidence level. To be conservative, a smaller error would be preferred, allowing a lower confidence level. For those radionuclides in the no-affinity group, error estimates are not required unless credit is taken for the small positive values of K_ds that may be measured in some experiments. In this case, the error levels would likely be determined by the capability of the experimental technique. If the error levels associated with the technique are too large to allow the assignment of a positive value for the K_d, a value of zero would have to be assigned to the K_d for the element.

The accuracy and precision required for the low- to intermediate-affinity elements are more difficult to define because of the probabilistic nature of the K_d assignment. The best that can be done is to include the experimental errors associated with the measured K_d values, for a given element in a given hydrologic unit, in generating the probability distributions for that K_d.

2.2.3 Simulation of Repository Conditions

The studies in this investigation are designed to address the sorption behavior of radionuclides in the far-field (i.e., outside the disturbed zone of the potential repository). Sorption in the far-field represents one of the multiple barriers to radionuclide transport between the potential repository and the accessible environment. No effort is made in this investigation to simulate near-field (i.e., inside the disturbed zone of the repository) conditions. Efforts will be made, however, to address present and future variations in far-field conditions such as atmosphere, ground-water composition, mineralogy of the host rock, and temperature to the extent that these conditions can be defined by other investigations. The "Sorption Strategy" discussed in the introduction to this section will be used to decide to what extent actual conditions, as opposed to bounding conditions, should be replicated in the experiments (see also Meijer, 1990).

The NRC (1987) has expressed concern regarding the use of crushed rock samples versus solid rock samples from Yucca Mountain in the batch sorption experiments. The concern is mainly that crushing of the rock material could result in the formation of particularly reactive sites on the surfaces of the crushed material. Because these "sites" would not be present in solid rock in the far-field of the potential repository, they could inject a nonconservative bias into the experimental results if radionuclides were preferentially bound to these "sites" in the laboratory experiments. Fortunately, data obtained to date suggest that the use of crushed materials may not be a serious problem for sorption experiments involving tuffaceous rocks (Daniels et al., 1982). For example, Rundberg (1987) has shown that sorption coefficients obtained for alkali and alkaline earth elements on crushed tuff were essentially equal to coefficients obtained for these elements on solid wafers of the same tuffaceous samples. There are at least two reasons why this may be the case. First, the crushed rock samples are pre-conditioned with the background water composition that is to be used in the sorption experiments (see Section 3.1.5.1). This allows any "active sites" that may have been produced in the crushing process to pre-react with the chemical constituents in the water. Second, the matrices in the tuffaceous rocks of Yucca Mountain are very fine grained (< 1-5 microns). Therefore, crushing to a 75-500 micron grain size results mainly in the separation of crystals along pre-existing grain boundaries. In contrast, for coarser grained rocks (e.g., granites), crushing would result in the fracturing of individual crystals, leading to the creation of new grain boundaries. To investigate whether or not crushing has an effect on the values obtained for sorption coefficients of other elements (e.g., actinides), solid wafer/crushed rock paired experiments involving these elements will be carried out in coordination with the Dynamic Transport Investigation (8.3.1.3.6).

The NRC (1987) also expressed concern over the large water/rock ratios used in the YMP sorption experiments relative to the water/rock ratios likely to exist in Yucca Mountain. As discussed in Wolfsberg et al. (1981), it appears the impact of variable water/rock ratios on sorption coefficients can be modeled by isotherm equations. In effect, a high water/rock ratio simply means there is more of the radionuclide available in the solution phase for sorption onto the solid phase. If the radionuclide has a nonlinear isotherm, this leads to smaller sorption coefficients in experiments with higher water/rock ratios. This suggests that the batch experimental technique used in the YMP should lead to conservative values for sorption coefficients.

Another aspect of the experimental technique that may result in conditions different than those in the rock volume near the repository concerns the degree of saturation of the host rock. The batch experiments are carried out under saturated conditions while the potential repository horizon is located in the unsaturated zone. Two observations are pertinent with regard to this issue. The first is that there is no reason to suspect that sorption reactions between ground water and rock/mineral surfaces under unsaturated conditions (70-80 percent saturation) would be significantly different from sorption reactions that take place under saturated conditions, assuming the background water compositions are the same. Ground water compositions used in the batch sorption experiments will bound the compositions found in the unsaturated zone. The second observation is that unsaturated column experiments will be conducted in the Dynamic Transport Investigation (SCP 8.3.1.3.6). These experiments will provide further tests of the applicability of the (saturated) batch experiments to unsaturated flow conditions.

Another further aspect of the experimental technique that may result in conditions somewhat different from those in the potential repository environment concerns the number of radionuclides present in a given batch experiment versus the number and concentrations of radionuclides present in the solutions that may emanate from the engineered barrier system (i.e., source term) of a potential repository. There will likely be more radionuclides in the repository source term compared to the batch experiments. The question is, how will this aspect be integrated into the K_ds used in performance assessment calculations? In order to answer this question in a quantitative manner, we would need data on the sorption capacity of all the rock/mineral surfaces in Yucca Mountain rocks, the relative affinities of all the radionuclides and the natural chemical constituents in ground water for these rock/mineral surfaces, and the concentrations of all chemical constituents in the ground waters, as well as other parameters (see Appendix A in Meijer, 1992). In the following, a more pragmatic approach is developed for use in this investigation.

Because most of the key radionuclides are isotopes of elements that have low to very low solubilities in Yucca Mountain ground waters and have high to very high affinities for the rock/mineral surfaces in Yucca Mountain; the maximum total concentration of these elements in solution will generally be low. For the purposes of this investigation, this group of radionuclides can be thought of as a single component with a concentration equal to the total concentration of the separate radionuclides in solution. The sorption coefficient for this hypothetical component may be smaller than the coefficients for the individual radionuclides because of the higher concentrations involved (i.e., the hypothetical sorption coefficient would be higher up on some sort of composite isotherm). However, as long as the minimum K_d for the high-affinity elements is less than the value for the K_d for the hypothetical component, no problems should arise involving retardation of these elements in the performance assessment calculations. Experimentally, the composite isotherm could be measured for a given radionuclide by using solutions saturated with non-radioactive compounds of the other high-affinity radionuclides or appropriate analogs.

The radionuclides representing the elements C, I, and Tc have very low affinities for rock/mineral surfaces in Yucca Mountain (Thomas, 1987); therefore, they will not compete successfully with other radionuclides for sorption sites. The migration rate for these radionuclides will be determined primarily by physical processes (e.g., dilution, diffusion, etc.) This leaves radionuclides of the elements U, Np, Ni, Cs, Se, and Pu for further consideration. The element Cs has higher affinities for zeolitic rocks than any of the other key radionuclides and the major constituents of Yucca Mountain ground waters (Thomas, 1987). This suggests zeolitic units will be the primary barriers for Cs migration in Yucca Mountain although other units will also retard Cs to a lesser degree (Meijer, 1990).

The sorption coefficients measured for Ni in Yucca Mountain ground waters are generally greater than 100 ml/g (Knight and Lawrence, 1987). These results are consistent with the fact that Ni is known to be strongly sorbed by soils (Bowman et al., 1981) and suggest that Ni competes favorably with the major ground water constituents for available surface sites but not as favorably as the high-affinity elements. Therefore, its K_d in the high-affinity, element-enriched zone around the waste package may be smaller than that measured in (single radionuclide) batch experiments. In the far-field, however, the batch K_d values should be appropriate. The element Ni is known to be strongly sorbed on soils (Bowman et al., 1981). The fact that the total inventory of the element Ni will be small relative to the actinide elements (DOE, 1988) is also a significant consideration.

The key radionuclides representing the elements U, Np, Se, likely will not compete successfully for sorption sites with the high-affinity radionuclides. In the zone of high-affinity elements near the waste packages, the K_ds for these radionuclides may be smaller than those measured in typical (single radionuclide) batch experiments unless multilayer adsorption (e.g., surface precipitation) is a significant process. Outside this zone, the K_ds for U, Np and Se will be determined by competition for sites among themselves and with the natural chemical constituents of the ground water. By using ground waters from the site in the batch experiments, the competitive effects involving the natural constituents are accounted for. This leaves the competitive effects between the radionuclides and the natural constituents in solution as the main parameters to be determined. The most straight forward way to determine these parameters is to carry out batch experiments containing all three of these elements.

