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Study Plan Title DIFFUSION

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DIFFUSION

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ABSTRACT

This study will measure the diffusivity and kinetics of sorption in a purely diffusive system (i.e., no advection). This study supports Activity 8.3.1.3.6.1.4, Fractured Tuff Column Studies, and overlaps with Activity 8.3.1.3.6.1.2, Mass Transfer Kinetics, by providing confirmatory results. The measured diffusivities will be used by Investigation 8.3.1.3.7, Studies to Provide the Information Required on Radionuclide Retardation by All Processes along Flow Paths to the Accessible Environment, and Issue 1.1, Will the Mined Geologic Disposal System Meet the System Performance Objective for Limiting Radionuclide Releases to the Accessible Environment as Required by 10 CFR 60.112 and 40 CFR 191.13 (SCP Section 8.3.5.13). Kinetic rate constants and effective diffusivities will be measured from the uptake of radionuclides on intact tuff as a function of time.

The work scope of the Diffusion Study of the Yucca Mountain Site Characterization Project consists of performing transport experiments with solid tuff (in the absence of advection) under various degrees of saturation. The first type of diffusion experiment planned consists of a cell with two chambers containing groundwater. The chambers are separated by a slab of tuff. Radionuclides of interest are placed in one of the chambers and the untraced chamber is monitored as a function of time for the arrival of the radionuclides.

The second type of diffusion experiment consists of studying the kinetics of sorption under diffusive conditions by immersing a wafer made of tuff in a solution containing the radionuclide(s) of interest. The uptake of radionuclides(s) by the thin wafers is determined. The actinides exhibit sorption onto non-geologic media (such as the walls of containers). The kinetics of sorption under diffusive conditions is studied utilizing containers made of tuff in the form of beakers. The solution containing the radionuclide(s) of interest is placed in the tuff beaker cavity and the uptake of the radionuclide(s) by the tuff is measured as a function of time.

Unsaturated diffusion experiments are also performed. A solution containing the radionuclides(s) of interest is injected into an unsaturated block of tuff. The distribution of radionuclide(s) in the tuff as a result of diffusion is determined by sectioning the block of tuff and measuring the radionuclide(s) concentration throughout the tuff block.

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DIFFUSION

1.0 PURPOSE AND OBJECTIVES OF STUDIES

1.1 Purpose

The goal of these studies is to experimentally determine diffusivities and mass transfer rates for consolidated tuff for use both in performance assessment calculations and in support of the studies described in Site Characterization Plan (SCP) (DOE, 1988) Section 8.3.1.3.6.2, Diffusion. The combined goal of this study plan and the study plan 8.3.1.3.6.1 is to investigate the effective retardation of radionuclides by dispersive, diffusive, and advective processes. Specifically, Issue 1.1, Total System Performance (SCP Section 8.3.5.13), needs experimental evidence that confirms or denies the theory of advective/ diffusive coupling of solute concentrations in matrix and fracture flow. This theory is embodied in the transport model for fracture flow currently used in the transport model of TOSPAC (Dudley et al., 1988) described in Issue 1.1. Issue 1.1 states that information on advective/diffusive coupling is crucial in establishing the credibility of transport phenomenology embodied in any models used to assess the consequences of the release scenarios involving water pathways.

1.2 Use of Results

This study will provide values for the effective diffusivity of aqueous chemical species contained in the pores of the matrix of each rock unit in the saturated and unsaturated zones needed for resolution of Issue 1.1. The parameter called for by Issue 1.1 is the empirical parameter measuring the effective diffusivity of the fracture matrix interface (constrictivity/tortuosity factor) for the saturated and unsaturated zones. An understanding of dispersal of radionuclides into the tuff matrix and the contributions of sorption to radionuclide retardation in an advective system is necessary to develop information on the parameters of Issue 1.1. The diffusion studies provide an additional means of measuring sorption and sorption kinetics. Issue 1.1 requires distribution coefficients for the rock matrix in both the unsaturated and saturated zones beyond the disturbed zone. The bulk of the sorption data will be gathered in Investigation 8.3.1.3.4, Studies to Provide the Information Required on Radionuclide Retardation by Sorption Processes along Flow Paths to the Accessible Environment, but, if these data are used in a dynamic system, sorption (distribution coefficients) must be evaluated in dynamic systems. The diffusion experiments will provide that evaluation and will support the use of the sorption data by Issue 1.1. The results of this study, however, will first be assessed by Investigation 8.3.1.3.7, Studies to Provide Information Required on Radionuclide Retardation by All Processes along Flow Paths to the Accessible Environment, before being used in Issue 1.1. The results from this study are also to be used in modeling and interpreting the experiments in the Dynamic Transport Column Experiments SCP Section 8.3.1.3.6.1.

2.0 RATIONALE

2.1 Approach

We will study the migration of radionuclides and nonradioactive analogs of radionuclides through tuff samples under a variety of conditions. The experiments are intended to investigate the effects of the kinetics of sorption and diffusion on the liquid phase transport of radionuclides. Current performance assessment models assume instantaneous reaction rates. The kinetic data from the kinetics and diffusion studies will either support this assumption or will provide the data needed to more correctly model repository performance. Diffusivities are needed to predict the migration of radionuclides in fractured tuff. Diffusivity is also needed as a lower limit to transport rates for the matrix. The diffusivity in rock depends on pore structure. The measurements conducted in this study will determine the variability of pore tortuosity and constrictivity in Yucca Mountain tuff. To accomplish this, we have subdivided our efforts into the following activities.

- Diffusion studies will investigate the rate of movement of radionuclides through tuff in the absence of an advective flux. The processes of interest are molecular diffusion and sorption. These measurements will be performed using tuff disks of several thicknesses ranging from 1 to 5 cm because pumice grains of about 1 cm may have a porosity and/or tortuosity in the pore structure different from porosity and tortuosity of the bulk tuff. If this is true, then thin slabs penetrated by these grains would yield a diffusivity that is not representative of the bulk rock. Thicker tuff disks are impractical because the time required to complete the experiments increases as the square of the thickness. The experiments designed will provide the necessary rock-dependent parameters, i.e., tortuosity and constrictivity, for calculating the rate of diffusion of radionuclides through tuff and additional data on sorption distribution coefficients.

- Kinetics studies using solid tuff will provide kinetic rate constants by determining the time dependence of the uptake of radionuclides in solid tuff. These studies take advantage of the fact that diffusion-controlled uptake of dissolved species is linear versus the square root of time. If the sorption is influenced by kinetics, the observed uptake as a function of time will deviate from that controlled only by diffusion. To observe the effect of reaction rates on the uptake of radionuclides, the time required to diffuse through the solid must be short compared with the reaction time. Rapid reactions, such as ion exchange, can be studied by examining the uptake of radionuclides by thin wafers. Kinetic effects on ion exchange have been observed in 2-mm-thick tuff samples (Rundberg, 1984). The actinides, particularly americium, present special problems for studying their sorption and kinetic properties. The actinides exhibit nonselective sorption on nongeologic materials, such as the walls of the sample containers. To overcome this inherent difficulty, the sorption of actinides will be studied

as a function of time by using rock beakers so that the actinides will contact only the tuff.

