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YUCCA MOUNTAIN SITE CHARACTERIZATION PROJECT
STUDY PLAN APPROVAL FORM

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Study Plan Title Groundwater Chemistry Model

Revision Number 0

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TABLE OF CONTENTS

TABLE OF CONTENTS
(continued)

TABLE OF CONTENTS
(continued)

LIST OF TABLES

LIST OF FIGURES

Effective Date: ________________

GROUNDWATER CHEMISTRY MODEL OF YUCCA MOUNTAIN

1.0 PURPOSE AND OBJECTIVES OF STUDY

1.1 Introduction and Objectives of Study

The purpose of the groundwater chemistry investigation (SCP 8.3.1.3.1) is to provide a model of groundwater chemistry at Yucca Mountain that will reflect groundwater compositions that will occur as a result of interaction with different chemical environments. The groundwater chemistry model will show the geochemical materials that control the composition of the present groundwater, will support site characterization activities, and will be used to support the resolution of Performance Assessment Issues 1.1 (Total System Performance), 1.8 (Siting Criteria), and 1.5 (Engineered Barrier Performance), In addition, the groundwater chemistry model will support the geochemistry program by providing actual or simulated data on water composition required by other investigations, studies, and/or activities.

The groundwater chemistry model will be developed in two phases through Site Characterization Plan (SCP) Activities 8.3.1.3.1.1.1 and 8.3.1.3.1.1.2. The purpose of Activity 8.3.3.1.1.1 is to develop conceptual models of groundwater chemistry that isolates the geochemical parameters with the greatest influence on groundwater composition. The purpose of Activity 8.3.1.3.1.1.2 is to develop mathematical models of groundwater chemistry. This model will be based on the conceptual model and will use the important variables and parameters to quantitatively predict the ranges of groundwater composition subject to fluctuations in overall chemical conditions due to changes in the Yucca Mountain environment.

1.1.1 Development of the Conceptual Model, Activity 8.3.1.3.1.1.1

A preliminary conceptual model of groundwater chemistry will be proposed to provide a qualitative understanding of the geochemical parameters and processes controlling the groundwater composition over time (Figure 1). The effects of chemical parameters and geochemical processes, such as pH, mineralogy, and sorption, on groundwater composition will be suggested in the preliminary model. Hypotheses about the variables, parameters, and geochemical processes most affecting groundwater composition will be formulated from the preliminary conceptual model. Section 1.2.2 of this study plan suggests several tests of the preliminary model and the hypotheses derived from it that will provide information on specific variables, parameters, and processes and will be used to refine the preliminary model. The behavior of different parameters will be examined by computer codes and tested through detailed experiments, and those parameters that most influence the groundwater composition will be included in a refined conceptual model. The final conceptual model will be the product of this activity and will provide the initial information for development of a mathematical model of groundwater chemistry at Yucca Mountain.

Developing conceptual models of groundwater composition requires a data base of the geochemical parameters, variables, and processes that could influence groundwater composition. The data base will be developed through tests of hypotheses generated from the preliminary conceptual model. previously published data on groundwater at Yucca Mountain or in the vicinity, and other studies, namely Studies 8.3.1.2.2.7 (Hydrochemical Characterization of the Unsaturated Zone) and 8.3.1.2.3.2 (Characterization of Saturated Zone Hydrochemistry) (DOE, 1988). The data base will be used with the conceptual model to develop and test the mathematical model in Activity 8.3.1.3.1.1.2. The data base will include data and calculations on processes that are important. such as pH. redox conditions, and sorption, as well as the concentrations of aqueous ions such as

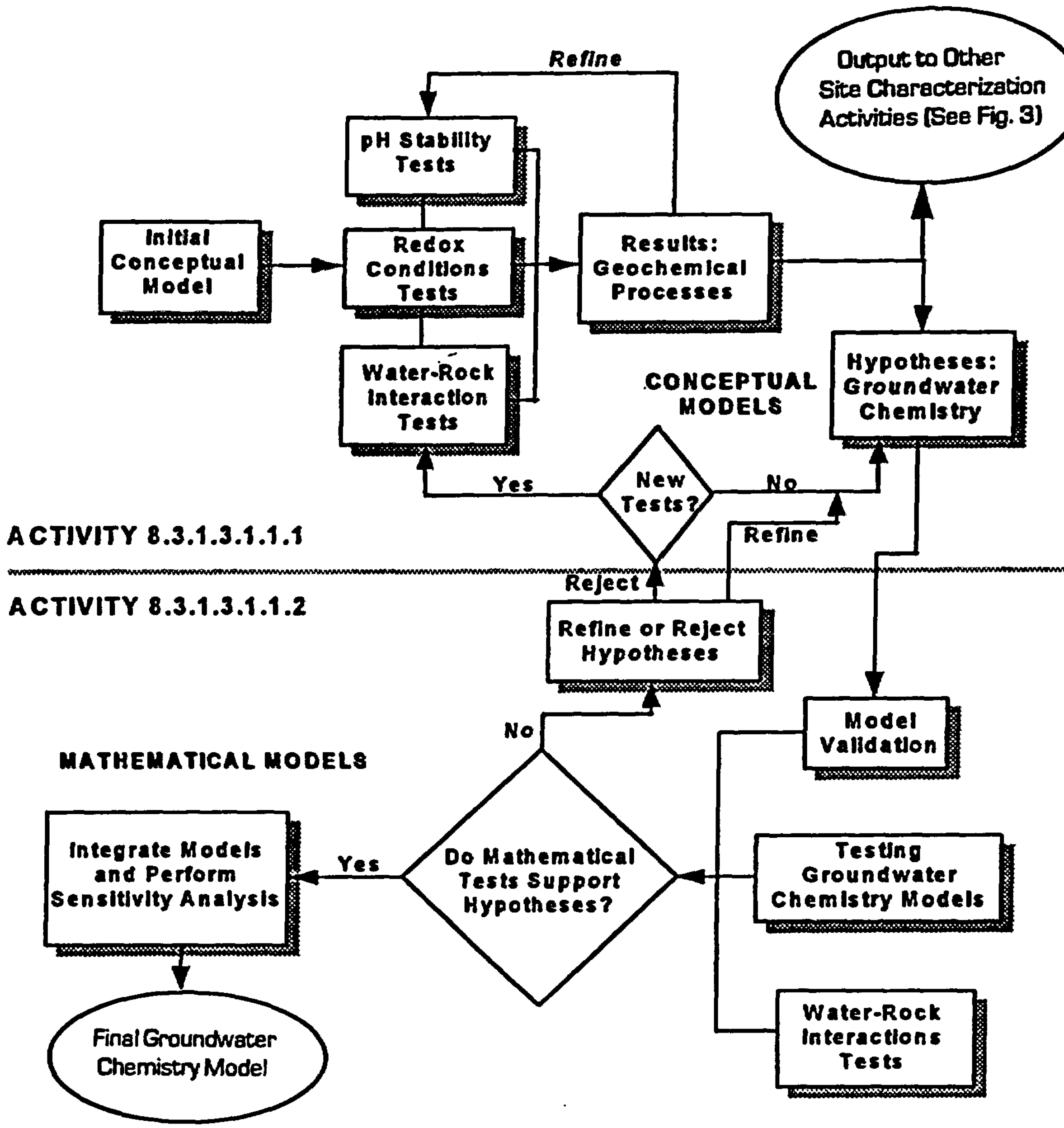

Figure 1. Diagram of Study 8.3.1.3.1.1. Different sections in diagram are discussed in Sections 2 and 3 of the Study Plan.

Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, F^{-}, HCO_3^{-}, Al^{3+}, Mn^{2+}, $Fe^{3+/2+}$, SiO_2 (aq), and other trace constituents. In addition, data and information on geochemical processes related to groundwater chemistry, such as secondary mineral precipitation, will be included as will data on mineralogy, petrology, and radionuclide solubility, and the array of environmental conditions to be used in the calculations. The information will show the variables and parameters primarily controlling groundwater composition. It will also show the constituents of least importance to groundwater composition. The completed data base with the conceptual model will be the initial input for development of the mathematical model in Activity 8.3.1.3.1.1.2. Relations between data in the data base will be further tested by the mathematical model.

1.1.2 Development of the Mathematical Model, Activity 8.3.1.3.1.1.2

After the conceptual model is completed (Figure 1), the mathematical model will be developed in Activity 8.3.1.3.1.1.2. The relationships between parameters and the results of calculations suggested by the development of the conceptual model cannot be quantified until the important geochemical parameters and processes are identified. Because of this limitation, details of the exact development of the mathematical model can only be supplied as the conceptual model nears completion. The goal of Activity 8.3.1.3.1.1.2 is to produce a mathematical model of groundwater composition that can be used to predict groundwater composition as a result of different chemical environments over time. The model will be used to calculate the results on the basis of input data distributions and on an estimate of the uncertainty in the calculations. The mathematical model will support the calculations of radionuclide retardation that ultimately will be used to support the resolution of Performance Assessment Issue 1.1.

1.1.3 Sources of Data for Development of Models

In order to develop a conceptual model and a mathematical model of groundwater chemistry, Study 8.3.1.3.1.1 will obtain data on major ion chemistry and on other parameters important to groundwater composition. Published reports (e.g., Benson and McKinley, 1985; Kerrisk, 1987) and other Yucca Mountain Site Characterization Project (YMP) studies (e.g., from Study 8.3.1.2.2.7, Hydrochemical Characterization of the Unsaturated Zone) will be used. Data on mineralogy and petrology of rock matrix minerals and fracture minerals will be obtained from Study 8.3.1.3.2.1 (Mineralogy, Petrology, and Chemistry of Transport Pathways), and information on the alteration of minerals will be obtained from Study 8.3.1.3.2.2 (History of Mineralogic and Chemical Alteration of Yucca Mountain). The mineralogical and petrological data define the minerals present at Yucca Mountain. This information will then be used to evaluate how these minerals control groundwater composition. The alteration history will provide information on the changes in minerals with time and will suggest possible changes in groundwater composition as a result of mineral transformation through time. Information on the kinetics of mineral dissolution and precipitation will be obtained from the literature.

Duffy(1985) showed that the kinetics of mineral transformations are important components to incorporate in the conceptual models for groundwater chemistry because few of the rock-water interactions (i.e., the interactions between rock and water) at Yucca Mountain are expected to reach true thermodynamic equilibrium. Some rock-water interactions appear to reach states of metastable equilibrium where solution concentrations are controlled by solid phases, present for relatively long periods of time. For example, cristobalite may control the activity of silica in Yucca Mountain groundwater eventhough cristobalite is metastable with respect to quartz.

Data from different studies will be used with groundwater chemistry data to determine the minerals that control groundwater composition, the stability of pH, and redox conditions of groundwater at Yucca Mountain, and the composition of the groundwater as a result of interactions between host rocks and different weathering environments over time. Timely exchange of data among these studies will be important so that the groundwater chemistry model can be developed and refined with the most recent data and interpretations gathered from other studies. In turn, the groundwater chemistry model will provide current information on groundwater composition to other studies for their continuing development.

1.1.4 Goals of Study 8.3.1.3.1.1

Study 8.3.1.3.1.1 will develop models of groundwater chemistry at Yucca Mountain under different environmental scenarios through time. Activity 8.3.1.3.1.1.1 will develop conceptual models of groundwater composition and will evaluate and refine the model through several tests and analyses of the effects of different geochemical processes and parameters on groundwater composition. In Activity 8.3.1.3.1.1.2 the conceptual models will be used to develop a mathematical model that can be used to predict groundwater composition through time when different sets of environmental conditions are imposed on the system.

1.2 Objectives for Activity 8.3.1.3.1.1.1

Three objectives must be met before the final conceptual model is complete. These objectives include detailed laboratory tests and use of different computer codes to evaluate different parameters and to calculate chemical speciation. The objectives and related tests are outlined in Sections 1.2.1, 1.2.2, and 1.2.3 and discussed in detail in Section 3. Similar objectives are developed for Activity 8.3.1.3.1.1.2.

1.2.1 Objective 1: Propose Preliminary Conceptual Model

A preliminary conceptual model of groundwater chemistry will include the effects of different parameters. First, the preliminary conceptual model will consider the composition of groundwater at Yucca Mountain and surrounding areas. These data will be derived largely from published reports, but data from other investigations in the Geohydrology and Geochemistry Investigations (Sections 8.3.1.2 and 8.3.1.3, respectively, DOE, 1988) will be used as they become available.

The conceptual model will consider the influence of the mineralogy of Yucca Mountain on the composition of groundwater. These data will show the relative importance of different primary minerals and secondary minerals (silicate phases, oxides, and zeolites) in controlling groundwater composition. Information on mineral alteration will also be included in the conceptual alteration of minerals. The information on mineral alteration will be used to suggest dissolution of existing minerals and precipitation of new phases over time.

The preliminary conceptual model will suggest those parameters that could significantly affect groundwater composition. The variables that determine the parameters will also be suggested as major controls on groundwater composition, and the function of HCO_3^- in controlling pH will be considered. The parameters that control pH, redox conditions, mineralogy, sorption, and mineral alteration are considered the main contributors to groundwater composition, but their relative importance remains to be demonstrated. These parameters will be examined in a preliminary conceptual model so that a more thorough conceptual model can be developed.

The conceptual model will include the influence of sorption processes on groundwater chemistry to account for changes in groundwater composition resulting from adsorption and desorption of chemical constituents on different secondary and primary minerals. Information on sorption of radionuclides will also be included to permit modeling of future groundwater compositions that include different concentrations of radionuclides.

Information on the hydrology of the system will be included. Data from hydrologic studies, e.g., Study 8.3.1.2.3.2 (Characterization of the Saturated Zone Hydrochemistry), will give information on flow rates through unsaturated and saturated material and will be used by this activity to estimate the rate of change of groundwater composition through time. Groundwater chemistry data will also be used in Study 8.3.1.3.7 (Radionuclide by All Processes) to calculate radionuclide release to the accessible environment.

Preliminary conceptual models will be examined, using the tests listed in the following sections, to refine and simplify the model. These tests of the preliminary model are important for several reasons. First, the test results will isolate the parameters and processes that most influence the water compositions and those that are relatively insignificant. Processes controlling organic concentrations are important to the overall groundwater composition in some settings but are expected to be less important in this study because of their low concentration at Yucca Mountain (Means et al., 1983).

Second, the information accumulated from these tests will be an important part of the data base around which the conceptual models are developed and from which the mathematical models are formulated. This data base is currently not complete enough to use for model development, and it must be augmented. The tests described below will provide information on pH control, redox conditions, and rock-water interactions that are important to groundwater composition, and information from Studies 8.3.1.2.2.7 (Hydrochemical Characterization of the Unsaturated Zone) and 8.3.1.2.3.2 Characterization of the Saturated Zone Hydrochemistry) will complete the data base.

Third, the results of the tests will help refine the conceptual model. The conceptual model will integrate information of the important parameters, and those variables that determine them, with existing information on groundwater composition models will also be examined as the preliminary model is refined. The final conceptual model will then be the initial input for the development of the mathematical model.

Fourth, the sensitivity of the conceptual model will be estimated along with the effects of changes in different parameters or omission of different parameters on predicted groundwater compositions. Information on the sensitivity of the conceptual model to changes in different parameters will be important in the development of the mathematical model.

1.2.2 Objective 2: Test Parameters Identified in Preliminary Conceptual Models

1.2.2.1 pH Stability of Groundwater in Saturated and Unsaturated Zones

This test will evaluate the stability of pH of Yucca Mountain groundwater under different chemical environments. Testing pH stability cannot be conducted without changing the composition of the water. Therefore, the pH Stability Test is also a test of water composition changes during induced pH variation. Kerrisk (1987) and Ogard and Kerrisk (1984) suggest that pH is well buffered by the activity of aqueous carbonate, bicarbonate, and the carbonate minerals that are present. If so, relatively small changes in pH of groundwater should be observed when water of different pH and/or different composition is added to the system. For example, the pH of the groundwater should remain relatively constant when the pH of recharge water is lower than that of the groundwater, when radionuclides are included in the system, or after continued contact between the host rock and the groundwater because bicarbonate and/or carbonate react to maintain pH. Stability of pH is the measure of how much bicarbonate or carbonate is present to react with the infiltrating water. Changes in pH will be observed as the bicarbonate, carbonate, or other buffering constituent are consumed.

The pH stability of saturated-zone water can be estimated from previously published information, but estimating the pH stability of unsaturated-zone water will require more effort to isolate the different processes that control pH. Research by Yang et al. (1988), detailed in other YMP studies, will be important to this part of Test 1.

