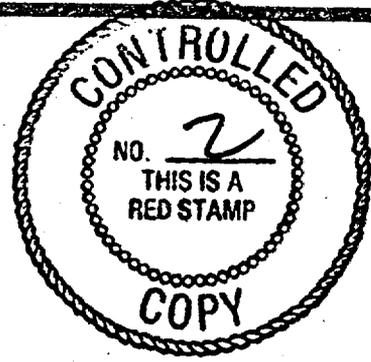


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TESTING OF THE C-HOLE SITES WITH REACTIVE TRACERS

Los Alamos National Laboratory

Abstract

This activity will characterize the chemical and physical properties of the geologic media in the saturated zone in the vicinity of the C-holes that will affect radionuclide retardation during ground water flow within the saturated zone.

A group of tracers will be selected that will aid in evaluating various controlling mechanisms of radionuclide sorption by the geologic media within the saturated zone in the vicinity of the C-wells. The tracers will be used in field tests, which are part of site characterization investigations.

A screening of potential tracers to define controlling sorption mechanisms in various minerals will be conducted from literature reviews and consultations with experts. Laboratory tests will be conducted to select those procedures and analyses (for geologic material and water) that can facilitate the distinction among prevailing sorption mechanisms. Modeling of sorption experiments will be conducted using both kinetics and equilibrium expressions. Geochemical modeling will assist in defining the prevailing sorption mechanisms in laboratory studies.

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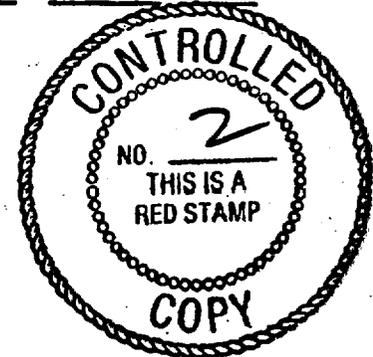


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1.0 PURPOSE AND OBJECTIVES OF ACTIVITY

1.1 Purpose

Models to assess performance of the candidate repository at Yucca Mountain, presented in Site Characterization Plan (SCP) Section 8.3.5.13 (DOE 1988) for resolution of Issue 1.1 (total system performance), use a retardation factor to represent the many geochemical processes that may occur. This activity, specified by SCP Section 8.3.1.2.3.1.7 (hereafter referred to as the reactive tracer study), will provide information to understand the use of the retardation factor in performance assessment calculations by investigating the behavior of reactive tracers, evaluated in laboratory investigations, under field conditions. The value of 1.0 that is currently assigned to the factor assumes that no retardation occurs. The needed confidence for this retardation factor for the saturated zone is medium (SCP Table 8.3.5.13-9), and, through field testing, this study will help to establish the level of confidence in the use of the factor.

Geochemical studies in site characterization depend primarily on laboratory experiments that use materials available at the site to develop information required to understand geochemical and transport processes for radionuclides. Activities that comprise the geochemical test program are described in SCP Section 8.3.1.3. Field experiments are required to demonstrate the applicability of laboratory-derived information, such as equilibrium and kinetics adsorption expressions, to the field scale.

The purpose of the reactive tracer study is to conduct field experiments to assess the application of laboratory-derived adsorption parameters to field-scale conditions found at the C-wells complex. The Nuclear Regulatory Commission (NRC) technical position on sorption (NRC 1987) indicated that evidence to demonstrate consistency of sorption parameters among various experimental approaches is needed to assess the effects of sorption on the performance of a high-level waste repository. The reactive tracer study will include both laboratory batch and column experiments to determine sorption parameters and a series of field tests to demonstrate the applicability of these sorption parameters. The reactive tracer study will use nonradioactive tracers because of regulatory and operational considerations that will be described in the following sections.

A variety of geochemical processes may affect the migration of an ion through the Yucca Mountain environment. These processes include chemical reactions, such as hydrolysis and complexation, with other species in solution; volatilization; biotransformations caused by microbial action; precipitation or solubilization; and adsorption on solid phases. Adsorption was selected as the principal geochemical process for this study in the assessment of Yucca Mountain as a repository because of its expected importance as a barrier to the migration of radionuclides.

This study recognizes the possible roles of other geochemical processes that may affect retardation but attempts to emphasize some processes and to minimize others. Although it is very difficult to effectively foresee the fate of a tracer in field studies, tracers will be selected that will not be significantly affected by mechanisms other than sorption. This can be achieved by selecting tracers (1) that are nonvolatile and nonbiotransformed, (2) that do not show potential for complexation or for which complexation is mostly defined by one or two major

species, and (3) that have concentration ranges that are predicted to be well below precipitation limits for the conditions involved.

By studying adsorption mechanisms in both SCP Section 8.3.1.3.4 (radionuclide retardation by sorption) and in this study, correlation of the behavior of tracers to the target radionuclides listed in SCP Section 8.3.5.13 can be made through the characterization of mechanisms. The fundamental information generated by the reactive tracer study will be used to determine the confidence that can be assigned to retardation caused by equilibrium and kinetics (rates) sorption conditions. This study will derive adsorption expressions and their parameters in the laboratory and will evaluate these expressions and parameters in field tests.

Diffusion of radionuclides into the matrix from fractures is another potentially important retardation mechanism. Not only does this matrix diffusion have implications for resolution of Issue 1.1, but it can be important in the resolution of Issue 1.6 (SCP Section 8.3.5.12), which pertains to pre-waste-emplacment ground water travel time. Also, the movement of radionuclides as colloids is being investigated by several studies in the geochemical test program (SCP Sections 8.3.1.3.4.1.4, 8.3.1.3.5.2, 8.3.1.3.6.1.5, and 8.3.1.3.7.1.1). Tracers are being used in the reactive tracer study to (1) help provide estimates for matrix diffusion by using tracers sufficiently large that they will not diffuse into the matrix pores and (2) provide some field data for modeling of colloid transport. The reactive tracer study is not considering colloid formation and disintegration processes because they are covered in the other activities listed.

An additional goal of the reactive tracer study is to provide data that can be used for model evaluation, particularly for the computer codes used by the geochemistry test program described in SCP Section 8.3.1.3.7. The proposed field experiment at the C-wells will be conducted in a high-permeability region of the saturated zone but at a scale that is larger than proposed experiments in the unsaturated zone. For example, infiltration tests in the exploratory shaft (Activity 8.3.1.2.2.4.2) will examine a maximum horizontal length of 12 m and a vertical length of 5 m. The scale of the C-wells experiments will be at a minimum of 30 m. Therefore, it will be possible to examine large-scale behavior of models and parameters. In addition, flow in the more permeable zones at the C-wells location is expected to be dominated by fractures. Therefore, components of computer codes that simulate flow and transport in fractures and interactions between rock matrix and fractures can be tested. Confidence in models can be increased if evaluating them relative to the proposed field experiments proves successful. However, scaling relationships developed from data obtained by the reactive tracer study for the saturated zone are not expected to be applicable to the unsaturated zone.

The reactive tracer study will aid in the characterization of the site before repository construction. Information will be collected on adsorption and retardation as noted in the previous paragraphs. In addition to reactive tracers, tracers will be used to investigate potential colloid migration, and, in conjunction with nonreactive tracers, matrix/fracture interactions may be assessed. This information may be useful in the resolution of both Issue 1.6 and Issue 1.1.

1.2 Objectives

The reactive tracer study will be conducted in conjunction with the United States Geological Survey (USGS). In an agreement (Dudley and Oakley, 1986) between the Technical Project Officer (TPO) at Los Alamos National Laboratory

(LANL) and the USGS TPO, the USGS will be the lead agency for hydraulic and conservative tracer tests with LANL as the support agency, and for the reactive tracer tests the roles will be reversed with LANL the lead agency and the USGS the support agency. The agreement defines responsibilities, review roles, and data flow between lead and support agencies. Both the USGS and LANL studies are described in SCP Section 8.3.1.2.3.

The rationale for the reactive tracer study given in the previous section leads to more specific objectives. These objectives are

- to select reactive tracers that are sorbed by a prevailing or controlling mechanism to be evaluated in field experiments,
- to evaluate the application of laboratory-derived sorption information and expressions to the field experiments, and
- to assess the effects of fractures and matrix/fracture interactions on solution transport.

Two objectives that result from the study and have benefits to other studies and investigations of the Yucca Mountain Project (YMP) are

- to investigate transport and adsorptive retardation in the saturated zone at the field scale and
- to provide field data of flow and transport of nonreactive and/or reactive tracers in the saturated zone at Yucca Mountain for evaluation of numerical models and their computer codes.

1.3 Use of Results

The reactive tracer study is part of the YMP investigations to describe the hydrologic system of the saturated zone at the site (SCP Section 8.3.1.2.3). Data for conservative tracers and hydraulic responses that will be collected during LANL's field tests can be added to the data obtained by the USGS in experiments described in SCP Sections 8.3.1.2.3.1.4 and 8.3.1.2.3.1.5. The following information describes the results and support provided by the reactive tracer study to related Project activities.

The geochemistry test program described in SCP Section 8.3.1.3 relies extensively on laboratory data to characterize the chemical behavior of radionuclides. The reactive tracer study is an initial step towards understanding the applicability of laboratory sorption information and expressions to field conditions. The reactive tracer study is expected to be one of the studies used to examine field-scale behavior of sorption. Study 8.3.1.3.7.2, Demonstration of Applicability of Laboratory Data to Repository Transport Calculations, will address the laboratory/field linkage in more detail, but the reactive tracer study is a necessary first step in this direction.

Activity 8.3.1.2.3.1.8 is Well Testing with Reactive Tracers Throughout the Site. Results from the C-wells activity will be used in making the decision on proceeding with similar experiments in other wells at Yucca Mountain. For instance, the type of information may be the effectiveness of single-well experiments in providing required information to describe site saturated zone

properties. Single-well experiments are generally less costly to conduct than multiple-well experiments. If both types of experiments yield the same information, single-well experiments are preferable.

Data from the C-wells experiments have been explicitly requested for two activities in SCP Section 8.3.1.3.7.1 pertaining to retardation sensitivity analysis. Activity 8.3.1.3.7.1.1 analyzes the physical and chemical processes affecting transport and intends to use data from the reactive tracer study. Also, Activity 8.3.1.3.7.1.2 will use an integrated geochemical/geophysical model of Yucca Mountain to make transport calculations to establish which physical and geochemical processes need to be included in performance assessment calculations for Issue 1.1 in SCP Section 8.3.5.13. For Activities 8.3.1.3.7.1.1 and 8.3.1.3.7.1.2, the C-wells data are needed for model evaluation. These two activities do not require the final analysis to be conducted as part of the reactive tracer study—that is, estimates of velocity and dispersion coefficients. The data to be transferred from each field test will be location, geometry, and dimensions of experimental settings; pumping rates and modes; piezometric information over the test periods; input concentrations and application modes of nonreactive and reactive tracers; breakthrough curves for nonreactive and reactive tracers; and any other pertinent experimental and operational information, such as temperature.

Data from experiments with polystyrene microspheres at the C-wells will be supplied to Activity 8.3.1.3.7.1.1 for use in testing a colloid transport model being developed in that activity. The specific data to be transferred from each field test will be location, geometry, and dimensions of experimental settings; pumping rates and modes; piezometric information over the test periods; influent concentrations and application modes of the polystyrene microspheres; tracer size distributions; breakthrough curves for the microspheres; and any other pertinent experimental and operational information, such as temperature.

In SCP Section 8.3.5.13, performance assessment calculations make the assumption that the retardation factor for fractures is essentially 1.0 (i.e., there is no retardation by sorption in fracture flow at Yucca Mountain). This assumption was based on calculations by Sinnock et al. (1984) in which the fracture was assumed to be smooth and the surface-area-to-mass relationship for sorbing minerals in the fractures was $50 \text{ m}^2/\text{g}$ of sorbing mineral. The reactive tracer study can assess the validity of this assumption. An estimate of matrix diffusion or diffusion into dead-end fractures can be made from the polystyrene microspheres and nonreactive tracers so that estimates of the retardation caused by sorption can be made. Additionally, estimates of dispersion coefficients and matrix diffusion can be used directly by the performance assessment models for resolution of Issues 1.1 and 1.6.

2.0 RATIONALE FOR THE TESTING OF THE C-HOLE SITES WITH REACTIVE TRACERS ACTIVITY

2.1 Approach

The reactive tracer study is divided into three tasks: (1) tracer identification and characterization, (2) field experiments, and (3) modeling. Tracer identification and characterization are a laboratory phase of this study to find tracers for use in the field experiments and to provide expressions of sorption behavior for use in modeling. Data from the field experiments will be used to verify the applicability of the laboratory-derived adsorption information and expressions to the field site. Modeling will be used in the design and analysis of the laboratory and field experiments. Each of these tasks is described in more detail in the following sections.

2.1.1 Tracer Identification and Characterization

Ideally, the radionuclides identified in SCP Section 8.3.5.13 (or isotopes of these radionuclides) would be the tracers used in this study. A direct field evaluation of radionuclides is the approach suggested by Pearson et al. (1987) in the design of similar field tests for the Waste Isolation Pilot Plant.

Three factors complicate the use of these radionuclides for the reactive tracer study. The first factor is the criteria governing the use of radioactive material at a candidate site. Section 113 of the Nuclear Waste Policy Act of 1982 requires that radioactive material used at a candidate site "be fully retrievable." For this study, "fully retrievable" is interpreted as 100% recovery; however, 100% recovery cannot be ensured. Another complication with using radionuclides as tracers is that if waste is emplaced at Yucca Mountain, the detection of radionuclides in ground water may lead to the erroneous conclusion that the integrity of the repository had been breached when, in fact, the radionuclides detected were introduced as tracers and not as components of the waste emplaced (Pearson et al. 1987).

The second factor is the high retardation exhibited by most of the radionuclides of interest. Table 1, which is taken from SCP Table 8.3.5.13-4, contains values for the distribution coefficients and the retardation factors based on the bulk density and moisture content values listed in the footnotes. A retardation factor greater than about 10 (more a range than a value) will require a long-duration test, and use of these tracers would not yield data early enough to be used for site characterization. The final complicating factor is the complex chemistry exhibited by many of the radionuclides of interest, particularly the actinides. Phenomena that may affect the radionuclides are being investigated as described in SCP Section 8.3.1.3.5. In particular, processes such as speciation, precipitation, and colloid formation may occur to different extents for the various radionuclides, which makes the understanding of adsorption more difficult. These factors significantly limit the consideration of the radionuclides that can be studied in the reactive tracer study.

An alternative to using radionuclides is to use natural analogs for various radionuclides. An analog exhibits some similarities in chemical behavior to the behavior of the radionuclide it represents, but the analog may not be radioactive and can be used as a surrogate for the radionuclide. An example of such a surrogate is rhenium for technetium. Analogs appear to alleviate environmental concerns associated with the radionuclides, but the analogs still have limitations imposed by their high retardation and complex chemistry.

TABLE 1
TYPICAL DISTRIBUTION COEFFICIENTS AND APPROXIMATE
RETARDATION FACTORS FOR WELDED AND NONWELDED
HYDROGEOLOGIC UNITS AT YUCCA MOUNTAIN^a

Element	Distribution Coefficient, $K_d^{a,b}$ (ml/g)		Retardation Factor, R_m^c	
	Welded	Nonwelded	Welded	Nonwelded
Americium	1,200	4,600	28,000	24,000
Carbon	0 ^d	0 ^d	1	1
Curium	1,200	4,600	28,000	24,000
Cesium	290	7,800	6,700	41,000
Iodine	0 ^d	0 ^d	1	1
Neptunium	7	11	160	58
Protactinium	64	140	1,500	740
Lead	5 ^e	5 ^e	120	27
Plutonium	64	140	1,500	740
Radium	25,000 ^f	25,000 ^f	580,000	130,000
Tin	100 ^e	100 ^e	2,300	530
Strontium	53	3,900	1,200	21,000
Technetium	0.3	0 ^d	8	1
Thorium	500 ^d	500 ^e	12,000	2,600
Uranium	1.8	5.3	27	45
Zirconium	500 ^e	500 ^e	12,000	2,600

a. From Table 8.3.5.13-4 in the SCP.

b. Unless otherwise indicated, distribution coefficients were taken from Table 6-25 (DOE 1986) or were inferred from the sorption ratios quoted by Daniels et al. (1982).

c. Calculated using values of moisture content of 10 and 28% and bulk densities of 2.33 and 1.48 g/cm³ for welded and nonwelded tuff.

d. No data available; assumed to be zero.

e. Inferred from the midrange retardation factor for tuffs compiled in Table 7-1 (National Research Council 1983).

f. Barium used as a chemical analog.

Another alternative is to use either inorganic or organic tracers whose chemistry is relatively well defined to study their mechanisms of adsorption. The behavior of the surrogate tracers must be correlated with the behavior of the radionuclides of concern for repository performance. This correlation is particularly difficult for the actinides because of the complex chemical behavior that they exhibit. For adsorption, the mechanism(s) that control the interaction between the solute and the solid can be used to relate radionuclides to nonradionuclides. By defining the mechanisms that govern adsorption for the radionuclides (SCP Section 8.3.1.3.4) and by selecting nonradioactive tracers whose adsorption is governed predominantly by one of these mechanisms, a connection to radionuclides can be established. This approach of linking surrogate tracers to adsorption mechanisms has been selected for this study.

Retardation of reactive tracers may result from a number of geochemical processes, but the reactive tracer study will limit its evaluation of retardation to adsorption processes. Adsorption may generally be defined as the interaction of a solute with a surface or interface (e.g., solid surface) (Schindler and Stumm 1987). Adsorption refers to interactions of solutes with a two-dimensional surface, and absorption refers to interactions of solutes with a three-dimensional phase (Westall 1987). Sorption includes both adsorption and absorption and is a general term used to represent both types of interactions (Morel and Gschwend 1987; Weber 1972). The term adsorption also describes the movement of dissolved species from the bulk solution to the surface (or interface), and desorption describes the movement of adsorbed species from the interface to the bulk solution (Schindler and Stumm 1987). Adsorption of dissolved species by interfaces may lead to dissolution or precipitation reactions (Schindler and Stumm 1987).

Adsorption processes can be divided into two general classes: physical and chemical (Cole 1983; Thomas 1987; Greenland and Hayes 1981; Gaspar 1987; Carberry 1976; Weber 1972; Faust and Aly 1987). Physical adsorption is caused by weak forces of attraction, such as intermolecular or van der Waals forces. The heat liberated in physical adsorption is generally in the range of 2-6 kcal/mol of species adsorbed. Physical adsorption is not site specific (i.e., the adsorbed molecules are free to cover the entire surface) and is reversible, enabling desorption to occur at the same temperature, although the process may be slow because of diffusion effects. The interaction is rapid and nonactivated, and the chemical nature of the adsorptive species is essentially preserved in the processes of adsorption and desorption. Chemical adsorption (or chemisorption) involves valence forces of the type that bind atoms to form chemical compounds. For chemical adsorption, the heat of adsorption is usually greater than 20 kcal/mol. The interactions in chemical adsorption are localized on specific sites and, therefore, are not free to migrate about the surface. Chemisorption is largely irreversible and usually involves an activation energy. Table 2 summarizes the major differences between physical and chemical adsorption. A third category of adsorption, which displays characteristics of both physical and chemical adsorption (Table 2), is intermediate. There is not a sharp boundary between the two classes of adsorption, although the extremes are easily distinguishable.

This choice of this approach to classification for use in this study was based on a review of the literature and communications with experts from fields such as environmental science and engineering, chemical engineering, soil science and geochemistry. These disciplines classify and refer to adsorption somewhat

TABLE 2
**CHARACTERISTICS OF PHYSICAL, CHEMICAL,
AND INTERMEDIATE SORPTION REACTIONS**

Characteristic	Controlling Process of Sorption Reaction		
	Physical Process	Chemical Process	Intermediate Between Physical and Chemical
Enthalpy, ΔH (kcal/mol)	Low <6-12	High >20	Low Intermediate between chemical and physical
Changes in Vibration Frequency	Small (~0.1%)	Large	Small to large
Bond Strength	Too weak to cause physical or chemical change	Strong enough to cause physical and chemical change	Similar to physical or chemical
Type of Bond	Nonspecific and reversible	Specific and irreversible	Similar to physical and chemical

Sources: Thomas 1987; Cole 1983; Greenland and Hayes 1981.

differently. For example, Westall (1987) used chemical reactions with surfaces and electrical interactions at surfaces, which correspond to the chemical and physical classes, respectively, used in this study. Stumm and Morgan (1981) classified adsorption processes as specific and nonspecific, which can again be related to chemical and physical adsorption, respectively.

Within these generic classifications, more specific interactions can be defined. Again referring to Westall (1987), the specific interactions within the chemical reaction class are surface hydrolysis, surface complexation, surface ligand exchange, and hydrogen bond formation. For electrical interactions, the specific types are electrostatic and polarization interactions. Describing the interactions between radionuclides and/or tracers at these specific levels would be ideal, but, as Westall noted, no single mechanism dominates adsorption in a natural system.

Therefore, the reactive tracer study will use the generic classes of physical and chemical adsorption as its basis for selecting tracers and distinguishing mechanisms.

Another approach to classifying adsorption in groups is through surface complex models (Sposito 1981) or electrochemical models (Westall 1987). Figure 1, taken from Westall (1987), is a pictorial representation of the triple-layer model for the solute/solid interface. At the surface plane and at the inner Helmholtz plane (IHP), the primary ions that determine the potential of oxide surfaces interact

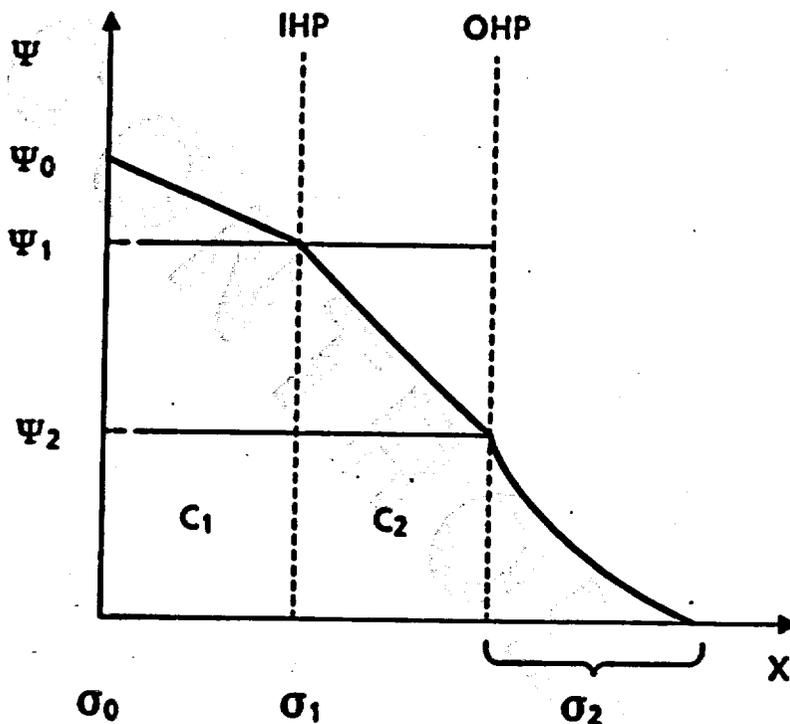


Figure 1. The Triple-Layer Model for Solid/Solute Interface. Ψ represents potential; σ represents charge; C is the capacitance; X is the distance away from the surface; IHP is the inner Helmholtz plane; and OHP is the outer Helmholtz plane (from Westall 1987).

chemically with the surface. The outer Helmholtz plane (OHP) is the inner boundary for the diffuse layer, where ions are affected by electrostatic forces only. Two other models, the capacitance model and the double-layer model, have also been proposed to describe surface/solute interactions at a molecular level (Sposito 1984; Stumm and Morgan 1981; Kent et al. 1986). For all three of these models, the charge and potential of the layers decrease from the surface to the bulk liquid. In the triple-layer model in Figure 1, H^+ and OH^- functional groups reside in the surface, where inner-sphere complexes, including metal cations or oxyanions, are formed. These interactions are also referred to as specific adsorption because no molecule of the bathing solvent is interposed between the surface functional group and the molecular unit it binds. Outer-sphere complexes containing the ions of a background electrolyte are associated with the IHP plane, where at least one solvent molecule is interposed between the functional group and the bound molecule. Beyond the OHP is the diffused region, where ions are nonspecifically bound. For the purposes of this study, chemical adsorption is associated with the formation of inner- and outer-sphere complexes, whereas physical adsorption is considered to occur in the region of the diffused ion swarm.