- Unsaturated diffusion experiments will investigate diffusivity as a function of saturation in blocks of intact tuff. The diffusivity of radionuclides is expected to decrease as the saturation decreases because the larger connections between pores will dry out first, which leaves a more tortuous path for radionuclides to migrate through. These studies will measure the change in the constrictivity/tortuosity parameter as a function of saturation. Small volumes of tracer will be injected into unsaturated tuff blocks in which the moisture distribution has been allowed to equilibrate for 0.5 to 2 yr. The tracer distribution after a diffusion period of 0.5 to 2 yr will be determined by sectioning the tuff blocks and measuring the concentration of radionuclid throughout the blocks.

2.2 Types of Measurements to Be Made

The types of measurements will include tracer concentrations using (1) gamma ray spectrometry, (2) liquid scintillation counting, (3) alpha spectrometry, (4) scintillating glass beta counting, and (5) ion chromatography. The porosity of rock matrices will be determined by measuring weight differences between saturated and dry samples. The analytical techniques used in these tests are standard techniques for this type of data acquisition.

Ancillary measurements will include bulk rock mineralogy (described in the mineralogy/petrology study plan for Investigation 8.3.1.3.2, Studies to Provide Information on Mineralogy, Petrology, and Rock Chemistry Within the Potential Emplacement Horizon and along Potential Flow Paths), tuff permeability, and batch distribution coefficients (described in the study plan for batch sorption studies for Investigation 8.3.1.3.4, Studies to Provide the Information Required on Radionuclide Retardation by Sorption Processes along Flow Paths to the Accessible Environment).

2.3 Rationale for Choosing the Types of Measurements to Be Made

The diffusivity of dissolved species in water can be calculated from ionic conductivities. The effective diffusivity of that aqueous species in rock depends on the porosity, the retardation factor, the tortuosity of the pore structure, and the constrictivity. Constrictivity is the result of the repulsion of the aqueous species by a charge on the mineral surfaces. The combined tortuosity/constrictivity factor can be measured by observing the rate of diffusion through rock because ionic diffusivity, porosity, distribution coefficient (K_d), and dry bulk density can be determined either by conducting an independent measurement or by reviewing the literature. The rate of diffusion will be observed by measuring the rate of movement of radionuclides through intact tuff in the absence of an advective flux. This method has been chosen because it is the closest simulation of the migration of radionuclides

through tuff under the zero ground water velocity limit. Another method for measuring tortuosity is to measure the electrical resistivity of rock, but this method cannot determine the constrictivity.

2.4 Constraints on the Study

One of the most significant constraints on this study is the extent of knowledge of potential transport pathways away from the repository. This constraint affects the selection of samples to be used for measuring diffusivity. Several samples from each unit will have to be tested to arrive at a measure of variability. In the absence of certain knowledge of what these pathways are, the lower and upper bounds on diffusivity obtained from this study will provide estimates of radionuclide transport.

Another constraint is the lack of knowledge of the chemical speciation of actinides and other multivalent elements under groundwater conditions at the proposed repository site. Investigation 8.3.1.3.5, Studies to Provide the Information Required on Radionuclide Retardation by Precipitation Processes along Flow Paths to the Accessible Environment, will address this limitation. Time will limit the scale on which the experiments can be carried out. The goal of achieving results within a few years limits the scale for nonsorbing tracers to about 10 cm. Sorbing tracers will be limited to a smaller scale because retardation will further slow diffusion.

2.5 Additional Factors for Consideration

2.5.1 Impact on Site

The analyses necessary for this study should have minimal additional impact on the site because most samples necessary for the study will be obtained from core from existing and planned drill holes or from surface outcrops. Large samples will be acquired from the exploratory studies facility (ESF).

2.5.2 Required Accuracy and Precision and Limits of Methods

Currently, the performance assessment of the site has a sufficient safety margin, based on hydrologic estimates, that accuracy requirements have not been established for geochemical retardation. The measurements to be performed are subject to accuracy and precision limits that can be considered normal for analytical chemical measurements.

3.0 DESCRIPTION OF TESTS AND ANALYSES

3.1 Diffusion Cells

Diffusion cells are constructed that have two chambers containing groundwater. The chambers are separated by a slab of tuff. After radioactive tracers are added to one of the chambers, the untraced chamber is periodically monitored for the presence of radioactivity. The only driving force is the chemical concentration gradient; thus, the solute flux is purely diffusive. The apparent time of arrival depends on the porosity, the heterogeneity of the pore structure, the retardation factor for a given radionuclide, and the sensitivity of radionuclide measurements. The rate of concentration increase in the untraced chamber depends on the ionic diffusivity, the porosity, and the tortuosity/constrictivity factor. Thus, by measuring the movement of sorbing and non-sorbing tracers through tuff slabs as a function of time, we can measure the rock-dependent diffusion parameters. In addition, the retardation factor, R_f, can be determined from the initial arrival of a sorbing radionuclide, which, in turn, can be related to the sorption distribution coefficient, K_d, by Eq. 1, derived by Hiester and Vermeulen (1952) who carefully described the assumptions required for this result.

$$R_f = 1 + \frac{\rho b}{\varepsilon} K_d, \qquad (1)$$

where ρ_b is the bulk density, and ε is the porosity of the rock.

The diffusion experiments described in this study plan will provide hydrologic information for describing the diffusion of non-sorbing radionuclides through Yucca Mountain tuffs. In addition, the diffusion experiments will test the assumptions inherent in using a sorption distribution coefficient to describe the transport of sorbing radionuclides. These assumptions are that (1) the sorption reaction is reversible and instantaneous, (2) there is only one chemical specie or, if more than one specie is present, the species interchange rapidly, and (3) the dependence of sorption on sorbing species concentration is described by a linear isotherm.

3.1.1 Test Methods

Diffusion cells consist of two chambers containing groundwater from Yucca Mountain. The chambers are separated by a slab of tuff. Sorbing and non-sorbing tracers are placed in one of the chambers and the untraced chamber is monitored as a function of time for the arrival of the tracers. Plexiglas is utilized for construction of the cell. The chamber for the traced solution is large enough to keep the solution concentration constant throughout the experiment. The tuff sample will be sealed into a Plexiglas holder with Silastic sealant. The receiving (untraced) chamber will have as small a volume as practical to make the measurement of the time of first arrival of the tracers as

accurate as possible. The porosity of the tuff will be determined by differences in wet and dry weight.

A model for matrix and fracture flow regimes in unsaturated, fractured porous media at Yucca Mountain has been provided (Nitao, 1991). This model provides a framework for assessment of the importance of matrix diffusion at Yucca Mountain. Solute transport in fractured rock in a potential radionuclide waste repository has been discussed (Neretnieks, 1990). Neretnieks concludes that most rocks (even dense rocks such as granites) have small fissures between the crystals. These microfissures interconnect the pore system containing water. Small molecules of radioactive materials can diffuse in and out of this pore system. The inner surfaces in the rock matrix are much larger than the surfaces in the fractures in which the water flows. The volume of water in the microfissures is much larger that the volume in fractures. Consequently, over a long time scale diffusion can play an important role in radionuclide retardation.

Calculations for tracer diffusion in fractured and unfractured Yucca Mountain tuffs have been reported (Birdsell et al., 1988). Based on these calculations, four types of tuff have been chosen for diffusion tests: Topopah Springs Member tuff, zeolitic tuff from the Calico Hills unit, vitric tuff from the Calico Hills unit, and tuff from the Prow Pass Member. In addition to measuring porosity for each tuff sample (which is required for data analysis of the diffusion cell tests), ancillary measurements will be performed. Ancillary measurements will include rock bulk mineralogy and tuff permeability.