Changes in pH resulting from different chemical conditions imposed on the test apparatus will be initially modeled with the EQ3/6 code (Wolery, 1983) and other codes if appropriate such as MINTEQ (Felmy et al., 1984) and PHREEQE (Parkhurst et al., 1980). Initial models will suggest possible reactions and processes controlling pH and water composition. The results of imposing pH conditions on water pH and composition will be measured by experiments with rock columns and crushed tuff obtained from Yucca Mountain. A discrepancy between measured and calculated results will require resolution and reexamination of calculations and measurements before information on pH stability and buffering capacity can be incorporated into the conceptual model. Agreement between measured and calculated results will indicate that the processes controlling pH stability were identified. Sets of hypotheses concerning processes and reactions that control pH and water composition will be formulated as Conceptual Models and passed to Activity 8.3.1.3.1.1.2 (Mathematical Modeling).

1.2.2.2 Controls of Eh in Saturated Zone

Performance Assessment Issues 1.1 and 1.8 require information about the redox conditions at Yucca Mountain. Because radionuclide solubility depends partly on the oxidation state of the dissolving species, information about the control of the oxidation potential in groundwater is important for calculating the release of radionuclides to the accessible environment. Oxidizing conditions (high Eh) can result in increased mobilization of radionuclides; therefore, more transport of aqueous radionuclides would be expected at high Eh values. Also, aluminosilicates and oxides are generally more stable at a high Eh, therefore, active radionuclide absorbers are expected to be present in the system in oxidizing conditions.

As in the pH Stability Test above, water composition will change as the imposed Eh varies, and the composition changes will be measured. Changes in pH as a result of variation of Eh will also be measured so that the combined effects of Eh on pH and composition can be considered. Carefully controlled conditions will provide the opportunity for the necessary measurements. The processes controlling the reactions will be identified and passed on the Mathematical Model that is discussed later in the Study Plan.

This test will suggest how reactions with minerals and geochemical processes influence groundwater Eh and will show changes in Eh as a result of fluctuations in the alteration environment or in the composition of infiltrating water, such as increased acidity or the introduction of radionuclides. Initially, groundwater composition will be assumed to reflect a well-poised, oxidizing system, buffered by the available atmospheric oxygen (Winograd and Robertson, 1981). This condition will be evaluated during Test 2. Oxygen buffering with depth at Yucca Mountain will use literature values as well as measurements made during the unsaturated-zone hydrochemistry study (Study 8.3.1.2.3.2). Redox potentials will be calculated with different computer codes and various minerals, and the composition of groundwater will be shown as a result of oxidation potentials controlled by oxygen partial pressure with depth and/or by different minerals. Redox potentials will also be measured by the concentrations of different ions of redox couples when possible. For example, the Fe^{3+}/Fe^{2+} ratio relates to specific redox conditions, and the ratio can be measured spectrophotometrically by complexation with 1,10 o-phenanthroline.

Gas chromatography methods for H_2 and O_2 measurement (Kashima and Sakai, 1984) could be used to discern the redox conditions in Yucca Mountain groundwater. The amount of H_2 in oxidizing waters is expected to be low and may limit the practicality of the gas chromatograph method, however. Measurement of dissolved oxygen, redox-specific ion concentrations, and gas chromatography of dissolved gasses are preferred to using Eh measurements made with standard platinum electrodes, i.e., system Eh (Nordstrom and Munoz, 1985; Stumm and Morgan, 1981).

It is expected that different minerals and partial pressures of oxygen will determine the redox conditions at Yucca Mountain. The system may not be well controlled or "poised," i.e., a small change in composition, such as a change in hydrogen partial pressure, could result in a large (>100 mV) change in redox conditions that may be of long or short duration. Lindsay (1979) illustrates the magnitude of the change in redox conditions when different minerals poise a system and a different hydrogen and oxygen partial pressures.

Kinetics of mineral transformations will also be important in understanding the redox conditions at Yucca Mountain. For example, manganese and iron fracture coatings indicate that oxidizing conditions prevail in some portions of the saturated and unsaturated zones.

Experiments with rock columns and with crushed material will be conducted to measure the redox conditions of water removing through these materials. Tests using water with high and low hydrogen partial pressure to control initial redox conditions will also be conducted so that the response of the material of interest can be understood. Discrepancies between calculated and measured values will require greater attention before the Eh information can be used in the refined conceptual model.

1.2.2.3 Tests to Isolate Water-Rock (Mineral) Interactions

The Water-Rock Interactions tests are designed to evaluate compositional, pH, and Eh data obtained during the pH Stability Test and Redox Conditions Test with regard to water-rock interactions that control pH, Eh, and composition. The minerals that could control the composition of saturated zone groundwater have been discussed in several reports (e.g., Benson and McKinley, 1985; Claassen, 1985; Duffy, 1985; Kerrisk, 1987, 1987; Ogard and Kerrisk, 1984), and saturated-zone water compositions appear to be controlled initially by glass dissolution and then by aqueous silica activity. Reaction path calculations (Duffy, 1985; Kerrisk, 1983) compare favorably with mineralogical/petrological data (Bish and Chipera, 1989; Carlos 1985, 1987) and suggest that the major geochemical processes controlling saturated-zone water composition have been identified. The results of previous work on saturated-zone water composition will be incorporated into the preliminary conceptual model of groundwater chemistry, and interpretations of previous data will be reexamined as needed and used in the refined conceptual model. Data on stable isotopes of C, O, and H will be included in the tests in order to further constrain the possible set of hypotheses that will result from the above tests. The isotope data will be supplied through Study 8.3.1.2.3.2 and related activities.

Few data on water composition from the unsaturated zone at Yucca Mountain have been reported. Yang et al. (1988) reported on water compositions extracted from unsaturated-zone material by triaxial compression. Benson (1976) reported similar data but from Rainier Mesa. Although more data will be made available from Study 8.3.1.2.2.7 (Unsaturated Zone Hydrochemistry), Activity 8.3.1.2.2.4.8 (Hydrochemistry Tests in the Exploratory Shaft Facility), and Study 8.3.1.2.3.2 (Characterization of Saturated Zone Hydrochemistry), the preliminary conceptual models will depend on computer simulations of water compositions in the unsaturated zone.

Yang et al. (1988) showed that the water content in material from the unsaturated zone at Yucca Mountain varied from 1-35% by weight at matric potentials of -0.55 to -0.1 MPa, respectively. This report also included the composition of water extracted from the unsaturated-zone material.

Bish and Chipera (1989), Caporuscio et al (1985), and Carlos (1985, 1987) reported on the mineralogy of the rock matrix and fractures of different units at Yucca Mountain. Data on water content and composition will be combined with the data on matrix and fracture mineralogy, and possible compositions of water from the unsaturated zone will be calculated. The EQ3/6 code will be used to investigate water-rock interactions that include but are not limited to (1) reactions between water and rocks along specific flow paths that may occur only on minerals surfaces and not the entire minerals matrix at Yucca Mountain, (2) rock-water interactions with respect to equilibrium with a metastable solid phase such as cristobalite or smectite clays, (3) rock-water interactions, and (4) strict thermodynamic equilibrium with stable minerals such as quartz.

1.2.3 Objective 3: Integrate Test Data and Hypotheses: Generating Conceptual Models

Ideas about control of groundwater composition proposed in preliminary hypotheses will be integrated with test results, calculations, and data. This integration implies significant data analysis and reduction and will lead to the development of sets of hypotheses about the processes and reactions that control groundwater pH, Eh, and composition. The ideas from the preliminary hypotheses and the information from the tests and analyses will be integrated with the parameters and processes most influencing groundwater composition, and will provide the opportunity to refine the conceptual models. Alternative conceptual models will be proposed and will comprise different sets of hypotheses. The product of this activity will be a set of conceptual models of groundwater chemistry at Yucca Mountain that will show the parameters and processes important to groundwater composition and will be the basis from which a mathematical model can be developed. The proposed conceptual models, or sets of hypotheses about controlling processes and reactions, will be the basis from which the Mathematical Models will be developed in Activity 8.3.1.3.1.1.2.

1.2.4 Objective 4: Develop Mathematical Models of Yucca Mountain Groundwater

The goal of the Groundwater Chemistry Model Study is to develop a mathematical model of groundwater chemistry that can be used to predict the water composition as a result of various potential environments at Yucca Mountain. The potential environments include but are not limited to the changes in the current conditions resulting from construction of a nuclear repository, long-term heating of the rock surrounding a repository, and climatic conditions such as cooler, wetter climates at Yucca Mountain. Activity 8.3.1.3.1.1.2 is designed to use the hypotheses generated from laboratory tests, preliminary mathematical modeling, and field tests and refine them into a set of mathematical models of Yucca Mountain groundwater. Testing the models using laboratory data, natural analogs of processes that occur at Yucca Mountain, and through sensitivity analysis, will provide data needed to either accept a given model or to refine it to improve its predictive capability.

In Activity 8.3.1.3.1.1.2 the validity of the modeling approach will be tested. Mathematical models will be used to predict the results of experiments or known processes. Successful prediction of processes that are well characterized will lend strength to the particular models chosen to model the processes in question. Uncertainty and sensitivity analyses will be conducted on the models so that the error (precision) and the accuracy of the predictions can be established.

Specific groundwater chemistry models will be tested in Activity 8.3.1.3.1.1.2. The models developed from the hypotheses in Activity 8.3.1.3.1.1.1 will be models of specific processes and models that are a combination smaller models of processes. The models will be tested to determine if they can predict the results of known experiments and test cases. Successfully tested models will be used to refine the concepts about the processes and reactions that determine the pH, Eh, and composition of Yucca Mountain groundwaters. Models that are not successfully tested will be reconsidered and either refined or discarded. The groundwater chemistry model will be shaped during the course of model testing.

Finally, the mathematical models will be used to predict the effects of long-term water-rock interactions on water chemistry. Based on processes occurring presently or that are expected to occur during the lifetime of a repository, the predictions of groundwater pH, Eh, and composition as a result of continued mineral alteration will be made. Several sets of potential conditions will be imposed upon the calculations, including but not limited to extended heating into the far field, control of silica activity by precipitation of opal C-T and amorphous silica phases, and added recharge from a wetter climate. The uncertainties associated with such predictions will also be calculated so that other investigators know the degree to which the model can be believed. The last phase of the Mathematical Model Activity will show the usefulness of the model for prediction and will also be ready for use as a a tool to predict the effects of a given change on Yucca Mountain. Figure 1 shows the expected course of Investigation 8.3.1.3.1.1.

1.3 Regulatory Rationale and Justification

Several performance assessment issues require information on groundwater chemistry to resolve the issues specified in 10 CFR 60. This section describes the role of the study in support of resolution of Issue 1.1 (Total System Performance), Issue 1.5 (Performance of the Engineered Barrier System), and Issue 1.8 (Siting Criteria). Figure 2 shows the relationships between the performance assessment issues, site characterization activities, and Study 8.3.1.3.1.1.

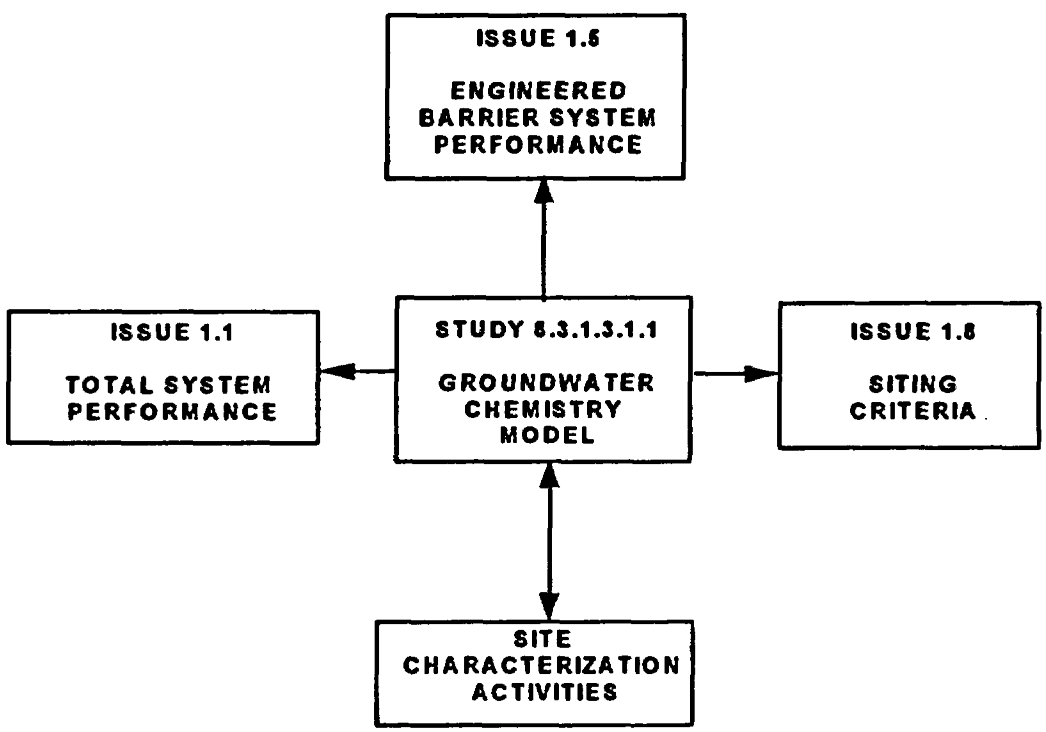

Figure 2. Relations Between Site Characterization Activities, Performance Issues, and Study 8.3.1.3.1.1

Issue 1.1. Total System Performance for Limiting Release of Radionuclides to the Accessible Environment

Support from Study 8.3.1.3.1.1 is required for the resolution of Issue 1.1 through Information Need 1.1.1 (Site Information Needed to Calculate Radionuclide Release to the Accessible Environment) and Information Need 1.1.4 (Determination of Radionuclide Release to the Accessible Environment in Association with Realization of Potentially Significant Release Scenario Classes). Scenario classes of importance to Issue 1.1 and relevant to Study 8.3.1.3.1.1 are detailed in Section 8.3.5.13 (DOE, 1988). Information from Study 8.3.1.3.1.1 will be used to evaluate parameters that relate to expected partial performance measures (EPPM) associated with different categories of scenario classes. Category E of the scenario classes is considered the nominal case and indicates no significant change in any natural barriers at Yucca Mountain. The parameters required for the nominal case and relevant to the groundwater chemistry study are the profiles of chemical constituents, including pH, Eh, and major and minor cations and anions. The current confidence in these parameters is low, but Study 8.3.1.3.1.1 will provide the required medium confidence level as defined in Issue 1.1. The parameters will be evaluated from data and calculations for both the unsaturated and saturated zones and will reflect the groundwater compositions, assuming no changes in the Yucca Mountain system occur.

Other performance parameters for Issue 1.1 required by Study 8.3.1.3.1.1 include support of the calculations of the radionuclide retardation factor (R_d) in both unsaturated and saturated zones. Relevant information, such as water compositions, will be supplied to Study 8.3.1.3.7 (Radionuclide Retardation by All Processes) for calculating radionuclide retardation and for resolving Issue 1.1. The EPPM for radionuclide release through water pathways is required to be at a high confidence level.

Categories C and D are also of interest to Study 8.3.1.3.1.1. Category C includes partial failure of the unsaturated-zone barriers because of increased flow of water through the unsaturated zone, a rise of the water table into the unsaturated zone, or greater release of radionuclides into the saturated zone from the unsaturated zone as a result of alteration of the geologic material. Category D involves partial failure of the saturated-zone barriers because of the emergence of new discharge points within 5 km of the candidate repository or an increased flow rate through the saturated zone.

Pathways for radionuclide release important to this study are releases via water movement through the unsaturated zone (Category C) and the saturated zone (Category D). As in Category E, the parameters of interest are chemical composition, pH, and Eh for both categories. In addition, parameters in both categories will include mineralogy, groundwater flow rates, and the geochemical processes controlling water composition, including soprtion and mineral alteration. Category C will be concerned with increased infiltration into Yucca Mountain and the associated changes in water composition and mineralogy that could occur. Increased infiltration could be caused by increased irrigation in the recharge area or increased precipitation. However, the primary concern for Study 8.3.1.3.1.1 and for the resolution of Issue 1.1 is the overall effect on groundwater composition. The effects of changes in groundwater composition will be used by Study 8.3.1.3.7 to calculate the release of radionuclides to the accessible environment under the conditions of increased infiltration. EPPMs for radionuclide release via water pathways for Category C are required at a high confidence level for both increased infiltration and radionuclide release resulting from changes in geologic materials of the unsaturated zone. A medium confidence level is required for a water table rise into the unsaturated zone. Category D will be concerned with radionuclide release resulting from new water discharge points within 5 km of the candidate repository. The groundwater composition to higher flow velocity through the saturated zone will be suggested. This information will be important in calculating the radionuclide release to the accessible environment required by Study 8.3.1.3.7 and in resolving Issue 1.1. The EPPM associated with new discharge points is required at a medium confidence level, whereas the EPPM for radionuclide release resulting from an increased flow rate through the saturated zone is at a high confidence level.