By grouping all solute/surface interactions in one of two classes, the adsorption of radionuclides based on the controlling or prevailing mechanism (here, mechanism is used at the generic class level) can be determined. The interactions of any ion with a surface are not totally governed by a single mechanism, so this study will look at the prevailing mechanism(s). The radionuclide sorption study (SCP Section 8.3.1.3.4) will examine sorption at a mechanistic level, and the tie from tracers used in the reactive tracer study to the radionuclides can be made at this fundamental level.

SCP Section 8.3.1.2.3.1.7, which describes this activity, indicates that electrostatic adsorption, molecular sieve, and chemisorption are the mechanisms to be used in the study. In the discussion above, Westall defines the electrostatic mechanism as a specific mechanism, but electrostatic will be used interchangeably with physical in this study plan. Molecular sieve is the process by which a molecule is trapped in cage structures common to zeolites and certain clays. Molecular sieve will not be considered any further in this study because of the difficulty in differentiating it from matrix diffusion. Chemisorption is defined essentially as chemical sorption, i.e., strong bonding between solute and surface and high heat of adsorption. Therefore, this definition coincides with the generic class definition used in this study.

Use of electrochemical models can also aid in establishing a tie between the radionuclides and tracers used in this study. The problem is that experimental data generally do not provide sufficient detail to resolve the many possible states of the model. A single mineral is often used in experiments as the solid phase, and model parameters are determined by fitting. Westall (1987) observed that mathematical manipulation is not sufficient to resolve the adsorption energy, and additional data derived from electrophoresis or electrochemical cells are needed. As part of the reactive tracer study, individual minerals identified by studies conducted in SCP Section 8.3.1.3.2 (mineralogy and petrology) will be used in experiments with the proposed reactive tracers. The purpose of experiments that involve individual minerals is to increase the understanding of mechanistic interactions that are not inherent in adsorption expressions (e.g., isotherms). Because these adsorption expressions (either for kinetics or for equilibrium) are used to account for retardation by adsorption in transport codes,

It is necessary to know as much as possible about their connection to more fundamental mechanisms. Knowledge obtained from experiments with individual minerals should increase effectiveness in transferring results from laboratory scale to field scale by improving the confidence of using isotherms to represent retardation by adsorption. For example, laboratory studies of lithium adsorption on individual minerals may show no detectable adsorption on feldspar, in contrast to a greater adsorption on montmorillonite and very high adsorption on hematite. If a tuff sample is composed of various percentages of these minerals and represents the zone where field tests will be performed, it may be inferred that the extent of adsorption will be controlled by hematite and montmorillonite. The extent of adsorption defines the prevailing mechanism(s). The transfer of information on the behavior of a tracer in the presence of a single mineral to samples that contain various minerals will be difficult, particularly because the number of minerals playing a significant role in the adsorption of the tracer increases. This outcome can only be known after the tracer has been evaluated with both single minerals and tuff samples.

A logical alternative is to use data from the individual mineral experiments with electrochemical models. This approach is not warranted for the field studies. Electrochemical models provide insight into processes or properties that control the reactions in the solid/solute system, but, as noted by Bolt and Van Riemsdijk (1987), heterogeneities at the micro- and macroscales prevent complete determination of model parameters. These authors indicated that a simple model, combined with additional knowledge of important processes, may be the best choice for field studies. This basic approach guides the philosophy of the laboratory experiments in the tracer selection tasks. Tracers will be selected on the basis of adsorption mechanisms (as well as other criteria), but adsorption will be modeled using less sophisticated adsorption isotherms. The rationale for this approach is that the heterogeneities in physical and chemical properties cannot be easily identified, and using the more complex model results in a fitting exercise. Isotherms are not intrinsically tied to a particular adsorption mechanism, but, by fitting the isotherms to experimental data and selecting tracers that are adsorbed by a prevailing mechanism, the parameter values of the isotherms can be related to particular adsorption mechanisms.

Another complicating factor is linking of complex geochemical codes to transport equations. Several studies (Cederberg et al. 1985; Lewis et al. 1987; Kirkner et al. 1984; Miller and Benson 1983) link geochemical codes to transport codes, but these codes are primarily one- or two-dimensional and do not include all of the processes that are occurring.

Although isotherms are considered empirical, some have been derived from fundamental concepts. For example, a general isotherm was derived from statistical mechanics by Sposito (1980), who assumed that the adsorption sites were heterogeneous and that adsorption on each site or groups of sites behaves according to Langmuir (1918) theory. Crickmore and Wojciechowski (1977) also derived the same equation from kinetics theory using similar assumptions. The resulting equation is termed the modified Freundlich in this study plan and is given as

$$S = \frac{S_{\max} A^{\beta} C^{\beta}}{1 + A^{\beta} C^{\beta}}, \quad (1)$$

where

S is the adsorbed phase concentration (M/M),
 C is the solution phase concentration (M/L³),
 S_{\max} is the maximum adsorption (M/M), and
 A and β are parameters.

This formulation is based on two assumptions: (1) the distribution of charges over the surface is very similar to a Gaussian or normal distribution and (2) at each charge site, the adsorption can be described by a Langmuir (1918) equation. Van Riemsdijk et al. (1986) used the same Langmuir assumption with skewed and symmetric distributions of charges to derive an isotherm with the same formulation.

The isotherm parameters (A and β) in Equation 1 represent the mean sorption energy and the spread of individual energies about the mean, respectively (Sposito 1980). Polzer and Fuentes (1987) suggested that these parameters can be interpreted in terms of reactive solute transport for equilibrium conditions, as A relates to the average time for breakthrough to occur and β represents the spread or dispersion of the solute caused by its adsorptive heterogeneity. This dispersion is in addition to hydrodynamic dispersion caused by flow.

The modified Freundlich is a general isotherm from which three other commonly used sorption expressions can be derived (Polzer and Fuentes 1987). For example, if the solute is in trace quantities so that $A^\beta C^\beta < 1$, then Equation 1 becomes

$$S = \alpha C^N, \quad (2)$$

where S and C have been previously defined, and α and N are parameters. This is the Freundlich isotherm. If Equation 1 were examined, α is equal to $S_{\max} A^\beta$ and N would be equal to β . The parameters in Equation 2 have been designated differently to reflect the fitting process and the fact that the quantities from Equation 1 may not be directly transferable to Equation 2. A β value of 1 in Equation 1 produces the following expression:

$$S = \frac{kbC}{1+kC}, \quad (3)$$

where S and C have been previously defined, and k and b are parameters. Again, k and b can be related to specific parameters in Equation 1, but the designation has been changed for the same reasons given for Equation 2. Equation 3 is the Langmuir isotherm, which was the basis for adsorption at a single site used in deriving the modified Freundlich. A β value of 1 in Equation 1 assumes a homogeneous charge distribution on the surface, so Equation 3 should come as no surprise. If both $A^\beta C^\beta \ll 1$ and $\beta = 1$, the resulting expression is

$$S = K_d C, \quad (4)$$

where S and C have previously been defined, and K_d is the distribution coefficient (Freeze and Cherry, 1979). By inserting Equation 4 into transport equations, analytical solutions to the governing mass transport equation are possible.

Equations 1-4 represent four of the available isotherms. Travis (1978) and Travis and Etnier (1981) present a more complete list of available isotherms. These four isotherms will be used to analyze experiments that use both individual minerals and tuff as the solid phase. Electrochemical models will be used to analyze only the single-mineral experiments. This fundamental approach used in conjunction with the isotherms will enhance the capability of extrapolating to conditions not observed in the laboratory.

Kinetics may play an important role in the transport of tracers under dynamic conditions. For the field tests, reaction rate will be important in predicting field behavior of the tracers in a heterogeneous ground water velocity field. By evaluating kinetics and estimating ground water velocities for various field test scenarios, conditions can be identified in which the local equilibrium assumption may not apply, and these particular test conditions can be avoided. For most adsorption processes in porous media, film and/or particle diffusion processes are rate-controlling under different conditions (Helfferich 1962). The effects on these processes were demonstrated by Boyd et al. (1947). Thus, any factor that decreases the rate of particle diffusion without causing a corresponding decrease in the film diffusion rate will favor control by particle diffusion, and any factor that increases the rate of film diffusion without causing a corresponding increase in the particle diffusion rate will also favor exchange controlled by particle diffusion (Sparks 1986).

Sparks (1986) discusses the following factors as determinants of whether adsorption in clays and soils is controlled by film or particle diffusion. (1) Vigorous mixing decreases the thickness of the film around a particle but does not entirely eliminate the film. (2) Slow flow velocities provide longer contact between the solution and the particle, whereas high flow velocities allow the system to remain dynamic. (3) The thickness of the hydrodynamic film may be affected by (a) stirring or shaking in a batch process, (b) flow in a column process, (c) the hydration status of cations, and (d) the ionic strength of the background electrolyte; thus, a change in film thickness affects film diffusion. (4) Large particles tend to favor control by film diffusion, although both film and particle diffusion are affected by particle size. (5) Processes controlled by film diffusion are usually favored in solutions of low concentration, and particle diffusion control is favored in solutes of high concentration. (6) The energy of activation tends to be lower for processes controlled by film diffusion and higher for processes controlled by particle diffusion.

Three primary techniques are usually used in studying kinetics reactions: (1) batch, (2) miscible displacement or flow technique, and (3) isotopic exchange (Sparks 1986). The batch technique will be used in the tracer selection study. The primary objective of these kinetics experiments is to determine the time needed to reach equilibrium in batch equilibrium experiments. A secondary objective is to determine in a qualitative way whether kinetics is controlled by film diffusion or by particle diffusion. This latter objective will be accomplished by varying the concentration of the adsorbing tracers and the rate of mixing. If the rate of adsorption is affected by the mixing intensity and by a change in tracer concentration, film diffusion is likely to be controlling. On the other hand, if the rate of adsorption is not affected by mixing intensity, particle diffusion is likely to be controlling. Determining the rate-limiting step is difficult and thus may not be accomplished.

The same laboratory techniques used in studying kinetics (batch, miscible displacement or flow technique, and isotopic exchange) can also be used to study

equilibrium conditions. The primary objective of the equilibrium experiments is to determine the equilibrium adsorption constants for the field experiments. The batch technique will be used for these experiments. One reason for using batch is that it is being used by the radionuclide sorption study (SCP Section 8.3.1.3.4), and increased confidence in extrapolating adsorption constants derived from that study to the field will be obtained if the same techniques are used. The parameters in Equations 1-4 will be derived from the results of these experiments, and a "best-fit" expression will be used for the column experiments.

Column experiments will be used to study the tracers selected by the batch experiments under dynamic conditions. These analyses represent an initial evaluation of the adsorption parameters from the batch experiments. A nonreactive tracer will be used to estimate the velocity and dispersion coefficients. These coefficients will be used in conjunction with a one-dimensional transport code to predict the response of the reactive tracers. Using all four isotherms (Equations 1-4) in this phase, an evaluation of the "best" isotherm for field use will be made.

In the C-wells tracer tests at Yucca Mountain, tracers will encounter fracture flow as well as matrix diffusion. Polystyrene microspheres of different sizes will be used as tracers to evaluate the relative amounts of matrix diffusion and fracture flow. An alternative to the polystyrene microspheres is biological tracers, such as bacteria and/or viruses, whose sizes are known. These biological tracers are stained or marked so that they can easily be detected. The polystyrene microspheres were selected for the following reasons. (1) A wide size distribution can be readily obtained, whereas, for microorganisms, several different organisms would have to be combined. (2) Surface charges for the microspheres are easily produced by doping them, whereas, if microorganisms are to be used, varying the charge can be achieved only by using different types of microorganisms. (3) The polystyrene microspheres are relatively stable and will not readily degrade and produce carbon dioxide, whereas, microorganisms might significantly enhance carbon dioxide production. This latter effect might interfere with studies that are dating ground waters at Yucca Mountain.

In field tests, Harvey and George (1987) found that the breakthrough in a sandy aquifer was faster for polystyrene microspheres than for a soluble nonreactive tracer (bromide), although the dispersion of the microspheres was greater than that of the bromide. These authors also found that the average size of the microspheres was larger (1.0 μm in diameter) at the observation location than the average size (0.3 μm in diameter) injected into the sandy aquifer. Their study also indicated that the peak abundance of uncharged microspheres more closely approximated that of the maximum breakthrough of a soluble conservative tracer than did the charged microspheres. They concluded that the filtration of the microspheres was affected by the size of the microspheres and by the charge characteristics of the microspheres and the porous medium.

The influence of surface characteristics of a colloid and of the porous medium is based on the double-layer concept at the interfaces (Ives and Gregory 1966). These surface forces at the interfaces have been discussed relative to types of adsorption mechanisms. A series of sized microspheres injected into a fractured medium could permit the evaluation of matrix diffusion and fracture flow. For example, small microspheres (<1 μm) could diffuse into the matrix, whereas the larger microspheres would move through fractures only because their large size would prevent them from entering the matrix. However, charge characteristics also need to be evaluated to assess size effects.

2.1.2 Field Experiments

Field experiments are considered a separate task because of the magnitude of the operation. Depending on the tracers selected, there may be special requirements for sampling and analytical chemistry equipment. The products of this task will be breakthrough curves that present concentration of tracer versus time for single- and multiple-well experiments that will have been conducted.

The transport and retardation of tracers will be investigated at the C-wells complex (UE-25c #1, UE-25c #2, and UE-25c #3) shown in Figure 2. A plan view of the C-wells complex in Figure 3 shows the relative distances between the wells. The stratigraphy of the three C-wells boreholes is given in Figure 4. At the location of the C-wells (Figure 2), the Calico Hills Member of the Crater Flat Tuff is at least partially located in the saturated zone. The remaining units are the Prow Pass, Bullfrog, and Tram Members of the Crater Flat Tuff formation. As described in SCP Sections 8.3.1.2.3.1.4 and 8.3.1.2.3.1.5, the USGS will identify the most permeable zones in the C-wells from hydraulic tests. These more permeable regions have been identified as the initial sites where tracer experiments will be conducted because the more rapid flow will provide a conservative estimate of the ground water velocity for the USGS. The reactive tracer experiments will use the more permeable zones because shorter travel times are expected for the retarded tracers. Therefore, the duration of the study will not be excessive.

The reactive tracer study will be coordinated with USGS hydraulic and conservative tracer experiments. Initial experiments by the USGS (SCP Section 8.3.1.2.3.1.4) will be hydraulic experiments in single and multiple wells. Packers will be used to isolate zones in the wells to identify communication between different zones and between the wells. One result of these experiments will be to characterize the hydraulic conductivity at the site.

The USGS will then conduct single- and multiple-well conservative tracer experiments to extend the hydrologic results. At this time, three designs have been proposed for the conservative tracer experiments: (1) interwell recirculation experiments consisting of injecting into one well and pumping at the same rate from another; (2) convergent experiments, in which tracer is deposited in a well and a second well is pumped; and (3) single-well drift/pumpback experiments in which a tracer is deposited in a well or packed-off zone, is allowed to drift with the natural flow (unperturbed beyond the effects of the well bore), and is then recovered by pumping the same well.

The reactive tracer experiments will also use single- and multiple-well designs in which the zones of interest are packed off. The single-well design is the most appropriate for investigating the chemical adsorption tracer because the tracer will be expected to be adsorbed a very short distance from the injection point. A multiple-well experiment, even along the shortest distance at the C-wells site (between C2 and C3), would require more time than is available for completing this study. Two designs of single-well experiments are proposed: (1) a drift/pumpback experiment, as proposed by the USGS and (2) an injection/withdrawal experiment design. For the injection/withdrawal experiment, the tracer is injected into a zone as uniformly as possible and is then pumped back into either the same zone or another zone that has been isolated. In the case of the drift/pumpback experiment, tracer is injected uniformly into a packed zone and allowed to drift for a specified duration with the prevailing ground water flow.

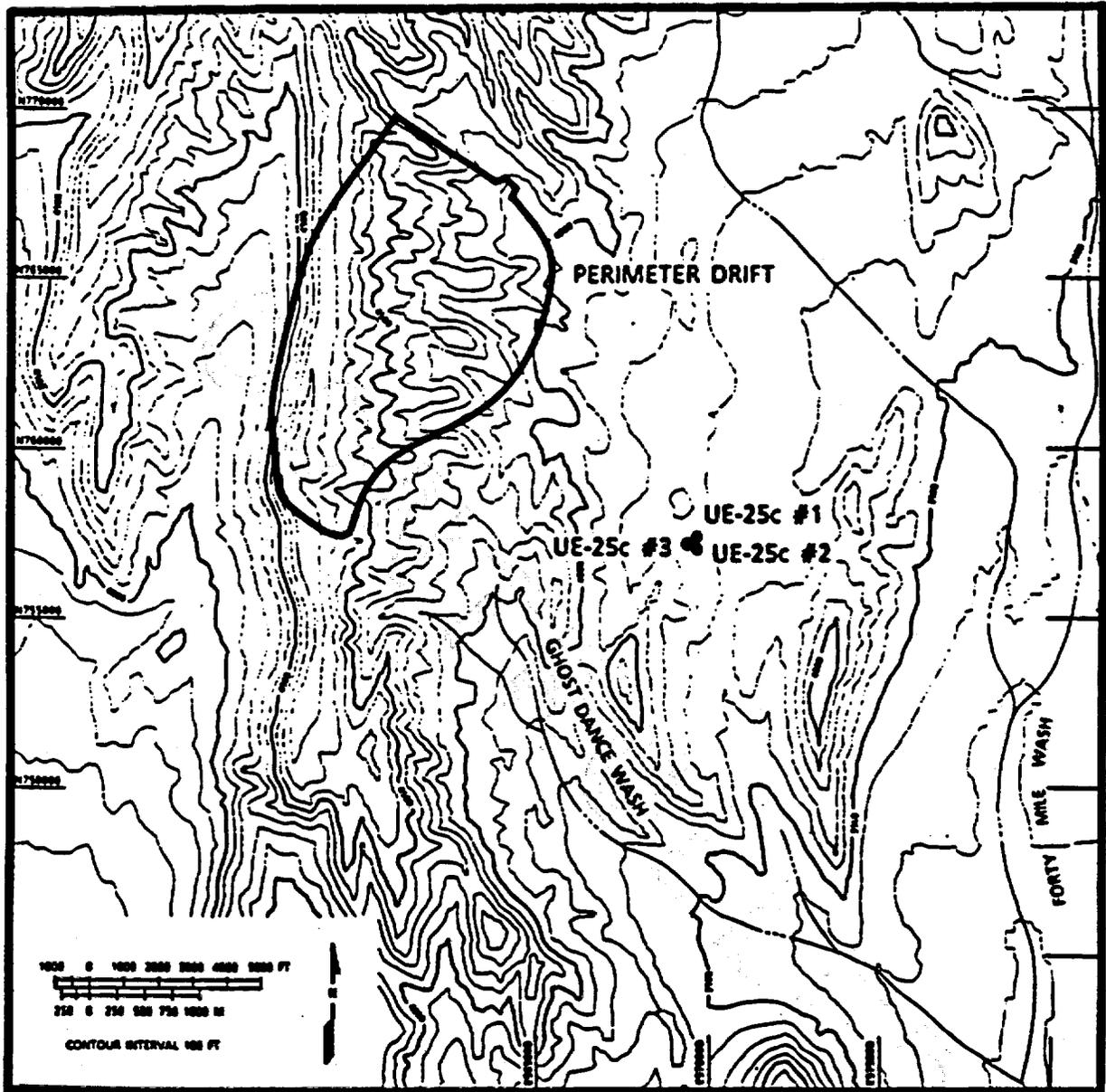


Figure 2. Location of the C-Wells Complex

C-WELLS COMPLEX YUCCA MOUNTAIN

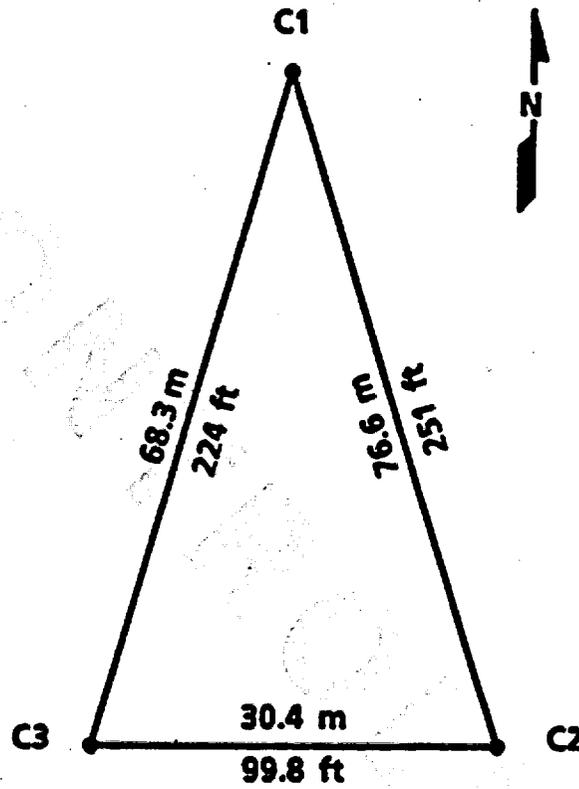


Figure 3. Plan View of the C-Wells Complex (not to scale)

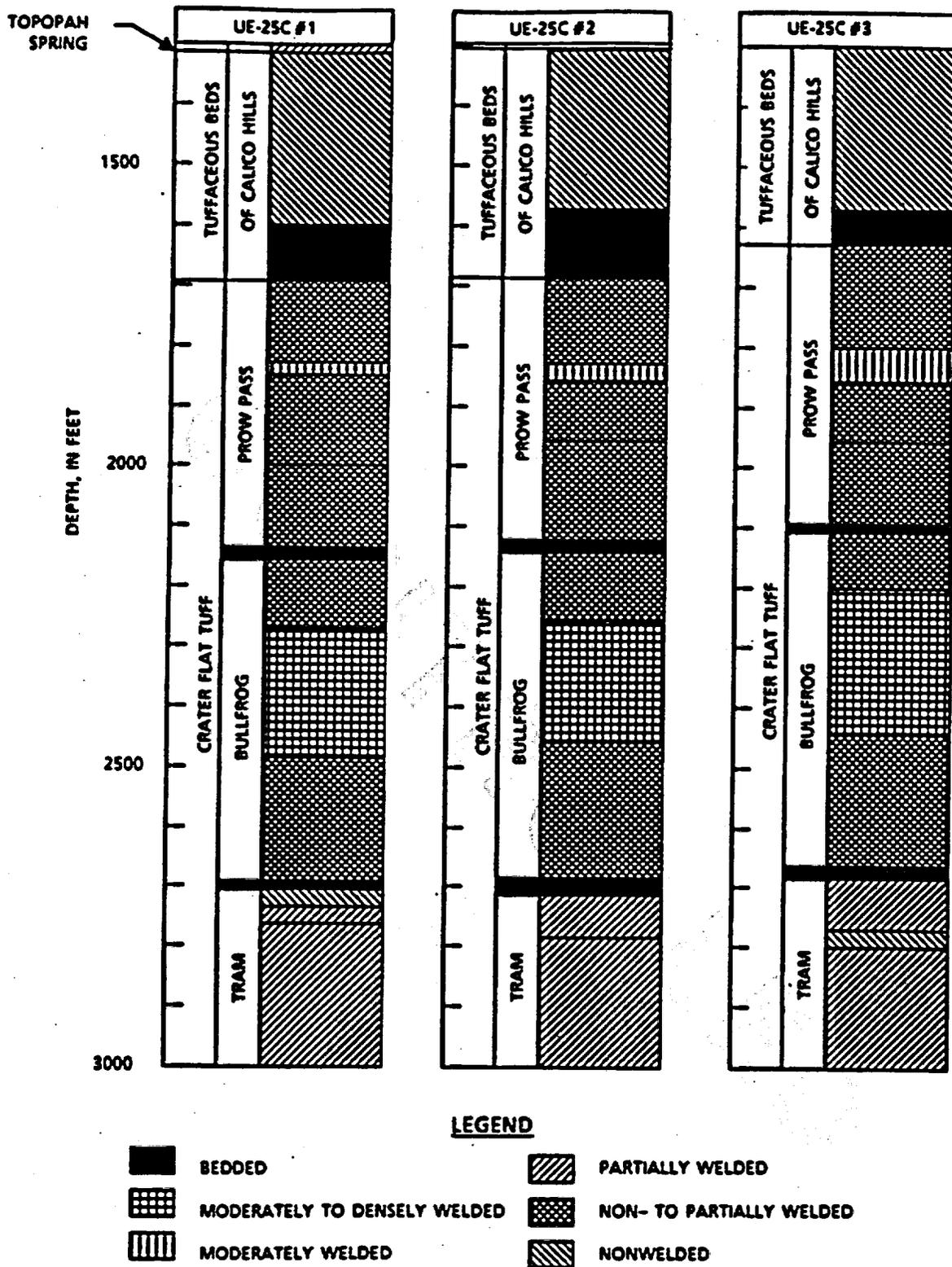


Figure 4. Stratigraphy of Each of the C-Wells (from SCP Section 8.3.1.2.3.1.3)

At the end of this drift period, the same zone is pumped and the tracer recovery is recorded.