Tritiated water will be used as a non-sorbing tracer to determine the diffusion through tuff of an uncharged molecule. Bromide will be used to determine the diffusion of a non-sorbing anion through tuff. Bromide is used as a field tracer and its use in these experiments will allow comparisons between the laboratory and field data. Technetium will be used as a tracer because it is part of the repository inventory and the Br and Tc data will allow the determination of the tuff constrictivity for anions. Both Br and Tc will exist as anions in Yucca Mountain groundwaters and will be excluded from tuff pores due to size and charge.

As already stated, the objectives of the diffusion tests in this study are to provide data on the diffusion of non-sorbing tracers through tuff and to validate the utilization of sorption distribution coefficients (obtained using crushed tuff in study 8.3.1.3.4.1) to describe radionuclide retardation in a dynamic system under diffusive conditions. Consequently, three sorbing tracers have been chosen for the diffusion cell tests: Np, U, and Pu. Neptunium and uranium have been chosen as priorities in the sorption strategy of "Batch Sorption Studies" (study plan 8.3.1.3.4.1). Plutonium exhibits very complicated sorption behavior due to the multiple oxidation states that can exist in solution. Ancillary measurements for the sorbing tracers will

include measuring sorption distribution coefficients using crushed tuff of the same type as the one used for the diffusion cell tests.

The effect of scale and parameters such as stress on the diffusion process that are different in the laboratory and the field will be addressed by comparing the values from these laboratory tests with the results of the *in-situ* diffusion tests planned for the Exploratory Studies Facility (study plan 8.3.1.2.2.5). Diffusion tests planned for the ESF include tests in the Topopah Springs Member and the Calico Hills unit. Bromide will be the field tracer utilized.

The diffusion cell tests to be performed are listed in Table 1 and possible analytical methods for tracer concentration measurements are listed in Table 2. The choice of tracers than can be utilized together (as shown in Table 1) is based on the compatibility of preferred analytical techniques that are utilized for tracer concentration measurements.

Prior to starting these tests, quality assurance grading will be completed in accordance with currently applicable procedures to control this effort. The details of the test methods are given in detailed technical procedures listed in Table 3. The technical procedures for ancillary measurements are given in study plan 8.3.1.3.2.1 "Mineralogy of Transport Pathways" and study plan 8.3.1.3.4.1 "Batch Sorption Studies."

Table 1: Diffusion Cell Tests

Solid Phase	Tracers	Groundwater	Test Duration
tuff from Topopah Springs Member	HTO + ^{95m}Tc + Br	from Well J-13	1 year
	HTO + ^{237}Np		1 year
	HTO + U		2 years
	HTO + ^{239}Pu		2 years
zeolitic tuff from Calico Hills unit	HTO + ^{95m}Tc + Br	from Well J-13	1 year
	HTO + ^{237}Np		1 year
	HTO + U		2 years
	HTO + ^{239}Pu		2 years
vitric tuff from Calico Hills unit	HTO + ^{95m}Tc + Br	from Well J-13	1 year
	HTO + ^{237}Np		1 year
	HTO + U		2 years
	HTO + ^{239}Pu		2 years
tuff from Prow Pass Member	HTO + ^{95m}Tc + Br	from Well J-13	1 year
	HTO + ^{237}Np		1 year
	HTO + U		2 years
	HTO + ^{239}Pu		2 years

All experiments listed in Table 1 will be performed at two different temperatures: 25 °C and 60 °C.

Table 2: Analytical Methods for Tracer Concentration Determinations

Tracer	Preferred Method	Alternate Method
HTO	Liquid Scintillation	
^{95m}Tc	Gamma Ray Spectrometry	
Br	Ion Exchange Chromatography	Ion Coupled Plasma Mass Spectrometry
^{237}Np	Liquid Scintillation	Gamma Ray or Alpha Spectrometry
U	Neutron Activation Analysis	Ion Coupled Plasma Mass Spectrometry
^{239}Pu	Liquid Scintillation	Alpha Spectrometry

Table 3: Details of Test Methods

Detailed Technical Procedures	Objective
TWS-INC-DP-66	provide experimental details for diffusion cell tests
TWS-INC-DP-62	provide details for obtaining and storing groundwater utilized for these tests
TWS-INC-DP-35	provide experimental details for measuring pH of groundwater and traced solutions utilized
TWS-INC-DP-83	provide details for storing and handling tuff core samples utilized in these tests
TWS-INC-DP-60	provide experimental details for manipulation of tuff core samples utilized in these tests
TWS-INC-DP-64	provide experimental details for determining tracer solution concentrations by gamma ray spectrometry
TWS-INC-DP-79	provide experimental details for determining tracer solution concentrations by liquid scintillation counting
TWS-INC-DP-45	provide experimental details for determining tracer solution concentrations by ion chromatography

3.1.2 Required Accuracy and Precision

As stated in Section 2.5.2, the accuracy and precision required for this activity are not limited by performance assessment. However, to be considered significant, deviations caused by scaling effects must be greater than an order of magnitude when laboratory experimental results are extrapolated to the field scale. Nonsorbing aqueous species will diffuse less than 10 m in 10^4 yr; thus, a 10% scale effect for laboratory experiments using a 10-cm disk is significant. A precision on the order of several percent would be adequate to observe this magnitude of effect. The individual measurements of concentration are compared with standards; thus, absolute accuracy is unimportant. The precision of individual measurements depends on the concentration of each sample and will be determined by making replicate measurements when possible. Otherwise, the uncertainty can be estimated on the basis of counting statistics.

3.1.3 Equipment Needed

Most equipment needed for these studies is currently available, including the equipment used for sample preparation (rock saws, wire saws, and polishers) and analytical equipment such as germanium gamma detectors, liquid scintillation counters, autogamma scintillation counters, silicon surface barrier detectors, Dionex ion chromatographs, and pH meters. All computer hardware necessary for data reduction is also available. Use of the current equipment will probably result in a need to replace equipment because of age and wear.

3.1.4 Data Reduction and Analysis

The measured concentrations for the diffusing tracers will be fitted to a one-dimensional diffusion model (Bradbury et al., 1986) which yields an analytic solution to diffusion through a slab. The diffusion equation solved by Bradbury et al. for a porous rock is given in Eq. (2) as

$$D_e \frac{\partial^2 C}{\partial x^2} = \alpha \frac{\partial C}{\partial t} \qquad (2)$$

where D_e = effective diffusivity = εD
ε = porosity of the tuff,
D = diffusion coefficient through tuff,
C = concentration of diffusing tracer in solution phase,
x = axis along direction of tracer diffusion,
t = time,
$\alpha = \varepsilon + \rho_b Kd$
ρ_b = bulk tuff density, and
Kd = sorption distribution coefficient.