The element Pu will be the most difficult to characterize in terms of sorption potential because it does not consistently appear to be a high-affinity element in relation to Yucca Mountain rock/mineral surfaces (Thomas, 1987). Interestingly, this is in contrast to the observations of Allard et al. (1984), who found Pu to be a very-high-affinity element on most common mineral surfaces (e.g., quartz, montmorillonite, biotite). In any case, Pu has much higher affinities (an order of magnitude or more) for rock/mineral surfaces in Yucca Mountain than elements such as U, Np, and Se (Meijer, 1990). The simplest approach for dealing with Pu sorption would be to ignore any sorption of Pu in the high-affinity zone close to the waste package and carry out batch experiments also containing U and possibly Np. Because U and Np have similar sorption coefficients on Yucca Mountain rock/mineral surfaces (Meijer, 1990) and because Pu has a much higher affinity for Yucca Mountain rock/mineral surfaces, the presence of only one of these elements (e.g., U) at a concentration near its solubility limit may be sufficient to gauge competitive effects with Pu. This would minimize the radiation exposure to the analyst.

A final issue relating to simulation of repository conditions concerns the possible influence of organic coatings on rock/mineral surfaces and organic complexes in the Yucca Mountain ground waters. The concentrations of organic constituents in Yucca Mountain ground waters appear to be very low (<3 ppm; DOE, 1988). However, no data are available on the presence or absence of organic coatings on rock/mineral surfaces in Yucca Mountain. By using rock and water samples from the site in the whole-rock sorption experiments, the possible influence of organics will be accounted to a significant, although quantitatively undetermined, extent.

2.2.4 Capability of Analytical Methods

The analytical methods used in this investigation are well established (see Section 3.1.3; TWS-INC-DP-05, R2) and fully capable of generating the required information, given proper concern for potential experimental artifacts (Meijer, 1990). Potential artifacts include: (1) oversaturation of the solution with a compound of the radionuclide of interest, (2) incomplete solid-liquid separations, (3) adsorption of radionuclide of interest to wall of experimental container, (4) incomplete equilibrium between species in solution, and (5) incomplete sorption equilibrium.

The oversaturation question can be addressed using the experimental results of the Solubility Investigation (SCP 8.3.1.3.5) and pertinent literature data. Questions concerning incomplete separations and adsorption to container walls are addressed in the current batch procedure (TWS-INC-DP-05, R2). Equilibrium between species in solution and in the sorption reactions cannot be directly tested. The approach taken on these equilibrium questions in previous work (e.g., Daniels et al., 1982) consisted of time-series experiments in which the same experimental system was allowed to "equilibrate" over a range of time intervals until a steady-state value was achieved for the distribution coefficient R_d. This steady-state value was called the K_d. The time required to reach steady state was generally less than six weeks. This will be the duration of the batch experiments carried out in this investigation.

2.2.5 Time Required Versus Time Available

Using the strategy detailed above (Section 2.2.3) for the derivation of sorption coefficients for performance assessment calculations, the time required to complete this investigation will depend mainly on the success of the experimental program, staffing, etc. There is no reason to believe this investigation could not be completed in 5-6 years.

2.2.6 Limitations of Equipment and Applicability to Field

The test planned for this investigation will not be limited by equipment capabilities or availability.

Questions relating to the applicability of the sorption coefficients measured in this investigation, to the field, are discussed in section 2.2.3.

Questions relating to the applicability of batch sorption coefficients to the field are also addressed in the Dynamic Transport Investigation (SCP 8.3.1.3.6).

2.2.7 Interference With Other Tests

The laboratory experiments carried out in this investigation will not interfere with other tests.

2.2.8 Limitations on Repeatability of Tests

The primary limitation on the repeatability of tests planned for this investigation is the availability of appropriate rock and ground water samples from the site.

3.0 DESCRIPTIONS OF TESTS AND ANALYSES

3.1 Batch Sorption Measurements as a Function of Rock and Mineral Composition (SCP Activity 8.3.1.3.4.1.1)

3.1.1 General Approach

This activity will focus on the sorption behavior of the key elements on mineral phases present in Yucca Mountain and on the determination of minimum sorption ratios for the high-affinity elements in whole-rock samples from Yucca Mountain. The technique used will be the batch method.

The goals of the mineral studies are: (1) to determine whether the major mineral phases in the rocks, particularly those that are the least sorptive, have sufficiently large affinities for the high-affinity radionuclides such that robust minimum K_ds can be derived for these radionuclides based only on these mineral phases, (2) to identify those mineral phases that dominate the sorption behavior of the low- to intermediate-affinity radionuclides, (3) to test whether the no-affinity radionuclides are sorbed on any of the mineral phases, and (4) to identify those solution parameters that control the sorption behavior of the key radionuclides on the appropriate mineral phases.

3.1.1.1 Key Parameters to be Measured

The key parameters to be measured in the pure-mineral tests will be:

- sorption coefficients for the key elements on representative mineral separates as a function of ground-water compositional parameters

The key parameters that will be measured in the whole-rock tests are:

- sorption coefficients for the high-affinity radionuclides of representative whole-rock samples

In addition, the following parameters will be obtained as part of this activity either by another activity in the LANL-YMP or by a commercial laboratory:

- effluent solution compositions

- rock or mineral compositions before and after sorption experiment

- cation exchange capacities of rock and mineral samples used in experiments

- surface areas for rock or mineral samples used in sorption experiments

- mineralogy of the rock samples used in the experiment

3.1.1.2 Experimental Conditions

The experimental conditions for the pure-mineral measurements will be:

- temperatures of 25°, 60°, and 90° C

- most reactive ground water composition for each of the high-affinity elements

- representative ground water composition for the low- to intermediate-affinity elements and low-affinity elements

- atmosphere with P_{CO2} appropriate to the pH desired

- mineral separates from Yucca Mountain or other appropriate sources

- maximum radionuclide concentrations associated with the solution phase near solubility limits for high-affinity radionuclides as a function of water chemistry and near source term concentrations for the other radionuclides.

The experimental conditions for the whole-rock measurements will be:

- temperatures of 25°, 60°, and 90° C

- atmosphere with P_{CO2} appropriate to the pH required

- 1 or more radionuclides in each experiment

- ground waters from Yucca Mountain

- crushed samples of rocks from Yucca Mountain

- radionuclide concentrations below but near solubility limits

3.1.1.3 Test Matrix

The test matrix for the pure-mineral experiments will be separated into two parts: one involving the high-affinity elements and the other involving the low- to intermediate-affinity and the no-affinity elements. For the high-affinity elements (Table 1), the objective is to determine the affinity of the elements for the least-sorptive rock type in contact with the most reactive water. This will require experiments with each high-affinity element on each of the selected mineral phases in Yucca Mountain rocks. The minerals were selected on the basis of pertinent sorption data available in the literature. The selection of the most-reactive water composition for each high-affinity element will be based on available literature data on the sorption behavior of each of the elements and any additional experiments that may be required. The matrix is shown in the following table:

TABLE 1

TEST MATRIX FOR MINIMUM K_d EXPERIMENTS

Elements (Radionuclide)			Major Mineral Phases (In Order of Abundance)
Am	Pu	Ra	Quartz
Cs	Sn	Zr	Alkali Feldspar
Cm	Th	Nb	Clinoptilolite

The total number of experiments for this part of the activity will be on the order of 30.

For the low- to intermediate-affinity elements, the objective is (1) to identify any mineral phases that may be present in Yucca Mountain rocks that have high affinities for these elements and (2) to identify the solution parameters that control the sorption behavior of these elements on the highly sorptive mineral phases. Any pertinent data available in the literature will be used to identify the highly sorptive phases and the dominant solution parameters. The most sorptive phases identified in the literature should be studied first using the most favorable water composition given the range of ground-water compositions identified at Yucca Mountain. The process of identification of these phases and parameters also should iterate with the results of whole-rock sorption experiments. Once one or more highly-sorptive phases have been identified that could explain the whole-rock sorption behavior of a given element, the other phases in the rock need not be further investigated. For the no-affinity elements, a similar procedure will be followed to identify whether any of the selected mineral phases show a positive sorption affinity. The experimental matrix will be as follows:

TABLE 2

TEST MATRIX FOR LOW- to INTERMEDIATE-AFFINITY AND "NO-AFFINITY" ELEMENTS

Element	Mineral Phase (In Likely Order of Importance)
Pu	Hematite
Np	Clinoptilolite
U	Mn Oxide
Ni	Calcite
Se	Quartz
C	
Tc	
I	

The total number of experiments in this part of the activity will be on the order of 350, assuming each of these mineral phases is studied. Two dominant solution parameters are identified for each radionuclide and 5 values for each of these parameters are studied within the range of variation of the given parameter in Yucca Mountain ground waters.