It is difficult to select either of these two designs based on current knowledge of the site and potential tracers. When more information is available, modeling can be used to provide a basis for choosing between the alternative single-well designs or for using both designs.

Multiple-well test designs for the reactive tracer study are (1) convergent; (2) two-well experiments with no recirculation, and (3) two-well experiments with recirculation. In the convergent experiments, a steady-state flow field will be established by pumping one of the three C-wells, and tracers will be injected into the zones of the remaining two wells. The concentration versus time of each tracer will be measured at the pumping well; therefore, at least two tracers will be needed to distinguish between the wells. Pearson et al. (1987) used a convergent scheme in their design of a sorbing tracer test because of the successful experience obtained by Kelley et al. (1987) for conservative tracer tests. The two-well design with recirculation again requires establishing a steady-state flow field between two wells. Fluid with tracer is injected into a packed-off zone in one well and is produced from an isolated zone in a second well. This design was used to measure transport parameters for a site for the Basalt Waste Isolation Project at Hanford (Gelhar 1982). The two-well experiment with no recirculation would necessitate the injection into a well of a fluid from another location, and the fluid produced from the second well would have to be disposed of. When fluid with tracer is reinjected during recirculation, a long tail (which is caused by recirculation rather than by dispersive effects), occurs on the concentration-versus-time curve, making analysis more difficult. The two-well design with no recirculation for the multiple-well experiment is preferred. The convergent design will require more tracers than may be identified and characterized by the time the field experiments start. The two-well test with recirculation leads to problems with analysis because the tracer is reinjected, so this design would be the second alternative.

2.1.3 Modeling

The modeling task will assist in the design of both field and laboratory experiments and in the analysis of the field experiments. Analysis of the laboratory experiments will be conducted as part of the tracer identification and characterization task.

It is expected that the field experiments will be conducted in the most permeable zones defined by the hydraulic and conservative tracer experiments performed by the USGS and that the more permeable zones at this site will be composed of fractured material. Recent studies in modeling flow and transport in fractured porous media indicate that behavior in terms of an equivalent porous medium may not always be exhibited, even at the scale of the well experiments proposed here (Karasaki 1987). Therefore, the different modeling approaches are suggested because the response of the various experiments cannot be predicted a priori. The three modeling approaches are porous medium continuum, dual porosity, and fracture network modeling. None of these approaches can currently be selected over the other, so all three will be used in the reactive tracer study.

The approach to be used in designing the field experiments is to select a range of parameter values for each modeling approach from the available data. Limited input will be available for the more complex model, so a range of values will be specified.

Analyses of the field experiments to achieve the primary purpose of this study will use all three modeling assumptions unless results from the USGS hydraulic or conservative tracer experiments indicate which approach is the most appropriate. For each reactive tracer experiment, an appropriate nonreactive tracer will be used to estimate the transport parameters, e.g., velocities and dispersivity for the advection/dispersion equation. Then, the parameters from the laboratory experiments for the appropriate retardation expression will be used in conjunction with the transport parameters to predict the field-observed breakthrough curve for the well experiments. The comparison of the predicted and observed breakthrough curves by a selected objective function will provide an evaluation of the application of the laboratory-derived data to field situations.

The three tasks--tracer identification and characterization, field experiments, and modeling--will be described in more detail in the following sections. Each task is dependent on the other two for successful completion of this study, e.g., the field experiments depend on the tracers from the tracer identification and characterization task, and the modeling task will assist in designing the field experiments. The field experiments, in turn, will provide data for modeling and testing the adequacy of the laboratory data in the field. The success of this study depends on completion of each task and continuous exchange of information between the modeling and tracer identification and characterization tasks. Simulation of potential experimental conditions that may occur in the field will allow the laboratory experiments to be conducted under conditions similar to those that will be encountered during the field experiments and that are important to adsorption.

2.2 Types of Measurements to Be Made

The objective of the laboratory experiments is to select tracers that retard primarily by physical and chemical adsorption (at least one tracer for each mechanism). A constraint placed on these selections is that the retardation of the tracers under flow conditions is minimal, so their breakthrough can be achieved within a reasonable period (e.g., <1 yr). Another important aspect of the laboratory experiments is that the data should provide a tie between the data obtained from the radionuclide sorption studies (SCP Section 8.3.1.3.4) and the data obtained from the C-wells field tests.

The batch studies will focus on kinetics and equilibrium experiments in either the adsorption or desorption modes. Geologic material and water from the Yucca Mountain vicinity will be used in these experiments. The Prow Pass, Bullfrog, and Tram Members of the Crater Flat Tuff are in the saturated zone at the C-wells (Figure 4). Although it would be ideal to use samples taken at appropriate depths from the actual boreholes, this does not appear feasible at this time. Instead, samples may be collected from outcrops located as near as possible to the field site, and this material is expected to have a mineralogical composition similar to that of the field test area.

If properly documented samples from the C-wells are available in sufficient quantity, they can be included in the experiments either to compare or to verify

the information obtained using samples from other sites or drillholes. The number of samples collected and available for the laboratory experiments will be small relative to the field test area and, therefore, may not adequately represent the distribution and range of composition of mineralogic components in the test area. Even if drilling and core samples were to become available in a reasonable period of time, efforts to characterize the effects of variable mineral composition on the behavior of selected tracers would be a time-consuming and expensive task whose need will have to be evaluated.

C-wells water, C-wells surrogate water, Well J-13 water, or distilled and deionized water are alternative liquids that could be used to introduce the tracers into the tuff samples. The choice of waters has limitations and disadvantages that should be recognized. Ideally, C-wells or C-wells surrogate waters would approximate in situ conditions. C-wells waters will probably not be available for the laboratory studies, and any water currently pumped from the wells is expected to come from a wide range of depths that are not specific to the intervals of the field tests. The reported composition of the C-wells waters (Table 3) represents an integrated sample of waters throughout the borehole, which does not permit reproduction of a C-wells surrogate water for individual field test zones at present. Use of surrogate water would provide better control of the chemical composition and would not raise questions pertaining to the specific application of the results if different waters are used. The selection of Well J-13 water to put tracers and tuffs in contact is based on the fact that it has been used in most experiments for the sorption of radionuclides (SCP Section 8.3.1.3.4) and dynamic transport (SCP Section 8.3.1.3.6); therefore, a better integration of results between those tasks and this study may be possible. Additionally, using the computer code PHREEQE (Parkhurst et al. 1980), it has been shown that the composition of Well J-13 water has an effect similar to that of lithium, as does the composition of the water currently available from the C-wells. C-wells waters will not be used in the experiments performed using single minerals because the variable compositions of the aqueous phase would complicate interpretation. Distilled and deionized water with various concentrations of electrolytes (NaCl or NaClO₄) will be the aqueous phase for experiments using single minerals.

Laboratory column experiments will also be conducted to evaluate the selected tracers for their relative behavior in a transport environment. These column experiments will simulate a range of influent and flow conditions to characterize both breakthrough and recovery. Additionally, retardation differences caused by differences in residence times will define equilibrium and kinetic adsorption. These experiments will also use tuff samples and Well J-13 water. Tuff samples may be disturbed or undisturbed, depending on the availability of cores.

Potentiometric and electrophoretic experiments will also be conducted in the batch mode using both individual minerals and tuff matrix samples to help evaluate mechanisms. These experiments, when performed with tuff matrix samples, will provide a measure of the interactions among minerals and may also serve as a qualitative criterion for differentiating between chemical and physical adsorption on individual minerals. Data from potentiometric and electrophoretic experiments will be incorporated in electrochemical models to provide a more quantitative evaluation to differentiate between mechanisms of adsorption (e.g., inner-layer surface complexation adsorption versus diffused layer adsorption). In the potentiometric and electrophoretic experiments, the solution phase will be distilled and deionized water with added electrolytes (e.g., NaCl and NaClO₄).

TABLE 3
COMPARISON OF WELL J-13 WATER WITH C-WELLS WATER^a

<u>Constituent^b</u>	<u>Well J-13 Water</u>	<u>C-Wells Water^c</u>
pH (onsite)	7.2	7.7
Calcium	12	11.3
Potassium	5	2
Lithium	0.040	0.11
Magnesium	2.1	0.38
Sodium	42	55
Strontium	0.02	0.04
Chloride	7.1	7.2
Fluoride	2.4	2.1
SiO ₂	57	54
SO ₄	19	22
HCO ₃ (lab)	124	142

- a. Source: Benson and McKinley 1985.
 b. All elements in milligrams per liter.
 c. Values are arithmetic average of reported values for three C-wells.

The use of individual minerals and the definition of their electrochemical adsorption conditions will aid in tying the radionuclide sorption study (SCP Section 8.3.1.3.4) to the reactive tracer study. The individual mineral samples will be purchased from suppliers because of the limited quantity of minerals that can be collected from the field and because of limitations involved in effectively separating the mineral phases from the matrix materials.

The interaction of the polystyrene microspheres with tuff material will be tested in batch and column experiments. The evaluation will focus on the relative retardation of various particle sizes. Ideally, the column experiments will be conducted with intact cores.

In the field experiments, injection or withdrawal rates will be measured in the zones being pumped. Pressure in the zones of interest in all three wells can be measured simultaneously. Temperature will also be measured at both injection and production points. Tracer concentrations for all three types of introduced

tracers—reactive, nonreactive, and polystyrene microspheres—will be measured at both injection and production wells.

2.3 Rationale for the Types of Measurements Made

Batch adsorption experiments are proposed because their simplicity facilitates an understanding of adsorption by evaluating the effect of more variables, such as temperature and pH, at each replication. The experiments will bring a range of tracer concentrations in Well J-13 water into contact with tuff samples for various lengths of time to ensure that equilibrium (or pseudo-equilibrium) will be reached. The kinetics experiments will provide the minimum equilibration times required for equilibrium experiments and, if performed in controlled mixing conditions, kinetics experiments can also provide data to define whether particle diffusion or film diffusion controls the rate of adsorption. Kinetics experiments to evaluate the controlling diffusion mechanism will be performed only if it can be determined that the local equilibrium assumption will be violated. Current expectations are that sufficient control of pumping will permit local equilibrium conditions to be maintained. Equilibrium experiments will provide data for developing isotherms, and, if performed at various temperatures (e.g., 20 through 50°C with an average measured temperature at the C-wells of 38°C), will provide data to estimate thermodynamic constants, such as enthalpy of adsorption. The kinetic and isotherm expressions derived from batch experiments will be validated to represent adsorption in the laboratory column and field tests. The results of adsorption and desorption experiments will also provide information on tracer hysteresis so that the extent of reversibility can be estimated. Enthalpy of adsorption estimates and extent of reversibility are criteria used to distinguish between physical and chemical adsorption.

Potentiometric and electrophoretic experiments to be performed in parallel with batch adsorption experiments will be conducted at equilibration times defined from kinetics experiments. Potentiometric experiments conducted with single minerals have a two-fold purpose: (1) to evaluate the role of each mineral in tracer adsorption over a range of ionic strengths and pH conditions and (2) to develop parameters for electrochemical adsorption models (e.g., the triple-layer adsorption model), which give a more mechanistic representation of the adsorption process. These results will help define the mechanisms controlling adsorption.

One way to discriminate between physical and chemical adsorption is to determine the zero point of charge (ZPC) of a system. The ZPC is the pH value at which the surface of a particle in suspension is uncharged. If the ZPC occurs at the same pH upon introduction of a tracer, the adsorption mechanism is suggested to be physical in nature (Stumm and Morgan 1981; Singh and Uehara 1986). Conversely, if the ZPC occurs at a different pH, the mechanism is suggested to be chemical. A chemically adsorbed cation should decrease the pH at the ZPC, and a chemically adsorbed anion should increase the pH at the ZPC (Stumm and Morgan 1981; Singh and Uehara 1986). The potentiometric data are also used in modeling adsorption according to surface complexation theory. The electrical properties of the solid/solute interface are determined as a function of pH and ionic strength, and site-binding constants are determined from adsorption isotherms of the tracer under varying pH and ionic strength regimes (Viani 1988).

Another way to discriminate between physical and chemical adsorption is to determine the isoelectric point (IEP) of a suspension of solid in solution. The IEP

is the pH value at which the particle in suspension is electrokinetically uncharged. Zero electrophoretic mobility (EM) is indicative of the IEP. Specifically adsorbed cations increase the pH of the IEP, and specifically adsorbed anions decrease the pH of the IEP (Stumm and Morgan 1981; Singh and Uehara 1986). Potentiometric experiments using tuff samples show the overall effect of interactions among various minerals when compared with data from single minerals.

Column experiments with disturbed (crushed) or undisturbed core samples will serve a two-fold purpose: (1) to validate the applicability of adsorption expressions (rates or isotherms) in continuous flow conditions and (2) to investigate the interactions between tracers when they are simultaneously applied to the columns under various influent conditions and flow regimes. These experiments will increase confidence in the expressions used to represent adsorption at the laboratory scale when they are compared with the breakthrough patterns obtained in the field tests.

The location of the C-wells has already been established by drilling (Figure 2). The number of single- and multiple-well experiments to be conducted will depend on the number of tracers that have been identified and characterized per adsorption mechanism. If only a single tracer is found for physical adsorption, three to five multiple-well tests can be conducted before the tracer remaining in the zone interferes with subsequent experiments. The same problems may evolve for single-well testing, so two single-well experiments per well for a total of six experiments are planned. More critical to the success of the reactive tracer study than the location of the C-Wells is characterizing the C-Well site in terms of physical and chemical properties so that retardation observed in field tests can be related to the laboratory-derived estimates of sorption.

Experiments will be conducted in the most permeable zones identified from experiments conducted by the USGS before LANL begins its experiments. These zones represent fast paths to the accessible environment and will permit conservative estimates of tracer travel times to be made. Also, the potential for the greatest recovery of total tracer mass will occur in the more permeable zones. In terms of tracer/solid interactions, the more permeable zones are likely to include pore velocities that will cause kinetics-controlled reactions, thus violating the local equilibrium assumption. Every effort will be made to use available data on the tracers and hydraulic characteristics of the C-wells complex and test zones so that the field experiments can be designed to avoid violating the local equilibrium assumption.

2.4 Constraints on the Testing of the C-Hole Sites with Reactive Tracers Activity

A major constraint on completing the reactive tracer study is the lack of core or other solid tuff material from the C-well site that is classified as quality assurance (QA) Level I. As noted in Section 3 of this study plan, this activity is Level I. In Section 4 several activities, in addition to this study, are listed that will benefit from obtaining QA Level I core at the C-well site. It will be difficult to achieve the primary objective of relating laboratory to field measurements without material from the C-holes. It is requested that a borehole designated UE-25c #4 be drilled at the C-well complex. This borehole will not only provide the required core but also serve as an observation hole in multiple-well

tests along one axis of the current design. The new borehole can provide additional information on scale dependency of hydraulic properties and solute transport parameters.

The new borehole should be drilled to a depth of 914.4 m (3,000 ft) to be consistent with current C-hole depths. Continuous coring of the hole beginning 22.9 m (75 ft) above the anticipated depth of the top of the saturated zone to the 914.4 m (3,000 ft) depth is also requested. Coring is required to support other activities listed in Section 4; and for activities at the C-holes, core is required because it is unknown where or in what interval tracer tests will be conducted. Data on fractures and mineralogy from this new borehole will be used to verify similar information from existing boreholes.

A number of constraints affect the kind, extent, and applicability of the laboratory and field experiments. A general constraint limits the selection of tracers to those that exhibit low retardation and some adsorption reversibility; thus, they can be studied both in the laboratory and in the field in a reasonable length of time (i.e., 2-3 yr for the entire study). In Table 1, those radionuclides whose release limits are defined in 40 CFR 191, Appendix A, with some additional radionuclides were listed. Only a few of these radionuclides listed in Table 1, such as neptunium, technetium, and uranium, show low retardation in tuffs, whereas high-priority radionuclides (Oversby 1987), such as americium and plutonium, have very high retardation. However, radionuclides listed in Table 1 cannot be used as tracers because of requirements to ensure 100% recovery, which is not practically achievable in field tests. Additionally, the chemistry of most radionuclides is affected by speciation, which complicates their characterization in the laboratory and in the field. If analogs of the radionuclides are considered, their similarly complex chemistry offers the same difficulties. This study will use surrogate tracers to represent various controlling adsorption mechanisms where these mechanisms can be related to radionuclide behavior. The use of surrogate tracers is a compromise approach used instead of radionuclides as tracers in laboratory and field tests. Thus, a constraint is created by the impossible task of mimicking all radionuclides listed in Table 1 by a few mechanism-based surrogate tracers. Nevertheless, information obtained from this study will provide fundamental knowledge of the effectiveness of transferring laboratory results to field scales.

The representativeness of geologic material and the solution phase used in the laboratory experiments is of major concern. Geologic samples should ideally represent the range of variability of the mineralogical composition of matrix and fractures (including fracture coatings) in the zone where field tests will be conducted. Limited availability of cores and a low expectation for additional drilling in the C-wells area reduces the selection of geological samples either to available cores or to samples collected from outcrops that are considered to be of comparable composition. In either case, the volume and original locations of the samples represent a very small percentage of the study area, and uncertainty appears related to effects of variability in composition on tracer adsorption. An aspect inherent to the variability is the potential presence and distribution of mineral coatings in fractures and minerals in the matrix with high adsorptive capacities (e.g., oxides) that could act as localized barriers. The characterization of these potential localized barriers is crucial in predicting retardation and in helping to explain tracer breakthroughs in field tests. An additional constraint is the availability of sufficient undisturbed core to perform column tests. It may be necessary to use crushed material, which would minimize any differences among columns.

C-wells waters from the depths of concern will probably not be available for the laboratory experiments that use tuff and mixed minerals. Assuming that these waters are available, a major concern will be to maintain in situ conditions during the laboratory experiments. For example, properties such as pH, gas content, and the oxidation reduction potential of the water in situ and after sampling will probably be different. The use of Well J-13 water would provide a basis for comparison of data, but the differences between in situ waters and Well J-13 waters must be evaluated to ascertain the applicability of results. These differences will be estimated through computer simulations with geochemical codes for each tracer in contact with the minerals of interest.

Potentiometric and electrophoretic experiments will support the characterization of mechanisms and their relation to specific minerals. Data from these experiments can be used to fit electrochemical models, such as the triple-layer model, recognizing that the data are only qualitative representations of the molecular behavior expressed by curve-fitted mathematical relations. Interactions among minerals and the effects of the interactions on tracer adsorption will be quantitatively evaluated, but a molecular understanding will not be possible using current techniques (i.e., electrochemical models).

The most permeable zones in which the field experiments will be conducted at the C-wells complex are expected to be fractured. The weathered linings and the washing of material from other layers into the fractures can create a mineralogy that differs from that of the porous matrix (Carlos 1985 and 1987). With three points of information for any zone (the three C-wells) and general problems in recovering core from fractured zones, the information required to reconstruct fracture minerals is limited. Changes in aqueous phase chemistry caused either by mineral variation or by pumping along the flow path will not be determined.

The hydraulics of flow and transport in fractured media are poorly understood and add to the uncertainty in analyzing the field experiments. Hydraulic parameters, such as transmissivity and porosity, have been shown to be spatially variable. Again, for multiple-well designs, the volume of rock investigated may be substantial, but the breakthrough curves will represent integrated effects over the flow domain. The estimation of parameters from these data is a vaguely posed problem with no clearly defined solutions. Knowledge of the hydraulic parameters is critical in predicting the retardation by adsorption.

2.5 Additional Factors for Consideration

2.5.1 Site Impacts

The C-wells have been drilled and completed; therefore, no additional site impacts are expected as a result of road construction, drilling pad construction, or drilling mud disposal. The primary expected site impact will be the disposal of water pumped during the single- and multiple-well field experiments. If the pumped water is allowed to infiltrate or is discharged down the existing natural drainage, studies of the unsaturated zone being conducted in the C-wells area may be influenced (Section 2.5.5).

Current efforts in the characterization and selection of tracers have concentrated on identifying nontoxic tracers that meet the requirements of this study. If a toxic tracer is used because no other tracer can fulfill the requirements, the appropriate YMP procedures will be followed to meet environmental regulations.

2.5.2 Need for Repository Conditions

Although construction of the repository and waste emplacement may affect the physical and chemical parameters governing radionuclide transport, the reactive tracer study does not need repository conditions to complete its objective. The tracer identification and characterization phase of the study will use geologic material available from the site or minerals characteristic of the site, and, if possible, water from the C-wells. The site for the field experiments has been determined by drilling the holes in a close proximity so that multiple-well testing can be conducted. In the attempt to link laboratory data to field data, it is more important to characterize the physical and chemical properties of the field site where the experiments are to be conducted than to impose repository conditions on the experiments.