The conditions used for solution of Eq. (2) are

at $x = 0$, a constant source concentration, C_0 is maintained, and

at $x = \ell$, where ℓ is the tuff slab thickness, the concentration measured at the initially untraced cell C_t is much smaller than C_0 ($C_t << C_0$)

The solution of this system is given in Eq. (3). The total quantity diffused through the tuff slab after a time t, Q_t is given by

$$\frac{Q_t}{A\,\ell\,C_0} = \frac{D_e t}{\ell} - \frac{\alpha}{6} - \frac{2\alpha}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\exp - \left(\frac{D_e n^2 \pi^2 t}{\ell \alpha}\right) \tag{3}$$

where A is the area of the tuff slab.

As $t \rightarrow \infty$ the asymptotic solution of Eq. (3) tends to

$$Q_t = \frac{A\,C_0\,D_e}{\ell}\,t - \frac{A\,C_0\,\ell\alpha}{6} \tag{4}$$

Consequently, a plot of Q_t against t yields the effective diffusivity, D_e, from the slope, and the rock capacity factor, α, from the intercept on the time axis of the extrapolated linear region. For a nonsorbing species ($K_d = 0$), $\alpha = \varepsilon$, and, for a sorbing species, K_d may be calculated from the value of α.

The difference between the diffusion coefficient for a tracer in the solution phase D_s and the diffusion coefficient obtained through the tuff pores D is given by Eq. (5).

$$D = \frac{\delta}{\tau^2} D_s \tag{5}$$

where δ = constrictivity, and
τ = tortuosity of the tuff pore structure.

3.1.5 Representativeness of the Tests and Limitations and Uncertainties

These tests will be performed on samples that are geochemically representative of the site to the extent that the analyzed core has a mineralogy and physical properties representative of the repository host rock. Limited time and manpower will restrict the number of tests that can be completed. The extent to which the results of these tests are representative depends on the variability

of the diffusivity of the rock. The variability is not known at this time. The statistical knowledge of the covariance of diffusion parameters, which will be required for performance assessment, is not known at this time either. Large scaling factors will also limit the representativeness of the tests. Again, the magnitude of scaling is not known at this time. However, comparison of the results of the laboratory diffusion tests with the results obtained in the *in-situ* diffusion tests planned for the ESF will provide information on scaling effects.

3.2 Kinetic Studies with Intact Tuff

The kinetics of sorption is discussed in the study plan for Study 8.3.1.3.6.1, Dynamic Transport Column Studies, in the context of the effect of kinetics on the shape of the breakthrough curve. The kinetic studies described here are a more direct means of observing the kinetics. If the time required for tracers to diffuse through a tuff sample is short compared with the chemical reaction time, the effect of these kinetics is directly observable. These studies are useful for gaining a complete understanding of the differences in sorption phenomena observed in batch and column studies. The kinetic rates observed in the laboratory are generally much more rapid than those that would be important in the field. Therefore, these rates need to be studied so that laboratory experiments can be properly interpreted and predictions of retardation in the field will not be underestimated. The slow reactions, such as mineralization, that can occur in the field are expected to incorporate or trap radionuclides in the mineral structure. Therefore, ignoring those reactions results in a conservative approximation from the standpoint of sorption. Reactions that convert strongly sorbing minerals to less sorbing minerals are a separate issue and are addressed in Investigation 8.3.1.3.3, Studies to Provide Information Required on Stability of Minerals and Glasses.

3.2.1 Test Methods

Two methods are to be used in the kinetic studies--one for rapidly sorbed radionuclides and another for actinides, which appear to be sorbed more slowly. Use of rapidly sorbed tracers requires that the time for diffusion be short, so thin tuff wafers are appropriate for studying sorption kinetics for rapidly sorbed radionuclides. A thin tuff wafer is suspended by a Teflon thread in a stirred solution. The aqueous radionuclide concentration is then monitored as a function of time. It is known that americium, and plutonium to a lesser extent, sorbs indiscriminately to any surface. To remedy this problem, rock beakers are to be constructed so that the traced solution will contact only the tuff. The concentration will again be monitored as a function of time by taking small aliquots from the solution in the beaker. The analytical method used to determine concentrations depends on the tracer used.

Tuff wafer experiments were utilized to study the uptake of sorbing radionuclides by tuff (Rundberg, 1984). A model for sorption kinetics was provided by Crank (1975) and tested by Rundberg (1984) for radionuclide uptake

on tuff. Rundberg's study (1984) indicated that sorption of Cs^{+}, Ba^{+2}, and Sr^{+2} on tuff is dominated by cation exchange in aluminosilicates such as zeolites and clays. The rate constants for uptake of the sorbing cations Cs^{+}, Ba^{+2}, and Sr^{+2} on tuff were consistent with a model that is diffusion limited (where diffusion occurs in two stages). First the cations diffuse into tuff through water-filled pores and then the cations diffuse into narrower intracrystalline channels. This diffusion model yielded sorption coefficients that agree well with sorption coefficients determined with batch techniques for the cations Cs^{+}, Ba^{+2}, and Sr^{+2}. Rundberg (1984) reports that actinide sorption onto tuff does not follow a cation exchange mechanism and/or that actinide species present in groundwater solutions are too large to fit into the intracrystalline space in clays and zeolites. Nitsche (1990) reports that actinide speciation depends on groundwater composition. Ogard and Kerrisk (1984) have provided data on the chemistry of groundwater along flow paths at Yucca Mountain. Based on the results of Rundberg (1984), Nitsche (1990), and Ogard and Kerrisk (1984), the wafer tests on Table 4 will be performed. The intent of the sorption experiments proposed in this study is to provide information to interpret the kinetics of sorption on the basis of dominant sorption chemical processes such as ion exchange or surface complexation.

Table 4: Wafer Diffusion Experiments

Solid Phase	Groundwater	Tracers	Test Duration
tuff from Topopah Springs Member	from Wells J-13, UE25p#1, and USW H-3	$^{137}Cs + ^{90}Sr + ^{133}Ba$	4 weeks
		^{237}Np	8 weeks
		U	8 weeks
zeolitic tuff from Calico Hills unit	from Wells J-13, UE25p#1, and USW H-3	$^{137}Cs + ^{90}Sr + ^{133}Ba$	4 weeks
		^{237}Np	8 weeks
		U	8 weeks
vitric tuff from Calico Hills unit	from Wells J-13, UE25p#1, and USW H-3	$^{137}Cs + ^{90}Sr + ^{133}Ba$	4 weeks
		^{237}Np	8 weeks
		U	8 weeks
tuff from Prow Pass Member	from Wells J-13, UE25p#1, and USW H-3	$^{137}Cs + ^{90}Sr + ^{133}Ba$	4 weeks
		^{237}Np	8 weeks
		U	8 weeks

All experiments listed in Table 4 will be performed at two different temperatures: 25 °C and 60 °C.

Rock beakers will be utilized to study the diffusion of actinides that tend to sorb to non-geologic media (such as Am and Pu). These tuff beakers will also be useful in the study of the diffusion of non-sorbing tracers such as Tc. When diffusion cells are used for the study of Tc diffusion, appearance of Tc retarded with respect to tritiated water can be due to Tc sorption onto tuff or anion exclusion effects. Utilization of rock beakers will resolve the dominant

mechanism. The experimental technique involves fabricating containers in the form of a beaker (made of tuff). The rock beaker sits on a Plexiglas container (surrounded by a layer of groundwater on the sides). A stopper is utilized to prevent evaporation. The beaker has a cavity with a radius of approximately 1.4 cm and length of 2.5 cm. The rock beaker has a length of approximately 5 cm and a radius of 3.1 cm. A groundwater solution containing the radionuclides of interest is placed in the cavity of the rock beaker. Aliquots of the solution containing the radionuclides of interest are taken as a function of time and analyzed for radionuclide concentration. The rock beaker tests on Table 5 will be performed.