Information Need 1.1.1 requires information on parameters important to site performance. Parameters important to site performance from the groundwater chemistry study are the major ion compositions, pH, and Eh, as discussed above and in Section 3. Information on these parameters will be collected and used with different environmental scenarios to estimate changes in groundwater composition over time.

Issue 1.5, Engineered Barrier System Performance

Some information necessary to resolve this issue will come from Study 8.3.1.3.1.1 through Information Need 1.5.3 (Scenarios and Models Needed to Predict Radionuclide Release for Waste Package and Engineered Barrier Performance). This issue is detailed in Section 8.3.5.10 (DOE, 1988) and requires that information on changes in groundwater composition with time under different scenarios be incorporated into calculations of radionuclide release. In addition, Information Need 1.5.3 includes activities and subactivities that call for development of a data base for geochemical modeling. Study 8.3.1.3.1.1 will contribute to the data base through the tests and analyses results outlined in Section 3.

Water quality information required in Information Need 1.5.3 will be evaluated so that different ranges of water compositions can be bounded for calculations of engineered barrier system (EBS) and waste package performance. Specific bounds on the water compositions will be established by the EBS and waste package tasks. Supplemental information on groundwater composition and change in groundwater composition from concentrations of radionuclides will be provided.

Issue 1.8, Siting Criteria-Favorable and Potentially Adverse Conditions

Issue 1.8 requires demonstration that the candidate repository site will contain radioactive waste for 10,000 to 100,000 years at the release limits stipulated in 10 CFR 60. This issue will evaluate several favorable conditions for radionuclide isolation and potentially adverse conditions that could compromise repository performance. Information on groundwater chemistry is required to evaluate the effects of different conditions on site performance. Two favorable conditions and four potentially adverse conditions require information from Study 8.3.1.3.1.1.

Favorable conditions include groundwater chemistry that promotes precipitation and/or soprtion of radionuclides; inhibits the formation of radionuclide particulates, colloids, and organic complexes; and inhibits transport of radionuclides. Study 8.3.1.3.1.1 will determine of these conditions exist and how stable they are over time and under different chemical environments.

Another favorable condition concerns the stability of the mineral assemblages at Yucca Mountain and the consequences of mineral weathering with time. Alteration of the present minerals into minerals with decreased radionuclide retardation capacity is undesirable, whereas it is considered favorable for the present minerals to change into those with increased ability to retard migration of radionuclides. Study 8.3.1.3.1.1, as outlined in Section 3, will evaluate mineral alteration and the resulting groundwater composition over time.

The first potentially adverse condition to be evaluated through this study is the present groundwater chemistry in order to determine any constituents or intensive parameters that could increase the solubility of the materials comprising the EBS. These conditions include pH, Eh, and compositions of water that could cause increased chemical alteration of the EBS, thus altering or destroying its capacity to retard migration of radionuclides. The result of such alteration could be the potential for transport of larger amounts of radionuclides and ultimately release to the accessible environment in excess of the limits set by 10 CFR 60.

A second potentially adverse condition involves circumstances that could reduce the sorption of radionuclides, degrade the rocks and minerals that are important to sorption of radionuclides, or change the geologic system so that radionuclides release to the accessible environment could increase over time. Groundwater compositions, under different scenarios, will play important roles in the evaluation of these potentially adverse conditions. Other information for this evaluation will come from studies in the geochemistry program on mineralogical/petrological mineral alteration, and mineral transformation kinetics.

The third potentially adverse condition to be evaluated by this study is the possibility for maintaining a reducing environment in the hydrologic flow system. The stability of the groundwater chemistry with respect to redox and specific redox levels will be important for radionuclide transport calculations because most radionuclides tend to be least soluble under reducing conditions. The effects of groundwater compositions on radionuclide solubility under different Eh and environmental conditions will be evaluated. Information from Studies 8.3.1.3.4 (Radionuclide Retardation by Sorption Process) and 8.3.1.3.5 (Radionuclide Retardation by Precipitation Process) will be used to assess this potentially adverse condition.

The fourth potentially adverse condition is the effect of surface impoundments on the transport of radionuclides to the accessible environment. This condition implies increased infiltration of water into the rocks and minerals of Yucca Mountain, a higher water table in locations near the impoundments, increased mineral alteration in the unsaturated zones because of alteration of groundwater composition in the unsaturated and saturated zones because of changes in minerals and rocks induced by increased infiltration. The effects of greater infiltration on groundwater composition and mineral alteration will be calculated, and the effects of changing groundwater compositions on radionuclide release will be estimated by this study and calculated through Study 8.3.1.3.7 (Radionuclide Retardation by All Processes).

2.0 RATIONALE FOR TESTS

2.1 Technical Rationale and Justification

2.1.1 Role of Study in Groundwater Chemistry Model

The goal of this study is to provide a groundwater chemistry model by developing conceptual models (Activity 8.3.1.3.1.1.1) and mathematical models (Activity 8.3.1.3.1.1.2) as discussed in Section 1. Initially, different preliminary conceptual models will be evaluated because several sets of parameters, geochemical processes, and chemical environments could affect groundwater composition. Considering the different aspects of the preliminary models separately is the most efficient way to examine the possibilities and to determine those factors important in developing the groundwater chemistry model. The tests and analyses outlined in Section 3 show how different chemical parameters will be identified and isolated. Testing and calculations will suggest the importance of parameters, such as pH and Eh, and will isolate the variables that determine them. Each test is designed to consider a specific parameter and different variables that could be important to groundwater composition. The product of the planned tests and analyses will be the integration of the test and calculation results into the preliminary models. The product of Activity 8.3.1.3.1.1.1 will be a set of relevant conceptual models used qualitatively to show different relationships between important parameters and groundwater chemistry. The conceptual model will be used in Activity 8.3.1.3.1.1.2 as initial input for the development of the mathematical model. The conceptual models will concentrate initially on both fracture flow and matrix flow. Data for one flow mechanism or the other can be disregarded should only one flow mechanism be deemed important to radionuclide transport.

2.1.2 Relationship to Other Site Characterization Activities

The unsaturated zone at Yucca Mountain could provide both a barrier and a pathway for radionuclide migration from the proposed nuclear repository. As discussed in Section 1, the release of radionuclides from a repository must be compatible with regulatory limits. Performance Assessment Issue 1.1 will evaluate the rate of radionuclide release to the accessible environment. In order to resolve the regulatory issues, a data base on groundwater chemistry is required that includes data on the rock-water interactions controlling such parameters as pH, Eh, and the ionic composition of groundwater.

The geochemical processes proposed using preliminary models cannot be developed satisfactorily without additional information on the parameters of interest. This information, which will come from other studies as well as this one, will include data on mineralogy and petrology, mineral alteration, mineral transformation kinetics, sorption of radionuclides and other constituents, climates in effect in the past, and data concerning composition of existing saturated and unsaturated zone water (Figure 3). These studies will provide information on the kind, abundance, and spatial variability of minerals (Study 8.3.1.3.2.1); possible reactions to which the minerals could be subjected (Study 8.3.1.3.3.2); the amount of radionuclides and other constituents that could adsorb onto different minerals (Studies 8.3.1.3.4 to 8.3.1.3.6); the composition of groundwater of Yucca Mountain and vicinity (8.3.1.2.2.3); the composition of water derived from the unsaturated zone (8.3.1.2.2.7); and past climates in the Yucca Mountain area (Study 8.3.1.5.1.2 and other studies in Investigation 8.3.1.5.1). Information derived from this study will more fully demonstrate the interaction between groundwater and rocks or minerals at Yucca Mountain through a series of tests, described below. The data from this and other studies will make possible a more specific description of water chemistry along potential flow paths and of the possible groundwater composition that could result from changes in chemical environments.

Some data exist on the interactions of rocks and groundwater, showing that these interactions can cause significant changes in groundwater composition and mineralogy (Delany et al., 1986;

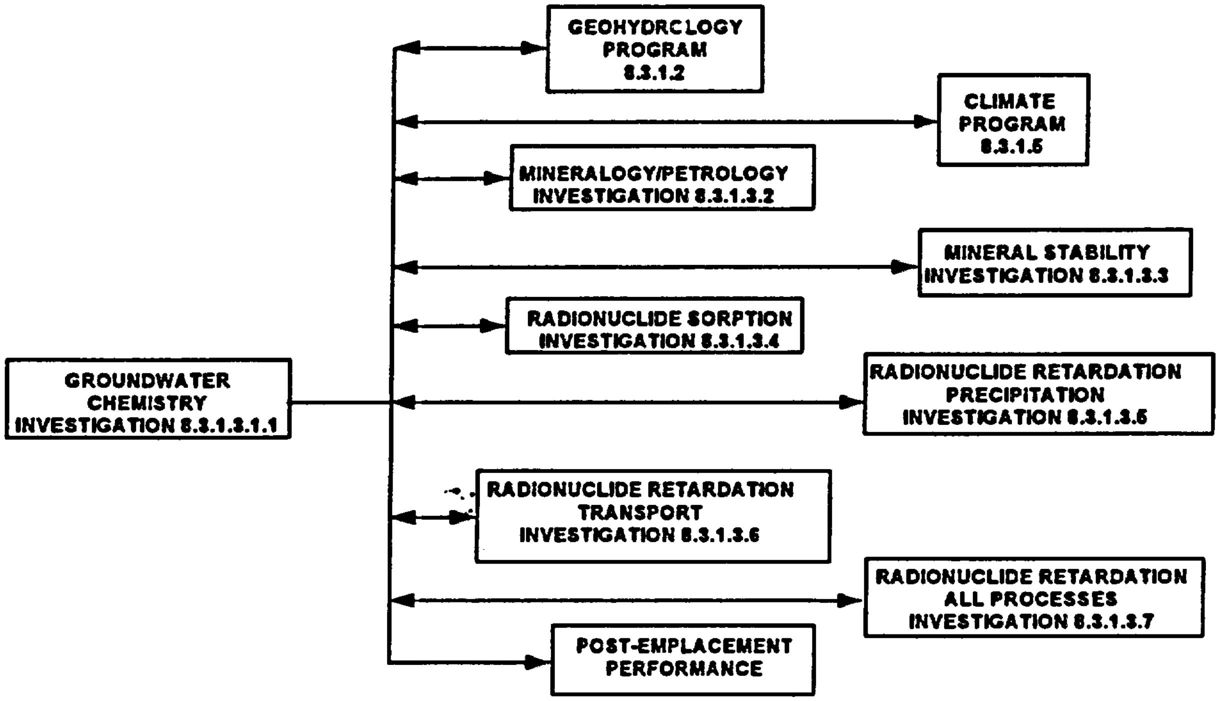

Figure 3. Schematic of the Relationship Between Study 8.3.1.3.1 and Other Site Characterization Activities

Knauss, 1984a, 1984b; Knauss et al., 1985, Knauss and Wolery, 1988; Oversby and Knauss, 1983). Few studies, however, show the specific effects of rock-water interactions on parameters such as pH because the tests are difficult to perform and the parameters are related to several geochemical processes.

The chemical composition of water is modified as it flows through different parts of Yucca Mountain. Water moving through the unsaturated zone is possibly in contact with minerals much longer than water moving through the saturated zone. The effects of long contact time on groundwater composition are continued dissolution of host rocks and possible precipitation of secondary minerals within relatively small rock volumes. The concentration of dissolved constituents in unsaturated-zone water is expected to be high because the volume of water is reduced by evaporation of water into the air in the unsaturated-zone pore space or by the decrease in the H_2O activity through hydration of different minerals. Data from Study 8.3.1.2.2.3 (Characterization of Percolation in the Unsaturated Zone--Surface-Based Study) and rate of evaporation or mineral hydration will be used to suggest conditions that could result in water with high concentration of dissolved constituents in the unsaturated zone.

Rock-water interactions appear to be a more continuous process in the saturated zone than in the unsaturated zone. Rock-water interactions in the saturated zone may even approach a steady state in geologic time. Periodic wetting and drying in the unsaturated zone, however, may slow mineral alteration significantly and/or result in the formation of greatly different secondary minerals than those found in the saturated zone. Thus, more mineral alteration is expected in the saturated zone and possibly more secondary mineral precipitation, owing to increased dissolution of host minerals. Study 8.3.1.2.3.2 (Characterization of Saturated Zone Hydrochemistry) will provide additional data on groundwater composition, and Study 8.3.1.3.2 (Mineralogic/Petrologic Investigation) will provide the mineralogy of new bore holes. This information will be used in modeling different reactions with minerals and water and in refining the conceptual model developed by this study so that a realistic idea of groundwater composition can be formulated.

Study 8.3.1.3.1.1 (Groundwater Chemistry Model) will use information from the unsaturated zone, saturated zone, and other studies mentioned above. The activity demonstrates interactions between rocks and water that control groundwater compositions. Computer codes employing calculations from thermodynamic data bases will be used with the water data and data from other studies to show plausible reactions and reaction paths that could produce the observed groundwater composition. Tests discussed in Section 3 will also be used to supply more detail on the variables that determine different parameters. The reactions suggested as a result of groundwater composition data and computer calculations will be refined, as needed, to show more specifically the role of Yucca Mountain rocks and minerals in the control of groundwater composition and to suggest how different chemical environments change groundwater composition through time.

Existing data on groundwater chemistry will be integrated into the Groundwater Chemistry Model, and different preliminary models of groundwater chemistry will be proposed. The preliminary models will be the starting point for further refinement of ideas and will provide a list of data needs so that a more realistic conceptual model can be developed. Consideration of alternate preliminary models will result in a conceptual model that examines different factors controlling groundwater chemistry. Elimination of preliminary models that are not supported by the data will result in a set of thorough conceptual models that will be fundamental to the development of more quantitative mathematical models.

The tests outlined above and discussed in Section 3 are proposed for three reasons. First, these tests will be used to evaluate different aspects of each preliminary model so that the model's validity can be tested in parts. The test results will indicate the importance of different parameters and also the relevance of the different models to the overall objective of this study. Those preliminary models remaining after testing will be considered further.

Second, the test results will provide substantial data for this study, other studies, and for activities in the geochemistry and hydrology investigations. The data base created will be used in Activity 8.3.1.3.1.1.2. Other task, such as Investigation 8.3.1.3.5 (Radionuclide Retardation by Precipitation Process), require information on groundwater chemistry to be included in the data base. The information obtained from these tests is required for the development of the final conceptual model and the mathematical model in Activity 8.3.1.3.1.1.2. This data base will be a continuing resource for other studies, activities, and tasks concerned with the chemical modeling of Yucca Mountain.

Third, the proposed tests will examine the preliminary models and will guide the refinement of preliminary models and formulation of the conceptual models. This process will make it possible to critically evaluate the preliminary models through test results and to eliminate or reduce the inadequacies of different preliminary models. Through this method, those aspects of the preliminary models that are not relevant to the goals of this study will be identified and eliminated while the most important elements to groundwater composition are studied further.

This method for developing conceptual models was chosen so that different preliminary models could be proposed initially, tested thoroughly, and a final models developed that illustrate the groundwater chemistry at Yucca Mountain. The method also allows for the inclusion and testing of different models, as discussed in the SCP, Section 8.3.1.1 (DOE, 1988). Each preliminary model consists of a set of hypotheses about the Yucca Mountain system, and the tests above prove or disprove them. This method of development also consolidates data on groundwater chemistry presently found in diverse sources and other studies within the YMP, thereby helping the development of the mathematical model and providing a valuable database for other studies and activities.