2.5.3 Required Accuracy, Precision, and Limits of Methods

Accuracy for both field and laboratory experimental results will be controlled by proper calibration of equipment against standards traceable to the National Institute of Standards and Technology (NIST), where possible, and by adherence to approved procedures in the analysis of chemical species and physical parameters, including the target tracers in liquid and solid samples. Analytical and experimental precision will be based on replication of sampling in all but those experiments in which trends are expected to be characterized by regression analysis. Error propagation will be used to examine the effects of errors on the experimental outcome. These procedures are described in Section 3 of this study plan.

2.5.4 Study Duration

Laboratory experiments for developing techniques to identify controlling adsorption mechanisms and for selecting tracers are expected to last 2 yr. The selection of two to five tracers, at least one per adsorption mechanism, is the desired goal of these laboratory studies. However, the availability of samples, equipment, and instrumentation may affect the laboratory selection process and initiation of the field experiments.

The duration of field tests will depend on pumping rates, connectivity of the wells, and detection limits of the tracers. Ideally, a field test should be continued until the concentration of tracer in the production well has decreased to below the detection limit. However, in certain cases, this goal may be unobtainable, especially if the measurement sensitivity for the tracer is great. In this case, the scientific judgment of the test operators will be used to decide when the point of diminishing returns for a given tracer test is reached. Equipment needed to service the C-wells field experiments may also be needed for other studies being conducted at Yucca Mountain during the same period. At this time, the schedule of activities is unknown, but contingency plans will be developed if scheduling becomes a problem.

2.5.5 Interferences

The reactive tracer study is third in a series of experiments to be conducted at the C-wells site. Interferences with the reactive tracer experiments by experiments begun earlier may result if stresses introduced by pumping during hydraulic testing fracture the zone around a well or if the conservative tracers

used by the USGS, particularly organic tracers, cause changes in solution chemistry.

In the case of fracturing, it should not be necessary to run geophysical logs to evaluate fracturing. To meet the goals of the reactive tracer study, the nonreactive tracer introduced with the reactive tracer will be used to determine hydraulic parameters; thus, conditions present during the reactive tracer field experiments will be assessed.

The use of organic tracers by the USGS may interfere with the reactive tracer study by enhancing biological activity in the vicinity of the C-wells and by changing the water chemistry from conditions used in the laboratory or from those found before the USGS experiment began. These effects cannot be evaluated until the USGS has selected tracers and has indicated the number of experiments planned. Also, potential biological activity at the depths at which the reactive tracer experiments will be conducted must be assessed. The only activity addressing the issue of biological activity below the surface is the biological sorption and transport activity (Study 8.3.1.3.4.2), but that activity is directed primarily at investigating the unsaturated zone. In this situation, the theoretical studies using single minerals will provide data by which to estimate relative parameter changes when changes in various governing properties such as pH have occurred. This study is currently the only study planned to address this potential interference.

The polystyrene microspheres to be used for studying matrix diffusion in the reactive tracer study may clog pores and fractures, thus changing flow patterns; therefore, experiments using polystyrene microspheres will be conducted last to avoid any interference with the reactive tracer experiments by the microspheres. Also, the zones where the microspheres will be used will be back-flushed after the experiments to remove as many microspheres as possible.

A major concern in the reactive tracer study is the disposal or use of fluid produced by the field experiments. One option, particularly for multiple-well designs, is to recirculate fluid, but this option presents problems (Section 2.1.2). Distributing the water on the surface may interfere with proposed studies in the unsaturated zone and with studies related to Fortymile Wash. In addition to recirculation, alternatives are (1) provision of a holding tank and subsequent transportation of the fluid to another location by truck, (2) building a pipeline whose outlet is below the sites of the Fortymile Wash studies, and (3) storing water in lined ponds to permit evaporation. Each of these alternatives has limitations, and more information is needed before a decision can be made.

The reactive tracer study is not expected to interfere with the exploratory shaft facility (ESF), nor are tests in the ESF expected to interfere with the experiments in the reactive tracer study.

3.0 DESCRIPTION OF THE TESTING OF THE C-HOLE SITES WITH REACTIVE TRACERS ACTIVITY

The proposed study is divided into three tasks: (1) tracer identification and selection, (2) field experiments, and (3) modeling. Ideally, experiments would use radionuclides as tracers to directly evaluate their potential retardation. Because regulatory restrictions preclude the use of radionuclides, a group of tracers will be used to "mimic" as closely as possible the prevailing mechanisms of retardation by adsorption. The product of the tracer selection task is a suite of tracers that are adsorbed primarily by one of two prevailing mechanisms: physical and chemical.

The first step in identifying suitable tracers is to perform literature reviews and to consult with experts. Tracers will be selected that provide suitable retardation and permit adequate recovery. Retardation and recovery properties may suggest controlling adsorption mechanisms in various minerals. Second, laboratory tests will be conducted to select those procedures and analyses (for geologic material and water) that can facilitate distinguishing among prevailing adsorption mechanisms. Third, modeling of adsorption experiments will be conducted using equilibrium expressions and kinetics expressions (if local equilibrium conditions do not apply). Geochemical and transport modeling will assist in the experimental design of laboratory investigations.

3.1 Tracer Identification and Characterization

A tracer selected for the field experiments must (1) be soluble in water so that it can follow flow patterns, (2) be stable within the range of expected field conditions, (3) be detectable in low concentrations so that the tail of the breakthrough curve can be accurately determined, (4) not adsorb so strongly that the duration of the field experiment becomes excessive, (5) meet applicable environmental regulations in the concentrations proposed for the field experiments, and (6) have a reasonable cost.

Currently, one tracer for each adsorption class has been identified. Lithium for the physical adsorption mechanism and boron for the chemical sorption mechanism are the candidate tracers.

This task will evaluate the interaction of manufactured polystyrene microspheres with tuff. The use of these spheres has been shown to be conservative, and their size (0.1-10 μ) is larger than the dissolved chemical species, so the microspheres travel the paths with the largest fracture or pores. It is expected that, in fractured media, the polystyrene spheres will provide some information on fracture aperture.

The rationale for using the two mechanisms (physical and chemical) as a basis for selecting the tracers is the assumption that these mechanisms will dominate in the adsorption of radionuclides at Yucca Mountain. Because it is necessary to recover the tracers within the expected duration of the field tests, nonradioactive tracers, which have low retardation, must be used in place of radionuclides, which have high retardation. This substitution does not reflect the high retardation expected for most radionuclides and their species. However, the fundamental determination of prevailing adsorption mechanisms of both tracers and radionuclides should be facilitated by the use of nonradioactive tracers.

The traditional approaches to evaluating adsorption have been empirical because simple formulations are easily incorporated in the transport equation. The commonest approach has been the linear isotherm or " K_d -approach," which is given in Equation 4. More sophisticated relationships that define the nonlinear dependence of sorption on solution concentration are also available (EPRI 1984a), and their applicability should be demonstrated with experimental data generated by this study. Some of the relationships are based on more formal theories (less empirical), such as Equation 3, the Langmuir isotherm (Langmuir 1918).

Recent approaches to represent adsorption by electrochemical models attempt to include multiple reactions of the target chemicals between the solid phase and the solution phase (Kent et al. 1986). This approach has the advantage of building a fundamental knowledge base that allows extrapolation of the results to conditions different from those for which the data were developed. The potentiometric and electrophoretic experiments will help to define the prevailing adsorption mechanism and provide data to implement electrochemical models. The most critical need is to characterize the interactions of each proposed tracer with individual minerals of the tuff and the tuff itself. These interactions will be used to analyze the prevailing or controlling mechanism of tracer adsorption on the tuff.

The tracer selection task will attempt to identify tracers whose reactions with solid materials under the conditions at Yucca Mountain will be by a prevailing mechanism. Isotherms will be derived to describe mathematically the generalized reaction of the tracers with the solid tuff. At the same time, experiments will be conducted with individual minerals present in the tuff to develop a fundamental data base for better interpreting the reactions of the tracers with the tuff on the basis of mineral/tracer interactions. In this manner, the applicability of isotherms to transport models will be supported by an improved understanding of the adsorption mechanism.

3.1.1 Preliminary Modeling

Mathematical modeling and computer codes are tools that aid in the experimental design of laboratory and field investigations by simulating anticipated situations and conditions based on assumptions and available information. Results from simulations can provide insight into the role that variables, such as water chemistry, geologic materials, flow regimes, temperature, and modes of tracer injection, may play in adsorption.

A first effort in mathematical modeling is the use of adsorption models to predict the extent and mode of tracer adsorption on materials from data found in literature. For example, smectite, which is a montmorillonite clay with a high adsorption capacity, has been characterized as a component of samples from the Prow Pass and Bullfrog Members in the C-wells area. Goldberg and Glaubig (1986) studied the adsorption of boron on several montmorillonites. Boron is being considered as a chemisorbent tracer for the reactive tracer study. Therefore, the data from Goldberg and Glaubig may serve as background information to predict the mode and extent of interaction between boron and smectite at low concentrations of boron (≈ 5 mg/l).

A second effort involves geochemical codes that consider processes, such as speciation in water solutions, precipitation, and solubilization of minerals in contact with the solution, and, in the case of some codes, adsorption expressions

for ion exchange or surface complexation. These codes constitute a means of defining those chemical substances and species that may control the solution chemistry, as well as any potential for precipitation or solubilization at different pH, temperature, or atmospheric conditions. Various codes offer advantages and disadvantages in regard to the number of defined processes, the quality and extent of thermodynamic data bases, and complexity. The following codes (EPRI 1984b) may be used for several purposes: PHREEQE (Parkhurst et al. 1980) is a relatively easy code to use that includes expressions for ion exchange but that has a limited thermodynamic data base; MINEQL (Westall et al. 1976) and MINTEQA2 (Felmy et al. 1984) incorporate adsorption as isotherms or surface complexation and have more extensive thermodynamic data bases; and EQ3/6 (Wolery 1983 and 1984) is being upgraded to include adsorption (Viani 1988) and to meet quality assurance (QA) requirements for the YMP. Adsorption and geochemical codes will assist in the design and interpretation of data for batch experiments (Section 3.1.2 provides more details). A limitation of geochemical codes is their lack of consideration of nonequilibrium reactions or interactions (kinetics) because they solve systems of simultaneous equations that represent stoichiometric balances of molecular reactions in solution or on solid surfaces under equilibrium conditions.

A third kind of mathematical modeling permits simulation of tracer transport for given initial and boundary conditions. These codes will be used primarily to design column experiments and to validate adsorption expressions developed in batch studies. Sections 3.2 and 3.3 present the types of field experiments and the transport codes considered for use in interpreting the data produced by the field experiments. The same transport codes can be used to design and interpret the column experiments.

3.1.2 Experimental Effort

The laboratory experiments consist of batch equilibrium, kinetics, and column transport experiments. Batch studies will be performed for the adsorption of a tracer on tuff material and on individual minerals. Kinetics experiments will evaluate the time needed to reach adsorption equilibrium. This information will be used in developing batch equilibrium experiments. Additional kinetics experiments may be performed to evaluate the type of diffusion that may control the rate of adsorption of the tracer (e.g., film diffusion or particle diffusion). This differentiation, if evaluated, will be qualitative in nature. In the equilibrium experiments, adsorption and desorption data will be obtained. Adsorption data will be obtained at three temperatures (25°C, 38°C, and 45°C), and desorption data will be obtained at only one temperature (38°C, the average temperature of the water in which the field tests will be performed). These equilibrium data will be used to estimate (1) isotherm parameters to be used in predicting transport of tracers in laboratory column experiments and in field tests and (2) thermodynamic indicators, e.g., enthalpies of adsorption, to differentiate between mechanisms according to the generic classification (physical versus chemical). Potentiometric titration and electrophoretic experiments will be performed on both tuff samples and individual minerals. In the case of the tuff material, the ZPC will be estimated to help differentiate between adsorption mechanisms. Experiments using individual minerals will permit parameter estimation for models that will be used to help extend the data base for adsorption mechanisms. In addition, batch equilibrium adsorption, potentiometric, and electrophoretic experiments will be performed using polystyrene microspheres to evaluate their interactions with tracers on both individual minerals and tuff matrix samples.

The objectives of the column experiments are (1) to verify estimates of adsorption parameters from batch experiments in a more realistic flow environment and (2) to evaluate the local equilibrium assumption to determine whether kinetics expressions will be needed for modeling tracer migration for the field tests. Also, column tests will be performed with and without microspheres to determine the transport properties of the microspheres under flow conditions.

Cores will be used in these column studies if they are available; if insufficient core is available, then crushed material will be used.

The experimental approach for each of the proposed laboratory experiments is described in the following sections. Preliminary estimates of the number of experiments required for each type of laboratory experiment will be given now. These numbers are subject to change as more information about the field site becomes available and experience with different techniques is obtained.

The first category is kinetics experiments to evaluate equilibrium conditions. For each tracer except polystyrene microspheres and each solid material, tuff and individual minerals, a total of 80 experiments will be required. This number of tests is based on 20 tubes for each kinetics experiment x 2 temperatures x 2 initial concentrations. These experiments will be repeated for each tracer and solid material. Controlled kinetics experiments will evaluate film and particle diffusion behavior of the tracers. An estimated total of 54 reactors (3 temperatures x 3 mixing rates x 3 initial tracer concentrations x 2 replications) will be required. The next category of experiments is the equilibrium batch. These experiments will be designed to evaluate both adsorption and desorption simultaneously. There will be 12 different initial concentrations x 3 temperatures x 2 replications x 2 conditions (adsorption and desorption) for a total of 144 experiments. The electrophoresis and potentiometric experiments will use aliquots from the same experiments. The total number of tubes required per solid material is 2 temperatures x 2 initial tracer concentrations x 2 replications x 6 pH values x 6 electrolyte conditions for a total of 288 tubes. Batch experiments to determine the interaction of polystyrene microspheres with the tuff will be required. This determination will require 3 diameters of polystyrene microspheres x 2 replications for a total of 6 experiments. Batch experiments will be conducted to determine the interactions of the physically and chemically adsorbed tracers if both are introduced simultaneously. The number of experiments required for this phase is 2 initial tracer concentrations x 2 tracers (physical and chemical) x 2 replications x 2 types (adsorption and desorption) x 4 combinations of high and low tracer concentrations for a total of 64 experiments. Column experiments will evaluate tracer behavior under dynamic conditions. Thirty column experiments will account for the various tracers, combinations of these tracers including the polystyrene microspheres, and replications.

3.1.3 Polystyrene Microspheres

To investigate various flow and transport mechanisms, manufactured polystyrene microspheres (very fine particles <10 μm in diameter) will be used. These tracers offer two advantages to the reactive tracer study: (1) the polystyrene microspheres appear to behave as conservative tracers and (2) because the polystyrene microspheres are larger than dissolved species, they should migrate preferentially down major flow paths such as fractures. The former advantage is important because of the difficulty in finding truly conservative tracers, that is, tracers that do not react biologically and/or chemically. The latter advantage is important because the polystyrene microspheres, in conjunction with nonreactive

solutes, may allow an estimate of matrix diffusion for the reactive tracer study and characterization of the fracture network by indicating the sizes that will flow between wells.

Recent field experiments conducted by Harvey and George (1987) have demonstrated the viability of using submicron polystyrene microspheres as conservative tracers. In these field experiments, the microspheres were shown to break through before anion species. The polystyrene microspheres are microscopic particles that can be formulated chemically to contain a fluorescent dye to permit easy detection and can be treated to be electrostatically charged or neutral.

Using the batch and column techniques outlined in Section 3.1.6 below, researchers will evaluate the polystyrene particles for potential interactions with tuff matrices and for potential clogging of pores in the rock matrix. Batch tests will be conducted to examine potential interactions between the microspheres and the tuff matrix. Column tests using tuff core will be performed to evaluate the transport characteristics of the microspheres and potential clogging of pores. Experiments with these particles in single fractures of welded tuff are also currently included in the dynamic transport study (SCP Section 8.3.1.3.6.1). Polystyrene microsphere concentrations can be determined by measuring the concentration of the fluorescent dye with a fluorometer either directly or by extracting the dye with toluene. Also, the size distribution of the microspheres will be measured for both input and effluent.

3.1.4 Equipment Needed

A variety of analytical instruments will be used in the measurement and characterization of liquid and solid samples. Liquid samples will be analyzed on a routine basis by inductively coupled plasma atomic emission spectroscopy (ICPAES) for cations with atomic weights less than 80, by inductively coupled plasma mass spectroscopy (ICPMS) for cations with atomic weights greater than 80, and by ion chromatography (IC) for anions. If conditions dictate, tracers or other ions may be determined by another method. For example, colorimetry may be used to determine boron concentrations when boron is used as a tracer. However, duplicates from some of those samples will also be analyzed by ICPAES so that concentrations can be normalized to a common standard. Readings of the pH of a solution will be made with a research-type pH meter system (e.g., Corning pH meter, Model 130, with an expanded scale and an Orion combination electrode having a precision of ± 0.02 pH units). A platinum electrode will be used to determine whether oxidizing or reducing conditions are present.

The mineralogic characterization of geologic samples (tuff and individual minerals) will be accomplished by x-ray diffraction (e.g., Siemens D-500 x-ray diffraction system). Surface area analysis of solid materials will be performed with a surface area analyzer (e.g., Quantasorb, Jr., instrument). Particle size distributions of the geologic tuff materials and minerals may be obtained with various instruments (e.g., US standard sieve series down to 44 μm and a Micro-metric sedigraph 5000D particle size analyzer for particles down to 0.2 μm in size).

Titrimetric measurements will be performed with a combination of a burette (e.g., Fisher burette, Model 394), a titrate stirrer (e.g., Fisher titrate stirrer,

Model 385), and a pH meter (e.g., Fisher electrometer, Model 380). Electrophoretic mobility measurements will use a Z-meter (e.g., Zeta meter 3.0 system). Batch experiments using containers such as 50-ml centrifuge tubes will be mixed by rotation (e.g., using a modification of a Patterson-Kelley twin shell dry rotator), and batch experiments performed in larger containers (e.g., 500-ml glass resin kettles) will be mixed with paddle stirrers (e.g., G. K. Heller GT21-18 stirrers).

A fluorometer will be used to detect fluorescent dyes that may have been encapsulated in the microspheres to be used as a colloid tracer. Balances will be used in routine work. Riffle splitters and pulverizers will be used for geologic samples, and centrifuges will be used for solute/solid separation. Experiment tests and measurements to be conducted at a constant temperature will be performed in either an environmental room with controlled temperature or a controlled temperature bath. Controlled temperatures will be maintained at $\pm 2^{\circ}\text{C}$.

3.1.5 Required Accuracy and Precision

The measurement of physical quantities to characterize experimental observations requires quantitative expressions for the accuracy and precision of each quantity. These expressions are a measure of the reliability of the observation and provide fundamental information pertaining to the propagation of errors in combined experiments and in mathematical models that include several measured quantities. Additionally, these expressions constitute basic information to test hypotheses and to make analyses and estimates of the uncertainty and sensitivity of variables. Two general kinds of error can be generated in measuring physical quantities: systematic errors and random errors. Although there is no strict definition of systematic errors, these errors arise from changes in conditions that could be corrected or considered. Systematic errors are associated with a lack of accuracy. Random errors are those left after the systematic errors have been taken into account. They may arise from ambiguities or uncertainties in the process of measurement or from fluctuations that are too irregular or too fast to be observed in detail. These types of errors are better characterized by increasing the number of replications and are defined by indicators of precision.

Accuracy will be ensured by proper calibration of equipment against either manufacturer's standards or, when applicable, to standards from the NIST or other standard methods that are accepted by either the scientific or the engineering community for specific methods and measurements. For example, the analysis of tracers in waters may follow the most recent edition of "Standard Methods for the Examination of Waters and Waste Waters." This publication, organized by the American Public Health Association and other professional societies, is accepted by the environmental community and by regulatory agencies. If cases occur for which standards are not documented or for which a discrepancy is found among available alternatives, a standard will be selected by the responsible investigator based on evaluation of references and input from appropriate experts. Additionally, experiments will follow procedures developed under the quality assurance program of the YMP, which are referenced to pertinent literature.

Precision will be characterized by defining deviation statistically for each measurement resulting from an instrument or from a procedure. Precision will

be defined by the adjusted standard error and the adjusted root mean square deviation. The first is the best estimate of the standard error or a measure of the accuracy with which the mean estimates the true value. The second provides the best estimate of the standard deviation. Both values are a function of the number of replicates (or measurements). If more than one instrument or procedure contributes to the generation of a numerical value, the error associated with each procedure will be propagated to provide the error for that value. This error could be based on any general deviation limit, such as the standard deviation or other measurement for error (for example, any deviation that encloses 50, 68, 95%, etc., of all the readings). A general equation to propagate errors for a function, $R = f(U, V, \dots, Z)$, may be expressed by the following equation:

$$W_r^2 = \left(\frac{\partial R}{\partial U} \right)^2 \cdot W_u^2 + \left(\frac{\partial R}{\partial V} \right)^2 \cdot W_v^2 + \dots + \left(\frac{\partial R}{\partial Z} \right)^2 \cdot W_z^2 \quad (5)$$

where W defines the selected deviation limit of concern. This equation assumes that the errors are distributed according to a normal distribution. Table 4 gives a list of specific equations of error propagation for a selected number of simple functions.

Experimental observations will be fitted to empirical and theoretical models (e.g., isotherms or electrochemical models), and constants that define the model will be obtained. These constants should also be bounded by precision statistics. These statistics permit the propagation of errors when these models are incorporated in more complex models, such as those for transport or performance assessment. They also provide a basis for evaluating the sensitivity of dependent variables to probable variations in measured quantities, which is an important aspect in analysis of uncertainty and consequently in risk assessment.

3.1.6 Experimental Procedures

Detailed technical procedures (DP) will be written for all experiments (Table 5). For those experiments in which the procedures are well developed, the DPs will be written before experimental work begins. For those experiments in which the procedures are not well developed, the DPs will be written after they have been developed. The development of those procedures will be included in the experimental design. A list of DPs and their status is given in Table 5. Some of those DPs are summarized below. They include sample preparation, kinetics batch sorption, equilibrium batch sorption, zero point of charge (potentiometric and electrophoretic) and column tracer transport.

Sample Preparation

This procedure includes the preparation of both solid and liquid materials. Well water to be used in these studies will be collected from specific water-bearing formations accessed by well bore. Bulk samples of water will be filtered through 0.45- μm membrane filter over a 0.05- μm membrane microfilter as a standard method of preparation before use in tracer experiments. Bulk rock material may

TABLE 4
EXPRESSIONS FOR THE PROPAGATION OF ERROR
FOR SIMPLE CASES OF COMBINATIONS OF MEASUREMENTS

Function	Best Estimate	
	Standard Error	Standard Deviation
Scale Factor $z = ax$	$Z_n = aX_n$	$s_n(z) = a s_n(x)$
Sum $z = x + y$	$Z_{nm} = X_n + Y_m$	$s_{nm}(z) = [s_n^2(x) + s_m^2(y)]$
Linear Combination $z = a + ax + by$	$Z_{nm...} = a + aX_n + bY_m$	$s_{nm...}(z) = [a^2s_n^2(x) + b^2s_m^2(y) + \dots]$
Logarithmic Function $z = \log x$	$Z_n = \log X_n$	$s_n(z) = s_n(x)/X_n$
General Product $z = ax^a y^b$	$Z_{nm...} = aX_n^a \cdot Y_m^b$	$s_{nm...}(z)/Z_{nm...} = [a^2s_n^2(x)/X_n^2 + b^2s_m^2(y)/Y_m^2 + \dots]$

$x, y, z =$ mean values; $s =$ adjusted mean square deviation; $n, m... = n, m... =$ measurements for x and y .

include whole-rock samples, core samples, core cuttings, fracture minerals, fracture coatings, and inclusions in host bulk rock. Representative minerals are primarily single-mineral crystals or clusters and may include quartz, albite, clinoptilolite, montmorillonite, and hematite. Initially, the solid materials will be washed with distilled water, and rock surfaces will be brushed with non-metallic bristles to remove contaminants such as drilling mud. Individual minerals will be visually sorted using a chisel and hammer. Poorly consolidated material will be washed by sonification. Consolidated material (used as crushed material) will be reduced to less than 500 μm in diameter by crushing, grinding, and sieving the material. The solid samples will be purified by a combination of particle size reduction and sieving or by sedimentation.