Table 5: Rock Beaker Tests

Solid Phase	Groundwater	Tracers	Test Duration
tuff from Topopah Springs Member	from Wells J-13, UE25p#1, and USW H-3	HTO + ^{95m}Tc	1 year
		HTO + ^{241}Am	2 years
		HTO + ^{239}Pu	2 years
zeolitic tuff from Calico Hills unit	from Wells J-13, UE25p#1, and USW H-3	HTO + ^{95m}Tc	1 year
		HTO + ^{241}Am	2 years
		HTO + ^{239}Pu	2 years
vitric tuff from Calico Hills unit	from Wells J-13, UE25p#1, and USW H-3	HTO + ^{95m}Tc	1 year
		HTO + ^{241}Am	2 years
		HTO + ^{239}Pu	2 years
tuff from Prow Pass Member	from Wells J-13, UE25p#1, and USW H-3	HTO + ^{95m}Tc	1 year
		HTO + ^{241}Am	2 years
		HTO + ^{239}Pu	2 years

For wafer and rock beaker experiments, the possible analytical methods for tracer concentration measurements are listed in Table 6. The tuff porosity will be determined by dry/wet weights. Ancillary measurements will include rock mineralogy and permeability. Ancillary measurements for the sorbing tracers will include measuring sorption distribution coefficients using crushed tuff of the same type as the one used for the sorption kinetic experiments.

Prior to starting these tests, quality assurance grading will be completed in accordance with currently applicable procedures to control this effort. The details of the test methods are given in detailed technical procedures listed in Table 7. The technical procedures for ancillary measurements are given in study plan 8.3.1.3.2.1 "Mineralogy of Transport Pathways" and study plan 8.3.1.3.4.1 "Batch Sorption Studies."

Table 6: Analytical Methods for Tracer Concentration Determinations

Tracer	Preferred Method	Alternate Method
HTO	Liquid Scintillation	
^{95m}Tc, ^{137}Cs, ^{90}Sr, and ^{133}Ba	Gamma Ray Spectrometry	Atomic Absorption Spectrometry
^{241}Am	Liquid Scintillation	Alpha Spectrometry
^{237}Np	Liquid Scintillation	Gamma Ray or Alpha Spectrometry
U	Neutron Activation Analysis	Ion Coupled Plasma Mass Spectrometry
^{239}Pu	Liquid Scintillation	Alpha Spectrometry

Table 7: Details of Test Methods

Detailed Technical Procedures	Objective
TWS-INC-DP-98	provide experimental details for wafer diffusion tests
TWS-INC-DP-67	provide experimental details for rock beaker diffusion tests
TWS-INC-DP-62	provide details for obtaining and storing groundwater utilized for these tests
TWS-INC-DP-35	provide experimental details for measuring pH of groundwater and traced solutions utilized
TWS-INC-DP-83	provide details for storing and handling tuff core samples utilized in these tests
TWS-INC-DP-60	provide experimental details for manipulation of tuff core samples utilized in these tests
TWS-INC-DP-64	provide experimental details for determining tracer solution concentrations by gamma ray spectrometry
TWS-INC-DP-79	provide experimental details for determining tracer solution concentrations by liquid scintillation counting

3.2.2 Required Accuracy and Precision

As stated in Section 2.5.2, the accuracy and precision necessary for this activity are not limited by performance assessments needs. However, to be considered significant, deviations caused by scaling effects must be greater than an order of magnitude when extrapolated to the field scale. Nonsorbing aqueous species will diffuse less than 10 m in 10^4 years so that a 10% scale effect for laboratory experiments of 10 cm size is significant. A precision on the order of several percent would be adequate to observe this magnitude of effect. The individual measurements of concentration are compared with standards, so absolute accuracy is unimportant. The precision of individual measurements depends on the concentration of each sample and will be determined by making replicate measurements when possible.

3.2.3 Equipment Needed

Most equipment needed for these studies is currently available, including the equipment used for sample preparation (rock saws, wire saws, coring tools, and polishers) and analytical equipment such as germanium gamma detectors, liquid scintillation counters, autogamma scintillation counters, silicon surface barrier detectors, and pH meters. All computer hardware necessary for data reduction is also available. Use of the current equipment will probably result in a need to replace equipment because of age and wear.

3.2.4 Data Reduction and Analysis

The data from the wafer experiments will be fitted to the one-dimensional diffusion equation considering a solute diffusing from a solution into a plane sheet of material of thickness 2a (Crank, 1975).

$$D\frac{\partial^2 C}{\partial x^2} = \frac{\partial C}{\partial t} + \frac{\partial S}{\partial t} \qquad (6)$$

where D = diffusion coefficient through tuff,
C = concentration of tracer free to diffuse within the sheet,
x = axis along direction of tracer diffusion,
t = time,
$S = \frac{\rho_b}{\varepsilon} F$,
ρ_b = bulk tuff density,
ε = porosity of the tuff, and
F = concentration of tracer immobilized by sorption onto the sheet, expressed as amount per unit mass of sheet.

The sheet occupies the space $-a \leq x \leq a$, and there is a restricted amount of solution which occupies the space $-\ell - a \leq x \leq \ell + a$. The concentration of the

tracer in the solution in contact with the sheet is always uniform and initially given by C_0.

In the general case,

$$\frac{\partial S}{\partial t} = k_1 C - k_2 S \tag{7}$$

where k_1 and k_2 are the rates of the forward and backward reactions, respectively. The immobilized tracer is formed at a rate proportional to the concentration of tracer free to diffuse, and disappears at a rate proportional to its own concentration. Invoking a reversible reaction for the sorption chemical reaction following diffusion yields an analytical solution (derived by Crank, 1975).

The initial conditions are:

$$S = C = 0 \qquad -a < x < a \qquad t = 0 \tag{8}$$

The boundary conditions state that the rate at which the tracer leaves the solution is equal to that at which the tracer enters the sheet over the surfaces $x = \pm a$.

$$\mp D \frac{\partial C}{\partial x} = \ell \frac{\partial C}{\partial t} \qquad x = \pm a \qquad t > 0 \tag{9}$$

The total amount of tracer both free to diffuse and immobilized in the sheet at time t, is given by Mt.

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{(1+\beta)\exp(p_n t)}{1 + \left\{1 + \frac{k_1 k_2}{(p_n + k_2)^2}\right\}\left\{\frac{a}{2\ell} + \frac{p_n}{2Dk_n^2} + \frac{p_n^2 \ell a}{2D^2 k_n^2}\right\}} \tag{10}$$

where the p_ns are given by the non-zero roots of

$$\frac{\ell p_n}{D} = k_n \tan k_n a \qquad\qquad k_n^2 = -\frac{p_n}{D}\frac{p_n + k_1 + k_2}{p_n + k_2} \tag{11}$$

and β and M_∞ are given by

$$\beta = \frac{\ell}{(k_1/k_2 + 1)\, a} \qquad\qquad M_\infty = \frac{\ell C_0}{(1+\beta)} \tag{12}$$

The numerical evaluation of these equations in order to obtain D, k_1, and k_2 is given by Crank (1975). It involves finding the roots p_n and $k_n a$ and evaluating M_t/M_∞ once the roots are found.