Tests 1 and 2 are designed to provide information concerning the processes and reactions that control composition, pH, and Eh of groundwater at Yucca Mountain. Knowledge of the rock-water interactions controlling the concentrations of different groundwater constituents is central to understanding both the present groundwater chemistry and the groundwater composition that could result from rock-water interactions under different chemical conditions over time. Changes in one of the parameters of interest in Test 1-2 will also change the values of the other parameters of interest. Thus, the relationship between the different parameters, such as pH, redox conditions, and different minerals that control or determine groundwater composition, can be examined in detail. The tests may also indicate that some of the parameters are stable over wide ranges of chemical environments, and the impact of these changes on the final conceptual model is minimal. Also, transport of radionuclides through Yucca Mountain in water depends upon groundwater composition, and solubility of radionuclides may be affected by pH, redox, and the minerals present. Understanding the role of each parameter on radionuclide solubility will lead to development of a more representative conceptual model that qualitatively predicts the possible fate of radionuclides in groundwater at Yucca Mountain over time. This type of qualitative prediction will be useful to other studies, especially Study 8.3.1.3.7 (Radionuclide Retardation by All Processes).

Development of the mathematical models in Activity 8.3.1.3.1.1.2 will integrate the different tests and hypotheses from Activity 8.3.1.3.1.1.1. Tests in the first activity will provide the information required to derive the conceptual models of groundwater chemistry, and the models will be tested and quantified in the second activity. Sensitivity and uncertainty analyses will be part of the testing phase mathematical models, and will provide necessary information about how reliable predictions of groundwater chemistry can be. Activity 8.3.1.3.1.1.2 will provide the groundwater chemistry model that is required in the SCP (1988).

The duration of tests will be approximately one year, or long enough to show no significant water composition changes over several weeks, i.e., "steady state" conditions. Calculation of the effects of changes in different parameters on water composition, however, will take considerably less time because no laboratory tests are involved. The rock column experiments, especially those with unsaturated-zone material and unsaturated flow conditions, will take the most time because of the complex test apparatus and slow flow rates anticipated. Replication of rock column experiments will be limited because of the duration of each experiment. However, replication of computer calculations will be done frequently because they take much less time.

The tests discussed in Section 3 will provide a more detailed understanding of the parameters and geochemical processes controlling groundwater composition. As discussed in Section 1, the test results will provide data on and initial estimates of groundwater composition for development of the mathematical model in Activity 8.3.1.3.1.1.2.

The tests were designed in kind and number to examine initial preliminary models and refine them into specific conceptual models to guide further work on groundwater chemistry at Yucca Mountain. Integration of test results and preliminary conceptual models will yield a final conceptual model providing information on groundwater composition at present and in the future, as changed by the influence of different environments.

2.2 Test Constraints

These tests will have little impact on the repository site. Samples for rock column experiments will be obtained from available drill cores through the Sample Management Facility (SMF). Data on mineralogy and petrology will be obtained on the samples, as needed, to ensure that well-characterized material is used in the tests.

The accuracy and precision of the analytical methods used in these tests will not limit the use of test results. Analyses of pH and soluble constituents are relatively simple, and the detection limits are low enough to provide useful information on the parameters of interest. Calculation of Eh using concentration ratios of redox couples such as H_2/H_2O, Fe^{3+}/Fe^{2+}, or Mn^{4+}/Mn^{2+} depend on the analyses of the redox couples. Gas chromatography analysis of $H_{2(g)}$ and spectrophotometric determination of Fe^{3+}/Fe^{2+} should not place undue constraints on the Eh values calculated. The procedures and the limits on precision and accuracy of different measurements made from these tests will be developed to reflect sound scientific practice. The accuracy of numerical values will be checked against National Institute of Standards and Technology (NIST) standards, and precision of measurements will be determined by obtaining values from multiple samples, when possible. If an estimate of the precision of a measurement from a given test cannot be made owing to the duration of a given test, this estimate will be made in a different medium. For example, replicate samples for measuring the pH of water moving through a rock column cannot be obtained, but the stability of pH measurements from a sample can be demonstrated by determining the pH of known standards or simulated water compositions. Also, care will be taken during experiments that do not permit replication so that the best measurements of different parameters are made.

Errors that propagate through computer calculations will be estimated with statistical methods (Iman et al., 1981a, 1981b; Iman and Helton, 1985; Siegel et al., 1987) to assess sensitivity to errors in input data. Errors enter into the calculations by uncertainty in the analytical values and error in the values that constitute the data base used by the chemical speciation codes. Because large uncertainty can result from error in data base values, the sensitivity of the data base used will be ascertained. The sensitivity analysis will be more fully developed in the later stages of Activity 8.3.1.3.1.1.1 and in Activity 8.3.1.3.1.1.2 as the mathematical model is developed, but initial estimates of model stability will be worked out in the former activity.

The main limitation of these tests is the amount of time needed to complete them. It is conceivable that data could be collected from rock column experiments for several years, but that time frame is longer than the scope of this study. Therefore, the time needed to establish the experimental conditions (e.g., the attainment of unsaturated flow or steady state flow in a column) will be minimized so that data collection can begin as soon as possible at the start of the experiment. The length of these tests and the complexity of the experimental apparatus will also limit the number of replications that can be completed. Replicate samples will be run to check the repeatability of the tests when flow rates through the materials of interest are rapid. When test apparatus is limited, or if column supports are limited, tests of different materials will be given preference over replicate runs of the same material. Because of the few replications planned in these tests, the experiments will be established in the most rigorous manner to minimize error in measured values.

Since these tests will be done remotely, they will not interfere with other tests or with the ESF design and construction. Repository conditions will not be simulated because this study is concerned with far-field effects, not those of the repository itself.

3.0 DESCRIPTIONS OF TESTS AND ANALYSES

3.0 DESCRIPTION OF TESTS AND ANALYSES

3.1 Description of Tests

This section provides detailed descriptions, lists of parameters, and expected results for each test and analysis. The number of test replications required is also discussed. Detailed technical procedures (DPs) are required for each test that is conducted that could affect the quality of work or data used for different Yucca Mountain Project purposes. A list of detailed procedures is not included in this study plan, however. The required DP's cannot be written until the exact structure of the tests is known. For example, the unsaturated-zone tests discussed in Section 3.1.1 call for sample collection at pressures below ambient atmospheric pressure. The apparatus for a test of this sort is available commercially, but writing a DP to use such apparatus dictates the apparatus that is to be used. If there are significant improvements in the apparatus, which there have been during each of the last few years, use of the improved equipment would require writing a new or revised procedure. In order to minimize the amount of time spent on establishing the procedures, the DPs will be written when the tests are in their final design stages. Since no quality-affecting work can be conducted until the procedures are written and reviewed, the final steps of the design phase will be to write the DPs. At that time a complete list of required DPs will be developed and writing them will commence. The list of DPs that is presently anticipated is attached to this study plan.

3.1.1 Test of pH Stability and Buffering Capacity of Water from the Unsaturated and Saturated Zones

3.1.1.1 General Approach

The pH Stability Test is the determination of pH stability of Yucca Mountain Groundwaters. The purpose of the test is to evaluate the stability of pH when human-caused or natural changes occur in the chemical environment of Yucca Mountain. The test cannot be completed at Yucca Mountain in situ because the number of indicated tests is too large and controlling experimental conditions is not likely on a Yucca Mountain scale.

One measure of pH stability, buffering capacity, is the ability of the water to maintain pH at a specific level when different chemical conditions are imposed. Changes in the chemical system include but are not limited to alteration of new or previously unaltered minerals, continued alteration of primary and secondary minerals, ion exchange, and introduction of water at a different pH than the ambient conditions. Chemical changes will be induced by exposing Yucca Mountain materials to different water compositions than current conditions and measuring the response in terms of pH and composition of effluent water. The range of introduced changes is designed to simulate the effects of mixing waters of different pH and/or composition on the resulting pH. The tests will be conducted on material derived from Yucca Mountain and will include, at the least, Calico Hills, Topopah Spring, and vitrophyre material. Solid material and crushed material will be brought to steady-state flow conditions and the desired testing will occur subsequently. Effluent pH and compositional parameters (Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-}, F^-, HCO_3^-, Al^{3+}, Mn^{2+}, $Fe^{3+/2+}$, SiO_2 (aq), and other trace constituents) will be measured to determine changes in both pH and composition as a function of the induced conditions.

The need to measure compositional parameters and pH concurrently is a result of the interactions between rock and solution. Changes in pH result from specific reactions such as mineral dissolution. During dissolution, basic cations (Ca^{2+}, Mg^{2+}, Na^+, K^+), acidic cations (metals), and different anions are released to solution and the fluid in contact with rocks is neutralized. A change in either basic or acidic ions in solution results in change in the amount of H^+ in the solution, thereby altering the pH. If the waters are well buffered, however, the change in pH will be minimal because liberated or retained ions that would change the pH are neutralized by a reaction with the buffer. A buffer with regard to groundwater is the pool of constituents in solution that reacts with H^+ or other ions and maintains the pH. The buffering capacity is the amount of buffer available for neutralizing acidic cations. The carbonate/bicarbonate system is a common buffer in naturally occurring groundwaters, and is ubiquitous at Yucca Mountain. Measuring the changes in pH is a measure of the buffering capacity of the water, and the measurements of the compositional parameters suggest the kinds of water-rock reactions and buffering reactions that occur. Measuring either pH or composition without the other would provide data that would be difficult to interpret to show the importance buffering reactions.

For this test the Eh is considered a constant, and will be determined by water in equilibrium with atmospheric O_2 introduced to the test material. The tests will be done so that no reducing conditions are introduced to the material. If reducing conditions occur due to water-rock interactions, the process will be allowed to continue to show the effect on groundwater chemistry.

Preliminary geochemical modeling will be conducted to determine some of the possible processes that could occur in the tests. More detailed and mechanistic mathematical modeling of the geochemical processes at Yucca Mountain will be done in Activity 8.3.1.3.1.1.2. The pH stability Test will provide the fundamental data for Activity 8.3.1.3.1.1.2 that will be used to test different hypotheses concerning groundwater chemistry.

3.1.1.2 Summary of Methods for the pH Stability Test

The goal of the test, as stated above, is to evaluate the pH stability and compositional changes of groundwater as natural and man-caused alteration of the chemical environment occur. In order to design the appropriate tests, detailed calculations of groundwater chemistry interactions with minerals must be investigated. As mentioned above, preliminary geochemical modeling will be conducted so that possible processes can be tested during the pH Stability Test. The probable reactions and processes include but are not limited to 1) mineral dissolution (e.g., calcite dissolution), 2) mineral precipitation (e.g., sepiolite and opal C-T formation), and ion exchange (e.g., Ca^{2+} for Mg^{2+} exchange).

The second part of the test is to alter the chemical conditions in actual lab experiments and measure the resulting changes in water composition. Intact columns of rock from at least the Calico Hills, Topopah Springs, and the vitrophyre stratigraphic units will be obtained from samples stored at the YMP Sample Management Facility (SMF). Rock columns will be placed into a column-testing apparatus that will allow water flow under saturated and unsaturated conditions. Synthetic water based on reported water compositions or natural water from Yucca Mountain wells will be pumped into the column apparatus and steady-state flow will be attained. Steady-state flow means that water composition and pH of the effluent water change little during several measurements at predetermined time intervals. After steady-state flow is established and verified, water of a new composition will be added to a supply reservoir and introduced into the column. The composition of the new water will be designed so that a particular chemical change is introduced. For example, synthetic J-13 water made at pH 6 instead of a nominal pH of about 7.5 might be introduced to the column. Changes in water composition and pH during the time the synthetic J-13 water flows through the column are the data needed to evaluate buffering capacity and to establish the possible reactions that occur. Measuring the pH and compositional parameters will occur at redefined intervals throughout the duration of the experiment.

Tests on intact core samples ("intact core" for the remainder of the study plan) removed from drill core stored at the SMF are required so that the influence of fracture flow and fracture minerals on water composition can be evaluated. Intact cores provide a realistic, albeit small-scale, example of the actual geologic material through which water will flow. Extrapolation from one solid core to the whole of Yucca Mountain is obviously tenuous, but the aim of the tests outlined here is to provide a set of plausible reactions and processes that occur in rocks of the same types as the samples. Tests on crushed material will also be conducted. The purpose of the tests on crushed materials is to observe potential compositional and pH changes in shorter amounts of time than in the intact core tests. The representativeness of conclusions from crushed sample tests is debatable. However, processes and reactions identified in the crushed material tests should be similar to those that occur in the solid column tests, even if the rates of the processes and reactions is much different between the two types of materials. In addition, tests on crushed material are more easily replicated than tests on intact columns, so that the precision of the pH and composition measurements can be determined easily. The data obtained from the crushed-material tests will be compared to data obtained from the intact core tests to show that the same or different processes affect intact material and crushed material. Crushed material tests will provide the opportunity to test a broader range of induced chemical environments, such as a wider pH range or both a wide pH range and temperature range.

The same set of measurements will be made during intact column tests and crushed tests, and these measurements will be pH, and the concentrations of Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, F^{-}, HCO_3^{-}, Al^{3+}, Mn^{2+}, $Fe^{3+/2+}$, SiO_2 (aq), and other trace constituents. The measurements will be made from samples of the effluent of each column apparatus, and each sampling will be collected at a predetermined time. The methodology outlined here will ensure that similar data sets from crushed material and intact core tests will be obtained as well as similar data sets from different replicates of the same test.

Steady-state flow will be established for the tests materials, and the materials will be allowed to equilibrate with the water for several days. The period of equilibration or time to reach steady-state will be determined by periodic measurement of pH and selected compositional parameters. As the pH and compositional parameters become stable from one measurement time to the next during equilibration, the column of intact or crushed material will be considered at equilibrium with respect to test conditions. At this point the introduction of water of different pH and/or composition will begin as will the measurement of pH and composition from the effluent of the column apparatus.

Test conditions will be varied to include several possible scenarios that might influence groundwater pH. A matrix of specific conditions will be prepared before any of the tests commences to ensure efficient experimentation and to avoid ambiguous test results caused by overlap of two tests. Each condition will be tested using fresh material, and three replicates of each test will be made. The range of tests conditions will include at least waters of pH 6 to 8.5 and compositions ranging from synthetic rain water to synthetic and actual water from well UE 25p#1. The range in pH values spans those measured at Yucca Mountain (Kerrisk, 1987) as well as the range of compositions that are reported for Yucca Mountain groundwaters. Additional conditions that will span the expected range of unsaturated zone waters will be designed if data from other studies (e.g., 8.3.1.2.2) indicate existing compositions that are not included in the range mentioned here. Duration of the tests, either intact column or crushed material, will be one year or until steady state is established under the new conditions. Samples will be analyzed at predetermined times during the tests so that comparisons between tests can be accommodated.

Groundwater temperatures measured in various wells at Yucca Mountain range from about 15° C to about 60° C in the saturated zone (Kerrisk, 1987). Tests simulating saturated zone conditions to about 40° C will be performed at similar temperatures in a temperature-controlled environment. Tests at temperatures greater than 40° C will require ovens or specially-modified facilities for intact column tests.

Intact columns and crushed material columns of unsaturated zone materials will also be tested. Wierenga and Van Genuchten (1989) show that column experiments under unsaturated conditions yield meaningful data on unsaturated flow conditions as well as contaminant flow. They also showed that several constraints in testing are imposed because of the nature of the apparatus. The column apparatus is driven by an applied vacuum at the effluent end of the column, creating the unsaturated conditions through the column. The effluent end, and therefore the sample collection location, is at a reduced pressure than the ambient atmosphere, thus analysis of gaseous products in samples is difficult if not impossible. Degassing of water samples before analysis is unwise because one of the major buffering constituents in Yucca Mountain groundwater bicarbonate. Not only will degassing affect bicarbonate concentration, but pH and most other compositional parameters will be affected. Thus, obtaining valid samples for analysis will be difficult.

Sampling and retaining the dissolved gases and the actual concentration of the dissolved constituents will be accomplished by using a gas-tight syringe. A sampling port that is closed to the ambient atmosphere will be installed in the effluent line but will be accessible from the ambient atmosphere. The gas tight syringe will be used to draw a sample from the effluent stream before it reaches the decreased-pressure vessel, thereby giving the most representative sample of the actual water exiting the column. The sample in the syringe will be analyzed immediately or stabilized for later analysis, but care must be taken to preserve the nature of the sample. Gas-tight syringes will be used to extract samples from the sampling ports in order to minimize degassing. Prototype testing of the sampling apparatus will be conducted with known and well characterized material (e.g., Ottawa sand) before actual Yucca Mountain material is used. Analytical measurements of pH and the constituents listed above will be obtained.

The temperature range of the unsaturated zone tests will be from ambient to about 40° C. Additional tests at higher and/or lower temperatures will be conducted if requested. As in the saturated zone tests, three replicates per test will be conducted and analyzed.