The material will then be conditioned (if necessary) for use in specific experiments. Conditioning may involve the equilibration of a bulk solution (e.g., well water) with the solid so that minimal system changes will occur upon the introduction of the tracer. Another typical treatment is the saturation of exchange sites with a single ion, converting the material to a monoionic system. All solids will be dried in one of three ways: air dry, 60°C oven dry, or 105°C oven dry. The dry samples will be homogenized before storage for use in the experiments. X-ray diffraction analysis will be performed to determine the purity of the samples and to identify impurities.

TABLE 5

**DETAILED TECHNICAL PROCEDURES FOR TRACER IDENTIFICATION
AND CHARACTERIZATION TASK**

Procedure Number	Procedure	Type	Date
TWS-HSE12-DP-301	Field Collection of Experimental Materials	Nonstandard	2/26/88
TWS-HSE12-DP-302	Cation and Anion Exchange Capacity	Nonstandard	12/2/88
TWS-HSE12-DP-303	Zero Point of Charge (potentiometric method)	Nonstandard	11/18/88
TWS-HSE12-DP-304	Zero Point of Charge (electrophoresis method)	Nonstandard	11/18/88
TWS-HSE12-DP-305	Equilibrium Batch Sorption	Nonstandard	12/23/88
TWS-HSE12-DP-306	Kinetic Batch Sorption	Nonstandard	12/23/88
TWS-HSE12-DP-307	Sample Identification and Control	Nonstandard	4/29/88
TWS-HSE12-DP-310	Calibration and Use of Phototachometer	Nonstandard	5/2/88
TWS-HSE12-DP-311	Sample Preparation	Nonstandard	5/2/88
TWS-HSE12-DP-312	Particle Size Reduction of Geologic Media	Nonstandard	5/2/88
TWS-HSE12-DP-313	Calibration and Use of Centrifuges	Nonstandard	5/2/88
TWS-HSE12-DP-314	Electrical Conductivity Measurement	Nonstandard	1/15/87
TWS-HSE12-DP-315	Calibration and Use of Temperature Measurement and Control Devices	Nonstandard	10/15/88
TWS-HSE12-DP-316	Preparation of Stock Solutions and Reagents	Nonstandard	5/2/88
TWS-HSE12-DP-317	Calibration and Use of Analytical and Top-Loading Balances	Nonstandard	5/2/88
TWS-HSE12-DP-318	pH Measurement, Acid-Base Solution Standardization, and Total Alkalinity	Nonstandard	5/2/88
TWS-HSE12-DP-319	Particle Size Analysis	Nonstandard	3/31/89

TABLE 5
DETAILED TECHNICAL PROCEDURES FOR TRACER IDENTIFICATION
AND CHARACTERIZATION TASK
(concluded)

<u>Procedure Number</u>	<u>Procedure</u>	<u>Type</u>	<u>Date</u>
TWS-HSE12-DP-320	Measurement of Dissolved Oxygen	Nonstandard	3/31/89
TWS-HSE12-DP-322	Magnetic Separation of Impurities	Nonstandard	3/3/89
TWS-HSE12-DP-323	Spectrophotometric Determination of Tracer Concentration	Nonstandard	12/23/88
TWS-HSE12-DP-324	Electrochemical Determination of Tracer Concentration	Nonstandard	3/3/89
TWS-HSE12-DP-325	Column Tracer Transport	Nonstandard	3/31/89

Zero Point of Charge (Potentiometric Method)

The potentiometric procedure involves titrating geologic (or mineralogic) materials suspended in an indifferent electrolyte with different amounts of added base or acid. An indifferent electrolyte (e.g., NaCl) does not specifically adsorb to the sample in solution or suspension. The pH of the supernatant solution is measured after a predetermined equilibration time (e.g., 48 hr). Amounts of consumed H^+ or OH^- are plotted against the resultant pH (measured) for a range of pH values (e.g., pH 2 to pH 12) and in electrolyte solutions of different strengths (e.g., 0.1 and 0.005 mol). The pH at which the titration curves of the two indifferent electrolyte concentrations cross is the ZPC. The same titration procedure is then conducted on a second but similar group of aliquots containing a specific concentration of tracer. If the replication is not affected by the addition of the tracer, physical adsorption is implied. An increase in the pH of the replication where the ZPC occurs implies chemical (specific) adsorption of cations, and a decrease in the pH is indicative of chemical adsorption of anions. This procedure is followed for two or more concentrations of tracer when the data are applied to surface complexation models. In the reactive tracer study, these models will be applied only to individual mineral data.

Zero Point of Charge (Electrophoretic Method)

The EM of colloids can be used to determine the isoelectric point (IEP) of a suspension of solid and solution. An EM of zero is indicative of the IEP. To accurately determine the IEP, the EM must be measured over a range of pH values that includes the condition of zero EM. It is desirable to track 30-50 colloids in each solution to enable an average EM to be estimated with a reasonably small variance. Sample preparation is the same as that for the potentiometric experiments. Further sample conditioning may involve either filtration, centrifugation, or reconstitution, depending on the needs of the experiment. For studies requiring a predetermined particle size range, filtration or centrifugation will be the method of choice, whereas reconstitution is valid for creating dilutions of the suspended solids without seriously changing the chemical status of the

supporting solution. Aliquots of the suspensions used for the potentiometric procedure may be used for the electrophoretic procedure.

Kinetic Batch Sorption

These experiments will be performed to meet two objectives: (1) to determine the optimum equilibration time for equilibration experiments and (2) to differentiate between reactions controlled by film diffusion and reactions controlled by particle diffusion. Two methods will be used: batch reactor and controlled reactor. The batch reactor method is intended to be a small-scale technique to determine optimum equilibration times. The controlled reactor method is designed to provide data for use in kinetics models. In the batch reactors, solid and water will be added to the reactors (e.g., 50-ml plastic centrifuge tubes) in a specified solid/solute ratio. Solids and water can be sterilized, if necessary, a minimum of 30 min at 248°F and 15 psi. Reactors, solids, and water will be conditioned for at least 24 hr before initiating the experiments. Temperature will be controlled throughout the entire experiment. Samples will be taken at specified time intervals to monitor reaction progress. Sampling will involve the use of filtration with a 0.45- μ m filter and plastic syringe. Centrifugation may be performed before filtration to ensure that adequate sample is recovered. The sample will be split; one part will be used to measure pH, and the other will be dedicated to chemical analysis. The controlled reactors are composed of a glass, polyethylene, or lucite container with baffles and lid, and have a mixing system with calibrated speed. Ports at the top of the reactor allow sampling and monitoring various conditions in the reactor (e.g., pH and conductivity). The sampling procedure will be the same as that for the batch reactors.

Desorption kinetics may or may not be evaluated for a given kinetics experiment. The desorption method is basically the same for the batch reactors and controlled reactors. After an adsorption period, the tracer solution will be removed using either filtration, centrifugation, decanting, or a combination of these methods. The amount of water remaining will be determined, and solids will be washed with distilled water to further remove nonsorbed tracer. An amount of desorption fluid (e.g., well water) will be added so that the solution volume is that specified for the experiment. Timing and mixing will be started immediately after addition of the desorbing electrolyte. The sampling procedure is the same as that for the adsorption experiment.

Equilibrium Batch Sorption

These studies are important to define the relationship between the solute concentration on the solid (adsorbed phase) and respective liquid concentration of the solute (dissolved phase) at defined environmental conditions (e.g., pH and temperature). The experiments will cover a range of tracer concentrations, which will allow development of models or isotherms to represent characteristic relationships. When studies are performed at several temperatures, it is possible to estimate thermodynamic parameters (e.g., enthalpy of adsorption) to be used in evaluating an adsorption mechanism (e.g., physical or chemical). Both equilibrium adsorption and equilibrium desorption batch studies will be performed for the tracers and solids of interest. A plastic centrifuge or test tubes will be used for the equilibrium reactors. Mixing will be either by hand or by blender (e.g., Patterson-Kelley). Solids and water will be added to the reactors in a specified solid/solute ratio. Solids and water can be sterilized in the reactors, if necessary

(e.g., a minimum of 30 min at 248°F and 15 psi). Temperature will be controlled throughout the experiment. Timing of mixing of the system will be started when the tracer is added to the system. Sampling will occur after an equilibration time established during the kinetics experiments. Sampling will follow the same procedure as that for the kinetics experiments. The preparation procedure to be followed for the desorption experiments will be the same as that for the kinetics experiments. Sampling will be the same as that for the adsorption experiments.

Column Tracer Transport

Column tracer studies will be performed to evaluate the prediction of tracer transport from isotherm parameters and to evaluate the matrix diffusion of tuff materials. Intact core will be used, if possible. Figure 5 gives the total core that was recovered during drilling of the C-wells. It is known at this time that some of this total core material has been previously used, so the total given in Figure 5 is not available. Also, the issue of the traceability of the core may prevent any QA Level I work from being done with these samples (Section 3.1.9). A request was made in Section 2.4 of this study plan to have a new borehole drilled at the C-well complex to provide the required core. Therefore, if intact core samples are not available, columns of crushed material will be used and matrix diffusion will not be evaluated.

The DP for the column transport experiments has not been developed; however, the main aspects of the procedures are as follows. For core samples, the core will be encased in a material such as epoxy after the exact size and weight of the core have been measured. The core will then be conditioned with the solution of interest (e.g., well water). The flow condition of the solution will be saturated steady state at the desired flow rate. After conditioning, the tracer will be added and the breakthrough of tracer will be monitored. The experimental setup of crushed material will be similar to that described by Fuentes et al. (1988). For example, lucite columns (3.81 cm inside diameter by 50 cm) can be fitted with an acetate filter pad having a pore diameter of 0.2 μm to retain the tuff material. The weight and density of the packed column will be measured. The column will be conditioned as described above, and the tracer will be applied in a predetermined mode and then monitored under saturated steady-state flow conditions. Tracers will be added individually and will include polystyrene microspheres.

3.1.7 Data Reduction and Analysis

Analytical results from kinetics and equilibrium experiments that measure the liquid-dissolved concentrations (e.g., concentrations of $<0.45 \mu\text{m}$) of the tracer or of other ions will be averaged when replicates are included, and those averages will be used to calculate the amount adsorbed on the solid phase, $S(\text{MM}^{-1})$, and to calculate the respective liquid concentration, $C(\text{ML}^{-3})$. These concentrations (S and C) will be used to evaluate parameters for Equations 1-4. Kinetics data and models provide a representation of nonequilibrium adsorption besides providing the equilibration times needed for isotherm information. The latter include the most common expressions used in transport codes, that is, linear, Freundlich, Langmuir, and modified Freundlich but are not limited to these expressions. Others could be used if results from laboratory columns and field tests require it. Enthalpy of adsorption will be determined from adsorption isotherms, S versus C , at two or more temperatures using the Van't Hoff equation (Argersinger et al. 1950).

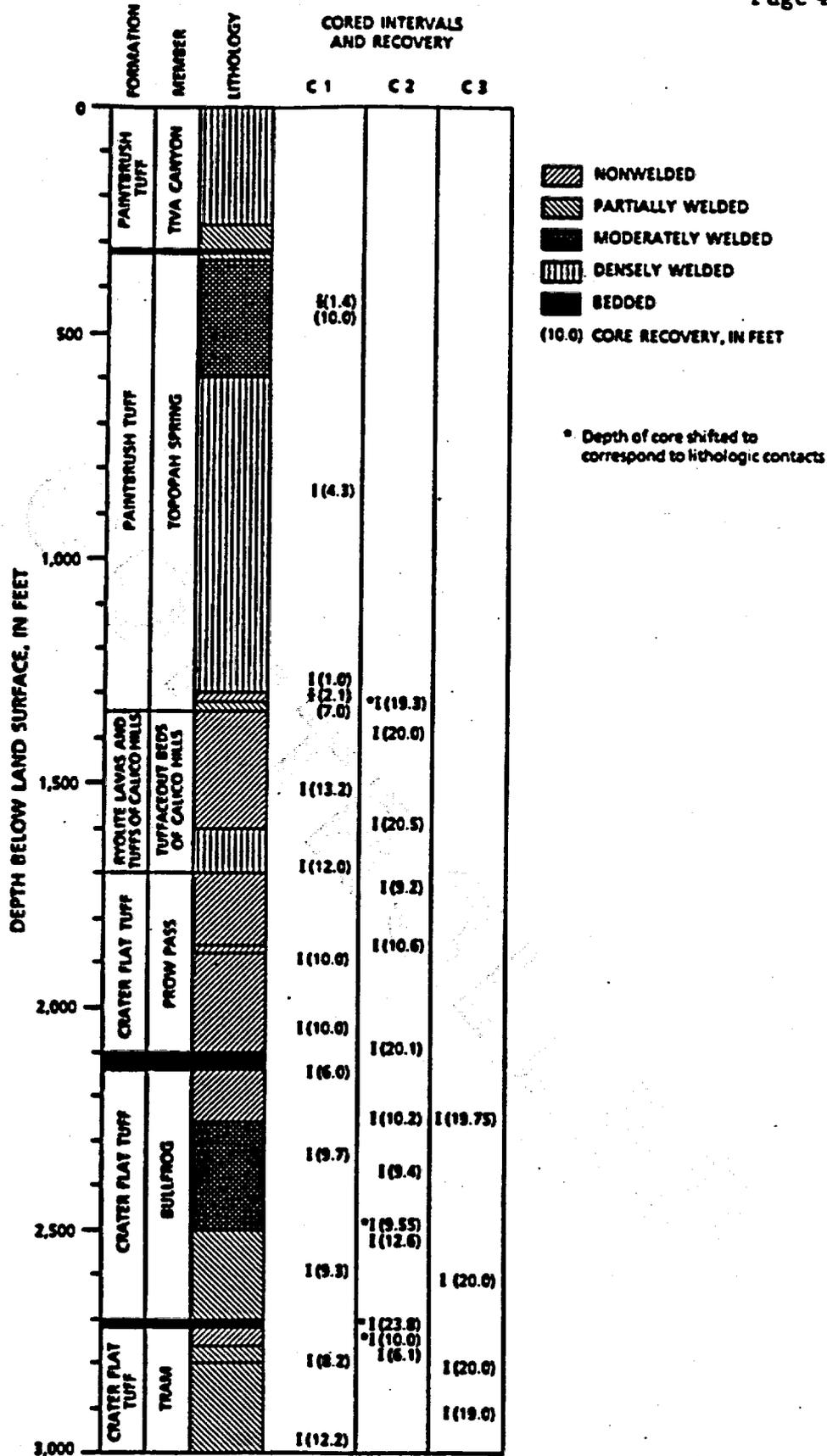


Figure 5. Core Recovery for the C-Wells

$$\frac{d \ln K_e}{dT} = \frac{\Delta H^0}{RT^2}, \quad (6)$$

which can be integrated over a range of temperatures to give

$$\Delta H^0 = \left[\ln \left(\frac{K_{eT_2}}{K_{eT_1}} \right) \right] \cdot \left\{ R / \left[\left(\frac{T_2 - T_1}{T_1 T_2} \right) \right] \right\}, \quad (7)$$

where

ΔH^0 is the enthalpy of adsorption,
 R is the gas constant,
 K_e is the equilibrium constant,
 K_{eT_2} is the equilibrium constant at temperature T_2 , and
 K_{eT_1} is the equilibrium constant at temperature T_1 .

The enthalpy of adsorption will assist in the evaluation of the adsorption mechanism. Chemical adsorption is expected to have a higher ΔH than does physical adsorption (Table 2). The equilibrium constants can be estimated from isotherm data, and various approaches are available. One approach is based on the law of mass action where adsorption can be represented as an exchange of two major ions (Helferich 1962). This equation can be written as

$$K_e = \frac{\bar{a}_A^{z_B} \bar{a}_B^{z_A}}{a_B^{z_B} \cdot a_A^{z_A}} \quad (8)$$

for the reaction



where

A, B are the ion species of the binary system in solution,

\bar{A}, \bar{B} are the ion species in the solid phase,

a_A, a_B are the activities of A and B , respectively, in the solution phase,

\bar{a}_A, \bar{a}_B are the activities of A and B , respectively, in the solid phase, and

z_A, z_B are the valences of A and B , respectively.

The equation for K_e can be expressed in terms of the following modified rational equilibrium constant,

$$K_e = K_r \cdot \frac{\bar{y}_A^{z_B}}{y_A^{z_A}} \quad (10)$$

so that

$$K_r = \frac{\bar{x}_A^{z_B}}{\bar{x}_B^{z_A}} \cdot \frac{C_B^{z_A}}{C_A^{z_B}} \cdot \frac{y_B^{z_A}}{y_A^{z_B}} \quad (11)$$

where

y_A, y_B are the activity coefficients of A and B, respectively, in the solution phase,

\bar{y}_A, \bar{y}_B are the activity coefficients of A and B, respectively, in the solid phase,

C_A, C_B are the molar concentrations of A and B, respectively, in the solution phase, and

\bar{x}_A, \bar{x}_B are the equivalent fractions on A and B, respectively, in the solid phase.

Therefore, the thermodynamic equilibrium constant can be expressed as follows

$$\ln K_e = (z_B - z_A) + \int_0^1 (\ln K_r) d\bar{x}_B \quad (12)$$

where

$$\bar{x}_B = \frac{z_B^{n_B}}{z_A^{n_A} + z_B^{n_B}},$$

and

n_A, n_B are moles of A and B, respectively, in the solid phase. The integral can also be expressed in terms of its components:

$$\int_0^1 (\ln K_r) d\bar{x}_B = z_B \int_0^1 \ln \bar{C}_A d\bar{x}_B - z_A \int_0^1 \ln \bar{C}_B d\bar{x}_B + z_A \int_0^1 \ln C_B d\bar{x}_B - z_B \int_0^1 \ln C_A d\bar{x}_B + z_A \int_0^1 \ln \gamma_B d\bar{x}_B - z_B \int_0^1 \ln \gamma_A d\bar{x}_B \quad (13)$$

which may be solved by several means, for example, graphically or analytically.

Another approach to estimating the thermodynamic equilibrium constant for adsorption in which ion exchange is not considered can be expressed as (Biggar and Cheung 1973; McCloskey and Bayer 1987)

$$K = \frac{\bar{a}_A}{a_A} \quad (14)$$

where

\bar{a}_A , a_A are the activities of A in the solid and solution phases, respectively.

The equation can be expressed as

$$K = \frac{\bar{\gamma}_A \bar{C}_A}{\gamma_A C_A} \quad (15)$$

where

$\bar{\gamma}_A$, γ_A are the respective coefficients of A in the solid and solution phases.

At infinite dilution, $\bar{\gamma}_A$ and γ_A equal unity; thus, the thermodynamic equilibrium constant can be calculated from the estimated values of \bar{C}_A and C_A at infinite dilution. A simple technique is available to estimate \bar{C}_A and C_A at infinite dilution and to calculate an overall equilibrium constant between the concentrations in the solid and in solution of the species or compound of concern (Biggar and Cheung 1973; McCloskey and Bayer 1987).

Results from potentiometric and electrophoretic studies will be converted to proton surface charge density (σ_H) and electrophoretic mobility (U) and plotted versus pH. From these graphs, the shift in either the point of zero net proton charge (PZNPC) or ZPC, which is caused by the presence of a tracer in solution in contact with a mineral or tuff sample, can be used as an indicator of the location and strength of the electrochemical bond formed between the tracer

and the solid surface. The same data will be used to estimate parameters for any of several electrochemical models, which may include the capacitance and the double- and triple-layer models. These models are a quantitative description of adsorption phenomena as a function of the spatial distribution of ions in the interfacial region. A detailed mathematical treatment of these models is presented by Sposito (1984), and their application is reviewed by James and Healy (1972a, 1972b, 1972c), Hohl and Stumm (1976), and Davis and Leckie (1978a, 1978b, 1978c).

Data pertaining to model development, to the characterization of accuracy and precision of error propagation, and to uncertainty and sensitivity analyses will be stored in computer files and hard copies. Data will be retrieved for mathematical handling, and any results from calculations will also be stored in computer and hard copies. Tables and graphs can be generated from these data for analysis and reporting purposes.

Equations 1-4 are general formulations used to describe adsorption regardless of the mechanisms involved. These expressions will be related to a mechanism by the tracer experiments through confirmation that the tracer is predominantly adsorbed by either a physical or chemical mechanism. Once the parameters have been fitted to the expressions, it is the parameter values that reflect a particular mechanism.

The parameters in Equations 1-4 will be fitted using linear regression, with appropriate transformations, if needed, or nonlinear regression. For each set of experiments, the parameters for all four expressions (Equations 1-4) will be determined. An initial comparison of the four equations will be made using conventional statistics, root mean-square error, coefficient of determination, and analysis of covariance, where appropriate. If a nonlinear least-squares algorithm is used to fit an equation, statistical tests are not applicable, and more qualitative comparison, such as minimum root mean-square error, will be used. At this point in the analyses, none of the four equations will be eliminated from consideration.

Desorption data will also be used to determine parameters for the proposed tracer. One complicating factor may be the hysteresis exhibited by the adsorption/desorption process. If substantial hysteresis is observed, two options are available: (1) perform additional characterization of adsorption/desorption behavior on the tracer to further define the main curves and scanning curves or (2) discard the tracer.

The column experiments are expected to distinguish among the four sorption expressions more readily than results of the batch experiments. A computer code, **SORBEQ**, will be written for design and analysis of the column experiments. This code will solve one-dimensional advection/dispersion using a finite difference numerical technique, and it will include the capability of selecting any one of the four sorption expressions. A nonreactive tracer will be included in the column experiments so that the hydrodynamic parameters--velocity and dispersion--can be determined for each experiment. Using the derived physical parameters and the parameters for the fitted sorption expressions from the batch experiments, the breakthrough (concentration-versus-time) curve for each tracer will be simulated and compared with the observed curve, both graphically and quantitatively, by computing the sum of squared differences. If two adsorption expressions provide equally good fits to the

observed data, the simplest expression will be used; e.g., the linear will be used before the Langmuir or Freundlich if the sum of squared differences between observed data are the same. Freundlich and modified Freundlich isotherms will be difficult to distinguish because they have the same functional form, and differences in terms of goodness of fit are expected to be small; therefore, the modified Freundlich may be used instead of the Freundlich, even though more information, that is, S_{max} , is required.

Results from the column experiments for the reactive tracers may not agree well with the results of the batch experiments. Reynolds et al. (1982) obtained poor agreement between batch and column experiments for cesium and strontium in a sand. It is hoped that some of the problems experienced by Reynolds et al. can be circumvented by using nonlinear isotherms. If predictions of column experiments are not adequate, the retardation will be determined by parameter fitting using SORBEQ. As noted by Reynolds et al., differences in the geochemical conditions in a flowing environment versus the essentially stagnant batch experiments may explain the discrepancy in the retardation parameter. In this instance, the results of experiments using individual minerals and characterization of the effluent from the columns may provide the insight to determine why the differences occurred.