The results of the rock beaker experiments will be modeled using TRACRN (Travis and Birdsell, 1991). Due to the complex geometry of the rock beaker, an analytical solution is not available for this system. The concentration profiles of the diffusing tracer are fitted to Eq. (13).

$$\nabla \bullet (\varepsilon D \nabla C) = \varepsilon \frac{\partial C}{\partial t} + Q \tag{13}$$

where ε = porosity of the tuff,
D = diffusion coefficient through tuff,
C = concentration of diffusing tracer in solution phase,
t = time,
Q = 0 for a non-reactive tracer,
$Q = \rho_b \frac{\partial F}{\partial t}$ for a sorbing tracer,
ρ_b = bulk tuff density, and
F = amount of tracer sorbed per unit mass of solid.

The mechanism of sorption determines the relationship between F and C. When sorption is linear, reversible, and instantaneous, the relationship between F and C is given by Eq. (14), where K_d is the sorption distribution coefficient.

$$\frac{F}{C} = K_d \tag{14}$$

Substitution of Eq. (14) into Eq. (13) yields Eq. (15). Equation (16) provides a means of comparing results for sorption coefficients obtained under diffusive conditions with the sorption coefficients obtained utilizing batch sorption experiments. The expression for the retardation factor R_f (given in equation 16) is only valid if sorption is linear, reversible and instantaneous. The Langmuir and the Freundlich isotherms are examples of non-linear relationships between F and C.

$$\nabla \bullet (\varepsilon D \nabla C) = \varepsilon R_f \frac{\partial C}{\partial t} \tag{15}$$

$$R_f = 1 + \frac{\rho_b}{\varepsilon} K_d \tag{16}$$

Consequently, fitting of concentration profiles for non-sorbing tracers will allow determination of the diffusion coefficient and fitting concentration profiles for the sorbing tracers will allow the determination of sorption parameters such as Kd.

3.2.5 Representativeness of the Tests and Limitations and Uncertainties

These tests will be performed on samples that are geochemically representative to the extent that the analyzed core has a mineralogy and physical properties representative of the repository host rock. Limited time and manpower will restrict the number of tests that can be completed. The extent to which the results of these tests are representative depends on the variability of the sorption kinetics of the rock, which is not known at this time. Neither is the covariance of kinetic rate constants known at this time.

Reaction rates significant on a geologic time scale cannot be investigated in laboratory experiments. This limitation will have to be dealt with by some other means, such as the study of natural analogs (SCP Section 8.3.1.3.7.2).

3.3 Unsaturated Diffusion Studies

Blocks of tuff from drill holes and outcrops will be machined, wetted to various degrees of saturation, and injected with tracer. The concentration profile in the tuff block will be measured after a fixed time. By fitting the observed profiles to a diffusion equation, the diffusivity will be determined. The diffusivity will thus be measured as a function of saturation. These experiments will provide the change in diffusivity caused by the increase in tortuosity and/or constrictivity as a function of saturation. These measurements are needed to properly model radionuclide transport in the unsaturated zone. The results of this test will be confirmed *in situ* in the ESF diffusion test (SCP Section 8.3.1.2.2.5).

3.3.1 Test Methods

A block of tuff is machined to prescribed dimensions, and a narrow hole is drilled to the center of the block. The porosity is determined by measuring the difference in weight between dry and saturated samples. After initial saturation, the block is allowed to dry until the desired moisture content is achieved. The block is then sealed in an airtight container and placed in a constant-temperature bath to allow the moisture distribution to equilibrate. It takes many months for the water to distribute evenly through the block because the permeability of Yucca Mountain tuff is low. The appropriate time for equilibration to occur will be calculated in each case using TRACRN (Travis and Birdsell, 1991 and Birdsell et al., 1988). After equilibration, a solution containing tracers is placed in the bottom of the injection hole. The tracers are allowed to diffuse for a fixed period of time (which will be determined using TRACRN). After this diffusion time, the block is frozen, sectioned, and each

section is analyzed using the analytical techniques listed in Table 9. The distribution of tracers in the tuff matrix will be fitted to a diffusion equation using TRACRN (see Section 3.3.4).

A model for matrix and fracture flow regimes in unsaturated, fractured porous media at Yucca Mountain has been provided (Nitao, 1991). This model provides a framework for assessment of the importance of matrix diffusion at Yucca Mountain. Calculations for tracer diffusion in fractured and unfractured Yucca Mountain tuffs have been reported (Birdsell et al., 1988). Based on these calculations, four types of tuff have been chosen for diffusion tests: Topopah Springs Member tuff, zeolitic tuff from the Calico Hills unit, vitric tuff from the Calico Hills unit, and tuff from the Prow Pass Member. In addition to measuring porosity and saturation for each tuff block (which are required for data analysis), ancillary measurements will be performed. Ancillary measurements will include rock bulk mineralogy and tuff permeability.

Tritiated water will be used as a non-sorbing tracer to determine the diffusion through unsaturated tuff of an uncharged molecule. Bromide will be used to determine the diffusion of a non-sorbing anion through unsaturated tuff. Bromide is used as a field tracer and its use in these experiments will allow comparisons between the laboratory and field data.

As already stated, the objectives of the diffusion tests in this study are to provide data on the diffusion of non-sorbing tracers through tuff and to validate the utilization of sorption distribution coefficients (obtained using crushed tuff in study 8.3.1.3.4.1) to describe radionuclide retardation in a dynamic system under unsaturated diffusive conditions. Consequently, two sorbing tracers have been chosen for the diffusion cell tests: Np and Cs. Ancillary measurements for the sorbing tracers will include measuring sorption distribution coefficients using crushed tuff of the same type as the one used for the diffusion cell tests.

The effect of scale and parameters such as stress on the diffusion process that are different in the laboratory and the field will be addressed by comparing the values from these laboratory tests with the results of the *in-situ* diffusion tests planned for the Exploratory Studies Facility (study plan 8.3.1.2.2.5). Diffusion tests planned for the ESF include tests in the Topopah Springs Member and the Calico Hills unit. Bromide will be the field tracer utilized.

The unsaturated diffusion tests to be performed are listed in Table 8 and possible analytical methods for tracer concentration measurements are listed in Table 9. The choice of tracers than can be utilized together (as shown in Table 8) is based on the compatibility of preferred analytical techniques that are utilized for tracer concentration measurements.

Prior to starting these tests, quality assurance grading will be completed in accordance with currently applicable procedures to control this effort. The

details of the test methods are given in detailed technical procedures listed in Table 10. The technical procedures for ancillary measurements are given in study plan 8.3.1.3.2.1 "Mineralogy of Transport Pathways" and study plan 8.3.1.3.4.1 "Batch Sorption Studies."