Validation of the pH Stability Test: Saturated Zone

The duration and nature of the tests makes sequential replication of the tests nearly impossible. Therefore, replicate experiments will be conducted simultaneously. Three replicates of complex experiments should give a reasonable probability of at least two of the tests being similar if not all three. The results of each test (i.e., the pH and composition measurements) should vary no more than 10% of the mean of all three tests. Wider variation means that the test results are either not reproducible, there is more spatial variability in the materials tested than originally thought, or the analytical methods are introducing considerable error in the determinations. Test results falling within 10% of the mean of all three samples may show only coincidental relationship (i.e., "false positives"). However, with three simultaneous experiments conducted with similar material, the probability of "false positives" should be low.

Data measured from the effluent of the columns will be compared to results generated from geochemical modeling of the assumed processes and reactions. Comparisons of measured values to predicted values will indicate if the assumed reactions and processes are reasonable or, if the two do not compare well, indicate that modifications are needed of the assumed processes and reactions. Uncertainty in both the analytical measurements (i.e., standard deviations) and in the calculated results will be included to develop confidence intervals for both sets of information. Favorable comparisons result when the confidence interval of the measured values overlaps with the confidence interval of the predicted results.

Test results from measurements of saturated zone and unsaturated zone tests will be compared to the results of appropriate calculations using the approach and criteria discussed here. Additional tests will be conducted to show reproducibility of the tests or statistical similarity of the measured data and the predicted values as needed or requested.

3.1.1.3. Equipment for pH Test Stability Test

Intact column and crushed material for each test will be obtained from SMF samples of the stratigraphic units mentioned previously. Equipment required for successful completion of the pH Stability Test consists of:

- stainless steel or glass cylinders to hold intact columns or crushed material;
- system of seals to ensure column materials are isolated from ambient atmosphere and to keep water from leaking down the sides of the vessel;
- an inlet mechanism that allows sampling of influent solution and continuous water input;
- a pump system or systems that will allow continuous water input for saturated and unsaturated conditions;
- a fractional collector that operates at reduced pressure and without attendance (for unsaturated zone experiments);
- a calibrated pH meter and necessary buffer solutions to maintain calibration;
- calibrated ion chromatograph for measuring composition of water samples and appropriate standards to maintain the calibration;
- miscellaneous glass and plastic water.

3.1.1.4 Accuracy and Precision

The expected range of pH in the effluent samples from both columns is between about 4 and 8.5. Water input to the columns will be at pH 4, 6, or 8. The range of expected concentrations in the samples is within a factor of 2 to 3 of the values reported by Kerrisk (1987). The accuracy of pH values and compositional values will be assured by use of calibration standards that are traceable to NIST standards. Buffers for pH measurements will span the range of observed values, and the pH meter will be calibrated at least daily during measurement periods. Standards for the dissolved constituents listed above will be obtained from NIST or NIST-traceable sources. Secondary standards that span the range of observed concentrations of each constituent will be prepared from the NIST traceable standards. The ion chromatograph will be calibrated before and after each batch of samples is analyzed, and an additional set of calibration standards will be run as samples during each batch run. The three sets of calibration curves must agree within 10% of the mean of the three curves. That is, the slopes of the calibration curves will be within 10% of the mean slope calculated for the three data sets. If the calibration curves do not all fall within this criterion, the analyses will be completed again. Analysis of process blanks will be a regular part of the batch analyses.

The precision of the pH measurements will be determined by analyses of known solutions during each set of pH measurements. The average pH value to two decimal places will be recorded in laboratory notebooks, and the mean and standard deviation of the measurements will be calculated during the measurements. Precision of the ion chromatograph measurements will be determined by analyses of several solutions of known composition and known concentrations. These known solutions will be analyzed routinely with the samples and standards. The means and standard deviations of each known solution will be calculated. The spread in the data will be the estimate of precision and the deviation of the mean from the known concentration for each constituent will be the measure of accuracy for the pH Stability Test. The detailed technical procedures for all aspects of the pH Stability Test and all the tests discussed in the this Study Plan will be developed and in place before any testing is conducted. The technical procedures will discuss sequential steps in the experiment from selecting geologic material for use to final reporting of concentrations and pH values.

3.1.1.5 Results

The pH Stability Test will provide laboratory data on the buffering capacities of different Yucca Mountain groundwaters or synthetic waters of compositions similar to Yucca Mountain waters. Results that indicate water with high buffering capacity will consist of a series of pH measurements that do not change significantly following input of water at higher or lower pH than the equilibration water. Slopes that result from graphing input water pH vs. effluent pH should be fairly flat with no strong inflection points. Results that indicate low buffering capacity of the water will consist of observed pH changes during the experiment and significantly greater slope in the input pH vs. effluent pH curve. High buffering-capacity waters are expected to dominate in the pH range of Yucca Mountain groundwaters, and therefore, should be the major result of the pH Stability Test. Since the hypothesis of high buffering capacity due to bicarbonate has not been tested, however, the expected result may not prevail during the tests.

The pH Stability Test will also provide fundamental information on the compositional changes in groundwaters or synthetic waters used in the tests. Since pH changes tend to correlate with solution and solid-phase composition changes, the composition of input water should be altered as it flows through the unsaturated or saturated material in a column. High buffering capacity may results in only slight composition changes due to ion exchange reactions or other processes especially if only bicarbonate is controlling pH. However, compositional changes coupled with pH changes during the experiments should reveal many of the processes and reactions that occur in the material. For example, a small change in pH but an increase in Ca^{2+} during the tests would indicate that the dissolution of calcite may be occurring to compensate a higher-pH water flowing into the system. The results of the pH Stability Test will show those constituents that vary as the chemical environment inside the column changes. The tests results will be important to discovering the processes and reactions that occur at Yucca Mountain.

Crushed material in columns should produce data that show a larger change in either pH, composition parameters, or both. Since the crushed material has considerably more surface area than intact column and because much more of the material is exposed to weathering (diagenetic) processes, the reactions between rock and water should be more extensive than in the intact columns. Thus, more of the constituents of the rocks in crushed material tests are released to solution or are available for formation of secondary minerals (e.g., hematite). Data from tests conducted with crushed material and intact core will be compared to show the effects of crushing on the results of the tests.

The data sets obtained from the pH Stability Test will also be compared to the results of preliminary modeling that will be conducted prior to the test. The comparison of measured values to predicted compositions allows for partial validation of the modeling approach. The comparisons of data and predictions also provide an opportunity for refining hypotheses about the possible processes and reactions that could control the pH and composition of Yucca Mountain groundwaters. Agreement between predicted compositions (including pH) and measured compositions generally means that the assumed reaction and/or process has been included in the models. However, a unique explanation of the data by a given reaction or process isn't necessarily determined at this point because several processes or reactions might explain the measured results. Using the comparisons and the preliminary hypotheses as starting points, sets of hypotheses that suggest the geochemical processes responsible for controlling water composition and pH at Yucca Mountain will be postulated. The hypotheses will be passed to Activity 8.3.1.3.1.1.2 where they will be tested further. Unique explanations of the measured compositions are the goal of the mathematical model and will be discussed in Section 3.2. Different sets of hypotheses, i.e., different conceptual models, for the unsaturated zone and the saturated zone are expected, although there will be overlap in the processes that occur in either zone. For instance, the buffering capacity may be controlled by bicarbonate concentrations in both the saturated zone and unsaturated zone.

but alteration of the Ca^{2+} composition in the unsaturated zone might be due to precipitation of a mineral whereas Ca^{2+} composition in the saturated zone may be a function of ion exchange.

The hypotheses will also cover a range of expected climatic conditions insofar as the climatic conditions influence the water that could infiltrate to groundwater. One set of hypotheses, i.e, one conceptual model, may pertain to a given set of climatic conditions whereas a separate set of hypotheses would pertain to a distinctly different set of climatic conditions. The different conceptual models will thus address the range of possible scenarios that must be considered in site characterization of Yucca Mountain.

The reproducibility of the column tests will be evaluated by comparing the data derived from replicate tests run simultaneously. Reproducible experiments will be indicated by similar measurements from each replicate for the same column material. Agreement, within about 10% of the mean of the replicates, is expected and will indicate that the replicates agree. Variation in greater than 10% of the mean suggests that the experiments were not reproducible and should be redesigned or repeated.

3.1.2 Redox Conditions and Water Composition in the Saturated and Unsaturated Zones

3.1.2.1 Approach

Since radionuclide solubility and, therefore, transport is controlled largely by redox conditions, the Eh of groundwaters at Yucca Mountain is of fundamental importance. One potentially adverse condition discussed in the SCP (1988) is the presence and persistence of oxidizing environments because radionuclide solubility tends to be higher in oxidizing conditions than in reducing conditions. Evaluating the prevalence of oxidizing or reducing conditions at Yucca Mountain and attributing specific processes or reactions to the conditions is the goal of Redox Conditions Test.

Redox or Eh has been measured using a Pt electrode and interpreted as an "overall" Eh or "system" Eh. Because redox potential can be controlled by many different reactions, and these reactions tend to be out of equilibrium, an "overall" Eh has little meaning unless it is tied to specific reactions or processes. Stumm and Morgan (1981) show that different Eh values can be calculated for sea water depending on the components chosen for the calculations. The Eh calculated from the concentrations of CO_2 and CH_4 in sea water yields an Eh of approximately -165 mV, but the Eh calculated from concentrations of NO_3^- and N_2 in the same water is approximately 625 mV. If the system were in equilibrium with respect to Eh, the two Eh measurements would be similar and an "overall" Eh would be sensible. Since there is no equilibrium in the example with sea water, however, the Eh and the reaction that determines the value must be known. The groundwater and rocks or minerals of Yucca Mountain reflect a geological system that is presently far from equilibrium when Eh is considered, and Eh must be measured by way of different sets of redox-sensitive ions such as the Fe^{2+}/Fe^{3+} couple or dissolved oxygen in the water. The Redox Conditions Test will provide the data necessary to define redox conditions within Yucca Mountain groundwater.

Both pH and compositional parameters will be measured in the pH Stability Test (Section 3.1.1). Changes in Eh, like changes in pH, will be accompanied by changes in different constituents. In addition, pH may also change as Eh changes, thus water composition and pH will be measured, and Eh will be calculated for different reactions as part of the Redox Conditions Test. The redox conditions of intact core or crushed materials will be carefully altered by introducing water of a different redox state into columns of material. The corresponding compositional and pH changes will be measured in the effluent of the columns, and Eh relative to different processes will be calculated from the data. The tests will be discussed in more detail in Section 3.1.2.2.

The materials of interest for the Redox Conditions Test are the same materials used in the pH Stability Test, but fresh samples of each material will be prepared for each experiment. The materials targeted for use include but are not limited to the Tuffs of the Calico Hills, Topopah Spring Tuff, and the material from the virtrophyre. The samples for use will be selected from samples at the SMF just as the samples for all other tests will be selected. Crushed material and intact core samples will be prepared from SMF material in the same manner that material for the pH Stability Test will be prepared. Testing additional materials is easily accommodated in the Redox Conditions Test as long as enough time is allowed to complete all tests and milestones.

Experiments will be run under saturated conditions for the Redox Conditions Test. Redox measurements in unsaturated material will likely be dominated by the presence of atmospheric or nearly atmospheric $O_{2(g)}$. Poising of the unsaturated zone by $O_{2(g)}$ will keep the unsaturated zone far from equilibrium and well into the oxidized regions of mineral stability fields. Should evidence of reducing conditions require testing, however, unsaturated zone experiments can be added to the Redox Conditions Test.

The Redox Conditions Test will provide the data necessary to postulate different hypotheses concerning redox conditions at Yucca Mountain. These hypotheses will be combined with those from the pH Stability Test, and different conceptual models will be constructed for further testing in Activity 8.3.1.3.1.1.2. Thus, the conceptual models tested during Activity 8.3.1.3.1.1.2 will include pH, buffering capacity, compositional changes, and redox conditions for Yucca Mountain groundwaters.

The Redox Conditions Test will show many of the chemical conditions that poise Yucca Mountain groundwater at oxidizing levels or allow for periods of reducing conditions. Determining the range of conditions that exist or could exist in the groundwaters is important to an overall understanding. Understanding the behavior of groundwater redox environments in the presence of radionuclides, however, is the more important part of the Redox Conditions Test. The processes and conditions that affect the redox of groundwater and minerals mean little unless those processes are considered with regard to radionuclides transporting with groundwater.

3.1.2.2 Summary of Methods

The Redox Conditions Test will involve initial geochemical modeling of possible reactions and processes that could affect redox in saturated zone groundwaters. The modeling will give a preliminary understanding of the range of processes that could occur in Yucca Mountain groundwaters and will guide the preparation of the laboratory experiments with geological material. A matrix of different test conditions will be developed in order to make the laboratory tests as efficient as possible and to assist in the analysis of the data generated during the experiments.

The mineral phases that contain most of the redox sensitive species (e.g., Fe-Ti oxides, amphiboles, biotite, sulfides, pyroxenes) will be identified on the basis of the results provided by Study 8.3.1.3.2.1 (Mineralogy, Petrology and Chemistry of Transport Pathways). Estimates will be made of the potential surface areas of these minerals which may contact groundwaters. Data from the literature will be used to develop preliminary models for oxidation reactions involving these minerals and Yucca Mountain groundwaters.

Rock samples from the main hydrologic units in the saturated zone at Yucca Mountain will be crushed to different grain sizes and contacted with either actual Yucca Mountain groundwater or synthetic water based on the composition of Yucca Mountain groundwaters. The Eh of these waters will be controlled prior to contact by reaction with different amounts of a reducing agent such as hydrogen gas. The stability of the redox potential in these waters will be evaluated by repeated measurement over time of the stock solutions. Once the stability of Eh in these waters has been established, they will be contacted with the rock samples crushed to various grain sizes in tightly sealed containers having at least one sampling port. The various rock-water combinations as well as several reference samples will be kept in a dark environment and allowed to react for an indefinite period of time. The waters will be sampled periodically and the samples will be analyzed for Eh, pH and major and minor constituents. Redox couples will be analyzed as appropriate.

If the batch redox experiments yield interpretable results, column experiments may also be carried out. The advantage of column experiments over the batch experiments would be that column experiments could be carried out on intact materials as well as crushed materials. Intact materials would be more representative of in situ rock units. The procedure for the column Eh experiments are similar to that used in the pH experiments except that the input solutions would have controlled redox potentials and the experiments would be carried out in a darkened environment. The column eluants will be sampled regularly and analyzed for the same parameters as the batch experimental solutions.

Special care will be taken to preserve and analyze redox-sensitive constituents under the same conditions as inside the columns during the tests. For example, analysis for total Fe alone in the effluent is not desired, but the analysis of total Fe and Fe^{2+} gives the information needed to calculate Eh with respect to the Fe^{2+}/Fe^{3+} redox couple. Isolating Fe^{2+} from the effluent sample is straight-forward using o-phenanthroline as an extractant/color complexant for the Fe^{2+}. Dissolved gases such as H_2 and/or O_2 may also be sampled and would require special sampling procedures. Dissolved H_2 can be detected using gas chromatography by purging a carefully collected sample of H_2 and delivering the H_2 to the gas chromatograph (Kishima and Sakai, 1984). Analysis of the CH_2/CO_2 redox couple can also be conducted using the same gas sample as for H_2. The use of H_2, CH_2, and/or CO_2 assumes that enough of each gas is present in the sample (Kishima and Sakai, 1984) so that small amounts of dissolved gas result in sufficient amounts for quantification. As part of the Redox Conditions Test, the detection limits for the gas chromatographic determinations of dissolved gases (or for any analytical method) will be determined before the method is used. Gas chromatograph sensitivity will be established before analysis of dissolved gases to ensure that accurate and precise results can be obtained. Dissolved O_2 can be analyzed in the same way as H_2 in addition to using a dissolved oxygen probe. Exact procedures governing the use of different analytical methods will be written as part of detailed technical procedures prior to the beginning of any part of the Redox Conditions Test.

The data collected from the different experiments that comprise the Redox Conditions Test will be analyzed to isolate different reactions and processes that control redox. Possible reactions include but are not limited to Fe^{2+} leaching from unaltered material and the possible formation of ferric oxides if oxidizing conditions are present or remaining as Fe^{2+} if reducing conditions are present. An example of a single process that could occur is the presence of an "oxidation front" could be detected as the water at poised at lower redox potential than the equilibration water moves through the column material. The front might be detected as a "spike" of low dissolved gases, high concentrations of redox sensitive constituents, or both. Numerous processes are possible, but the experiments of the Redox Conditions Test should reveal those processes that are the most prominent with regard to groundwater chemistry.