If the results of the column experiment cannot be described, it is doubtful that the primary purpose of this study can be achieved. The column experiments are viewed as a first test of the Project. One reason for using crushed tuff in at least one set of column experiments is to ensure that an anomaly of a core, such as an inclusion, is not disrupting the flow or transport. Such anomalies may also occur in the field test, but the first step in validating the use of the batch data for predicting transport should use a simple porous medium continuum.

3.1.8 Representativeness, Limitations, and Uncertainties of the Tests

The most representative tracer would be one of the radionuclides given in Table 1, but the use of these radionuclides is not considered a viable alternative at this time for reasons discussed in Section 2.1.1 of this study plan. In addition to this limitation, operational constraints exist, namely, time and resources, that also limit the selection of tracers to those that show finite but low retardation in the mountain tuffs. As discussed in Sections 1 and 2 of this study plan, the approach used is based on selecting a group of tracers that presumably react in the subsurface by the same prevailing adsorption mechanisms that control the interactions of the radionuclides listed in Table 1 and the saturated tuffs of the mountain. If this approach is accepted as a practical compromise, the issue of representativeness between the results of tracer tests and those expected for radionuclides can be bridged by mimicking a generic behavior rather than by mimicking any specific response. The restrictions on using radionuclides obviously generate uncertainties with regard to objective observation of their exclusive behavior but do not exclude the understanding of their more general behavior. Resulting uncertainties can be defined if tracers are selected that interact with tuffs by a prevailing mechanism.

The question of representativeness affects two major aspects of the laboratory experiments in the reactive tracer study. First, the geologic samples and water used in the laboratory experiments will be limited in their quantity and quality. They may come from within the C-wells area but will not necessarily originate in the zone of the proposed field tests. Furthermore, current sampling will not

allow characterization of features that vary three dimensionally. Cores may be disturbed, which may force the use of crushed materials. Thus, availability of sufficient samples and their degree of disturbance are limitations that affect the representativeness of the results. To determine that the samples are as representative of the zones as possible, results from Study 8.3.1.3.2.1 will be used. The water used in experiments such as those for isotherm development using tuff samples also introduces questions of representativeness if the water does not come from the proposed field test area or if its chemical composition is altered during laboratory experiments. As in the case of the geological samples, availability and changes in water composition can also cause an impact on any experimental results.

A second question pertaining to representativeness relates to the type of laboratory experiments and their ability to represent field conditions. Because this question is precisely one of the objectives of the study, it cannot be fully answered in advance. Undoubtedly, the small scale of the laboratory experiments defines itself as nonrepresentative of any field conditions. However, it provides a basis for understanding and modeling phenomena that will be more applicable to the field if the experiments simulate as closely as possible the range of expected variables affecting any field test. These variables are either physical, such as velocity fields; chemical, such as water composition, pH, redox potential, and dissolved gases; or biological, such as microbial activity.

To minimize the uncertainties caused by the lack of representativeness, an attempt will be made in this study to use materials and water from the proposed field test area or to use alternatives that simulate the field conditions as closely as possible. The experiments will also be designed to represent the range of field variables within the limitations imposed by conventional laboratory techniques. The use of information available on the site and potential tracers, in combination with computer codes, such as geochemical codes, will assist in the evaluation of the effects of variables, as well as improve the selection and design of laboratory experiments and measurements.

3.1.9 Quality Assurance Requirements

Quality Level I has been assigned to the activities in this study plan in accordance with Paragraph 5.2.1d in procedure TWS-MSTQA-QP-18. The data produced by this study may be used in the license application for assessing ground water travel times and radionuclide retardation by sorption or matrix diffusion in the saturated zone. These data have a direct bearing on the assessments of waste isolation to be used in the license application. The applicable criteria from NQA-1 that apply to this study are shown in Table A-1 of this study plan, along with procedures and other documents that will satisfy these criteria. The quality assurance level assignments (QALA) for this study are also given in Appendix A. The QALAs in Appendix A were approved in 1986. Revised QALAs are currently being developed using new procedures that implement NUREG-1318. When the new QALAs are approved, they will supersede the QALAs in Appendix A, and the new QALAs will be provided as a revision to this study plan.

Detailed procedures will be used to describe the laboratory experiments in the tracer identification and characterization task. All of these procedures are nonstandard. A listing of these procedures is given in Table 5.

3.2 Field Experiments

Reactive tracer field experiments at the C-wells complex will be carried out in concert with the USGS hydrologic and conservative tracer studies. It is preferable to conduct reactive tracer experiments in the same wellbore configuration and in conditions similar to those used for the USGS conservative tracer experiments so that the hydraulic information from the USGS tests can be applied to the reactive tracer field studies. This collaboration means that the schedule, wellbore configurations, and operating conditions for the reactive tracer experiments will be influenced strongly by the USGS schedule.

The types of field experiments using reactive tracers--interwell recirculation, drift/pumpback, and convergent--are discussed as possible methods of evaluating tracer sorption. These experimental arrangements are described in SCP Section 8.3.1.2.3.1.7. The use of a reactive tracer will be accompanied by a nonreactive tracer to provide a direct comparison between the two. This practice will be essential to model field results of the reactive tracer tests.

When attempting to perform multiple tests in the same well or set of wells, the experimenter runs the risk of altering the physical or chemical nature of the system so that subsequent tests are conducted in a system that differs from that in which the first experiment was conducted. For example, irreversible adsorption on the rock surface or, in the case of polystyrene microspheres, retention by filtration could alter the behavior of the tracer in subsequent tests. To prevent these problems, several tracer tests will be performed simultaneously whenever possible, thereby eliminating the need to conduct many consecutive tests. Laboratory experiments are planned to minimize interactions that may affect the transport behavior of tracers. Also, field tests will be carried out at low concentrations to minimize these problems. Nevertheless, the problem must be addressed, especially because conservative tracer experiments will have been conducted by the USGS before the reactive tracer tests. LANL will work with the USGS during the tracer identification process to make sure that conservative tracers do not compromise subsequent reactive tracer studies. Finally, the effect of consecutive tracer tests on transport behavior will be tested directly by repeating at least one test in the same zone.

3.2.1 Interwell Recirculating Tracer Experiments

The USGS plans to conduct multiple-well, recirculating tracer experiments by using conservative solutes in the intervals exhibiting the highest permeability from borehole surveys and hydraulic stress experiments (Activity 8.3.1.2.3.1.5). Current information available from the USGS indicates that at the C-wells these intervals are located in the lower part of the Bullfrog Member and in the upper part of the Tram Member of the Crater Flat Tuff.

The reactive tracer experiments will follow a similar strategy if information available from the USGS conservative tracer experiments does not reveal problems in the selected intervals. Reactive tracers will be injected and produced in zones that exhibit maximum tracer recovery in the conservative tracer field experiments. Three to five multiwell experiments are planned.

In the conservative tracer experiments, the USGS will have located packers to isolate permeable regions in each wellbore. It is scientifically advantageous and operationally more efficient to use the same wellbore configurations. With the

use of injection pumps and submersible pumps, a steady-state flow field will be established between two wells at a flow rate between 50 and 200 gpm. After the injection and production well pressures have stabilized, the tracers will be injected at the surface as a short and concentrated slug of known tracer mass. The tracer mass selected will depend on both the amount of dilution that occurred in the USGS conservative tracer experiments and the estimated adsorption from the laboratory experiments. Water samples will be collected at the surface in the production well to measure conservative and reactive tracer concentrations. Sampling frequency will be every 15-30 min during the initial tracer response and every 1-2 hr after the peak tracer concentration is measured and the tail of the response curve is approached. This sampling frequency should be sufficient to accurately determine the first arrival of tracer. An automatic sampling and analysis device would be superior, and, for tracers for which automatic sampling is possible, an automatic procedure will be implemented. The steady-state flow field and water sampling will continue until nearly all tracer has been recovered or until the concentration reaches pretest levels or becomes unmeasurable for a predetermined period.

To plan the tests more thoroughly and to assess the validity of the local equilibrium assumption, preliminary modeling of the tests will be carried out. For now, a very simple calculation will suffice for estimating the test duration and likely operating conditions. Despite the likelihood of anisotropic permeability in a fractured medium, it is assumed that fluid injected into the injection well travels radially away from the injection point. A first approximation indicates that the tracer will reach the production borehole after sweeping the pore volume from a disc-shaped region of rock. The dimensions of the volume of rock are assumed to have a 77-m radius (the distance between C1 and C2) and a thickness of 30 m (the height of a packed-off region envisioned for the experiments), resulting in a rock volume of $5.6 \times 10^5 \text{ m}^3$. This rock volume, when multiplied by a typical value of fracture porosity at Yucca Mountain of 10^{-3} (Erickson and Waddell 1985), yields a fracture pore volume of 560 m^3 . At a typical injection flow rate of $6.3 \times 10^{-3} \text{ m}^3/\text{s}$ (100 gpm), the estimated fluid travel time is 25 hr.

To measure the tail of the response curve, the experiment will have to be run for considerably longer than 1 day. Furthermore, a reactive tracer will reach the production well later because of adsorption. Given this approximate residence time for a conservative tracer, a tracer with a retardation factor as high as 10 could probably be used in a test lasting 1 mo. Higher retardation factors would probably result in an undesirably long field test.

In a two-well recirculating tracer experiment, the fluid produced contains a significant fraction of the injected tracer. If this fluid is reinjected directly, the concentration-versus-time curve at the outlet will eventually be affected by recirculation, and the response will no longer be to a simple pulse input of tracer. Robinson and Tester (1984) outlined a technique for deconvoluting a tracer response for the case of produced fluid recirculation to obtain the response to a pulse input of tracer. This technique is strictly valid only for conservative tracers or tracers with a linear adsorption isotherm. In some cases, the isotherm will be linear enough for the deconvolution technique to be adequate. For nonlinear isotherms, this technique must be tested using sensitivity studies. For other reactive tracers with highly nonlinear isotherms, direct mathematical deconvolution is not possible except by modeling the concentration input as a pulse of tracer followed by the concentration versus time input caused

by recirculation. Regardless of the method for deconvoluting the data, recirculation may lead to a lowering of the quality of the data. Thus, recirculation will be avoided unless the operational obstacles of injecting fresh water are insurmountable.

The options for disposing of the fluid produced are (1) pump the water offsite, (2) inject the fluid into the third C-well or another borehole, and (3) store the fluid at the surface either temporarily in holding tanks until it can be hauled away by truck or in a lined pond, where it can evaporate. A selection will be made after reviewing each of these options and the recirculation option. The disposal method will be selected after the circulation and other options have been reviewed for operational feasibility and effect on the data.

3.2.2 Drift/Pumpback Experiments

Two or three drift/pumpback reactive tracer experiments will be conducted in the interval(s) in which the USGS drift/pumpback experiments are most successful. Exact flow rate, drift and pumpback times, and tracer mass injected will be based on the results of the USGS conservative tracer experiment. The experiments will be carried out by isolating a permeable region in the wellbore using a straddle packer. Tracer is placed in the interval using a specially designed logging tool that deposits the tracer at the desired depth. The tracer drifts from the wellbore via the prevailing ground water flow for a specified period. In the pumpback phase, a submersible pump is installed and water is withdrawn at a low rate. Initially, samples are collected frequently at the surface and less frequently during the tail of the tracer response until concentrations are below detection limits or until a point of diminishing returns is reached for the experiment. Again, the option of using automatic sampling equipment will be considered.

The drift/pumpback tracer experiment requires travel time estimates for both phases of the experiment. The drift phase time must be long enough to permit the tracer to move out of the near-wellbore region into the main body of the fracture system. If it is assumed that this distance is about 10 m and a linear flow velocity estimate of 0.15 m/day is used (Glover 1986), the result is a drift phase duration of about 2 mo. A typical pumpback duration may be calculated by assuming radial inflow of tracer from a distance of 10 m through a zone 10 m thick. Assuming a fracture porosity of 10^{-3} and a flow rate of 6.3×10^{-4} m³/s (10 gpm), the estimated backflow time is about 75 min. Thus, one day should be sufficient to recover most of the injected tracer.

In this experiment, the fluid produced will ideally be stored or discarded at the surface. If these options are impossible, the integrity of the test could be jeopardized because injection into another well could affect the flow field during the pumpback portion of the test. One possible solution is to inject into a different zone of another wellbore, where pressure communication with the zone being tested is minimal. It cannot be determined whether this option is feasible until the hydrologic studies have been carried out.

3.2.3 Convergent Tracer Experiments

One or two convergent tracer experiments with reactive tracers are planned in the regions used by the USGS in its convergent tracer experiments. Packers will be installed in permeable regions of two wellbores. Water will be pumped from

one wellbore until a steady-state flow field is developed. The tracer will be deposited downhole in the isolated region of the second borehole and will be allowed to travel to the production well. Water samples will be collected at the surface from the pumping well at a high frequency during the initial tracer response and the peak tracer response. Pumping and sampling will continue until concentrations attain pretest levels or become unmeasurable. Automatic sampling equipment will be used if possible.

Until more sophisticated modeling is carried out, the tracer transit time estimate for the convergent tests is assumed to be the same as that for the two-well recirculating test. Thus, similar test durations and requirements for the retardation factor are estimated for these tests.

As in the case of the injection/backflow test, if reinjection is necessary to discard the fluid, it must be into a zone that shows no pressure communication with the zone being tested. If such a zone cannot be found and if disposal at the surface is not possible, the convergent test cannot be performed.

3.2.4 Required Accuracy and Precision

Both the accuracy and precision of the tracer concentration measurements should be at least 95% to ensure reliable tracer response curves. The accuracy and precision of fluid flow rates should be at least 90-95%.

3.2.5 Equipment Needed

Until appropriate tracers are identified, a complete list of the equipment needed cannot be made. It is likely that a downhole injection tool, and possibly a downhole fluid sampler, will be necessary. If samples are collected at the surface, an apparatus to collect samples will be needed. The design of the apparatus will depend on the properties of the tracer and amount of sample needed to perform a chemical analysis. Analytical chemistry equipment will be needed, preferably on the site or close by, to perform the analyses in real time. The equipment needed depends on the tracers selected.

Downhole pumps, pressure gauges, and flow meters will be needed to control and monitor fluid flow. Packers will be set to isolate zones in the wellbores so that the flow system can be better defined. This equipment will already be in place from the USGS conservative tracer experiments. Finally, if the two-well recirculating tracer experiment is run in open-loop mode without reinjecting the produced fluid, provisions need to be made to store fluid temporarily at the surface while injecting fluid from a different source. To make this approach worthwhile, capacity to store at least 100,000 gal of water would be needed.

3.2.6 Data Reduction and Analysis

Because the duration of the experiment depends on the length of time necessary for the tracer to reach the production well, samples should be analyzed as they are collected to monitor the progress of the experiment. Concentration and flow data will be integrated to give the total mass of tracer that has been recovered. Data will be plotted in several forms: concentration versus time, concentration versus produced volume, and normalized concentration versus time for use in the modeling task discussed in Section 3.3 of this study plan. The normalized concentration is QC/m , where Q is the volumetric flow rate, C is the concentration,

and m is the mass of tracer injected by slug injection equipment. This normalization is carried out so that the integral of this curve over time equals unity at large times. Once the data have been reduced in this way, the various models described in Section 3.3 will be used to interpret the results.

3.2.7 Representativeness, Limitations, and Uncertainties of the Tests

A field experiment of solute transport is potentially more representative of radionuclide migration than a laboratory test because the solute undergoes flow and transport processes that cannot be duplicated in the laboratory. Nonetheless, several factors must be addressed to ensure the representativeness of the C-wells experiments. First, to be relevant to radionuclide transport in the saturated zone, the experiments will be conducted in the most permeable zones. Higher flow velocities in these zones will provide greater potential for nonequilibrium or kinetics effects. A conservative estimate of travel time for the conservative tracers and retardation for the reactive tracers will be obtained. Also, to complete tracer field experiments in a reasonable length of time, injection or pumping must be used, thus raising the issue of changes in flow and transport patterns from those of the natural state. Some examples of these phenomena include non-Darcy flow near injection and production wells and possible hydrofracturing if the injection pressure reaches the minimum confining earth stress. These issues will be addressed primarily through modeling efforts.

One factor that may affect experimental results is dispersion of the tracer in injection and withdrawal pipes after the tracer has flowed distances of 500-800 m. Robertson et al. (1987) found that pipe dispersion affected estimates of formation dispersion coefficients and porosity for the two-well tracer tests at the Basalt Waste Isolation Project (Gelhar 1982). This effect cannot be quantified until well-testing equipment has been installed and test zones have been selected. The potential effects will be determined, but no further details can be given until well-testing equipment has been purchased.

The main limitation in analyzing field experiments is the "nonuniqueness" problem: different porous medium or fracture network properties and models for flow and transport fit the measured data equally well yet differ when predicting some other facet of system behavior. Though this problem is to some extent inherent in all field experiments, a graduated approach using models of increasing complexity should allow us to achieve an adequate understanding of the processes involved. Finally, there will be uncertainty in extrapolating data from one site in the saturated zone to predict the behavior of the entire saturated zone. To reduce this uncertainty, experiments in wellbores at other locations around Yucca Mountain should be considered.

3.2.8 Quality Assurance Requirements

Quality Level I has been assigned to the activities in this study plan in accordance with Paragraph 5.2.1d in procedure TWS-MSTQA-QP-18. These data may be used in the license application for assessing ground water travel times and radionuclide retardation by sorption or matrix diffusion in the saturated zone, which have a direct bearing on assessments of the site's suitability for isolating waste to be used in the license application. The applicable criteria from NQA-1 that apply to this study are shown in Table A-1, along with procedures and other documents that will satisfy these criteria. The QALAs for this study are also given in Appendix A. The QALAs in Appendix A were approved in 1986. Revised

QALAs are currently being developed using new procedures that implement NUREG-1318. When the new QALAs are approved, they will supersede the QALAs in Appendix A, and the new QALAs will be provided as a revision to this study plan.

Detailed procedures for the field experiments task will be used to guide operational activities, e.g., establishing pumping rates, injecting tracers, and sampling. All of these procedures are classified as nonstandard. A listing of the procedures is given in Table 6. It is expected that the USGS will develop procedures for its conservative tracer experiments, and the reactive tracer study will be adapted from the USGS procedures.

TABLE 6
PROPOSED PROCEDURES FOR FIELD EXPERIMENTS TASK

<u>Procedure</u>	<u>Type</u>	<u>Status</u>
Single-well experiment with physical sorbing tracer	Nonstandard	TBD*
Single-well experiment with chemical sorbing tracer	Nonstandard	TBD
Multiple-well experiment with physical sorbing tracer	Nonstandard	TBD
Multiple-well experiment with chemical sorbing tracer	Nonstandard	TBD
Single-well experiment with polystyrene microspheres	Nonstandard	TBD
Multiple-well experiment with polystyrene microspheres	Nonstandard	TBD

*TBD--to be determined.

3.3 Modeling Analyses

This section is concerned primarily with design and analyses of the field experiments. Modeling of adsorption for the tracer identification and characterization task is described in Section 3.1 of this study plan.

A critical requirement for modeling the results of the reactive tracer experiments is understanding the physical phenomena governing flow and transport of a reactive tracer in a field experiment. In particular, the flow velocity, dispersion, and matrix diffusion must be known in order to use the laboratory-derived estimates of adsorption parameters to predict the observed breakthrough curves for the reactive tracers from the field experiments. Both nonreactive and polystyrene microspheres will be used as tracers to estimate the physical

parameters previously listed. After a general discussion of modeling, techniques will be presented that can be used to estimate values for velocity and dispersion. The estimates for dispersion generated by this effort will be used in site characterization (SCP Table 8.3.1.2-1).

Once the physical parameters have been estimated, they will be entered in transport codes along with laboratory-estimated adsorption values, and the response from the field experiments will be predicted. This approach is favored over the alternative approach of estimating adsorption parameters from field data because of the way the radionuclide adsorption data generated by activities in SCP Section 8.3.1.3.4 will be used. Performance assessment will predict radionuclide behavior, and a favorable comparison of the predicted and observed breakthrough curves in the reactive tracer study will increase confidence in the application of laboratory-derived adsorption estimates to the Yucca Mountain site. On the other hand, estimation of the adsorption parameters from the observed data will be of limited use because the inverse problem is vaguely defined and the estimates are not unique. Therefore the assumptions in the fitting procedure are crucial to the "best-fit" value.

The basis for modeling is the governing equations for flow and transport with appropriate initial conditions, boundary conditions, and source or sink terms. In the modeling of the results of a tracer test at the scale of the C-wells, many different formulations can be proposed and solved, each providing a system response (Karasaki 1987). Questions immediately arise as to the validity of the different approaches and the derived parameters, but this is a fundamental issue whenever modeling is used and the data available are limited. The governing equation for flow in saturated porous media, assuming a porous medium continuum, is (Freeze and Cherry 1979).

$$S_s \frac{\partial H}{\partial t} = \frac{\partial}{\partial x_i} \left[K_{s,ij} \frac{\partial H}{\partial x_j} \right] + W, \quad (16)$$

where

S_s is the specific storage (L^{-1}),

H is the hydraulic head (L),

$K_{s,ij}$ is the saturated hydraulic conductivity tensor (L/T),

W is the source or sink term (T^{-1}),

x_{ij} is the three-dimensional spatial coordinate $i, j = 1, 2, 3$ (L), and

t is the time coordinate (T).

When a saturated hydraulic conductivity (K_s) and specific storage (S_s) are included in Equation 16, a finite volume of material [representative elementary volume (REV)] is assumed to exist for which storage and hydraulic properties are defined. For flow in fractured media, Equation 16 may not be appropriate. If few fractures exist at the scale of the wells or if there is poor connectivity of fractures between the wells, a discrete fracture approach is the most appropriate model for analysis. This approach involves using an equation that is similar to Equation 16, with perhaps a different definition of conductivity, and

the geometry of the fracture must be assumed. Well logs can be used to locate fractures, but fracture size cannot be readily determined. Data from the USGS's hydraulic tests will be used to estimate apertures, and model sensitivity analyses using different fracture characteristics will be needed to determine the importance of shape if the discrete fracture approach is adopted.

The advection/dispersion equation is generally used to describe mass transport in a porous medium. For a sorbing solute in a saturated medium, the equation is (Freeze and Cherry 1979)

$$\phi \frac{\partial C}{\partial t} + \rho_b \frac{\partial S}{\partial t} = \frac{\partial}{\partial x_i} \left[D_{ij} \frac{\partial C}{\partial x_j} \right] - q_i \frac{\partial C}{\partial x_i} \quad (17)$$

where

- ϕ is the porosity (L^3/L^3),
- C is the concentration in solution (M/L^3),
- ρ_b is the bulk density (M/L^3),
- S is the concentration in the sorbed phase (M/M of solid),
- D_{ij} is the dispersion tensor (L^2/T),
- q_i is the Darcy flux obtained from the solution of Equation 17 in the i coordinate,
- direction $i = 1, 2, 3$,
- t is the time coordinate, and
- x_i and x_j are the three-dimensional spatial coordinates $i, j = 1, 2, 3$.