The test matrix for the whole-rock tests will focus on high-affinity elements including Am, Cm, Nb, Sn, Th, Zr, and Ra. The elements Cs, Pu, and Ni may also be included. Rock samples will be chosen for this activity on the basis of the pure-mineral experiments. The objective will be to choose, with respect to each of the high-affinity elements, a minimum sorbing rock sample (i.e., a sample with the lowest affinity for the elements of interest) from each of the hydrologic units identified at Yucca Mountain. The water composition to be used in these tests will also be chosen on the basis of the pure mineral experiments. The compositions chosen will be those compositions, in the range of compositions expected at Yucca Mountain, that would result in the highest concentration of each of the high-affinity elements in solution.

Assuming there are 6-7 hydrologic units identified in Yucca Mountain, this part of the activity would involve a minimum of 210 individual tests.

This brings the total number of experiments for the activity to around 590.

3.1.2 Summary of Test and Analysis Methods

3.1.2.1 Test and Analysis Methods

3.1.2.1.1 Batch Technique

A standard batch-sorption technique has been developed (Daniels et al., 1982) and incorporated in the LANL Quality Assurance Manual as detailed technical procedure TWS-INC-DP-05, Sorption, Desorption Ratio Determination of Geologic Materials by a Batch Method. In this procedure, the rock sample is pretreated for at least 2 weeks by contact with ground water. At the end of the pretreatment time (usually 3 weeks), the solid is separated from the solution by centrifugation, and an aliquot of the resulting moist sample is taken for determination of its water content. Contact of the radionuclide containing ground water with a 1-g aliquot of the moist sample is started within 2-24 hours. At the end of the contact time (usually 6 weeks), the solution is separated from the solid phase by either ultracentrifugation or ultrafiltration. For experiments involving devitrified tuffs, ultracentrifugation appears to be adequate (Daniels et al., 1982). For zeolitic tuffs, ultrafiltration is required for complete separation. After separation of the phases, the amount of radionuclide in each phase is determined and a sorption coefficient is calculated as follows:

$$K_d = \frac{\text{amount of radionuclide on the solid phase/gram of solid phase}}{\text{amount of radionuclide in solution/milliliter of solution}} .$$

After the solid phase has been sampled for counting or when counting is complete, desorption measurements are begun. Twenty milliliters of pretreated water are added to the remaining solid phase. The sample is placed in a shaker and agitated at 200 rpm for a predetermined length of time (usually 6 weeks), after which the phases are separated and counted as already described.

3.1.2.1.2 Actinide Tracer Preparation and Characterization

Actinide tracers in known, stable, and well-characterized oxidation states are needed for use in this activity. Most actinide elements in near-neutral solutions and at expected repository conditions can exist in more than one oxidation state, each of which may exhibit different sorption behavior. In order to characterize these behaviors, well-characterized solutions of the individual oxidation states must be available in concentrations representative of those that could be found in ground waters along flow paths from the repository. Plutonium will be prepared with different oxidation states in a carbonate buffer approximating the carbonate concentration of water from Well J-13 and other wells as appropriate. The concentration prepared will be the lowest possible in which the pertinent species present can be identified with standard techniques (normally by spectroscopy ~10^{-6} M). These solutions will be diluted with the ground water of interest to create tracer solutions. These will be immediately used in sorption measurements with the presumption that the species distribution is not changed during the experiment. The remaining stock solution will be monitored during the course of the sorption experiments to assess the stability of the prepared oxidation state.

A preferred alternative to the standard spectroscopic technique for the characterization of species in solution is PAS (photo-acoustic spectroscopy). This technique is capable of determining solution speciation at concentrations as low as 10^{-9} M. The PAS technique would allow us to prepare the actinide tracer solution and to measure directly the species present. It could eliminate the uncertainty associated with the assumption that the dilution step described above did not cause any changes in speciation. The PAS technique may also be capable of identifying the speciation and oxidation state of the actinide activity remaining in the aqueous phase after a sorption experiment has been completed-something not presently possible. This technique is under development and is discussed in the study plan for the solubility investigation (SCP 8.3.1.3.5). If this technique cannot be used to determine speciation in the experimental solutions used in the sorption experiments, solution speciation will remain uncertain.

3.1.2.2 Tolerance, Accuracy, and Precision and Expected Range of Results

3.1.2.2.1 Tolerance, Accuracy, and Precision

The tolerance, accuracy and precision required in these tests are similar to those discussed in Section 2.2.2.

However, because the data obtained in the pure-mineral experiments will be used mainly to select whole-rock samples on which sorption coefficients will be measured for use in performance assessment calculations, the requirements for accuracy and precision are not as stringent in these mineral experiments as in the whole-rock experiments.

3.1.2.2.2 Expected Range of Results

For the whole-rock experiments, the available data suggest that the elements Am, Cm, Nb, Ra, Sn, Th, and Zr should have sorption coefficients > 1000 ml/g in essentially all the water/rock/mineral systems to be investigated in this study (e.g., Daniels et al., 1982; Thomas, 1987). Such large values for sorption coefficients should provide a firm basis for the derivation of minimum K_d values in the range of 100-1000 ml/g. For the experiments involving the high-affinity radionuclides the expectation is that high sorption coefficients will be obtained, even in the system involving quartz and a most active ground water. This expectation is based on the results of similar experiments reported by Allard et al. (1984). For the experiments involving the radionuclides of low- to intermediate-sorption affinity, the expectation is that sorption coefficients will be highest for hematite and Mn oxide, lower for clinoptilolite and possibly calcite, and lowest for quartz. This expectation is also based on results published in the literature (e.g., Allard et al., 1984). For the no-affinity radionuclides (i.e., C, Tc, I), the expectation is that there may be very limited sorption of Tc and C on hematite but not on the other phases. In fact, there will likely be negative sorption (i.e., anion exclusion) for I, and for Tc and C on the other phases.

3.1.3 Technical Procedures to be Used

Prior to starting these tests, quality assurance grading will be completed in accordance with currently applicable procedures to control this effort. The technical procedures that will be used are all nonstandard technical procedures. All nonstandard technical procedures will be approved 60 days prior to their use in laboratory experiments and all procedures will be approved prior to use.

3.1.4 Equipment List

Equipment to be used in the batch experiments includes pulverizers, American Society for Testing and Materials sieves, orbital shakers, ultra- and superspeed centrifuges, Ge(Li) gamma-ray detectors, NaI detectors, solid-state and proportional and alpha-particle detectors. Equipment to be used in obtaining supporting data includes an ion chromatograph, 20-channel emission spectrograph, alkalinity titrator, x-ray fluorescence spectrometer, x-ray diffraction spectrometer, and BET surface area analyzer. All of this equipment is commercially available.

3.1.5 Test and Analysis Results

3.1.5.1 Data Reduction and Analysis Techniques

The computer codes RAYGUN, GAMANAL, and SPECANAL are used to reduce gamma ray spectra to corresponding atom ratios of gamma-emitting radionuclides in the aqueous and solid samples. Alpha-counting data are reduced by hand, with desk top calculators, or with commercial spread-sheet programs. Final sorption ratios are calculated by hand or with commercial spread-sheet programs using the definition of K_d given in Subsection 3.1.2.1.1. Standard counting statistics will be provided for each sample analyzed by counting techniques.

3.1.5.2 Representativeness of Tests and Analyses

The pure-mineral tests are not meant to be strictly representative of the environment in the far field of the potential repository. They are intended to provide a basis for the selection of whole-rock and ground-water samples from the site to be used to measure sorption coefficients for the key elements that can be used in performance assessment calculations. The main issue regarding representativeness in these experiments is the relationship between the composition of the surfaces of mineral grains in Yucca Mountain and the composition of the mineral surfaces used in these experiments. The best way to deal with this issue is to obtain the mineral separates for the experiments from Yucca Mountain rock samples. In those cases where this is not feasible and mineral separates are obtained from other localities, special care must be taken in applying the results to the selection of samples from Yucca Mountain for use in whole-rock experiments.

Another issue regarding the representativeness of these tests is whether the appropriate set of pure minerals has been chosen for experimentation. The lists given above reflect expert judgment based on all the data available at the present time. If new data become available that impact the selections made, new lists of pure minerals could be formulated for use in this activity.

The whole-rock tests and analyses will be representative of the repository environment to the extent that representative samples are chosen for the least-sorptive samples in each hydrologic unit and for the most-reactive water composition for each of the high-affinity radionuclides. Additional discussion of the representativeness of these tests and analyses is presented in Section 2.1.3.