Limited testing of Unsaturated Zone material is planned for the Redox Conditions Test because of the probability that the unsaturated zone is poised by atmospheric oxygen. Unsaturated zone material will be prepared for one experiment to illustrate the hypothesis that the excess oxygen in the system maintains oxidizing conditions unless reducing conditions prevail for long periods, i.e., the unsaturated zone becomes saturated or is otherwise isolated from the atmosphere. Should the limited testing of unsaturated zone material disprove the hypothesis, however, additional testing will be conducted in parallel with the saturated zone testing.

Temperatures of interest for the Redox Conditions Test will be similar to those of the pH Stability Test and will cover ambient laboratory conditions to about 60° C. Increasing the temperature range can be accommodated if necessary.

Validation of the Redox Conditions Test

Validation of the Redox Conditions Test will be accomplished through replication of the experiments and through comparison of predicted results of different experiments to measured results of the same tests.

Replication will be conducted in a manner similar to that in the pH Stability Test. Experiments will be done in replicate at the same time using similar material for each of the replicates. Reproducibility will be assumed if the composition and pH measurements of the replicates agree within 15% of the means of the three replicates. Since there is added uncertainty in maintaining the exact concentration of redox-controlling constituents in the water pumped through the column compared to the pH Stability Test, a slightly larger comparative standard is set. Reproducibility among the replicates, however, is only part of the validation of the Redox Conditions Test. Predicting the results of a test using geochemical modeling codes must also be demonstrated in comparisons of measured data and predictions.

Successful prediction of an experiment means that the reactions and processes assumed to control Eh of the water used in the experiment are identified and included in the code, and that the results of the exercise produce a water composition similar to the measured comparison. Favorable comparison would be within 15% of the measured concentration. The possibility of reproducing redox experiments through modeling will be investigated using less complex problems such as pyrite oxidation or uranium reduction in water. The results of these and other comparisons of different geochemical systems will be used to refine the comparison standard of 15% if needed. A separate phase of the validation will be to include simulations of existing and relatively well known geological systems such as geothermal areas that produce a variety of temperature-redox-composition conditions. One area of interest is the Jemez geothermal field near Los Alamos, another is the area surrounding the Oklo natural "reactor." Incorporating simulations of natural analogs as part of the validation of the Redox Conditions Test overlaps somewhat with Activity 8.3.1.3.1.1.2, but the potential benefit is higher confidence in the predicted water concentrations in redox-affected groundwaters and actual laboratory tests to measure redox effects.

3.1.2.3 Equipment for the Redox Conditions Test

The same equipment listed for the pH Stability Test is required for the Redox Conditions Test with some additions. The Redox Conditions Test requires a system of mixing and monitoring the gases above the reservoir of water used in the column experiments. The reservoir must be isolated from the ambient atmosphere, as must the test column from input port to effluent port. The reservoir could be a glass or compatible plastic container that is sealed from the ambient atmosphere and equipped with input ports to allow gas mixtures to flow through and maintain a desired atmosphere. Additional equipment includes analytical capabilities for measuring dissolved oxygen, the concentration of selected redox couples such as Fe^{2+}/Fe^{3+}, and dissolved gases.

3.1.2.4 Accuracy and Precision

The expected Eh range is from about -100 mV to about 700 mV. This range covers Eh values measured at Yucca Mountain and could be modified as the investigation continues. Evaluation of different processes and reactions that control Eh may indicate that the lower boundary is too negative and is the result of man-induced changes that are not expected to occur during construction of the repository. Corresponding changes in composition and pH are expected in the laboratory tests, and the range of such changes may be as much as a factor of 2 to 3 with regard to composition and up to 2 pH units.

The accuracy of measurements will be verified against NIST-traceable analytical standards that will be used routinely. Where NIST standards are not available, efforts will be made to procure or produce standards that will be legitimate substitutes for NIST standards. Procuring standards for dissolved gases is one example of relying on non-NIST standards. The use of any standards, NIST or otherwise, will be specified in the detailed technical procedure that will be written to cover tests conducted as part of the Redox Conditions Test.

Precision of the measurements made during the Redox Conditions Test will be determined from repeated measurements of standards and samples. The required precision will be measured by the standard deviation of repeated measurements and should be less than 5 to 10% of the mean for composition measurements. Measurements of pH will be within 0.05 pH units of the mean pH determined from multiple measurements. Dissolved oxygen will be within 0.5 mg/L of the mean of repeated measurements. Precision of all measurements used for the Redox Conditions Test will be reported with the analytical results for a particular set of samples as will the mean values and a comparison of standards with measurements.

3.1.2.5 Results of the Redox Conditions Test

The Redox Conditions Test will provide several overall results important to the groundwater chemistry model. The Eh values measured from the laboratory tests will be provided for all sets of test conditions. The results of the laboratory tests will include the analytical results as well as a detailed description of the initial conditions and the experimental apparatus that was used. The results will include estimates of the uncertainty in the measurements, the results of comparison with known standards, and the estimates of precision and accuracy for those data. Composition data will also be measured during the Redox Conditions Test and reported in the results. The same set of complimentary information as for Eh (precision, uncertainty, etc.) will be reported.

The relationships between Eh, composition and surface areas will be considered from the laboratory test data. The relationships that exist will be described in a way to support hypothesis formation about processes and reactions that control Eh. Different hypotheses about the processes and reactions may take the form of simple statements and/or statistical statements that imply a specific test of the data. The list of hypotheses will be collected and used to provide test cases for Activity 8.3.1.3.1.1.2.

Relationships between pH and Eh are of particular interest in understanding the water-rock interactions at Yucca Mountain and also for use by radionuclide modeling tasks. Since radionuclides are the important species in the performance assessment of Yucca Mountain, Eh/pH stability diagrams will be drawn to aid those conducting the performance assessment in determining the chemical form of radionuclides. Eh fields also show the significance of different processes and reactions as well as the limits on the kinds of environments in which those processes are active.

The final result of the Redox Conditions Test is developing a set of hypotheses or conceptual models concerning the processes and reactions at Yucca Mountain that can be passed to Activity 8.3.1.3.1.1.2 for more rigorous mathematical testing. The results will be integrated with the hypotheses from the pH Stability Test and the tests in Section 3.1.3 to provide several conceptual models. The conceptual models will be the starting point for the development of mathematical models of groundwater chemistry at Yucca Mountain.

3.1.3 Tests to Isolate Water-Rock (Mineral) Interactions

3.1.3.1 General Approach

The Water-Rock Interactions Test is designed to evaluate the major and minor constituent compositional data obtained during the pH Stability and Redox Conditions Tests. The major and minor constituent information from these two tests will be assessed to evaluate the importance of possible reactions on groundwater composition and to specify particular reactions that are important. The Water-Rock Interactions Test will involve analyzing the data from Tests 1 and 2 using geochemical modeling tools to address questions such as: 1) With which mineral phases is the solution over-saturated and what is the degree of oversaturation in each case? 2) What is the degree of undersaturation of other minerals likely to be important? 3) Are there constituents in the waters that appear to be buffered by the rock materials? If so, which constituents are they? 4) What does the degree of oversaturation or undersaturation of various mineral phases say about the kinetics of the mineral-water interactions? Is this consistent with literature data that may be available for the phases involved? and 5) what is the importance of ion exchange and sorption processes to water compositions. The tests will be conducted using the EQ3/6 code and other appropriate geochemical codes as appropriate.

3.1.3.2 Summary of Methods

The method for the Water-Rock Interactions Test consists of calculating the speciation of the constituents in solution, determining saturation indexes, examining possible relationships between water compositions and the mineralogy of the batch tests and the columns, and quantifying, as much as possible, the reactions that control mineral dissolution and precipitation from the waters and effects such as ion exchange with test materials on water composition.

The data obtained from the tests discussed previously will be used as input to the EQ3NR portion of EQ3/6. The data will initially be checked for charge balance; solutions that exhibit a charge balance within 10% of neutral will be considered balanced. In previous use of data obtained from water samples, charge balance within 5% to 10% is almost always attained except when data are in error and, therefore, deficient in either cations or anions. Compositions that do not adequately charge balance will be reexamined for completeness and either retested or not used for further calculations.

Chemical speciation will be calculated using the EQ3NR section of the EQ3/6 package. Input information will be the composition measurements from the pH Stability Test and the Redox Conditions Test, including dissolved oxygen and pH, and the temperatures at which the particular tests were conducted. The speciation of each dissolved constituent will be calculated based on the thermodynamic data in the EQ3/6 package. The calculations will show not only the constituents and their amounts, but also the form the constituents take in the waters of interest. These calculations will show the relationships between test conditions (pH, temperature, and Eh) and solution speciation. Speciation calculations will also show the predominant and minor species in the waters, and will provide fundamental solution information for radionuclide sorption and solubility tasks.

Saturation indexes, as defined by Wolery (1983), are the log of the ratio of the ion activity product (IAP) to the dissociation constant (K) for the dissolution reaction of a solid. Saturation indexes greater than 0 indicate oversaturation which could lead to precipitation of a particular mineral, whereas saturation indexes less than 0 indicate undersaturation of a solution with respect to a mineral which would lead to dissolution of the mineral if it were present in the solid phase. Saturation indexes will be calculated for a variety of minerals, many more than could possibly exist in the test columns and/or in the rocks at Yucca Mountain. The number of saturation indexes calculated will be reduced by knowledge of the mineralogy of the rocks involved. The usefulness of the large number of calculations is to show the saturation conditions for minerals that may have been omitted from consideration by the investigator or those minerals that may not have been considered as important for a number of reasons. The saturation indexes will be examined, and probable mineral-water interactions (ion exchange, dissolution, and precipitation) will be considered.

Although saturation indices provide an indication of whether a given mineral phase is oversaturated or understurated in the water of interest, the extent to which the mineral dissolves or precipitates in a given experiment is a function of the kinetics of the mineral-water reactions. There are now data in the literature regarding the mineral-water reaction kinetics for some of the major mineral phases found in Yucca Mountain tuffs. This information will be included in the EQ3/6 calculations discussed above. However, the available data is limited and there will likely be pertinent reactions for which no kinetic data are available. In this case, the data from batch and column tests will provide the primary data set on water-rock interaction rates.

The different calculational results will be compiled and analyzed to formulate additional hypotheses about the reactions and processes controlling water composition, pH and Eh. the Water-Rock Interactions Test will also provide initial conditions for the Mathematical Model tests discussed in Activity 8.3.1.3.1.1.2.

Validation of the Water-Rock Interactions Test

The calculation methods used in the Water-Rock Interactions Test have a history of validation exercises published in the geochemical literature. The concepts and theory of using saturation indexes is developed fully by Parkhurst et al (1980) and Wolery (1983) and will not be developed further in this study plan. Use of the geochemical code EQ3/6 (or other codes if such are used) requires that reproducible results from a known set of "benchmark" inputs be attained to show that the code is performing as it should. There is an extensive body of test input files and a library of corresponding outputs that will be used to test the performance of the geochemical code. The repeated use of test cases during the Water-Rock Interactions Test will show that the code is or is not performing as expected.

Validation of the calculations concerning speciation and/or mineral-water interactions will be achieved by comparison of predicted results to measured results when measured results are known. Repeated simulation of calcite dissolution and subsequent measurement of a calcite-water system will be employed for validation purposes. Other similar systems will be designed and used periodically to show the correspondence between measurement and prediction. The body of evidence developed through comparisons of predictions and measurements will show that the methods used for the Water-Rock Interactions Test are reproducible and agree with actual experiments or that the methods need adjustment and should be carefully reviewed to ensure that the predicted results are representative of the system being measured.

Validation of the kinetic data and calculations used in this test will be more difficult. Basically, validation will be defined by the degree to which the data and calculations allow successful modelling of blind batch and column tests. The blind tests will involve prediction of water compositions that would result from water-rock interactions conducted under conditions different (e.g., different pH, ionic strength, etc.) from those used to define an original model.

3.1.3.3 Equipment for Test 3

The equipment for test 3 is as follows: the geochemical code or codes of choice (EQ3/6 nominally), the necessary documentation to run the code or codes, a set of "benchmark" examples that have been previously and independently tested, and the appropriate computer for code execution. Additional laboratory equipment may be required for small-scale validation exercises, but the required materials are standard in most laboratories.

3.1.3.4 Accuracy and Precision

The accuracy of the results of the Water-Rock Interactions Test depends on (1) the completeness of the conceptual model on which the calculations are based, (2) the precision with which the experiments were carried out, (3) the accuracy of chemical analyses of waters and mineral samples, (4) the accuracy and completeness of the thermodynamic database used with EQ3/6 and (5) the accuracy and completeness of kinetic data used in the calculations. The thermodynamic database will not be reviewed or developed as part of the groundwater chemistry model investigation. However, data in the EQ3/6 database are a project resource and have been reviewed under current QA/QC programs. Therefore, accuracy in the database is assumed and will not (and need not, in most cases) be shown.

Accuracy of the predictions depends on the reactions and processes that are defined as part of the modeling efforts. If reactions are incorrect or improperly described, there will be large discrepancy between the predicted and measured results. The accuracy of the predictions also depends on accurate information in the input used for the calculations. Reactions included in the calculations will be checked for appropriateness before and after the calculations are made. The input data will be checked against the original data so that typographical errors can be corrected before the calculations are run.

The precision of the Water-Rock Interactions Test depends on the precision of the data used for the calculations. The inherent precision (or uncertainty) in measured values will be incorporated into the calculations. Doing so will provide an estimate of the range of values that a calculated parameter can assume. The precision of the predicted results will show the combined effects of the precision of all the variable that went into a calculation. Using the precision of the input data as the source of precision in the calculations will provide the most realistic values for constituent speciation, mineral dissolution/precipitation reactions, and ion exchange processes in the rocks.

3.1.3.5 Results of Water-Rock Interactions Test

The Water-Rock Interactions Test will provide the geochemical calculations required to relate the data from the pH Stability Test and the Redox Conditions Test to the reactions and processes important in controlling the overall composition of groundwaters in Yucca Mountain. Speciation calculations based on the results of the previous two tests will show changes in speciation as water moves through different geologic materials. Changes in pH and/or Eh will be examined with regard to changes in speciation to determine compositional differences in water in the columns during each test. Changes in speciation during the course of the tests will also provide data on groundwater differences with time to other tasks such as radionuclide sorption and radionuclide solubility.

Calculations of saturation indexes using data from the pH Stability and Redox Conditions Tests will provide information about the mineralogical control on water composition, pH buffering capacity, and water-rock interactions that control Eh. The pH Stability and Redox Conditions Tests will provide composition data in different geologic materials as well as composition data over relatively long time intervals. Thus, one of the more important results of the Water-Rock Interactions Test will be the changes predicted and observed in saturation indexes during the laboratory column tests. The information about saturation indexes will be fundamental in identifying water-rock interactions heretofore omitted as well as describing known or suspected interactions in a manner that will allow mathematical testing. Mathematical testing in Activity 8.3.1.3.1.1.2 will integrate several elementary processes including but not limited to calcite precipitation (or dissolution) into the overall model of groundwater chemistry at Yucca Mountain.

Data will be synthesized on the possible mechanisms of how groundwater composition will change in time and with imposed chemical environments such as those induced by construction of a repository. These data will be obtained during Tests 1 and 2 and during the data analysis of those tests. The hypotheses generated in the earlier tests will be critically evaluated using the full data set, and either the hypotheses will be rejected during the Water-Rock Interactions Test or they will be refined and passed on to Activity 8.3.1.3.1.1.2 as conceptual models.

The Water-Rock Interactions Test is the integrating test for Activity 8.3.1.3.1.1.1. Not only will several working hypotheses be tested with experimental data, but sets of hypotheses concerning the groundwater chemistry of Yucca Mountain will be generated from the hypothesis testing. The pH Stability and Redox Conditions Tests are designed to give information about different reactions and processes that occur as a result of specific geochemical conditions. the Water-Rock Interactions Test takes the results of those tests and combines them into conceptual models of groundwater chemistry changes through time at Yucca Mountain. The final set of hypotheses, or the set of conceptual models, will be prepared in the Water-Rock Interactions Test and passed to Activity 8.3.1.3.1.1.2 for further testing. The results of the Water-Rock Interactions Test will include a summary of the processes and reactions that are supported and refuted by the data in the pH Stability and Redox Conditions Tests and the geochemical analysis in the Water-Rock Interactions Test.

The final part of the Water-Rock Interactions Test and of Activity 8.3.1.3.1.1.1 will be to formulate into starting models the hypotheses generated by integration of data and geochemical testing. The hypotheses so generated will be tested further using detailed geochemical codes and by comparison to natural analogs that incorporate many if not all of the processes identified at Yucca Mountain. The importance of establishing the processes and reactions in the saturated and unsaturated zones is that the descriptions of these processes are the foundation for building a more predictive mathematical model of groundwater chemistry.