Using Equation 17 to simulate conservative tracers means that the second term on the left-hand side is zero. Again, this equation is for a porous medium continuum. For transport through fractures, Equation 17 can be applied with the appropriate definition of the parameters. Of particular interest for transport through fractures is the diffusion of solutes, either conservative or nonconservative, into the porous matrix. Rasmuson and Neretnieks (1981) presented a one-dimensional formulation for transport through fractures that considered matrix diffusion into spherical blocks and radioactive decay. Their formulation, without radioactive decay or sorption, is

$$\frac{\partial C_f}{\partial t} + U_f \frac{\partial C_f}{\partial z} - D_L \frac{\partial^2 C_f}{\partial z^2} = -\phi_m D_m \left(\frac{\partial^2 C_m}{\partial r^2} + \frac{z}{r} \frac{\partial C_m}{\partial r} \right) \quad (18)$$

where

- C_f is the concentration in the fractures (M/L^3),
- U_f is mean flow velocity in the fracture (L/T),

D_L is longitudinal dispersion (L^2/T),
 Φ_m is porous matrix porosity (L^3/L^3),
 D_m is the diffusivity in the matrix (L^2/T),
 C_m is liquid concentration in the porous matrix (M/L^3),
 r is the radial coordinate (L),
 z is the spatial coordinate in the direction of flow (L), and
 t is the time coordinate (T).

The equation can be modified for prismatic rather than spherical blocks and for solute reaction with fracture fill material or within the rock matrix.

To achieve the primary goal, the velocity, dispersion, and diffusion parameters in Equations 17 and 18 must be estimated. The dispersion coefficient in particular has been shown to exhibit scale dependency (i.e., it increases in magnitude as the experimental scale increases). This effect will be discussed in more detail in the following sections. Dagan (1987) defined the local scale as a formation whose depth is of the same order as the horizontal extent. This distance is on the order of meters, rather than kilometers used to describe regional scales. Thus, the field experiments will be conducted and are applicable on a local scale.

The modeling analysis to be conducted as part of the reactive tracer study will span the number of approaches available for analysis of flow and transport in porous and fractured media. The simplest models that assume a porous medium continuum will be applied with various techniques to determine the parameters governing flow and transport. The study is concerned with field verification of the reactive processes affecting the movement of solutes through the saturated zone. Matrix diffusion incorporated in Equation 18 is a physical process that can be an important retardation mechanism in transport through fractured media. Matrix diffusion will be examined using nonreactive tracers in conjunction with polystyrene microspheres. An early breakthrough of the polystyrene microspheres when compared with the breakthrough time of the nonreactive tracer is presumably caused by diffusion of the dissolved tracer into pores that are not available to the larger polystyrene microspheres. Modeling this type of behavior may provide insight into matrix diffusion and allow for estimation of a matrix diffusion coefficient.

3.3.1 Estimation of Physical Properties

The purposes of the analyses described in this section are to provide estimates of velocity, dispersion coefficients, and matrix diffusion coefficients to be used in the analyses of the field experiments. This activity is normally termed calibration or fitting of the model parameters. By using this approach, the conditions that occur during each reactive tracer experiment are incorporated in the estimates of these parameters.

The estimated parameters will be obtained for conditions occurring at the C-wells site during a given field experiment. Sensitivity or uncertainty analyses are not planned as part of this phase of the modeling. These analyses will provide estimates of dispersion coefficients and matrix diffusion coefficients that can be used in performance assessment calculations for the saturated zone for Issue 1.1.

Three techniques to be used in this phase of the study are presented in the following sections. All three methods are inverse techniques, but it is proposed to use the method of moments and residence time distribution theory as two simplified techniques. A more general inverse technique is also presented.

3.3.1.1 Method of Moments

In the simplest case, a porous medium continuum is assumed, and the classical advection/dispersion equation is used to describe transport. A simple technique for determining the parameters for the advection/dispersion equation is the method of moments. Gelhar et al. (1985) state that an advantage of the method of moments is that assumptions about the constancy of dispersivity in time are not made; thus, the method can be used to determine whether dispersivities are constant or are growing with time or travel distance. Freyberg (1986) and Roberts et al. (1986) have used the method of moments to identify both transport and retardation parameters in a natural gradient experiment in a sandy aquifer. Valocchi (1985) presents moment estimators for equilibrium and nonequilibrium formulations of the advection/dispersion equation. The general technique is described by Turner (1972).

Spatial or temporal moments can be defined and used to calculate the parameters for the transport equation. Assuming a single observation well, the temporal moments are defined as

$$M_0 = \int_0^{t_0} Q C(x,y,z,t) dt, \quad (19)$$

$$M_1 = \int_0^{t_0} Q t C(x,y,z,t) dt, \quad (20)$$

$$M_2 = \int_0^{t_0} Q t^2 C(x,y,z,t) dt. \quad (21)$$

where

M_0 is the zero moment,

M_1 is the first moment,

M_2 is the second moment,

$C(x,y,z,t)$ is the tracer concentration at given spatial and temporal coordinates (M/L^3),

Q is flow rate (L^3/T),

t_0 is the duration of the breakthrough curve, and

t is a dummy variable for integration.

M_0 is used to normalize M_1 and M_2 for calculation of the velocity and dispersion coefficient using relationships provided by Jury and Sposito (1985) and Duffy and Al-Hassan (1987) for the one-dimensional, advection/dispersion equation:

$$\frac{M_1}{M_0} = \frac{LR}{u} \quad (22)$$

$$\left[\frac{M_2}{M_0} - \left(\frac{M_1}{M_0} \right)^2 \right] = \frac{2DLR^2}{u^3} \quad (23)$$

where

L is the distance from the source to the sampling location,
 R is the retardation factor,
 u is the pore water velocity, and
 D is the dispersion coefficient.

All analyses conducted in this section assume that R is equal to 1.0 for the nonreactive tracer.

Goltz and Roberts (1987) presented moments analysis for the three-dimensional advection/dispersion equation for equilibrium and nonequilibrium conditions. In the case of the C-wells, there will be at most two locations in the horizontal plane where samples can be taken, and this number of samples is insufficient to apply the spatial moments technique.

The method of moments represents a simple technique for analysis of tracer concentration data. The integrals in Equations 19-21 can be estimated by a numerical quadrature formula such as Simpson's rule or the Gauss-Legendre quadrature.

3.3.1.2 Residence Time Distribution Modeling

Residence time distribution (RTD) modeling is also being developed to analyze the tracer experiments. Given a conservative tracer response, these RTD-based models offer a way to place bounds on the adsorbing tracer response for interwell experiments. The models automatically match the conservative tracer RTD for the extremes of the earliest or latest possible mixing of molecules of different residence times.

Zwietering (1959) showed that these RTD models can place bounds on the steady-state conversion of a chemical reaction. These models can also be used to place bounds on adsorbing tracer response. The fundamental principle used in these "micromixing" models is that models that match the conservative tracer RTD differ only in the earliness or lateness of mixing of molecules of different residence time, which gives rise to different behavior for solutes undergoing nonlinear processes. The two extremes of micromixing are depicted in Figures 6 and 7. The latest possible backmixing or minimum mixedness occurs when the RTD is represented by a network of plug flow reactors connected in parallel.

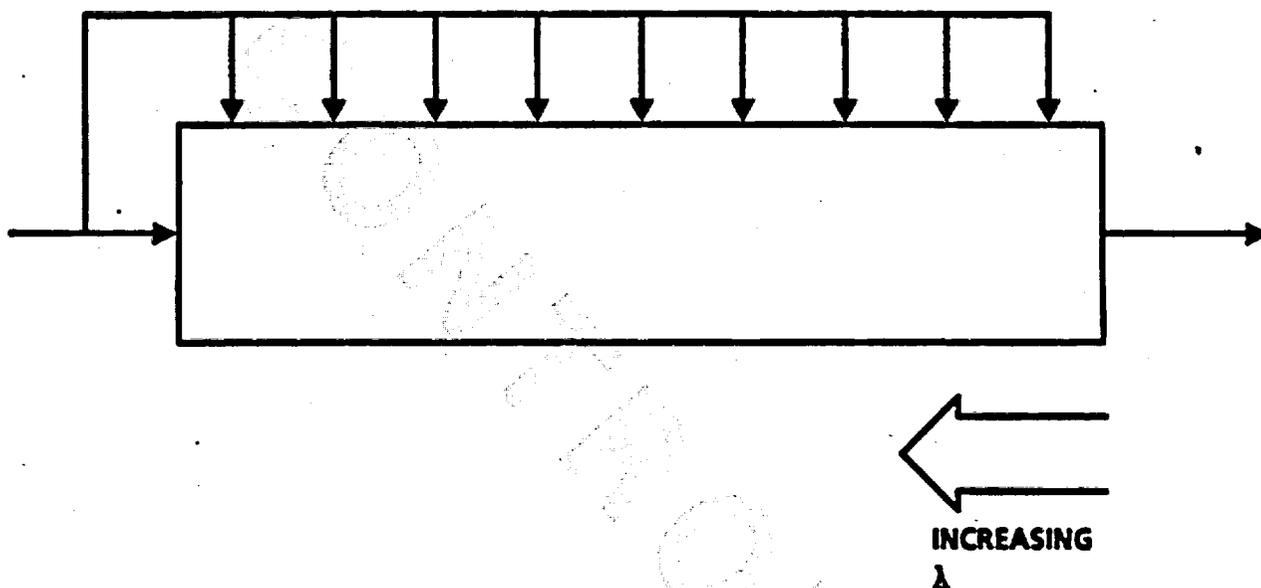


Figure 6. Schematic of the Maximum Mixedness Model of a Plug Flow Reactor with Side Entrances with Life Expectancy (λ) Increasing from the Outlet

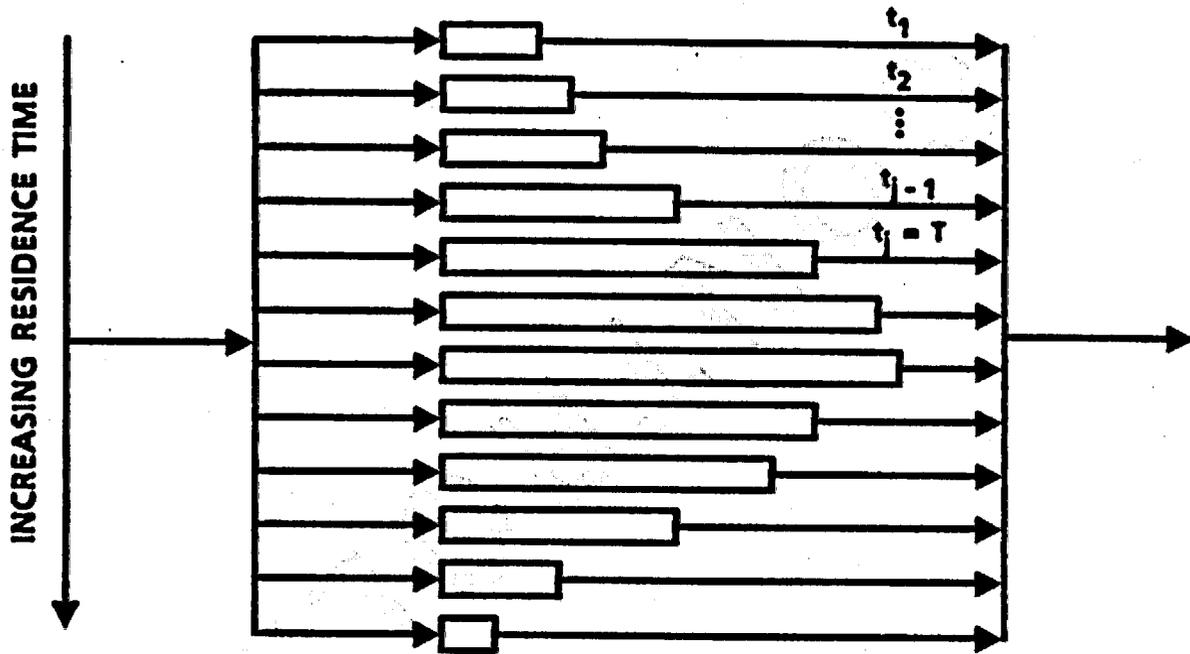


Figure 7. Schematic of the Minimum Mixedness Model of Parallel Plug Flow Paths

Fluid and tracer of different residence times remain unmixed until they reach the outlet manifold. The volumes and flow rates of each path are adjusted to approximate the measured nonreactive tracer response. The maximum mixedness reactor is a plug flow reactor with side entrances whose positions and flow rates are also adjusted to match the RTD. Because fluid mixes with other fluid of longer residence times immediately upon entering the system, the system has the earliest possible mixing of fluid of different residence times. These models can also be used to predict tracer behavior for different tracer inputs such as slug, step injection, or slug injection with recirculation.

3.3.1.3 Inverse Techniques

Inverse techniques use the proposed equations governing reactive tracer transport and an optimization scheme to determine parameter values. Analytical or numerical solutions to the governing equations in one, two, or three dimensions can be used in this approach. The inverse technique can use either manual trial and error or automatic methods to determine optimal parameter values.

Parker and van Genuchten (1984) have developed an automatic fitting algorithm for analyzing the one-dimensional, advection/dispersion equation with the following terms: linear equilibrium adsorption, zero-order production and/or first-order decay, two site/two region for nonequilibrium conditions, and field-scale stochastic hydraulic fluxes. Application of this program is based on the assumption that the porous medium can be described as a continuum, i.e., the fractures do not invalidate concepts for flow in porous media.

Dual-porosity models have been proposed for analyzing fractured porous media when the density of fractures is so great that discrete fracture models cannot be used. Because the dual-porosity models assume two overlapping continua--the porous matrix and the fractures--an assumption must be made about the interaction between the fluid in the fractures and the rock matrix. Neretnieks and Rasmuson (1984) used diffusive transport between the fracture and the porous matrix and inside the porous matrix. A computer code to solve the inverse problem for dual-porosity media with transport has not been published; therefore, a manual calibration may be used to estimate parameters for this case.

3.3.2 Numerical Models

Flow and transport in fractured porous media can be assumed to be either a porous medium continuum, a dual-porosity medium, or a discrete fractured medium. Two numerical models have been selected that are capable of simulating all three of these assumptions.

3.3.2.1 Finite Element Heat and Mass

The finite element heat and mass (FEHM) code calculates two-phase (liquid and vapor) water, heat, and solute flow (Zyvoloski et al. 1987). FEHM will be used for both the continuum and dual-porosity simulations for both single- and multiple-well experiments in the reactive tracer study. FEHM uses a finite element solution technique and is capable of simulating two-dimensional radial and rectangular geometries and three-dimensional rectangular geometries. Solute transport in FEHM is treated by solving the advection/dispersion equation.

Another component of FEHM is the solution of the energy balance equation. The USGS has conducted hydraulic experiments at the C-wells (SCP Section 8.3.1.2.3.1.3), and preliminary data have shown that pumping causes changes in temperatures. By measuring temperature during a field experiment, an additional state variable is available that may allow for more accurate prediction of the flow field and may provide information for temperature effects on tracer reactions.

3.3.2.2 Fracture Network Simulator

Karasaki (1987) has shown that under certain conditions the response of wells to hydraulic stresses cannot be described either by a porous medium continuum or a dual-porosity approach. In this case, a discrete fracture representation can be used. Fracture network simulators, such as those used by Long et al. (1982) and Schwartz et al. (1983), are an approach to simulating the response. These simulators create a fracture network representative in a statistical sense of the network found at an experimental site. Schwartz et al. (1983), while studying macrodispersion using a stochastic modeling approach, found the dispersivity to be variable and showed that simple functions relating dispersivity to velocity could not be determined. These results were attributed to the sensitivity of dispersivity to velocity fluctuations that were a function of fracture characteristics. The network generator used by Schwartz et al. (1983) randomly located fractures, oriented fractures, and set fracture length and apertures. Particle-tracking techniques were used to describe solute transport through the fracture network. Smith and Schwartz (1984) conducted a sensitivity analysis of transport in fracture networks using the same model and found that parameters that increased the chance for a more circuitous pathway increased the mean and standard deviation of the breakthrough curves.

A fracture network model (FRACNET) is currently being developed to determine the steady-state fluid flow and solute transport properties in a two-dimensional fracture network. The model randomly generates a fracture network with a given fracture density and assumes statistical distributions of fracture orientation, aperture, and length. The pressure boundary conditions are constant pressure line segments to represent wellbore sources and sinks, and the outer boundary is a no-flow boundary; thus, the model realistically simulates the flow field during an interwell tracer experiment.

The code solves the pressure field and tracer response for a two-well recirculating tracer experiment. Particle-tracking techniques are being developed to account for phenomena such as dispersion within a fracture, reversible adsorption, and matrix diffusion.

Several techniques will be used to determine the input parameters of the model. First, well logs will allow estimation of the fracture density and orientation distribution. Hydraulic tests will be used to estimate the average hydraulic aperture of fractures by matching the measured pressure drop across the flow systems. Fracture lengths are difficult to determine, and the effects of fracture lengths will be estimated using sensitivity studies. Matrix porosity will be determined from cores. Finally, a parameter in the model that relates the hydraulic and tracer apertures will be adjusted within the likely range of values to provide a fit with the nonreactive tracer response. Then, these parameters, along with the laboratory-determined adsorption parameters, will be used to calculate the predicted reactive tracer response curve.

3.3.3 Field Experimental Design

This phase involves estimating tracer response for reactive, nonreactive, and polystyrene microsphere tracers before the experiments begin. These analyses will use data from Czarnecki and Waddell (1984), Robinson (1984), Erickson and Waddell (1985), and information available from the C-wells site generated by Activity 8.3.1.2.3.1.3, which analyzes previously completed hydraulic stress tests. Using data and information from these sources, this analysis will try to bracket expected conditions to assist in determining sampling schemes and experiment durations.

3.3.4 Single-Well Tracer Experiments

The USGS is proposing to conduct single-well experiments in addition to multiple-well experiments in the vicinity of the C-wells. These experiments will provide information on local hydrologic and chemical properties and parameters that can be used in the multiple-well experiment. It is not possible to provide a detailed description of the analysis of the single-well experiments until the experiments have been completed. Interpretation of the data from these experiments will follow a general pattern of starting with the simplest analysis—method of moments—and proceeding to a more complex technique if the results based on the simpler technique have been shown to be inadequate. In all cases, results from the same analysis using a conservative tracer will provide the estimated velocity and dispersion parameters. Initially, laboratory values for the retardation properties can be used and compared with the observed data. The inability to match observed data with established criteria will necessitate fitting the retardation coefficients. Conditions for equilibrium and nonequilibrium will be based on laboratory experiments to discern the threshold.

The constraints on analyzing this experiment are obtaining a complete (or nearly complete) breakthrough curve and obtaining knowledge of the porosity of the material to assist in estimating the hydraulic conductivity. A preliminary analysis conducted by Robinson (1987) indicated that conventional drift/pumpback experiments with reactive tracers will not provide any additional information on the retardation properties of the porous medium. As noted, single-well experiments are useful in providing local values of the hydraulic and transport parameters, velocity and dispersivity. The utility of these data for the multiple-well experiments can be substantial if the single-well experiments are conducted in sufficient numbers to characterize the vertical distribution of properties in the borehole. Molz et al. (1986) described a multiple-well tracer experiment that used the vertical distribution of hydraulic conductivity obtained from single-well experiments and a local dispersivity value. Molz et al. were able to successfully simulate the multiple-well experiment using the parameter values from the single-well experiment. Another consideration in planning a drift/pumpback experiment is the diffusion of tracer into the matrix and/or dead-end pores. This diffusion may be particularly prevalent in experiments conducted using natural ground water flow.

3.3.5 Multiple-Well Tracer Experiments

As opposed to single-well experiments, multiple-well experiments are used to provide aquifer average or global information. In the analysis of multiple-well experiments, the scale-dependency phenomenon must be considered. The importance of scale dependency is primarily related to the analysis of radionuclide

migration, which can be inaccurate if scale-dependent behavior is not included. Dagan (1987) indicated that injection/withdrawal experiments had two limitations in determining transport properties of porous media: (1) only short-time behavior is reflected and (2) the results are dependent on radial flow conditions around the wells.

Various theories have been developed to describe the scale dependency of macrodispersivity (Matheron and de Marsily 1980; Gelhar and Axness 1983; Güven et al. 1984; Domenico and Robbins 1984), and the common theme of these theories is that heterogeneities control the developing dispersivity. Matheron and de Marsily (1980) and Gelhar and Axness (1983) used stochastic approaches that required the variability and correlation structure of the velocity field or hydraulic conductivity field to describe the developing dispersion pattern. In the analysis by Güven et al. (1984), the aquifer is considered to be perfectly stratified, and velocity variations for each stratified layer are known and used to determine the macrodispersivity. In another explanation of scale-dependent behavior of dispersion, Domenico and Robbins (1984) attributed the scaling of parameters to the fitting of an n -dimensional system by a model with dimensions no higher than $n-1$. Another factor cited by Domenico and Robbins, which may lead to increased dispersion in analyzing field tests, is the location of samples in the plume. If sampling is off the center line and the solution to the governing transport equation assumes that the concentration data come from the center line, the dispersion coefficient must be increased for a given velocity to reflect the lower observed concentrations, even if both the system and the model are n -dimensional. In field situations, it is difficult to determine the plume center line, particularly when the gradient between sampling locations is low and the number of samplers is limited.

An analysis of the C-wells field experiment will be conducted before the actual field test to assist in planning for field sampling. To account for scale dependency, one approach is to use current theory to derive a value for macrodispersivity at the scale of the C-wells and to use a continuum model to predict tracer transport for various pumping rates. Another approach is to use a random field generator to provide a realization of hydraulic conductivities for either a finite difference or finite element mesh and to use local values for dispersivity. Again, a series of pumping rates can be applied. Finally, fracture network simulations can be conducted. In all cases, adsorption parameters obtained from laboratory experiments will be used. Before performing any of these analyses, more information will be needed about the distributions of hydraulic conductivity and the characteristics of the fracture networks. Some of the information will come from the USGS analyses of the hydraulic response of the C-wells.

The analysis of the multiple-well experiments will use a phased approach, beginning with the simplest model and proceeding to more complex models if the simpler models are shown to be inadequate. A data-fitting approach using a least squares difference objective function will be used to judge the goodness of fit. However, other more qualitative criteria must be used when evaluating models. First, it must be determined whether the model provides a useful, realistic description of the transport process with a minimum of adjustable parameters required to achieve the fit. Also, the derived model parameters must have realistic values in terms of other information provided by the C-wells. Thus, in addition to simply fitting the data, more subjective criteria will be used to evaluate the efficacy of a model.

Analysis of a conservative tracer will provide the transport parameters, and laboratory values will be used for initial estimates of the adsorption parameters. If the laboratory-determined adsorption values cannot be used to describe reactive tracer retardation, these data will be fitted to the models, along with an analysis identifying possible sources of the discrepancy. Further laboratory and modeling efforts may then be needed to resolve the differences. Every attempt will be made to identify all phenomena that may have an effect on the results before running the tests. However, if unexpected results are obtained, an attempt will be made to examine other possible physical and chemical effects suggested by the results but not considered in the initial modeling effort.

Constraints on this analysis are knowledge of the hydraulic and chemical properties of the flow path. The influence of the fracture network on macrodispersivity has not been studied. Changes in mineralogy or water composition along the flow path may lead to developing a false set of retardation estimates. Problems of multidimensional flow and transport become more prevalent at larger scales, and an estimate for transverse dispersivity is necessary. Although these experiments are a direct measure of system performance for the specified conditions, the difficulty in integrating the effects of processes that occur along the flow path complicates predictions.