3.1.5.3 Limitations and Uncertainties of Results

Care must be taken to address potential problems with the batch technique described in Section 3.1.2.1.1 including slow sorption kinetics, mineral fractionation during sample preparation, oversaturated stock solutions of sparingly soluble radionuclides (e.g., Am), imperfect solid/liquid separations, and sorption to the wall of the experimental container. In the batch sorption experiments carried out to date by the YMP, these problems have mostly led to underestimation of the true sorption coefficient for high-affinity radionuclides (Meijer, 1990). The main exception is the problem involving sorption on the wall of the experimental container. This problem is now addressed by analyzing both the solid and the solution in those experiments in which it is suspected this problem may come up. The other problems are addressed in the present detailed procedure for batch sorption measurements.

3.1.5.4 Relationship to Performance Goals and Confidence Levels

The performance goals and confidence levels set for sorption coefficients for the key radionuclides/elements in the Site Characterization Plan (i.e., SCP Table 8.3.5.13-17) are minimal and should be easy to meet given our current knowledge (e.g., Thomas, 1987; Meijer, 1990). However, recent performance assessment calculations (Barnard et al., 1992) have pointed to the need for more stringent performance goals and confidence levels for sorption coefficients of many of the key radionuclides/elements. The high-affinity radionuclides/elements have sufficiently high sorption coefficients so that even the higher performance goals and confidence levels should be met with the minimum K_ds derived from this activity. The data obtained in the pure-mineral experiments may be useful in modeling retardation in fracture-flow scenarios. The sorption coefficients obtained for the key radionuclides/elements on pure mineral separates could be converted to K_as for use in modeling transport during fracture flow.

3.2 Batch Sorption Measurements as a Function of Sorbing Element Concentrations (Isotherms) (SCP Activity 8.3.1.3.4.1.2)

3.2.1 General Approach

This activity will focus primarily on the determination of sorption coefficients for the intermediate- and low-sorption-affinity elements (e.g., Pu, Ni, U, Np, and Se) as a function of radionuclide concentration. The approach will be to select a representative sample of each of the major rock types in Yucca Mountain and carry out batch sorption experiments using several end-member ground water compositions and a range of radionuclide concentrations.

3.2.1.1 Key Parameters to be Measured

The key parameters that will be measured in these tests are:

- isotherms for the low- to intermediate-affinity radionuclides on representative whole-rock samples

The following parameters will be obtained as part of this activity either by another activity in the LANL-YMP or by a commercial laboratory:

- effluent solution compositions

- rock composition before and after sorption experiment

- cation exchange capacities of rock samples used in experiments

- surface areas for rock samples used in sorption experiments

- mineralogy of the rock samples used in the experiment

3.2.1.2 Experimental Conditions

The experimental conditions for these measurements will be:

- ambient laboratory temperature

- atmosphere appropriate to the pH required

- 1 or more radionuclides in each experiment

- ground waters from Yucca Mountain

- crushed samples of rocks from Yucca Mountain

- several radionuclide concentrations up to solubility limits

3.2.1.3 Test Matrix

This activity will focus on the determination of representative isotherms for low- to intermediate-affinity radionuclides including Pu, Ni, U, Np, and Se. Isotherms may also be determined for C, I, or Tc if pure mineral experiments provide an indication of positive K_d values for any of these radionuclides. Experiments will be carried out with representative samples of each of the four major rock types in Yucca Mountain and each of the three major end-member ground-water compositions (DOE, 1988). The four major rock types to be utilized are zeolitic, vitric, and devitrified tuff from the Calico Hills unit and tuff from the Topopah Spring Member. The groundwaters to be utilized will be representative of the waters at Yucca Mountain: UE-25p#1, USW H-3, and J-13. In addition, the experiments will be carried out with several different radionuclide concentrations. Two separate sets of experiments will be conducted: one with a mixed spike of U, Np and Se, and the other with Pu, U and Ni. The minimum number of separate experiments in this activity will total at least 144.

3.2.2 Summary of Test and Analysis Methods

3.2.2.1 Test and Analysis Methods

The test and analysis methods used in this activity will be the same as those described in Section 3.1.2.1.

3.2.2.2 Tolerance, Accuracy, Precision and Expected Range of Results

3.2.2.2.1 Tolerance, Accuracy, and Precision

The accuracy and precision required in these tests will be greater than those required for the high-affinity radionuclides because the measured sorption coefficient values will be used directly in performance assessment calculations, unlike the minimum values used for the high-affinity radionuclides. Although the performance goals listed for these radionuclides in the SCP (Table 8.3.5.13-9) are minimal, more recent performance assessment calculations have pointed to the need for more stringent performance goals for these radionuclides (Barnard et al., 1992). The implication is that a high degree of accuracy and precision will eventually be needed to evaluate properly the performance of the site with respect to the low- and intermediate-affinity radionuclides. As an estimate, the analytical errors associated with the sorption coefficient determinations should probably be less than 25% of the measured values for Pu, Ni, U, Np, and Se.

3.2.2.2.2 Expected Range of Results

The available data on sorption coefficients for the key radionuclides on rocks from Yucca Mountain (e.g., Thomas, 1987) suggest the values for the Pu sorption coefficient will be in the range of 50-10,000 ml/g; for Ni, 50-500 ml/g; for U, 0-25 ml/g; for Np, 0-20 ml/g; and for Se, 0-35 ml/g.

3.2.3 Technical Procedures to be Used

The technical procedures to be used in this activity are described in Section 3.1.3 and listed in the attachment.

3.2.4 Equipment List

The equipment to be used in this activity is listed in Section 3.1.4

3.2.5 Test and Analysis Results

3.2.5.1 Data Reduction and Analysis Techniques

The data reduction and analysis techniques used in this activity will be essentially the same as those listed in Section 3.1.5.1. However, the data will also be analyzed in terms of isotherm fitting parameters as discussed in Section 3.6.

3.2.5.2 Representativeness of Tests and Analyses

These tests and analyses will be representative to the extent that the shapes of the isotherms obtained are representative of the isotherm shapes appropriate to the sorption behavior of low- to intermediate-affinity radionuclides in the far field of the potential repository.

3.2.5.3 Limitations and Uncertainties of Results

The limitations and uncertainties of data obtained by this activity are similar to those discussed in Section 3.1.5.3.

3.2.5.4 Relationship to Performance Goals and Confidence Levels

Although the performance goals and confidence levels set for sorption coefficients for the key radionuclides in the Site Characterization Plan (e.g., SCP Table 8.3.5.13-9) should be easy to meet, more recent site-suitability calculations have pointed to the need for more stringent performance goals for these coefficients (Barnard et al., 1992). Because the results of the new calculations have not yet been fully evaluated by the project, new performance goals and confidence levels for sorption coefficients for the low to intermediate affinity radionuclides have not yet been defined.

3.3 Batch Sorption Measurements as a Function of Ground Water Composition (SCP Activity 8.3.1.3.4.1.3)

3.3.1 General Approach

This activity will focus primarily on the influence of variations in ground-water composition on the sorption coefficients of the low- to intermediate-affinity radionuclides in whole-rock samples from Yucca Mountain. Representative whole-rock samples will be selected for each of the major hydrologic units at Yucca Mountain, based on the pure mineral studies described in Section 3.5 and other available data. Representative ground-water samples will be chosen on the basis of models and experimental data developed in the Ground Water Characterization and Modeling Investigation (SCP 8.3.1.3.1) and study 8.3.4.2.4.1 "Chemistry and Mineralogy of the Near Field Environment." Values for those ground-water compositional parameters that have the greatest impact on the sorption behavior of these radionuclides will be varied over the ranges anticipated in the Yucca Mountain flow system.

3.3.1.1 Key parameters to be measured

The main parameters to be measured in this activity will be:

- sorption coefficients for the low- to intermediate-affinity elements in representative rock types from Yucca Mountain as a function of those ground water compositional parameters that have the greatest impact on the concentration of these elements.

The following parameters will be obtained as part of this activity either by another activity in the LANL-YMP or by a commercial laboratory:

- effluent solution compositions

- rock composition before and after the sorption experiment

- cation exchange capacities of rock samples used in experiments

- surface areas for rock samples used in sorption experiments

- mineralogy of the rock samples used in the experiment.