Table 8: Unsaturated Diffusion Tests

Solid Phase	Tracers	Groundwater	Test Duration
tuff from Topopah Springs Member	HTO + Br	from Well J-13	1 year
	HTO + ^{237}Np		3 years
	HTO + ^{137}Cs		4 years
zeolitic tuff from Calico Hills unit	HTO + Br	from Well J-13	1 year
	HTO + ^{237}Np		3 years
	HTO + ^{137}Cs		4 years
vitric tuff from Calico Hills unit	HTO + Br	from Well J-13	1 year
	HTO + ^{237}Np		3 years
	HTO + ^{137}Cs		4 years
tuff from Prow Pass Member	HTO + Br	from Well J-13	1 year
	HTO + ^{237}Np		3 years
	HTO + ^{137}Cs		4 years

All experiments listed in Table 8 will be performed at three tuff moisture contents and two different temperatures: 25 °C and 60 °C

Table 9: Analytical Methods for Tracer Concentration Determinations

Tracer	Preferred Method	Alternate Method
HTO	Liquid Scintillation	
Br	Ion Exchange Chromatography	Ion Coupled Plasma Mass Spectrometry
^{237}Np	Liquid Scintillation	Gamma Ray or Alpha Spectrometry
^{137}Cs	Gamma Ray Spectrometry	Atomic Absorption Spectrometry

Table 10: Details of Test Methods

Detailed Technical Procedures	Objective
TWS-INC-DP-81	provide experimental details for unsaturated diffusion tests using blocks of tuff
TWS-INC-DP-62	provide details for obtaining and storing groundwater utilized for these tests
TWS-INC-DP-35	provide experimental details for measuring pH of groundwater and traced solutions utilized
TWS-INC-DP-83	provide details for storing and handling tuff core samples utilized in these tests
TWS-INC-DP-60	provide experimental details for manipulation of tuff core samples utilized in these tests
TWS-INC-DP-64	provide experimental details for determining tracer solution concentrations by gamma ray spectrometry
TWS-INC-DP-79	provide experimental details for determining tracer solution concentrations by liquid scintillation counting
TWS-INC-DP-45	provide experimental details for determining tracer solution concentrations by ion chromatography

3.3.2 Required Accuracy and Precision

As stated in Section 2.5.2, the accuracy and precision required for this activity are not limited by performance assessment needs. To be considered significant, changes in diffusivity caused by changes in water content should be greater than an order of magnitude over the saturation range expected for field conditions. The individual measurements of concentration are compared with standards; thus, absolute accuracy is unimportant. The precision of individual measurements depends on the concentration of each sample and will be determined by making replicate measurements when possible.

3.3.3 Equipment Needed

Most equipment needed for these studies is currently available, including the equipment used for sample preparation (rock saws, wire saws, drills, and polishers) and analytical equipment such as germanium gamma detectors, liquid scintillation counters, autogamma scintillation counters, silicon surface barrier detectors, Dionex ion chromatographs, and pH meters. All computer hardware necessary for data reduction is also available. Use of the current equipment will probably result in a need to replace equipment because of age and wear.

3.3.4 Data Reduction and Analysis

The tracer concentrations measured as a function of space within the unsaturated tuff will be fitted to Eq. (17) using TRACRN (Travis and Birdsell, 1991) to obtain diffusion coefficients for non-sorbing tracers and sorption information for sorbing tracers.

$$\nabla \bullet (\varepsilon D(\theta) \nabla C) = \frac{\partial \theta C}{\partial t} + Q, \tag{17}$$

where θ = moisture content.
ε = porosity of the tuff,
D = diffusion coefficient through tuff,
C = concentration of diffusing tracer in solution phase,
t = time,
Q = 0 for a non-reactive tracer,
$Q = \rho_b \frac{\partial F}{\partial t}$ for a sorbing tracer,
ρ_b = bulk tuff density, and
F = amount of tracer sorbed per unit mass of solid.

The mechanism of sorption determines the relationship between F and C. When sorption is linear, reversible, and instantaneous, the relationship between F and C is given by Eq. (14), where K_d is the sorption distribution coefficient. Consequently, fitting of concentration profiles for non-sorbing tracers will allow determination of the diffusion coefficient and fitting concentration profiles for the sorbing tracers will allow the determination of sorption parameters such as K_d.

3.3.5 Representativeness of the Tests and Limitations and Uncertainties

These tests will be performed on samples that are representative to the extent that the analyzed core has a mineralogy and physical properties representative of the repository host rock. Limited time and manpower will restrict the

number of tests that can be completed. The extent to which the results of these tests are representative depends on the variability of the rock in terms of diffusivity, which is not known at this time. Neither is the covariance of diffusion coefficients known at this time. Large scaling factors would also limit the representativeness of the tests. Again, the magnitude of scaling is not known at this time. The destructive analysis required for these experiments results in uncertainty caused by the variation in pore structure from sample to sample. This uncertainty overlies the measured dependence of diffusivity on saturation.

4.0 APPLICATION OF RESULTS

The information derived from the activities described in Section 3.0 is summarized in Table 11.

Table 11: Derived Information

Test	Data Measured	Data Derived	Expected Value	Reference
Diffusion Cells (Section 3.1)	tuff porosity and bulk density; Concentration of diffusing tracer	Diffusion Coefficient	10^{-7} - 10^{-5} cm^2/s	Triay et al., 1992
		K_ds for Np, U, and Pu	10 - 1,000 ml/g	Thomas, 1987
Tuff Wafers (Section 3.2)	tuff porosity and bulk density; Concentration of diffusing tracer	Diffusion Coefficient	10^{-7} - 10^{-5} cm^2/s	Triay et al., 1992
		k_1 for diffusing tracers	10^{-3} - 10^{1} sec^{-1}	Rundberg, 1984
		k_2 for diffusing tracers	10^{-6} - 10^{4} sec^{-1}	Rundberg, 1984
Rock Beakers (Section 3.2)	tuff porosity and bulk density; Concentration of diffusing tracer	Diffusion Coefficient	10^{-7} - 10^{-5} cm^2/s	Triay et al., 1992
		K_ds for Am and Pu	100 - 10,000 ml/g	Thomas, 1987
Unsaturated Blocks (Section 3.3)	tuff porosity, bulk density, and saturation; Concentration of diffusing tracer	Diffusion Coefficient	10^{-8} - 10^{-6} cm^2/s	Birdsell et al., 1988
		K_ds for Np and Cs	10 - 1,000 ml/g	Thomas, 1987

The derived information will be used in the following information needs, investigations, and issues.

Information Needs

1.1.1 Site Information Needed to Calculate Releases (SCP Section 8.3.5.13.1)

The diffusion experiments described in this study plan provide kinetic rates, matrix diffusion coefficients, and retardation factors. These parameters are needed to calculate release rates.

1.1.2 Potentially Significant Release Scenario Classes (SCP Section 8.3.5.13.2)

Scenarios that involve the transport of radionuclides in fractures are sensitive to matrix diffusion. The coupling of diffusion to transport in the fractures will in part determine the significance of these release scenario classes.

1.1.3 Calculational Models for Release Scenario Classes (SCP Section 8.3.5.13.3)

The diffusion of radionuclides into the tuff matrix depends on the pore structure of the tuff and may even be scale-dependent. If scaling is observed, a strategy for modeling the scale effect will need to be developed. The spatial distribution of diffusivity may also need to be incorporated in the model.

1.1.4 Radionuclide Releases for Scenario Classes (SCP Section 8.3.5.13.4)

The diffusion coefficients will be used in the calculation of radionuclide releases.

Investigations

Radionuclide Retardation by Sorption Processes along Flow Paths to the Accessible Environment (8.3.1.3.4)

The initial breakthrough of activity is strongly dependent on the retardation factor. This high sensitivity makes diffusion measurements an excellent method for measuring distribution coefficients less than one. The information from this study is complementary to the measurements in the sorption task.