3.2 Activity 8.3.1.3.1.1.2: Description of Tests and Analyses for the Mathematical Model

The Mathematical Model consists of three components: 1) the conceptual models developed from data obtained in previous tests and formulated in the Water-Rock Interaction Test; and 2) testing of the conceptual models against possible scenarios imposed by changing climates;, construction and emplacement of a nuclear waste repository; and other activities of man in the Yucca Mountain vicinity; and 3) validating the techniques and methods used to develop a quantitative model of groundwater chemistry. The approach to developing a mathematical model of Yucca Mountain groundwater depends on validation of the methods used to obtain data for the conceptual models and the methods of testing the concepts or hypotheses mathematically. Conducting laboratory experiments for the lifetime of the repository is impossible, so extensive modeling must be used to show the possible influence of a repository on groundwater chemistry. In order to lend credibility to the modeling efforts, the soundness of the mathematical methods must be ensured. Activity 8.3.1.3.1.1.2 is the testing and development phase that will result in a model or set of models that will predict groundwater chemistry during the lifetime of the repository.

3.2.1 Validation of Mathematical Methods

3.2.1.1 Approach

The overall approach is to validate the methods that will be used to develop the mathematical model. The validation task becomes impossible when the 100,000 year lifetime of the repository is considered. There is no rational means to providing test data for that time period, so even the best models will be plagued by being untestable in the 100,000 year span. Through careful testing, however, the mathematical methods used to predict water composition in a variety of conditions should correspond to measured data of the same affects. Therefore, the methods that will be used for the mathematical model will also show that they can predict the results of different laboratory tests and the results of geochemical processes at work on known systems in the field. Demonstration of the capabilities to model laboratory and field systems will lend significant credibility to estimating the effects of emplacement of a repository at Yucca Mountain. The inherent uncertainties in the mathematical models will be estimated to show the effects of the uncertainties on the predictions. The sensitivity of the models to uncertainty in the input parameters will also be evaluated to ascertain those reactions and/or processes that are most influential in determining the groundwater composition

3.2.1.2 Summary of Methods

The method used to test the hypotheses will be geochemical modeling of water composition data obtained from the field (e.g., Kerrisk, 1987) and from laboratory experiments in Activity 8.3.1.3.1.1.1. EQ3/6 is the code that will be used to provide most if not all of the geochemical modeling; other codes (e.g., PHREEQE, Parkhurst et al, 1980) could be used if or when testing of processes is required for which EQ3/6 has no capability. Such processes would include but are not limited to surface complexation or adsorption of radionuclides onto clay minerals.

Several studies (e.g., Knauss, 1984a, 1984b; Knauss et al 1985) show that geochemical models can be used to successfully predict the water chemistry resulting from laboratory tests of diagenetic processes with rocks. The same principles will be used in Activity 8.3.1.3.1.1.2 to demonstrate that the results of the column tests in Activity 8.3.1.3.1.1.1 can be predicted by way of geochemical modeling codes. The hypotheses generated from Activity 8.3.1.3.1.1.1 will provide the initial models from which the predictions will begin. Initial predictions of water composition, pH, and/or Eh will be made, then compared to the laboratory test results. Individual processes and reactions in the models tested will be refined in order to provide the best possible mathematical description of the processes at work. Predictions will be made with the refined models and again compared to the laboratory data.

Continued occurrence of discrepancies between predictions and laboratory data could have several causes. One is an inadequate description of the processes of interest. The mathematical interpretation of the processes may be flawed and require reinterpretation or additional fine tuning. Alternatively, the hypotheses upon which the descriptions are based may have been incorrectly generated during Activity 8.3.1.3.1.1.1 and therefore require reconsideration. Another cause for discrepancy is inadequate data in the geochemical database to support modeling of the processes in a model. This could likely be the case when modeling clay mineral reactions, or modeling radionuclide speciation and solubility. Thermodynamic data for clay minerals and most radionuclides is not very well known or has a wide range of values. Therefore, the uncertainty in calculations involving these species is large. Use of species with uncertain values in modeling may result in a large range in the predicted values. Another potential cause for discrepancies is that the laboratory tests were not conducted properly, thereby providing data on a different set of processes or under different conditions than expected. Using a mathematical description to model a laboratory test would be obviously flawed if the laboratory data were generated under a different set of test conditions than the nominal ones. Analyses of the laboratory tests during and after the tests are conducted will ensure that the processes measured are accurately described.

3.2.1.3 Results

The mathematical modeling conducted in Activity 8.3.1.3.1.1.2 will show that the processes and reactions tested in Activity 8.3.1.3.1.1.1 can be predicted accurately. The comparison of predicted results to laboratory data will show where the model best describes the processes and where discrepancies remain. The comparisons will also show the limits concerning the conditions for which a particular model can be used. For example, a model that successfully predicts the results of pH changes in the pH Stability Test may not correctly predict Eh changes of the Redox Conditions Test under all conditions. In the case or cases where there are obvious limits to usefulness of a model, those limits will be fully stated to ensure the proper use of the model. It is expected that one to four mathematical models will result from this activity. Each will have a description of the conditions for which it is valid and not. The set of models and the caveats about their use will be the final product of this investigation. The models developed in Activity 8.3.1.3.1.1.2 will be used to evaluate different scenarios for their effects on groundwater chemistry and for subsequent use by other tasks. The results will include sensitivity and uncertainty analyses that will be fundamental in establishing the limits on the usefulness of the models. The uncertainty analysis will provide confidence limits on the predictions and sensitivity analyses will show the processes, reaction, or possibly parameters that most affect water composition, pH, and Eh. Sensitivity and uncertainty analyses will be discussed in more detail in Section 3.2.1.4.

3.2.1.4 Accuracy and Precision in Model Validation

Uncertainty in predictions or values used as input to models is considered a measure of error or precision for the purposes of this study plan. Sensitivity of predictions is related to accuracy and serves to indicate which of the many processes in a model most influences the outcome or prediction. Estimating both sensitivity and uncertainty is of fundamental importance to presenting the results of the Mathematical Model Activity and building strength in the predictions.

Uncertainty and sensitivity analyses will be discussed in relation to a general model such as:

$$Y_i = f(X_j, X_{j+1}, \dots, X_n),$$

where Y_i is the prediction (or response) of a model that uses values of X_j through X_n in order to calculate the value of Y_i. Neter et al (1985) and Iman and Shortencarier, 1984) give detailed descriptions of analytical expressions and numerical models of the same form as above and a more in-depth discussion of uncertainty and sensitivity analyses. In the above general example, the value Y_i has an error term or some uncertainty associated with it. Sometimes this uncertainty would be the ± value attached to the estimate such as 10 ± 2. The uncertainty arises from several sources. First is the inherent uncertainty in the values for X_j through X_n. Since each variable X_j is an estimate of a parameter, there is an associated uncertainty in each X_j. Thus, each value that goes into the calculations of Y_i adds its own uncertainty to the uncertainty of Y_i. The calculation of Y_i reflects, therefore, the uncertainties of all the values used. A second source of uncertainty in Y_i comes from the processes that are included in the model of Y_i. For example, process A of the model might under predict a part of Y_i whereas process B might over predict part of Y_i but not as much as process A under predicts. The result is somewhere between over- and under-prediction of Y_i.

The sensitivity of Y_i to different variables within the set of X_j to X_n is similar to the uncertainty. Besides uncertainty in each value, one or several of the variables X_j to X_n may cause the prediction of Y_i to become smaller or larger at a rate greater than other variables. Alternatively, one or more of the variables may carry a greater or lesser weight and thereby influence the value of Y_i. Determining the variables that most influence the prediction of Y_i is the object of sensitivity analysis. Sensitivity analyses can be used to show the variables where expenditure of more time or resources are required in order to produced significantly more accurate and/or precise predictions from a given process in addition to simply indicating the processes that are the most important in a prediction. Sensitivity analysis will be pursued in the groundwater chemistry model development to show the processes that influence pH, Eh, and composition the most, given specific environmental scenarios. The information will also indicate the processes that must be described in the most detail or the best understood, as well as showing the processes that can be used with less understanding.

Uncertainty analysis will show the error or the variation in the predicted values of pH, Eh, and water composition. The uncertainty will also show the overall uncertainty related to the uncertainty of each of the parameters in the model. The uncertainty of the prediction will indicate if the uncertainties in the model parameter is of adequate quality; if not, the understanding of the process must be refined and/or the values that represent that process for the conditions being tested must be more carefully determined. Ideally the values of pH, Eh, and composition, plus or minus the uncertainty, that are predicted with the Mathematical Model would be about the same as the values measured in the tests, plus or minus their uncertainty. Therefore, the accuracy and the precision of the predictions can be established for the conditions being tested. The methods of sensitivity and uncertainty analysis are described in greater detail by Iman et al (1981a, 1981b), Vaurio (1983), and McKay et al (1979).

3.2.2 Testing Groundwater Chemistry Models

3.2.2.1 Approach

A major input to the mathematical model consists of the hypotheses generated during Activity 8.3.1.3.1.1.1. The hypotheses will include ranges of compositions, pH, and Eh that will limit testing of mathematical models to those conditions that are proposed or most likely at Yucca Mountain. The hypotheses will be included into the geochemical model by translating the processes and reactions into a form compatible with the model. For example, a hypotheses that states that precipitation of calcite is important between pH 6 and 7 in waters with Ca^{2+} concentrations of 50 to 100 mg/L will be written as a series of statements compatible with the format of the geochemical code.

Individual processes will be tested for their appropriateness if those tests were not a part of the hypothesis development during Activity 8.3.1.3.1.1.2. Grouping of related hypotheses into cohesive "units" of processes will be made to provide a comprehensive model or models of the processes that control groundwater composition, pH, and Eh. Testing the groups of processes will result in either the statement of a formal mathematical model or a proposed model will be modified so that it can be stated as a formal model. The postulated reactions and processes not supported by predictions and the laboratory data will be eliminated during the testing, whereas the processes and reactions that are supported by the laboratory data and test favorably will be used in formal descriptions of the processes. The large number of hypotheses expected from Activity 8.3.1.3.1.1.1 will be reduced to several groups of hypotheses that will be formulated as mathematical models.

Since testing of the models with laboratory or field data for the life of the repository is not possible, testing the models will mean that particular scenarios are tested using the group of mathematical models, and the resulting predictions will describe a range of groundwater compositions. The range of predictions will be the part of the input for performance assessment calculations and other tasks requiring the range of probable water compositions from a given scenario. The approach to the testing is to provide the range in groundwater composition, pH, and Eh that would result in the future if specified conditions exist.

3.2.2.2 Identification and Range of Input Parameters

The compositional parameters such as Ca^{2+}, pH, and Eh will be identified during Activity 8.3.1.3.1.1.1. Those parameters that are important to the groundwater composition as determined during different testing scenarios will be specifically named and listed as part of the mathematical model formulations. The ranges of the values of the parameters will be given so that accurate testing and reasonable measures of uncertainty can be estimated in the predicted results. The probability distribution of values of a given parameter will be included in the description of the parameter where possible so that reasonable uncertainty analyses can be performed. The result of testing in Activity 8.3.1.3.1.1.1 will be a "catalog" of parameters and their values, important processes, and reactions that describe the processes. The possible scenarios that involve groundwater chemistry will also be specified as test conditions. The scenarios will include but are not limited to possible increase in atmospheric $CO2_{(g)}$, a long-term change in climate that results in cooler, wetter conditions, and a repository releasing more of its inventory than expected.

3.2.2.3 Summary of Test Methods

The sets of hypotheses generated in Activity 8.3.1.3.1.1.1 provide the set of testing conditions for the mathematical model. The parameters and the distribution of the values that determine pH, Eh, and water composition will be the input variables to the models, and the geochemical processes and reactions that control pH, Eh, and composition will be formulated into the modeling code. This modeling scheme provides the opportunity to systematically test the variety of chemical conditions that may be imposed on the repository as a result of emplacement of nuclear waste.

The results of the testing will show which sets of hypotheses, or which conceptual models, describe the test conditions the best. For example, one set of hypotheses may state that groundwater composition in ambient current conditions is controlled by ion exchange of Ca^{2+} and Na^{+} whereas a second set of hypotheses may suggest that Ca^{2+} is controlled by calcite dissolution and Na^{+} from mixing of tuff-derived water with Paleozoic carbonate water. Testing these hypotheses by way of the geochemical codes and the laboratory test data will show which set of hypotheses is consistent with the data. The hypotheses remaining after the tests will be the models for predicting groundwater composition during the lifetime of the repository. These hypotheses will be restated and will be assigned to the conditions for which they are appropriate. For example, the set of models that describes Eh changes as a result of possible radionuclide release will not be used to predict groundwater chemistry that could result from rain-water percolating through the unsaturated zone because the scenario and the model are not an appropriate combination. A test matrix will be developed to show the scenario that is being examined, the hypotheses about the processes and reactions that control geochemical conditions, and the values of the parameters (and their distribution). The results of the tests will also be added to the matrix to show which parts of the set of hypotheses are supported or refuted by the testing. Predictions of groundwater chemistry using the models that survive testing will be conducted in a similar way. A matrix of conditions, processes and parameters will be developed, the tests will be run, and the results will show the possible range of water compositions based on the models used.

3.2.2.4 Results

The results of testing the sets of hypotheses from Activity 8.3.1.3.1.1.1 will be the set of mathematical models that can be used for prediction of groundwater chemistry. The sets of hypotheses that are not supported during the testing will either be refined, tested again, or discarded. The models that are supported will consist of the set of hypotheses, the conditions for which the model is valid, the parameters that are required, and the list of geochemical processes and reactions that are important in the model. The tested mathematical models will have predictive capability and can be used to test specific conditions that occur presently or are considered probable in the future of the repository.

The possibility of more than one set of hypotheses explaining water composition, pH, and Eh under specific conditions is not neglected. One set of hypotheses about a specific process may explain the observations and describe processes adequately, but the probability that there is another set of hypotheses that will also explain the same process increases as the number of scenarios, model parameters, and processes of interest increases. Since the nature of the groundwater chemistry model is to show the possible groundwater chemistry as a result of continued water-rock interactions, the non-unique solutions must be included as alternate sets of hypotheses or alternate models. Testing alternative models relevant to particular scenarios will be conducted to show the effects of all competing models on groundwater composition. The results of testing competing models should provide a range of composition values, and these values will be incorporated into the uncertainty analyses for the predictions.

Predicted water compositions will also be one set of results from the testing of the models. As discussed previously, the models that are supported by testing using the geochemical codes will be used for predictive purposes. The results of the predictions will be a set or range of compositions, pH, and Eh values for the particular scenario tested. Each prediction will be accompanied by an estimate of uncertainty that will indicate the confidence with which conclusions can be drawn about the effects of a scenario on water composition.

3.2.2.5 Accuracy and Precision

The accuracy of testing the conceptual models will be impossible to demonstrate over the 100,000 year life of the repository. However, accuracy of the tests on a shorter term can be demonstrated by comparison of predictions with data from previous laboratory tests and field data from other geological settings. The accuracy of the descriptions of individual processes and reactions that comprise the mathematical models will determine the accuracy of the predictions. Assessing whether the predicted values are the same as the actual values of specific processes, however, will be complicated by the fact that the actual values may not be known with much certainty. A better measure of how predictions and measured values compare, or the reliability of predicted values of possible future events, is the range of the predicted values. Variation of the predicted values is a measure or precision more than accuracy if the actual values are not known. Therefore, the precision of the predictions is the measure of their reliability or the indicator of confidence in the predictions.

Uncertainty analysis will provide the estimates of the range of predicted values. There will be uncertainty associated with each part of each hypotheses, including uncertainty in the reactions that control pH to uncertainty in the processes that control sorption of radionuclides on mineral surfaces. The uncertainty estimated for the predictions will reflect all the uncertainty in the different part of the process. Including the information such as variation in water composition, variation in pH and Eh values, and variations in the actual conditions tested will produce estimates with definite ranges. The ranges of the predicted values will be the guidelines used to determine if the occurrence of a particular environment or chemical condition at Yucca Mountain will result in groundwater compositions that are beneficial to or detract from repository performance. Uncertainty and sensitivity analysis are discussed in more detail in Section 3.2.1.4.