3.3.1.2 Experimental Conditions

The experimental conditions for these measurements will be:

- temperatures of 25°, 60°, and 90° C

- atmosphere with P_{CO2} appropriate to the pH required

- 1 or more radionuclides in each experiment

- ground waters from Yucca Mountain

- crushed rock samples from Yucca Mountain

- radionuclide concentrations representative of the source term compositions.

3.3.1.3 Test Matrix

This activity will focus on the determination of the effects of variations in key solution parameters on the sorption behavior of the low- to intermediate-affinity elements. Experiments will be carried out with representative whole-rock samples from each of the main hydrologic units defined in Yucca Mountain and with each of the three end-member, ground-water compositions. The key parameters to be varied will be identified in the pure-mineral activity (Section 3.5). Between one and three key parameters will be varied over the ranges of values expected within the Yucca Mountain ground-water flow system. There will be two separate sets of experiments: one with U, Np and Se, and the other with Pu, U, and Ni. The total number of experiments will be on the order of ~600.

3.3.2 Summary of Test and Analysis Methods

3.3.2.1 Test and Analysis Methods

The test and analysis methods used in this activity will be the same as those described in Section 3.1.2.1.

3.3.2.2 Tolerance, Accuracy, Precision, and Expected Range of Results

3.3.2.2.1 Tolerance, Accuracy, and Precision

The tolerance, accuracy, and precision required of these tests and analyses will be the same as those described in Section 3.2.2.2.1.

3.3.2.2.2 Expected Range of Results

The ranges of expected values for the sorption coefficients of the low- to intermediate-affinity radionuclides will be similar to those given in section 3.2.2.2.2.

3.3.3 Technical Procedures to be Used

The technical procedures to be used in this activity will be the same as those described in Section 3.1.3 and listed in the attachment.

3.3.4 Equipment List

The equipment to be used in this activity will be the same as that listed in Section 3.1.4.

3.3.5 Test and Analysis Results

3.3.5.1 Data Reduction and Analysis Techniques

The data reduction and analysis techniques will be essentially the same as those discussed in Section 3.1.5.1. However, the results obtained will be closely compared for consistency to the results obtained in the pure mineral studies (Section 3.5).

3.3.5.2 Representativeness of Tests and Analyses

These tests and analyses will be representative to the extent that (1) the rock samples selected from each of the main hydrologic units are representative, (2) the end-member ground-water compositions are representative, and (3) the key solution parameters chosen for each radionuclide are representative.

3.3.5.3 Limitations and Uncertainties of Results

The limitations and uncertainties of data obtained in this activity are similar to those discussed in Section 3.1.5.3.

3.3.5.4 Relationship to Performance Goals and Confidence Levels

The relationship of these tests and analyses to performance goals and confidence levels are the same as those discussed in Section 3.2.5.4

3.4 Batch Sorption Measurements on Particulates and Colloids (SCP Activity 8.3.1.3.3.1.4)

3.4.1 General Approach

The goal of this activity is to determine the degree to which the key radionuclides may sorb onto colloids and particulates that may be present in ground waters along potential transport pathways to the accessible environment. This effort will interact with others described under SCP Investigations 8.3.1.3.5 (Solubility) and 8.3.1.3.6 (Dynamic Transport) and with SCP Study 8.3.1.3.4.2 (Biological Sorption and Transport).

SCP Activity 8.3.1.3.6.1.5 (Filtration) will examine the transport and filtration of colloids and particulates through porous matrices and through fractured tuff columns. The results of these transport experiments will determine the scope of this sorption activity. If colloid transport is found to be a viable transport mechanism in Yucca Mountain, then the experiments discussed in the remainder of this section will be carried out. These experiments will also be guided by the identity and concentrations of colloidal and particulate material found to occur in the Yucca Mountain ground-water flow system and by estimates of what K_d values would lead to significant transport of the key radionuclides on the colloids and particulates found. Data generated in this activity will not only support SCP Investigation 8.3.1.3.6 but will also contribute to the sorption database and may be used in support of performance assessment calculations.

3.4.1.1 Key Parameters to be Measured

The main parameters to be measured in this activity will be:

- sorption coefficients for the key radionuclides on colloid and/or particulate samples from the Yucca Mountain ground water flow system.

The following parameters will be obtained as part of this activity, either by another activity in the LANL-YMP or by a commercial laboratory, assuming sufficient sample material is available:

- effluent solution compositions

- colloid/particulate composition before and after sorption experiment

- cation exchange capacities of colloid/particulate samples used in experiments

- surface areas for samples used in sorption experiments

- mineralogy of the samples used in the experiment

3.4.1.2 Experimental Conditions

The experimental conditions for these measurements will be:

- the ambient laboratory temperature

- atmosphere with P_{CO_2} appropriate to the pH required

- 1 or more radionuclides in each experiment

- ground waters from Yucca Mountain

- colloid/particulate samples from Yucca Mountain

- radionuclide concentrations obtained from the study on Integrated Radionuclide Release; Tests and Models (SCP 8.3.4.2).

3.4.1.3 Test Matrix

The test matrix will be determined by the results of the colloid filtration study (SCP 8.3.1.3.6.1.5). If colloids/particulates are found to be a viable transport mechanism for the key radionuclides, attempts will be made to obtain colloid/particulate samples from the Yucca Mountain ground water flow system and batch sorption experiments will be carried out on those colloid/particulate samples that may become available. The total number of tests will likely be less than 30.

3.4.2 Summary of Test and Analysis Methods

3.4.2.1 Test and Analysis Methods

The test methods for this activity will consist of two separate subactivities (1) sampling of colloid/particulate material from the Yucca Mountain ground-water flow system and (2) batch sorption experiments on the colloid/particulate materials obtained in the field. Sampling of colloid and/or particulate material will be attempted by filtering ground water pumped from various wells on Yucca Mountain. Filters with 0.05-micron pore size will be used.

Because the samples obtained will likely be small in mass, batch testing over the range of radionuclide concentrations, ground-water compositions, and other variables may not be practical or necessary. Based on the results of the studies described above, the variables and conditions showing the greatest influence on sorption of each of the key radionuclides can be selected for study in order to set up a smaller test matrix.

The experimental methods to be used in this activity for batch sorption measurements are those described in Section 3.1.2.1.

3.4.2.2 Tolerance, Accuracy, Precision and Expected Range of Results

3.4.2.2.1 Tolerance, Accuracy, and Precision

The tolerance, accuracy, and precision required in these tests are similar to those discussed in Section 3.2.2.2.1. Note that actual measured values will be required for the high-affinity radionuclides as well as the other radionuclides.

3.4.2.2.2 Expected Range of Results

For the colloid-sampling subactivity, we expect to recover silica and iron colloids with or without minor amounts of clays. The quantity of colloidal material recovered is expected to be small.

The results expected for the batch sorption experiments on colloidal samples include: (1) high K_a values on both silica and iron colloids for the high-affinity elements and (2) relativity of high K_a values (50-200 ml/g) for intermediate-to low-affinity elements on iron colloids and low K_a values for these elements on silica colloids.

3.4.3 Technical Procedures to be Used

The technical procedures to be used in this activity will be the same as those described in Section 3.1.3 and listed in the attachment.

3.4.4 Equipment List

The equipment to be used in this activity will be the same as that listed in Section 3.1.4.

3.4.5 Test and Analysis Results

3.4.5.1 Data Reduction and Analysis Techniques

The data reduction and analysis techniques will be essentially the same as those discussed in Section 3.1.5.1. However, the results obtained will be closely evaluated for consistency with the results obtained in the pure mineral studies (Section 3.1).

3.4.5.2 Representativeness of Tests and Analyses

These tests and analyses will be representative to the extent that (1) the colloid/particulate samples used in the batch sorption experiments are representative of the intervals pumped to obtain the samples, and (2) the key solution parameters and concentrations chosen for the experiments on the key radionuclides are representative of the conditions in the environment of a potential repository at Yucca Mountain. Proving that colloid/particulate materials sampled from deep wells are representative of in-situ materials in the interval(s) pumped has always been problematic.

3.4.5.3 Limitations and Uncertainties of Results

In addition to the limitations and uncertainties associated with batch sorption tests discussed in Section 3.1.5.3, these tests are subject to sampling problems (e.g., representativeness, etc.) and problems in experimental determination of sorption coefficients on small amounts of material. These problems can lead to large measurement errors. Until the samples are in hand, the magnitude of the possible uncertainties cannot be reliably estimated.