3.3.6 Input Requirements

To conduct the modeling analyses, the following input parameters are needed. It may be necessary to measure these parameters in the field using geophysical techniques, laboratory techniques, and/or tracer experiments with conservative (nonreactive) tracers. Three model formulations have been proposed (continuum, dual porosity, and fracture network), so input parameters for all three models are included. The input parameters are

- saturated hydraulic conductivity—distribution in space for composite porous media, matrix, and fractures;
- effective porosity for continuum models—distribution in space;
- matrix porosity for fracture network and dual-porosity models—distribution in space;
- molecular diffusion coefficient for tracer;
- tortuosity;
- fracture apertures—distribution in space;
- fracture lengths;
- dispersivity—local and global values;
- tracer input distribution—distribution in time and total mass;
- equilibrium adsorption expressions and their parameters;
- kinetics-based adsorption expressions and their parameters;

- temperature profiles--changes in time;
- pumping rates--continuous measurement;
- nonreactive tracer breakthrough curves--at observation and production wells in time; and
- reactive tracer breakthrough curves--at observation and production wells in time.

This list is extensive, and several of the information needs cannot be determined directly. For example, all property values labeled "distribution in space" will be very difficult to determine, even using information from geophysical techniques planned for the C-wells (SCP Section 8.3.1.2.3.1.3). Sensitivity studies will be carried out to determine how important uncertainties in various parameters are to the model results. At the other extreme, several of the input parameters will be measured directly in the C-wells study. These parameters are the tracer input distribution, the equilibrium sorption expressions, the kinetics-based sorption expressions (if necessary), temperature profiles, pumping rates, and conservative and reactive tracer breakthrough curves.

3.3.7 Representativeness, Limitations, and Uncertainties of Analyses

The preceding sections describe a modeling analysis of the reactive tracer experiments and analysis for radionuclide migration at the scale of the proposed reactive tracer experiments. Several issues affect the results of these analyses. Some of these issues, particularly the spatial variability in the flow velocity or hydraulic conductivity of the medium, have been noted already; other potential factors have not been explicitly identified.

A critical need is data pertaining to the spatial variation in hydraulic conductivity or velocity field to analyze for dispersivity. Single-well tracer experiments can provide the vertical distribution of hydraulic conductivity at individual wells. The multiple-well experiments provide an integrated aquifer average over the distance of the experiments, which may be more appropriate for an aquifer that is not perfectly stratified.

The most permeable zones in the C-wells vicinity are fractured, and several factors are currently unknown about the response of material from fractured porous media. The stress effects from pumping can alter the dimensions of fractures, thus affecting flow and transport characteristics. For experiments conducted under natural conditions, the influence of diffusion into the matrix and dead-end pores must be considered. The difference in the minerals that line fractures and the minerals in the matrix affects retardation of the reactive tracers.

The pumping of the aquifer can create conditions where assumptions pertaining to the local equilibrium of solute interaction may be violated; therefore, laboratory verification of these conditions must be made using column experiments. Other factors, such as borehole storage or the presence of a skin on the borehole, can affect results through delayed sampling or enhanced retardation. When rapid pumping rates are used in highly fractured material, the potential exists for non-Darcian flow to occur in the vicinity of the borehole.

Although state-of-the-art computer codes are being used in these analyses, the problem is still identification of parameters in a distributed system with many degrees of freedom available. Measurements will be made at a few locations in a system in which the numerical mesh may have thousands of unknowns. If all available data are used, the uncertainty can be reduced, but uncertainty remains about the horizontal distribution of fractures and velocity. Uncertainty analyses, which incorporate the unknown features of the system, are viewed as the primary alternative to the solution of these problems.

3.3.8 Quality Assurance Requirements

Quality Level I has been assigned to the activities in this study plan in accordance with Paragraph 5.2.1d in TWS-MSTQA-QP-18. These data may be used in the license application in assessing ground water travel times and radionuclide retardation by sorption or matrix diffusion in the saturated zone, which have a direct bearing on site assessments concerning waste isolation to be used in the license application. The applicable criteria from NQA-1 that apply to this study are shown in Table A-1 of this study plan, along with procedures and other documents that will satisfy these criteria. The QALAs for this study are also given in Appendix A. The QALAs in Appendix A were approved in 1986. Revised QALAs are currently being developed using new procedures that implement NUREG-1318. When the new QALAs are approved, they will supersede the QALAs in Appendix A, and the new QALAs will be provided as a revision to this study plan.

4.0 APPLICATION OF RESULTS

The results from this study will be used in other site characterization studies and in performance assessment.

The resolution of Issue 1.1 (SCP Section 8.3.5.13) for total system performance will take credit for any retardation factor greater than 1 for the saturated zone. The reactive tracer study will provide field estimates of retardation for matrix diffusion. Adsorption estimates for the radionuclides will be made in Investigation 8.3.1.3.4 using laboratory experiments to determine the parameters. Estimates of adsorption made by the reactive tracer study can be used in performance assessment to the extent that the adsorption parameters identified for the physical or chemical adsorption mechanisms are applicable to the radionuclides. A specific effort to correlate the behavior of the tracers selected for the reactive tracer experiments with the behavior of the radionuclides is not planned as part of the reactive tracer study. Any correlation will be indicated by the adsorption mechanisms.

The resolution of the ground water travel time performance issue (Issue 1.6) involves dispersive and diffusive fluxes as barriers (SCP Section 8.3.5.12) in the saturated zone. Estimates of matrix diffusion from the field experiments with the polystyrene microspheres and dispersion coefficients estimated at the scale of the C-wells will provide this information.

Data obtained from the field experiments can be used to validate performance assessment models for the saturated zone, although care must be taken not to use calibrated parameters from the reactive tracer study in a computer code that solves the same equations as those in Section 3.3 of this study plan. This approach cannot be considered validation because, if this approach were used, parameter estimates would not be obtained independently.

A site characterization activity that will use data from the reactive tracer study is retardation sensitivity analysis (SCP Section 8.3.1.3.7.1). This activity will use data from the field experiments for testing the TRACR3D (Travis 1984) computer code. Also, the retardation sensitivity analysis includes investigation of the transport of radionuclides as colloids using polystyrene microspheres to represent the colloid behavior. Data from the reactive tracer study can be used in developing and testing the colloid transport model.

Acquisition of the QA Level I core from a proposed new borehole that was discussed in Section 2.4 of this study plan will support other site characterization activities. Activity 8.3.1.2.3.1.5 will require QA Level I core to identify and characterize conservative tracers for the same rationale as required by the reactive tracer study. Activities 8.3.1.2.3.1.4 and 8.3.1.2.3.3.2 both will use C-well core to characterize fractures and calibrate geophysical techniques to describe the geology of the C-hole complex. Activity 8.3.1.2.3.2.2 will use core to examine matrix water in adjacent saturated and unsaturated zones. Activity 8.3.1.3.2.1.2 can use the core to obtain data on minerals from deep drill holes to assess mineral distributions between host rock and the accessible environment, and Activity 8.3.1.3.2.1.3 can use the core to obtain data on minerals in fractures with depth.

The reactive tracer study will also provide information for further field experiments that may need to be conducted at Yucca Mountain. Study 8.3.1.3.7.2 is

intended to demonstrate the applicability of geochemical data derived in the laboratory and to evaluate the data for use in resolution of Issue 1.1 (SCP Section 8.3.5.13). The field portion of the reactive tracer study is intended to aid in the integration of laboratory and field data. Results from the reactive tracer study will be used to guide further testing in the field. The reactive tracer study's companion activity, Well Testing with Reactive Tracers Throughout the Site (Activity 8.3.1.2.3.1.8), will also depend on the results of C-wells testing.

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5.0 SCHEDULE AND MILESTONES

5.1 Tracer Identification and Characterization

The laboratory phase of this study requires time to develop and evaluate laboratory methods designed to distinguish the two adsorption mechanisms. Initial development will use tracers that literature review has indicated to be predominantly adsorbed by the physical adsorption mechanism. After completion of this initial phase, tracers retarded by chemical adsorption will be evaluated. Column studies will then be initiated to evaluate the tracers and the polystyrene microspheres in a dynamic flow environment.

5.2 Field Experiments

The start of LANL's field experiments depends on when the USGS conducts its hydraulic and conservative tracer tests. A minimum of three multiple-well tests is planned with a duration of approximately 4 wk each. Allowing for equipment problems and problems in scheduling personnel, LANL's field experiments will take 12-20 wk. If more experiments are conducted, additional time will be needed.

5.3 Modeling

Modeling analyses will be conducted throughout the study. Initially, modeling will be used to define physical parameters, flow velocities, and diffusion rates for laboratory experiments. As retardation parameters are supplied by the laboratory experiments, models will be used to design the field experiments. Sensitivity analyses will be used to evaluate pumping schemes and uncertainty in porous media properties for the field experiments. The data from the field experiments will be analyzed using both analytical and numerical models.

The modeling task depends on the availability of data. The sensitivity analyses require some idea of the distribution, at least a mean and variance, of the important parameters and properties of porous media. Analysis of the field experiments cannot begin until the field data have been collected.

5.4 Proposed Schedule and Milestones

Table 7 shows the milestones, which are depicted graphically in Figure 8. All milestones listed in Table 7 are reports.

TABLE 7

MILESTONES FOR THE TESTING OF THE C-HOLE SITES WITH REACTIVE TRACERS

<u>Milestone Number</u>	<u>Milestone</u>
<u>Tracer Identification and Characterization</u>	
R379	Identification and Characterization of Reactive Tracers for C-Wells Reactive Tracer Investigations
T425	Characterization of Reactive Tracers for C-Wells Field Experiments I: Electrostatic Adsorption Mechanism, Lithium
New	Characterizing Chemical Adsorption Using Individual Minerals
New	Characterization of Reactive Tracers for C-Wells Field Experiments II: Chemical Adsorption Mechanism
New	Preliminary Selection of Reactive Tracers for C-Wells Field Experiments Using Batch Experiments
New	Column Experiments to Characterize Reactive Tracers and Polystyrene Microspheres for the C-Wells Field Experiments
(F) ^a New	Characterization of Reactive Tracers and Polystyrene Microspheres for C-Wells Field Experiments
<u>Modeling</u>	
R487	Predictive Modeling of In Situ Retardation of Reactive Tracers During C-Wells Testing at Yucca Mountain, Nevada
T426	FRACNET--Fracture Network Model for Water Flow and Solute Transport
New	FEHMN--Finite Element Heat and Mass Model for Use on the Yucca Mountain Project
New	SORBEQ--One-Dimensional Advection/Dispersion Equation with Nonlinear Adsorption for Design and Analysis of Column Experiments in the Reactive Tracer Study
New	Evaluation of FRACNET for Use on the Yucca Mountain Project
New	Evaluation of FEHMN for Use on the Yucca Mountain Project
(H) New	Design of Field Tests for the C-Wells Reactive Tracer Experiments
(N) New	Analyses of the C-Wells Reactive Tracer Experiments (This milestone is being added to the SCP through an Interim Revision Notice, dated 6/28/89)
<u>Field Experiments</u>	
New	Data from the C-Wells Reactive Tracer Field Experiments

a. Letters refer to entries in Table 8.3.1.2-11 of the SCP (DOE, 1988).

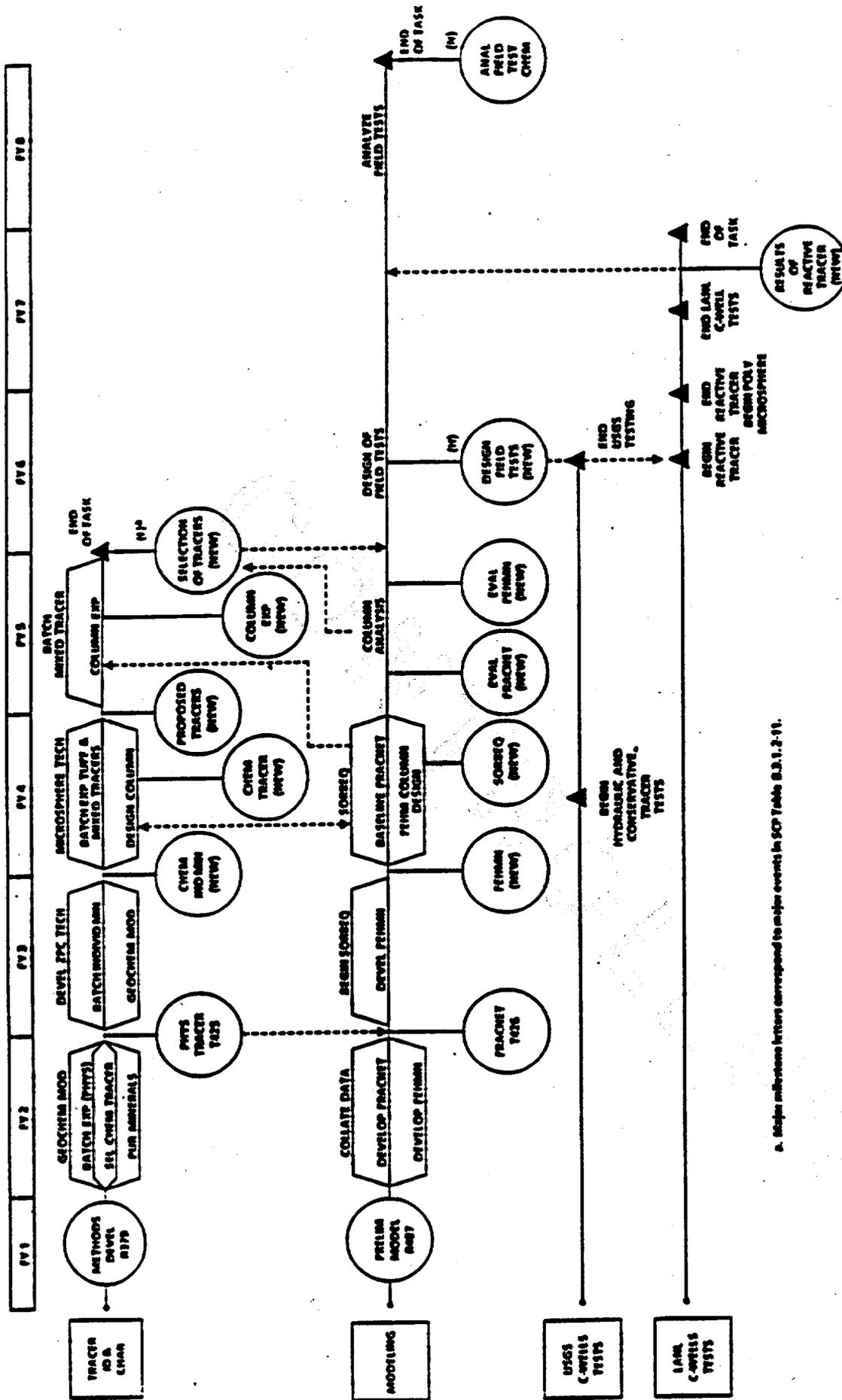


Figure 8. Schedule and Milestones for the Testing of the C-Hole Sites with Reactive Tracers Activity

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APPENDIX A
QUALITY ASSURANCE SUPPORT DOCUMENTATION

CONTROLLED

This appendix is composed of two parts. Table A-1 presents the applicable criteria from NQA-1 together with the procedures that implement these criteria. The second part is the quality assurance level assignments (QALA) for the work in this study. These QALAs were approved in 1986 and are not completely consistent with Table A-1. Revised QALAs for this study plan are currently being developed using a new procedure that implements NUREG-1318. When the revised QALAs are approved, they will supersede the 1986 QALAs and will be provided through controlled distribution as a revision to this study plan.

TABLE A-1

**APPLICABLE NQA-1 CRITERIA FOR SCP STUDY 8.3.1.2.3.1.7
 AND HOW THEY WILL BE SATISFIED**

NQA-1 Criterion	Documents Addressing These Requirements	Anticipated Date of Issue
1. Organization	The organization of the Office of Civilian Radioactive Waste Management (OCRWM) program is described in Section 8.6 of the SCP. The LANL QA program is described in the LANL-YMP-QAPP and includes a program description addressing each of the NQA-1 criteria. The LANL QA program contains quality administrative procedures (QP) further defining the program requirements.	
	TWS-QAS-QP-01.1 Interface Control	1/31/89
	TWS-QAS-QP-01.2 Stop Work Control	1/31/89
	TWS-QAS-QP-01.3 Conflict Resolution	2/21/89
2. QA Program	The LANL QA program is described in the LANL-YMP-QAPP and includes a program description addressing each of the NQA-1 criteria. An overall description of the YMP QA program for site characterization activities is described in Section 8.6 of the SCP.	
	TWS-QAS-QP-02.1 Personnel Selection, Indoctrination, and Qualification	1/31/89
	TWS-QAS-QP-02.2 Personnel Training	1/31/89
	TWS-QAS-QP-02.3 Readiness Review	5/31/89
	TWS-QAS-QP-02.4 Management Assessment	5/31/89
	YMP AP-5.4Q Assignment of Quality Assurance Level	1/24/89
3. Design and Scientific Investigation Control	This study is a scientific investigation. The following QPs apply:	
	TWS-QAS-QP-03.1 Software QA Plan	4/30/89
	TWS-QAS-QP-03.2 Technical and Policy Review	4/30/89
	TWS-QAS-QP-03.3 Preparation of SCP Study Plan	5/31/89
	TWS-QAS-QP-03.5 Documenting Scientific Investigation	2/29/89

TABLE A-1
APPLICABLE NQA-1 CRITERIA FOR SCP STUDY 8.3.1.2.3.1.7
AND HOW THEY WILL BE SATISFIED
(continued)

NQA-1 Criterion	Documents Addressing These Requirements	Anticipated Date of Issue
	TWS-QAS-QP-03.6 IDS Design and Interface Control	5/31/89
	TWS-QAS-QP-03.7 Peer Review	5/31/89
	TWS-QAS-QP-03.8 IDS Technical Assessment Review	5/31/89
	TWS-QAS-QP-03.11 Software Configuration Management	6/16/89
	TWS-QAS-QP-03.12 Scientific and Engineering Software and Software Libraries	6/16/89
	TWS-QAS-QP-03.13 Auxiliary, Commercial, and Utility Software	6/16/89
	TWS-QAS-QP-03.14 Design Input for ESF	2/3/89
	TWS-QAS-QP-03.15 TMO Design and Interface Control	5/31/89
4. Procurement Document Control	TWS-QAS-QP-04.1 Procurement	12/14/88
	TWS-QAS-QP-04.2 Acceptance of Procured Services	1/31/89
	TWS-QAS-QP-04.3 Qualification of Suppliers	1/31/89
5. Instructions, Procedures, and Drawings	TWS-QAS-QP-05.1 Preparation of QPs	12/14/88
	TWS-QAS-QP-05.2 Preparation of DPs	12/14/88
6. Document Control	TWS-QAS-QP-06.1 Document Control	1/31/89
7. Control of Purchased Material, Equipment, and Services	Applicable parts of this criterion are covered in Item 4 (see above).	
8. Identification and Control of Materials, Parts and Samples	TWS-QAS-QP-08.1 Identification and Control of Samples	5/31/89
	TWS-QAS-QP-08.2 Control of Data	5/31/89
9. Control of Special Processes	This criterion has been determined to be inapplicable to the scope of work of the LANL YMP.	
10. Inspection	This criterion has been determined to be inapplicable to the scope of work of the LANL YMP.	

TABLE A-1
APPLICABLE NQA-1 CRITERIA FOR SCP STUDY 8.3.1.2.3.1.7
AND HOW THEY WILL BE SATISFIED
(concluded)

NQA-1 Criterion	Documents Addressing These Requirements	Anticipated Date of Issue
11. Test Control	This criterion has been determined to be inapplicable to the scope of work of the LANL YMP.	
12. Control of Measuring and Test Equipment	The control of instrument calibration and data collection is described in the technical procedures referenced in Section 3 of this plan. The following QPs also apply:	
	TWS-QAS-QP-12.1 Measuring and Test Equipment	5/31/89
	TWS-QAS-QP-12.2 Control of Operator-Calibrated Equipment	5/31/89
13. Handling, Storage and Shipping	TWS-QAS-QP-13.1 Handling, Shipping, and Storage	3/17/89
14. Inspection, Test and Operating Status	This criterion has been determined to be inapplicable to the scope of work of the LANL YMP.	
15. Nonconforming Materials, Parts or Components	TWS-QAS-QP-15.1 Nonconformances	12/14/88
16. Corrective Action	TWS-QAS-QP-16.1 Corrective Action	4/28/89
	TWS-QAS-QP-16.2 Trending	5/31/89
17. Quality Assurance Records	TWS-QAS-QP-17.1 Resident File	12/14/88
	TWS-QAS-QP-17.2 Records Processing Center	12/14/88
18. Audits	TWS-QAS-QP-18.1 Audits	4/28/89
	TWS-QAS-QP-18.2 Surveys	3/17/89
	TWS-QAS-QP-18.3 Auditor Qualification	3/31/89

QUALITY ASSURANCE LEVEL ASSIGNMENT SHEET (QALAS)
AND
QUALITY LEVEL ASSIGNMENT CRITERIA SHEET (QLACS)

SIP No. 8G/A.1.1/C-Wells
Rev. 0
Activity Reactive Tracer Tests in C-Wells and Other Wells
Tasks: Subtask A. Identification and characterization of reactive
tracers to be used in tracer tests.
D. Reactive-tracer tests in C-wells.
C. Reactive-tracer tests in other wells in Yucca
Mountain vicinity.

TABLE A-2

QUALITY ASSURANCE LEVEL ASSIGNMENTS FOR STUDY 8.3.1.2.3.1.7

NNWSI QUALITY ASSURANCE LEVEL ASSIGNMENT			
Items/Activities	QA Level	QA Requirements	Technical Justification
Reactive Tracer Tests in C-Wells and Other Wells	I	1,2,3,4,5,6,7,8,10,11,12,13,15,16,17,18	NNWSI SOP-22-22: para.5.2.1b. (activity will provide site characterization data), and
		See attached QLACS	para.5.2.1.d (activity will provide data that will be utilized for a license application).
			Step 2 of QA Level Assignment checklist.
APPROVALS (Signature and Date)			
PI	<u>Paul F. Brunner</u> 10/20/86	TPO	<u>R. J. [Signature]</u> 10/20/86
QAL	<u>Chris F. Keller</u> 10/24/86	WMPO (TECH)	<u>Maxwell Blandard</u> 10-27-86
QAIA	<u>Paul Brunner</u> 10/21/86	WMPO (PQM)	<u>James Blaylock</u> 10/28/86
PI FINAL REVIEW <u>Paul F. Brunner</u>			

QUALITY LEVEL ASSIGNMENT CRITERIA SHEET (QLACS)SIP No. 86/4.1.1/C-WellsRev. 0

Activity: _____

Task: Reactive Tracer Tests in C-Wells and Other WellsPI: Lee F. Brown

QA Criterion	Applies	Does not Apply	Comments
1. QA Organization	x		
2. QA Program	x		
3. Design and Scientific Investigation Control	x		Only scientific investigation requirements apply
4. Procurement Document Control	x		
5. Instructions, Procedures, and Drawings	x		
6. Document Control	x		
7. Control of Purchased Material, Equipment, and Services	x		
8. ID and Control of Materials, Parts, Components, and Samples	x		
9. Control of Processes		x	Activities performed under this WBS are not considered to be special processes as per definition in Appendix A SOP-02-01
10. Inspection	x		Applicable for surveillance requirements only
11. Test and Experiment/Research Control	x		
12. Control of Measuring and Test Equipment	x		

QA Criterion	Applies	Does not Apply	Comments
13. Handling, Shipping, and Storage	x		
14. Inspection, Test, and Operating Status		x	No hardware generated in this task.
15. Control of Nonconformances	x		
16. Corrective Action	x		
17. QA Records	x		
18. QA Audits	x		

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