Radionuclide Retardation by All Processes along Flow Paths to the Accessible Environment (8.3.1.3.7)

Matrix diffusion is one of the processes needed to calculate the overall retardation.

Description of the Unsaturated Zone Hydrologic System at the Site (8.3.1.2.2)

Diffusivity is one of the hydrologic parameters. Diffusivity will be measured as a function of saturation in this study.

Description of the Saturated Zone Hydrologic System at the Site (8.3.1.2.3)

Matrix diffusion is an important hydrologic parameter, particularly when the water is flowing through fractures.

Issues

1.8 Nuclear Regulatory Commission (NRC) Siting Criteria (SCP Section 8.3.5.17)

The NRC siting criteria stated in 10 CFR 60 (NRC, 1986) require the presence of several favorable conditions, including favorable geochemical conditions, such as matrix diffusion.

1.9(b) 100,000-yr Releases (SCP Section 8.3.5.18)

The release rate will be determined by the hydrologic flow rate, dispersion, matrix diffusion, retardation, and chemical species. These studies will provide diffusivities, retardation factors, kinetic rates, and possibly information on chemical speciation.

5.0 SCHEDULE

Data required from other investigations are listed in Table 12; output of data from this study to other investigations is described in Table 13. The schedule showing the estimated length of study and milestones are presented in Figure 1 and Table 14.

Table 12: Data Needed

Designation (in Figure 1)	Investigation	Input Needed by this Study
A	8.3.1.3.1	water chemistry along potential flow paths
B	8.3.1.3.2	mineralogy along potential flow paths
C	8.3.1.3.4	sorption data by batch experiments
D	8.3.1.3.5	speciation and solubility of actinides along potential flow paths

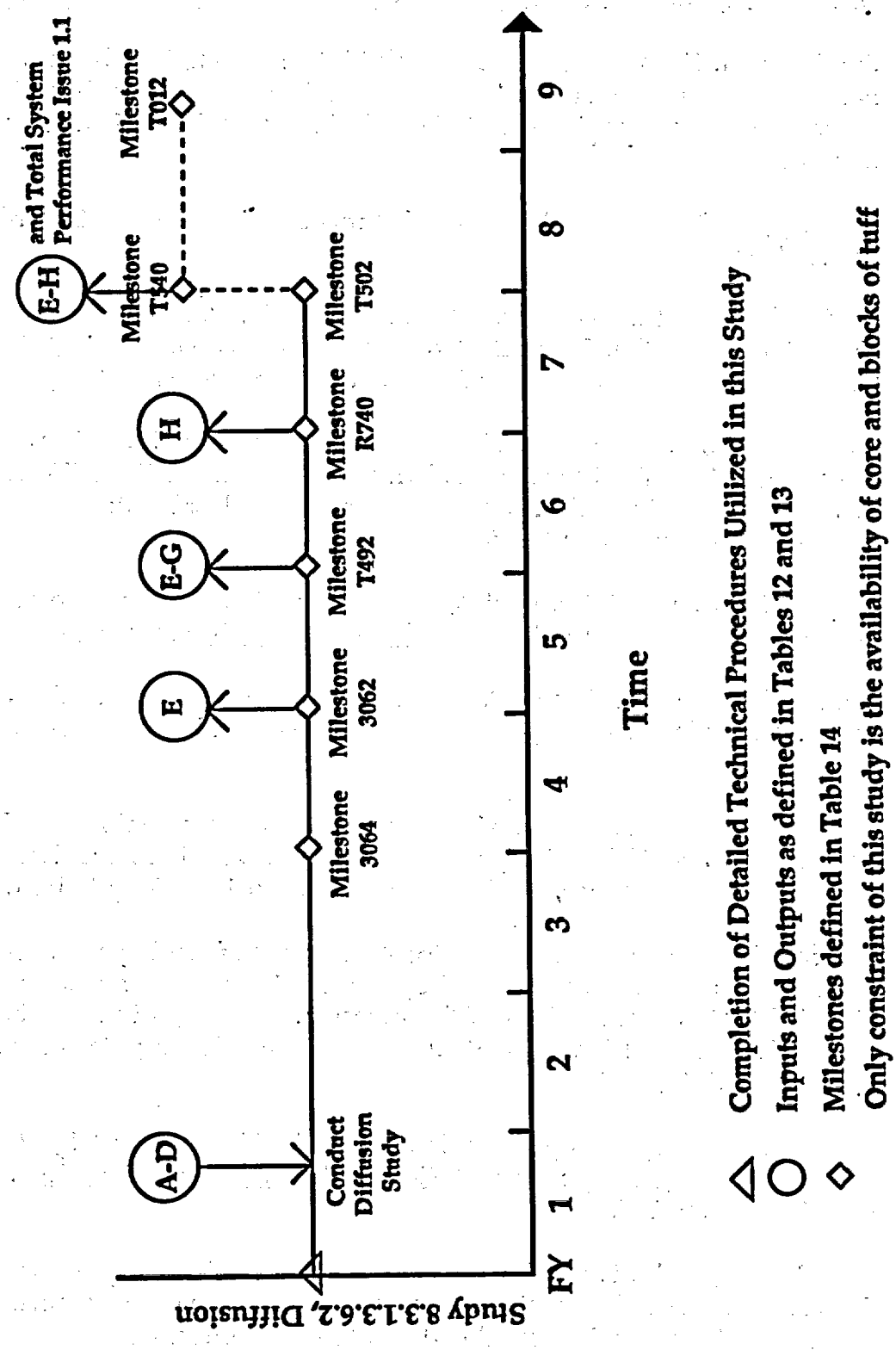
Table 13: Output to Other Investigations

Designation (in Figure 1)	Investigation	Information Derived in this Study Required by Other Investigations
E	8.3.1.3.6	Data on sorption kinetics will be combined with data obtained in activities 8.3.1.3.6.1.2 and 8.3.1.3.6.1.4 to fully describe the kinetics of sorption
F	8.3.1.3.7	Study 8.3.1.3.7.1 requires data on radionuclide transport under diffusive conditions to fully describe the retardation of radionuclides along potential flow paths and validate codes developed in study 8.3.1.3.7.1: TRACRN and FEHM.
G	8.3.1.2.3	Data on diffusion through saturated tuff is required to describe flow through the saturated zone
H	8.3.1.2.2	Data on diffusion through unsaturated tuff is required to describe flow through the unsaturated zone (a specific output is to study 8.3.1.2.2.5, for the *in-situ* diffusion tests in unsaturated tuff)

Table 14: Milestones for Diffusion Study

Milestone	Description
3064	Report on the techniques to study diffusion through unsaturated tuff
3062	Report on the kinetics of sorption
T492	Preliminary Report on retardation by diffusion
R740	Report on diffusion in unsaturated tuff
T502	Summary Report on retardation by diffusion
T540	T502 feeds information to Milestone T540 (which is generated from study 8.3.1.3.6.1) to describe the transport data required for transport calculations
T012	Milestone T540 feeds information to Milestone T012 (which is generated from Investigation 8.3.1.3.7) to describe the retardation of radionuclides by all processes along potential flow paths

Figure 1. Schedule for Diffusion Study



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