3.4.5.4 Relationship to Performance Goals and Confidence Levels

The relationship of these tests and analyses to performance goals and confidence levels was not clearly spelled out in the Site Characterization Plan. However, recent modeling efforts (Barnard et al., 1992) suggest accurate evaluation of radionuclide transport along fast-flow paths (e.g., fractures, bedded ash layers) may be critical to proper assessment of the performance of the site. In these fast-flow scenarios, colloid/particulate transport may be a significant transport mechanism. If true, this suggests a high degree of confidence may be required for sorption coefficients of the key radionuclides on colloids and particulates.

3.5 Statistical Analysis of Sorption Data (SCP Activity 8.3.1.3.4.1.5)

3.5.1 General Approach

The goal of this activity is to produce state-of-the-art statistical analysis techniques and experimental designs as they relate to the sorption task. A proper statistical analysis and experimental design effort is essential to establish the quality of the data and to ensure sound data inferences. Experimental designs will be produced that minimize the number of tests required to assess the influence of mineralogy, particle sizes, concentrations, and ground waters in Activities 3.2., 3.3, and 3.4 of this Study Plan. These designs, while minimizing the number of experimental tests needed will not result in a great loss of information. Regression diagnostics and regression techniques will be used to assess the quality of the selected isotherms of Activity 3.2. Error analysis on the regression fits will be done to reveal the uncertainties in the chosen isotherm.

3.5.1.1 Key Parameters to be Measured

In order to ensure proper statistical design, the effort involving statistics must begin with developing the test matrices in Activities 3.2, 3.3, and 3.4.

The parameters to be derived from statistical analysis of sorption data include the following:

- correlations of sorption isotherms with numerous variables,
- bounds on sorption ratios under various conditions,

- estimated errors on isotherm fits, and
- evaluation of experimental designs for experiments in Activities 3.2, 3.3, and 3.4.

3.5.1.2 Experimental Conditions

There are no laboratory experiments associated with this activity.

3.5.1.3 Test Matrix

The test matrix for this task will include the following parameters:

•Sample/ID: identification of the sample number of the rock used for the sorption measurements.

•Particle Size: the range of particle sizes used for the sorption measurements.

•Temperature: the temperature conditions during the batch sorption measurements.

•Atmosphere: the atmospheric composition under which the measurements were made.

•pH: the pH of the aqueous phase of batch experiments at the completion of the experiments.

•Comment: general comments on experimental conditions not included in the data fields.

•Element: the element analyzed in the experiments.

•Concentration: the absolute concentration in Molarity (M) of the sorbing element in the starting tracer solution.

•Sorption/Time/Days: the contact time of the sorption experiment in days.

•Sorption/Rd1 and Sorption/Rd2: the batch sorption ratios of duplicate measurements expressed in units of ml/g.

•Desorption/Time/Days: the contact time of the desorption experiments in days.

•Desorption/Rd1 and Desorption/Rd2: the batch desorption ratios of duplicate measurements expressed in units of ml/g.

•References: the published reference for the batch sorption information.

Initial investigations will concentrate on the elements barium, cesium, strontium, cerium, and europium and will consider the effects of temperature, particle size, mineralogy, waste-element concentration, and sorption time. These elements and variables have been chosen for initial analysis because they have the greatest number of data points available and because, as discussed in Thomas (1987), they exhibit the simplest and most easily understood patterns of sorption behavior. The next series of investigations will include effects of ground-water composition on sorption of these same elements. The analyses will be extended to include the key actinide elements when sufficient data have been generated in the previously described sorption activities.

3.5.2 Summary of Test and Analysis Methods

3.5.2.1 Test and Analysis Methods

Regression techniques, including regression diagnostics, will be used to investigate factors that may significantly influence sorption isotherms. The SAS and the BMDP statistical packages will be used for these analyses. The analyses will be done on VAX 11/780 and SUN 3/110 computers. The computer package of SOSI, data base management (sorting), and DATATRIEVE, a data management package, will also be used. Sorption data are entered into the DATATRIEVE data base management system on a VAX 11/780.

The sorption data set, stored in DATATRIEVE as explained above, will be evaluated and edited to provide the highest quality data before statistical analysis. The data editing is accomplished using procedure KDALL2 in DATATRIEVE on a VAX 11/780. The data set used for this study can be reproduced at any time in the future by running the procedure KDALL2. The sorption data base will be refined to remove three sources of data variance: (1) sorption measurements made during the development of experimental techniques, (2) particle-size effect, and (3) semiquantitative measurements of the mineralogical composition of rock samples using XRD techniques.

3.5.2.2 Tolerance, Accuracy, Precision and Expected Range of Results

3.5.2.2.1 Tolerance, Accuracy and Precision

This task will determine the appropriateness of the fitted isotherm, including an assessment of those data points that unduly influence the regression fits. The design aspect of this task should ensure reasonable estimated isotherms. Error estimates for the fitted isotherms will be given in terms of confidence intervals on predictions. Thus, the true uncertainty in the sorption isotherm will be reflected.

3.5.2.2.2 Expected Range of Results

Statistical analysis should allow identification of those physical and chemical parameters that most influence sorption ratios. This will allow the experimental design to be optimized so that the best estimates concerning sorption ratios as a function of mineralogy, concentration, and other test conditions can be derived. Optimal design of batch and isotherm experiments will reduce the uncertainty in these parameters. Regression diagnostics will delineate points or ranges of points where more experimentation is needed.

3.5.3 Technical Procedures to be Used

Technical procedures are described in the documentation that accompanies the software

3.5.4 Equipment List

Standard computer capabilities are required. A VAX 11/780 and a SUN 3/140 are used routinely.

3.5.5 Test and Analysis Results

3.5.5.1 Data Reduction and Analysis Techniques

This topic is addressed in Section 3.5.2.

3.5.5.2 Representativeness of Tests and Analyses

The statistical tests and analyses to be performed in this activity will be representative of conditions at Yucca Mountain to the extent that the parameters evaluated and the values for these parameters are representative of those conditions.

3.5.5.3 Limitations and Uncertainty of Results

The main limitations on the statistical analyses to be performed in this activity are the availability of sufficient data points for meaningful analysis. The greater the number of data points available for a given parameter, the less uncertainty there will be in the analysis for this parameter.

3.5.5.4 Relationship to Performance Goals and Confidence Levels

The statistical analysis to be performed in this activity will provide statistical parameters that will allow evaluation of the degree to which the experimental data obtained in Activities 3.2 to 3.4 achieve the performance goals. Among the statistical parameters to be derived in this activity will be confidence levels for the sorption coefficient values generated in this task.

3.6 Development of Sorption Models (SCP Study 8.3.1.3.4.3)

3.6.1 General Approach

The goal of this activity is to evaluate interactively the data obtained in the other activities of this investigation and to derive an appropriate set of sorption coefficients for use in performance assessment calculations. This activity will interact with the experimental activities in this investigation to provide feedback on the adequacy of the data obtained and provide guidelines for prioritization of the experimental program. The evaluation and modeling of the data obtained in the experimental program will include (1) critical comparison of results on whole-rock and pure mineral experiments with literature data on similar systems, (2) evaluation of experimental and theoretical factors responsible for measured values of sorption coefficients in whole-rock and pure-mineral experiments, and (3) isotherm modeling.

3.6.1.1 Key Parameters to be Measured

No experimental data will be obtained in this activity. However, the following parameters will be calculated or otherwise derived:

- minimum sorption coefficients for the high-affinity radionuclides in each of the hydrologic units defined at Yucca Mountain

- probability distributions for sorption coefficients of the low- to intermediate-affinity radionuclides in each of the major hydrologic units defined at Yucca Mountain

- Isotherms for each of the low- to intermediate-affinity elements on representative whole-rock/ground-water samples from each of the hydrologic units identified at Yucca Mountain.

- estimates of sorption coefficients for the key radionuclides on fracture-lining-mineral phases

3.6.1.2 Experimental Conditions

Because no experiments will be conducted in this activity, no experimental conditions need be defined.

3.6.1.3 Test Matrix

The test matrix for this activity will include the derivation, through measurement or calculation, of the following:

(1) Minimum sorption coefficients for the following elements in each of the major hydrologic units in Yucca Mountain:

Am, Cm, Cs, Nb, Ra, Sn, Th, and Zr,

(2) Isotherms for the following elements on representative whole rock samples from each of the hydrologic units in Yucca Mountain:

Pu, U, Np, Ni, and Se,

(3) Probability distributions for sorption coefficients for each of the following elements in each of the hydrologic units in Yucca Mountain:

Pu, U, Np, Ni, and Se.

(4) Estimates of sorption coefficients for each of the key radionuclides on selected mineral phases identified in fracture at Yucca Mountain.

3.6.2 Summary of Test and Analysis Methods

3.6.2.1 Test and Analysis Methods

This activity is concerned with data analysis and will not include experiments.

3.6.2.2 Tolerance, Accuracy, and Precision and Expected Range of Results

3.6.2.2.1 Tolerance Accuracy and Precision

Because the tolerance, accuracy, and precision required for sorption coefficients are yet to be determined through performance assessment calculations, it is difficult to assign requirements for tolerance, accuracy, and precision to the results of this activity at the present time.

3.6.2.2.2 Expected Range of Results

The range of minimum K_ds measured for the high-affinity radionuclides is expected to be from 100 to over 10,000 ml/g, depending on the radionuclide and the sample selected as representing the least sorptive rock in a given hydrologic unit. The range of values expected for isotherm parameters is more difficult to quantify. However, isotherms for the low- to intermediate-affinity radionuclides appear to fit the Langmuir equation within experimental error on the basis of available data (Fuentes et al., 1987).

The range of probability distributions expected for the low- to intermediate-affinity radionuclides cannot be quantified at the present time.

The sorption coefficients expected for the pure-mineral separates have a wide range. For the high-affinity radionuclides, the sorption coefficients will be >1000 ml/g for nearly all the minerals to be studied. Only quartz may have K_ds smaller than this. For the low- to intermediate-affinity radionuclides, the K_ds expected will vary greatly, depending on the mineral phase and the radionuclide. Radionuclides of the elements U, Np, Se, and Ni will likely show large affinities for iron and possibly manganese oxides/oxyhydroxides but small affinities for silicates and aluminosilicates. Hematite is apparently the dominant Fe-oxide phase in Yucca Mountain tuffs. For the no-affinity radionuclides, only hematite may show a small affinity for Tc and C under favorable conditions (i.e., low pH).

3.6.3 Technical Procedures to be Used

No detailed technical procedures will be developed for this activity.

3.6.4 Equipment List

No analytical equipment will be used in this activity.

3.6.5 Test and Analysis Results

3.6.5.1 Data Reduction and Analysis Techniques

3.6.5.1.1 Derivation of minimum K_ds for each high-affinity radionuclide in each hydrologic unit.

The technique used to derive minimum K_ds for each of the high-affinity radionuclides involves the identification of minimum-sorbing, major mineral phases, identification of the most active water composition for each radionuclide in contact with these mineral phases, radionuclide concentrations in solution near the solubility limits, and data on the detailed mineralogy of the hydrologic units defined at Yucca Mountain. Using this information, evaluations will be made to determine whether the least-sorptive rock composition in a given hydrologic unit, inferred on the basis of the pure-mineral studies, has a K_d for each high-affinity radionuclide that is above the minimum K_d required to meet the regulations for releases of these radionuclides to the accessible environment. Whole-rock experiments will be carried out in Activity 3.1.1 to test the minimum K_d inferred for minimum-sorbing rock compositions on the basis of the pure-mineral experiments. If the K_d measured in the chosen rock exceeds the minimum K_d required to meet the regulations for releases to the accessible environment, the experiments for this radionuclide will be ended. If the minimum K_d measured for a given radionuclide is smaller than that required by performance assessment calculations, this radionuclide will be assigned to the low- to intermediate-affinity group in the given hydrologic unit. The required minimum K_ds should be derived through preliminary performance assessment calculations (e.g., Barnard et al., 1992).

3.6.5.1.2 Derivation of probability distributions for each low- to intermediate-affinity radionuclide in each hydrologic unit.

The technique used to derive probability distributions for the low- to intermediate-affinity radionuclides will involve identification, on the basis of pure-mineral experiments, of representative rock compositions for each hydrologic unit defined at Yucca Mountain, identification of the solution parameters that dominate the sorption behavior of each of the low- to intermediate-affinity radionuclides, and identification of representative background water compositions. Once these parameters are identified, experiments will be carried out with the representative whole-rock compositions, water compositions, and radionuclide concentrations, varying the value of dominant solution parameters (as described in Section 3.3.1). The sorption coefficient values derived from these experiments will be combined with distributions of the values of the dominant solution parameter(s) expected in a given hydrologic unit as derived in the Ground Water Characterization and Modeling Investigation (SCP 8.3.1.3.1), to obtain probability distributions for the sorption coefficients for each of the low- to intermediate-affinity radionuclides in each of the hydrologic units. Any additional data that may be available on sorption coefficients for any of the low- to intermediate-affinity radionuclides on rock samples from any of the hydrologic units at Yucca Mountain (e.g., Thomas, 1987) will be used to test the derived probability distributions.

This approach could also be applied to the no-affinity radionuclides if any minerals are identified in the pure mineral experiments that have a significant affinity for these radionuclides.

3.6.5.1.3 Derivation of isotherm parameters for low to intermediate affinity radionuclides.

Isotherm experiments will be performed as described in Sections 3.2.1 and 3.2.1.3. Isotherm parameters will be derived for each of the low to intermediate affinity radionuclides using techniques described in Fuentes et al. (1987).

3.6.5.1.4 Derivation of pure mineral K_as for fractures.

Sorption coefficients will be obtained for the low, intermediate, and high affinity radionuclides on selected pure-mineral phases as described in Section 3.5. Surface areas measured for these pure-mineral separates will be used to derive K_as. These sorption coefficients could be used to derive sorption coefficients appropriate for fracture-flow scenarios using detailed mineral distributions in fractures in Yucca Mountain.

3.6.5.2 Representativeness of Tests and Analyses

The representativeness of the sorption coefficients derived by the techniques discussed above is largely dependent on the representativeness of the samples used in the experimental activities in this investigation.

3.6.5.3 Limitations and Uncertainties of Results

The limitations and uncertainties associated with the sorption coefficients and distributions derived in this activity have been discussed in Sections 2.2.3, and in the limitations and uncertainties sections in each of the experimental activity discussions.

3.6.5.4 Relationship to Performance Goals and Confidence Levels

The relationship of the results of this activity to performance goals and confidence levels has been discussed in Sections 2.2.3, 3.1.5.4, and 3.2.5.5.

4.0 APPLICATION OF RESULTS

4.1 Use in Performance Assessment Calculations

The sorption coefficients derived in this investigation will be used in addressing Information Needs 1.1.1, 1.1.3, 1.1.4, and 1.1.5 (see SCP Table 8.3.5.13-17). These information needs will support the calculation of system performance in relation to Issue 1.1 (e.g., Barnard et al., 1992).

The data obtained in this investigation will also be used to address the NRC siting criteria as discussed in Section 8.3.5.17 of the Site Characterization Plan.

4.2 Use in Other Site Characterization Activities

The data and models generated in this study will also be used in the dynamic transport investigation (SCP 8.3.1.3.6), the retardation sensitivity investigation (SCP 8.3.1.3.7), and reactive tracer field test activities (SCP 8.3.1.2.3.1.7 and 8.3.1.2.3.1.8). In the dynamic transport investigation, the data and models will be used primarily to interpret column transport experiments. Because the column experiments involve a number of variables (e.g., flow rate, dispersion, diffusion, and sorption kinetics) in addition to the equilibrium sorption coefficient, knowledge of the value of this coefficient for the particular radionuclide used in a given set of experiments is essential to the proper interpretation of the experiments. The retardation sensitivity analysis study will use the sorption data, models, and statistical methods to (1) assess, in a three-dimensional representation, the significance and relative importance of the various physical and geochemical processes that will be involved in radionuclide transport in Yucca Mountain, (2) examine and define the limits of applicability of laboratory-measured sorption ratios to the field situation at Yucca Mountain, (3) evaluate the applicability of sorption ratios obtained under saturated conditions in laboratory experiments to the transport of radionuclides under unsaturated conditions, and (4) assist in the future design of sorption experiments. The reactive tracer field tests activity (SCP 8.3.1.2.3.1.7) may use the sorption data and models to select appropriate tracers.

The EQ3/6 geochemical modeling code will have a sorption-modeling option that may be used to model the sorption of radionuclides in the near field of the proposed repository (Viani, 1988). In order to use this option, experimental data will be required on the characteristics of sorbing substrates present within Yucca Mountain and on sorption reaction parameters involving the appropriate solutions and substrates. These types of data will be generated in this task although not specifically for the EQ3/6 modeling effort.

The data obtained in this investigation will also be used in support of column transport studies in the dynamic transport investigation (SCP 8.3.1.3.6), biological sorption study (SCP 8.3.1.3.4.2), and the retardation sensitivity investigation (SCP 8.3.1.3.7). The retardation sensitivity investigation will use the sorption data to assess the significance and relative importance of physical and chemical processes involved in radionuclide transport.

5.0 MILESTONES AND SCHEDULE

This work will result in the production of the milestone reports illustrated in Figure 1 and listed in Table 6. The study numbers and titles corresponding to the time lines are shown on the left of the figure. Points shown on the time lines represent major events or important milestones associated with the studies. Solid lines represent study durations. Dashed lines represent interfaces. The data input and output at the interfaces are shown by circles. Ticks on the time scale represent 1-yr. increments.

The points on the time lines and the data input and output at the interfaces are described in Table 4.

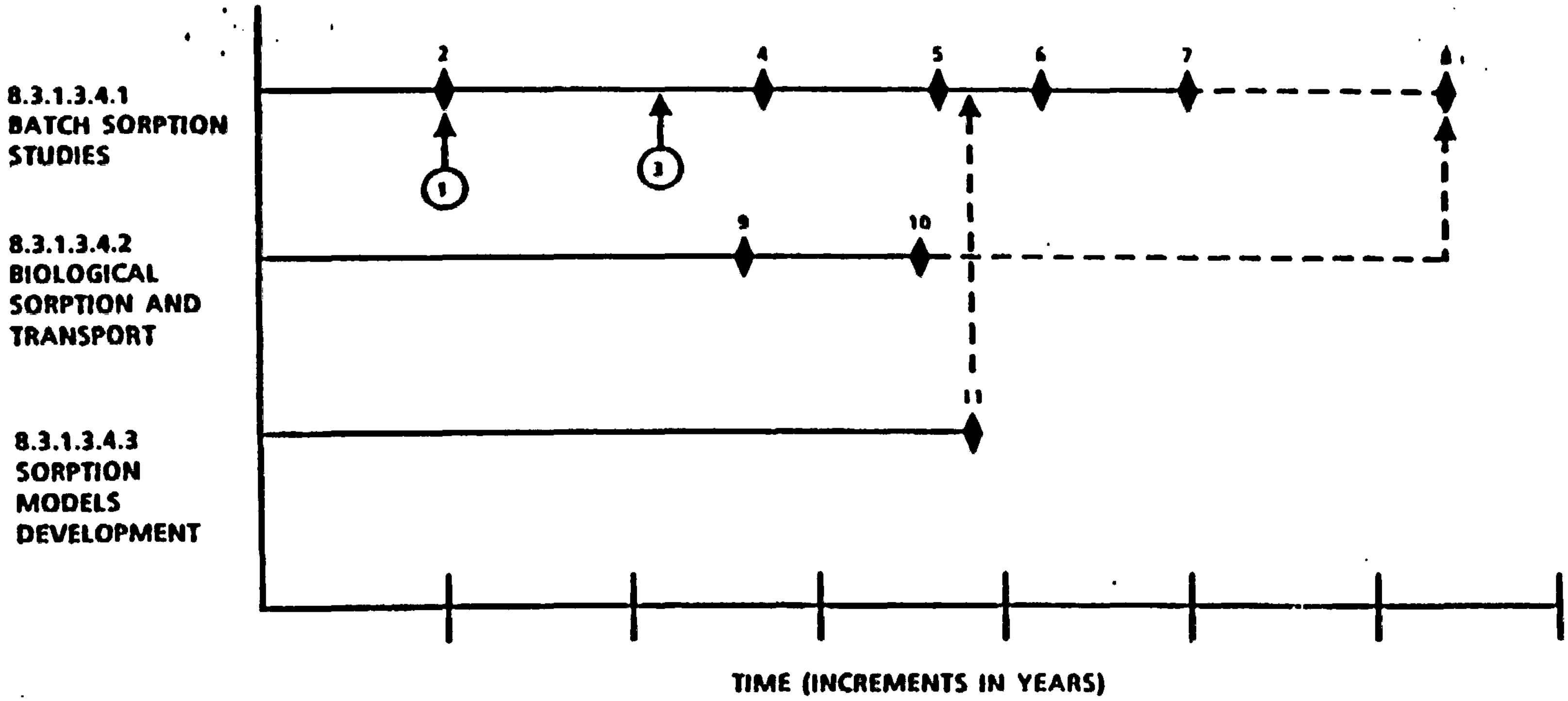

Figure 1. Milestone Schedule

TABLE 3

DESCRIPTION OF MILESTONES

Point Number	Description
1	Milestone R505. Summary report available on effects of ground-water composition on sorption. A large part of the experimental work for this study assumes a groundwater composition for the unsaturated zone. However, before the experimental data are considered finalized, this ground-water composition must be confirmed by data from SCP Investigation 8.3.1.2.2.
2	Data on the potential for particulate transport from SCP Investigation 8.3.1.3.6.
3	Milestone R382. Report available on sorption on particulates.
4	Milestone M315. Final report available on sorption isotherms.
5	Milestone R384. Report available on probability distributions for dominant ground water parameters.
6	Milestone M376. Final sorption report available. The report completes this study as well as the investigation. The data generated from this investigation will be combined with the data from SCP Investigations 8.3.1.3.4 through 8.3.1.3.7 to provide the retardation factors needed for radionuclide transport calculations for the range of conditions at Yucca Mountain, both nominal and disturbed.
7	Milestone Q002. Report available on the summary of results defining radionuclide retardation at Yucca Mountain. This higher-level report summarizes the results of SCP Investigations 8.3.1.3.4 through 8.3.1.3.7 and will be compiled as part of SCP Study 8.3.1.3.7.1.
8	Milestone P378. Report available on the sorption of actinides by micro-organisms indigenous to Yucca Mountain.
9	Milestone P382. Final report available on the magnitude of microbial activity on retardation and transport of nuclear waste elements at Yucca Mountain.
10	Milestone R385. Final progress report available on sorption modeling. This report completes the study. The results will feed SCP Study 8.3.1.3.4.1.

11 Milestone NEW. Final report on sorption studies.

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Technical Procedures
for Study Plan 8.3.1.3.4.1 and 8.3.1.3.4.3
"Batch Sorption Studies and Development of Sorption Models"

Reference	Title of Technical Procedure
TWS-INC-DP-05	Sorption, Desorption Ratio Determination of Geologic Materials by a Batch Method
TWS-INC-DP-26	Preparation of Aqueous Solutions for Analysis, Use in Experiments, or as Standards for Water Sample Analysis
TWS-INC-DP-27	Elemental Concentration Determination by Direct-Current-Plasma-Atomic-Emission-Spectroscopy
TWS-INC-DP-35	pH Measurement
TWS-INC-DP-62	Bulk NTS Well Water Samples
TWS-INC-DP-63	Preparation of NTS Core Samples for Crushed Rock Experiments
TWS-INC-DP-78	The Preparation of Solutions of Pure Oxidation States of Neptunium, Plutonium, and Americium
TWS-INC-DP-83	Storage and handling of Solid Samples
TWS-ESS-DP-16	Siemens X-Ray Diffraction Procedure
TWS-ESS-DP-24	Calibration and Alignment of the Siemens Diffractometers
TWS-ESS-DP-07	Microprobe Operating Procedure
TWS-ESS-DP-110	Zeolite Purification/Separation Procedure
TWS-ESS-DP-112	Operating Instructions for International Scientific Instruments Model DS-130 Scanning Electron Microscope and Tracor Northern Series II X-Ray Analyzer for Evaluation of YMP Geologic Materials
TWS-ESS-DP-116	Quantitative X-Ray Diffraction Data Reduction Procedure
TWS-ESS-DP-122	Preparation of Electron Microprobe Standard Mounts
TWS-ESS-DP-125	Certification of Standards for Microanalysis
TWS-HSE12-DP-302	Cation and Anion Exchange

Enclosure 2

SCA OPEN ITEMS ANALYSIS

Comment 25

The section in Study Plan 8.3.1.3.4.1/3, "Batch Sorption Studies and Development of Sorption Models," that addresses Comment 25 is Section 3.3.1, General Approach.

Comment 96

Comment 96 will be addressed in the Study Plan 8.3.1.3.6.1, "Dynamic Transport Column Experiments." In this study plan the sorption coefficients obtained using both sorption experiments will be validated under various conditions, including unsaturated and saturated flow. Section 4.0, *Application of Results*, of the "Batch Sorption Studies and Development of Sorption Models" study plan, 8.3.1.4.1/3, serves as the link to the columns' experiments; specifically, Section 4.2, Use in Other Site Characterization Activities.

Enclosure 3