Sensitivity of the predictions to particular parts of the conceptual models will show the degree to which each of the hypotheses influences the conceptual model. The hypotheses that comprise a conceptual model can be ranked as to their importance to that model. The precision of the predictions can be analyzed in terms of the hypotheses that cause the majority of the variation in the range of predicted values. Improving the precision of the predicted values becomes a process of refining the most sensitive hypotheses in the conceptual model being tested. Refining the hypotheses could mean constraining the range of values to a smaller range, altering a statistical distribution of a particular set of parameters, or other related reconsiderations of the process or processes in question. The object will be to provide predictions over the smallest range possible using models that are developed from sound testing and evaluation.

3.2.3. Modeling Long-Term Water-Rock Interactions

3.2.3.1 Approach

Tested conceptual models will be formulated into mathematical models, and geochemical codes will be used to predict the results of specific scenarios on the groundwater chemistry at Yucca Mountain. The process of modeling potential changes in groundwater composition as a result of different scenarios is considered long-term water-rock interactions modeling. Long-term is the length of time from emplacement of nuclear waste through the 100,000 year regulatory time of concern. The nature of groundwater chemistry is a function of interactions of groundwater with the rocks and minerals of Yucca Mountain during the lifetime of the repository. Predicting the results of these interactions is one goal of the groundwater chemistry model investigation, and the models developed through the investigation will provide the information to meet the goal.

The approach to modeling long-term water-rock interactions will be to exercise the tested mathematical models using appropriate data and potential environmental scenarios that could exist at Yucca Mountain during the lifetime of a repository. Modeling exercises will give estimates of changes in groundwater chemistry as well as potential changes in the rocks and minerals involved. One example of the kinds of predictions resulting from the mathematical models is showing the effects of silica activity on water composition through time as well as suggesting the composition of the silica phases that form and/or dissolve. Parallel compositional change in rock and water will be shown in order to show the entire domain of changes resulting for particular processes. The predictions will also show the estimates of the uncertainty inherent in the calculations, and the estimates will be derived using uncertainty analysis. The sensitivity of the predictions for specific parts of the models will also be estimates so that important processes influencing rock and water compositions can be identified.

3.2.3.2 Geochemical and Environmental Conditions

A range of scenarios to be tested give different geochemical and/or environmental conditions that will influence groundwater composition. The scenarios include but are not limited to atmospheric $CO_{2(g)}$ changes with time; climatic shifts to colder, wetter climates; increased infiltration into the saturated zone and/or unsaturated zone; and alteration of the surrounding rocks and ambient conditions by construction of the repository. The possibility of a spatially and temporally extended zone of heating has recently become a condition of interest that may provide a scenario for long-term testing, even in the far-field. The models will be developed in activities and tasks discussed previously to include the full range of geochemical conditions that could be encountered during the lifetime of the repository and are considered important. Sufficient testing on the laboratory scale, comparison of hypothesized processes occurring at Yucca Mountain with natural analogs in different areas, and testing of known systems will provide the opportunity to show that the mathematical models predict reasonable short-term effects. Extension of the models to long-term predictions of water-rock interactions will necessarily contain large uncertainties, but the impact of the uncertainties will be estimated and should show that the extrapolation over time is not unreasonable.

3.2.3.3 Methods and Geochemical Codes for Water-Rock Testing

The methods discussed in Sections 3.2.1 and 3.2.2 result in a set of mathematical models that are validated over specific ranges of conditions. The validated models should show agreement between predictions and data from laboratory experiments and/or comparison to natural systems, and will be used to predict the water-rock interactions in the long-term. Models that do not show agreement will be reconsidered. Data on initial conditions such as pH, Eh, and water composition will be used as input to the geochemical codes. The predictions will be based on the scenario chosen for evaluation, the initial data, and the relevant processes described in the mathematical model. The model will be exercised using the range of variables or their distributions of values and scenario conditions to provide estimates of the effects of those scenarios on water chemistry.

The EQ3/6 code will be the main geochemical code used. Other codes could be employed if required processes are not adequately accommodated in the existing EQ3/6 code. One process that is not used in the EQ3/6 code is surface complexation. If surface complexation is a process of importance to groundwater composition, a different code may be used. The code and the use of the code will be selected at a more appropriate time.

3.2.3.4 Results

The predictions of water composition, pH , and Eh are the desired results of modeling long-term water-rock interactions, as are the changes in rock composition as a result of the modeling. The composition of the rocks ties to other Investigations, most notably Mineralogy and Petrology, Investigation 8.3.1.3.2 and Radionuclide Adsorption, Investigation 8.3.1.3.4. Changes in water composition indicate new chemical conditions in the groundwater-rock (mineral) system, and could alter the performance of the geologic barrier to radionuclide migration. The predicted water compositions are the interest of the groundwater chemistry investigation, but the potential changes in rock and minerals will be of interest to other tasks investigating the geochemical aspects of Yucca Mountain.

3.2.3.5 Accuracy and Precision

The accuracy and precision of the predicted water compositions and predicted water-rock interactions will be a function of the accuracy of the processes included in the mathematical models as discussed in section 3.2.1.4. The range of predictions will indicate the possible changes in water composition, and the potential changes in water composition will show possible alteration of rocks and minerals. The range of the predicted values indicates the precision and accuracy or the water compositions. Therefore, the range of predicted values will also indicate the accuracy and precision of the possible compositions of the rocks and minerals. Improving the accuracy and precision in these predictions means refining the hypotheses and/or refining the estimated values for the parameters in the model as discussed previously.

Activity 8.3.1.3.1.1.2 will provide the mathematical models or formulations of the conceptual models that will be used to predict groundwater chemistry as a result of long-term water-rock interactions. The mathematical models will be based on the hypotheses of the important processes and reactions that occur between rock and groundwater. The mathematical models will be the predictive tools that will be used to ascertain the effects of imposed scenarios on water compositions at Yucca Mountain and the importance of future water compositions on performance of Yucca Mountain as a nuclear waste repository.

4.0 APPLICATION OF RESULTS

4.1 Performance Issues

The performance issues important to this study are listed and discussed in Section 1.3. This study will not be used as the sole source of information for resolution of Issues 1.1, 1.5, or 1.8. However, the groundwater chemistry study will supply data, results of calculations, and predictions to other studies (e.g., 8.3.1.3.7) that will calculate the performance of the candidate repository under different environmental scenarios. The information needed for these calculations will be developed by Study 8.3.1.3.1.1 (Groundwater Chemistry Model) and augmented by information from other appropriate studies. For example, Issue 1.1 (through Information Need 1.1.1) requires data and predictions on major and minor cations and anions in groundwater at the present time, and over a period of time, to evaluate the performance of the candidate repository under the nominal case. This information will be supplied together with information on the limits within which it can be used (i.e., experimental data, results of calculations, etc.). Section 1.3 detailed the types of information needed from this study to support the resolution of these performance assessment issue.

4.2 Interface with Other Site Characterization Studies

Results of this study will also be used to support site characterization activities in the geochemistry (8.3.1.3), geohydrology (8.3.1.2), and climate (8.3.1.5) programs. Not only is information from each program important to the development of the groundwater chemistry model, but also Study 8.3.1.3.1.1 will supply information important for completion of tasks in these programs at different times during site characterization activities. The following discussion summarize the interfaces with the other programs, investigations, and studies.

Study 8.3.1.3.1.1 (Groundwater Chemistry Model) derives information from several studies in the geochemistry and geohydrology programs. Studies 8.3.1.2.2.7 (Hydrochemical Characterization of the Unsaturated Zone) and 8.3.1.2.3.2 (Characterization of the Saturated Zone Hydrochemistry) will provide fundamental data on water composition from the unsaturated and saturated zones. These data and data from the literature are the primary sources to be used in developing the conceptual model and ultimately in developing the mathematical model. Studies 8.3.1.2.2.7 and 8.3.1.2.3.2 will involve collection of data and samples for studies of groundwater chemistry from new bore holes. The resulting data will be important for the continued development of the conceptual and mathematical models of Study 8.3.1.3.1.1 because they will be the only new data collected on water composition for this project. An efficient means of communicating the new data will be established so that timely use can occur.

Data on climate changes through time will also be required and will be provided by investigations under the climate program (8.3.1.5). This information will be important to estimating the effects of different climates on the variables controlling groundwater chemistry. Climatic data will also be important for the simulations discussed in Section 3, because the conceptual and mathematical models depend largely on interactions of rocks and water under chemical conditions different from those present today. The climatic data of interest will include rainfall compositions, amounts, and patterns; concentrations of atmospheric gases and other gases that could change groundwater composition; and the effects of acidic precipitation on the composition of recharge water.

Several studies within the geochemistry program will provide information to Study 8.3.1.3.1.1 and will also receive necessary information from Study 8.3.1.3.1.1. Study 8.3.1.3.2.1 (Mineralogy, Petrology, and Chemistry of Transport Pathways) will supply data on mineralogy and petrology, including information on the kind of amount of minerals of interest to Study 8.3.1.3.1.1 Data on mineral Alteration (Study 8.3.1.3.2.2, History of Mineralogic and Geochemical Alteration of Yucca Mountain) and mineral transformation kinetics (Study 8.3.1.3.3.2, Kinetics and

Thermodynamics of Mineral Evolution) will show the processes and rates of reactions that could affect groundwater chemistry over time. This information will be important both for the simulations in Study 8.3.1.3.1.1 and the interpretation of the proposed tests discussed in Section 3.

Information on sorption of radionuclides and other constituents will be obtained from Investigation 8.3.1.3.4 so that the effects of sorption on groundwater composition can be included in the conceptual model. Groundwater chemistry information will be an important input parameter for the sorption experiments performed in Investigation 8.3.1.3.4, and therefore the most current data and interpretations on groundwater chemistry are required. Investigation 8.3.1.3.5 will also require groundwater composition information for experiments designed to determine the solubility of different radionuclides. The bounds of possible water compositions will be established in Study 8.3.1.3.1.1 with required information on radionuclide solubility and speciation so that information on precipitation and dissolution of radionuclides can be incorporated into the conceptual model.

Ultimately, the calculations from studies discussed previously will be integrated into Investigation 8.3.1.3.7 by calculations of radionuclide retardation sensitivity to resolve Performance Assessment Issues 1.1 and 1.8. This discussion shows, however, that several interfaces exist between Study 8.3.1.3.1.1 and the other studies and investigations involved in site characterization activities. Figure 3 is a schematic diagram of the interfaces among the different investigations in the geochemistry, geohydrology, climate and engineered barrier programs.

5.0 SCHEDULE AND MILESTONES

5.1 Duration of Principal Test Activities

The duration of the principal test activities, including preparation of technical procedures, experiments, and reports, are shown schematically in Figure 4.

5.2 Timing of Tests

As discussed previously, Study 8.3.1.3.1.1 depends on information from other YMP studies in order to develop the conceptual models and mathematical models of groundwater chemistry. Many of these data can be incorporated into Study 8.3.1.3.1.1 at intermediate stages of model development, so that the timing of tests of other investigations does not severely restrict the model development. The exceptions are data from the unsaturated-zone tests, Study 8.3.1.2.2.7. Since few data exist on unsaturated-zone groundwater composition, information from Study 8.3.1.2.2.7 should be available to Study 8.3.1.3.1.1 as soon, and as often, as possible. Without this information little preliminary calculation of testing on unsaturated-zone groundwater composition can be done. Results from tests in Study 8.3.1.2.3.2 (saturated-zone groundwater) are also important for the development of the saturated-zone tests. Data exist on saturated-zone water compositions, and these can be used for preliminary model stages.

Delays in the tests and analyses of this study may delay experiments in Studies 8.3.1.3.4 and 8.3.1.3.5, but the impact should be small because groundwater composition data of usable quality can be obtained from Study 8.3.1.3.1.1 at any time during the project. Final radionuclide retardation calculations and performance assessment could be delayed considerably if the groundwater chemistry tasks are delayed.

5.3 Interrelations of Activities

The interrelations of the activities in the geochemistry, geohydrology, and climate programs are suggested in this study and are shown in Figures 3 and 4. The major milestones for this study are listed in Table 1.

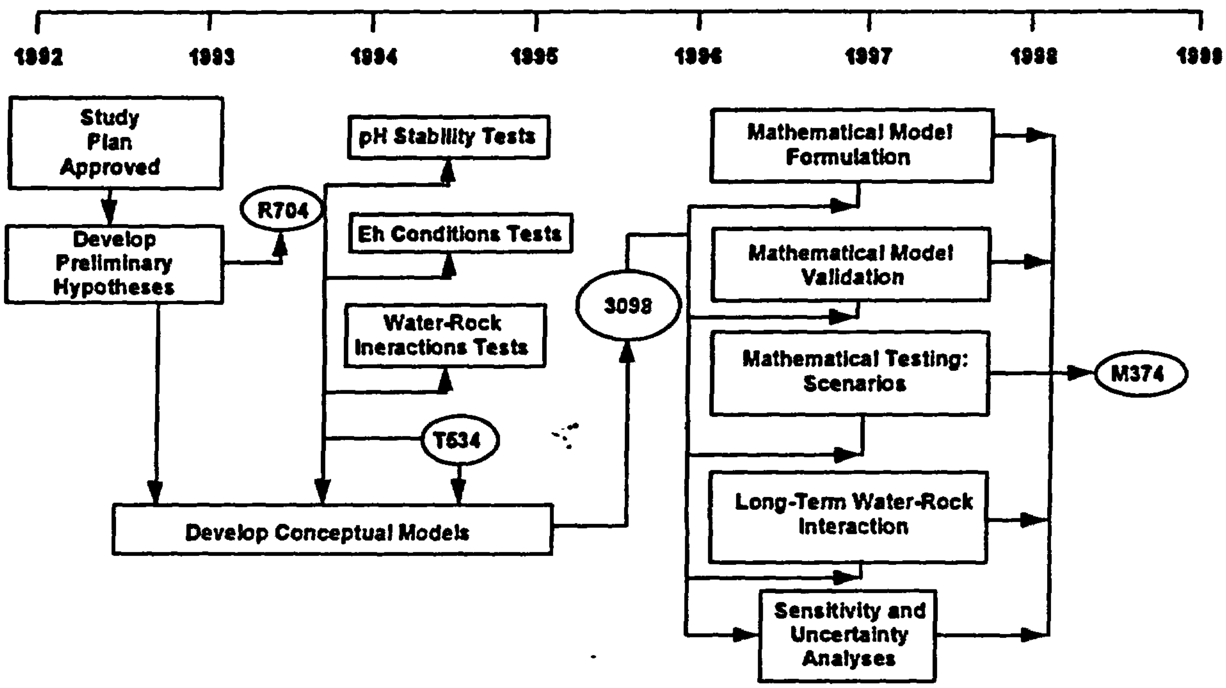

Figure 4. Schematic Showing Timing of Activities and Milestones. See Table 1 for Milestone Identification.

TABLE 1

MILESTONES FOR GROUNDWATER CHEMISTRY STUDY

Milestone	Description
R704	Interim Report of Groundwater Chemistry
T534 (3387)	Modeling and Experimental Results of Groundwater Chemistry
3098	Conceptual Model of Groundwater Chemistry
M374	Final Report, Groundwater Chemistry Model, Yucca Mountain

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GROUNDWATER CHEMISTRY MODEL OF YUCCA MOUNTAIN

The following detailed technical quality assurance procedures will be used in this Study:

LANL-INC-DP--15	Crushed Rock Column Studies
LANL-INC-DP-60	Preparation of NTS Samples for LANL YMP Solid Core Experiments
LANL-EES-DP-16	Siemens X-Ray Diffraction Procedure
LANL-EES-DP-25	Clay Mineral Separation and Preparation for X-Ray Diffraction Analysis
TWS-HSE12-DP-302	Cation and Anion Exchange
TWS-HSE12-DP-307	Sample Identification and Control
TWS-HSE12-DP-311	Sample Preparation
TWS-HSE12-DP-312	Particle Size Reduction of Geologic Media
TWS-HSE12-DP-314	Electrical Conductivity Measurement
TWS-HSE12-DP-315	Calibration and Use of Temperature Measurement and Control Devices
TWS-HSE12-DP-316	Preparation of Standard and Reagent Solutions
TWS-HSE12-DP-317	Calibration and Use of Analytical and Top-Loading Balances
TWS-HSE12-DP-318	pH Measurement, Acid-Base Solution Standardization, and Total Alkalinity Determination
TWS-HSE12-DP-320	Measurement of Dissolved Oxygen
TWS-HSE12-DP-323	Spectrophotometric Determination of Constituent Concentrations in Solution
LANL-EES15-DP-326	Ion-Chromatographic Determination of Constituent Concentrations in Solution
LANL-EES15-DP-328	Use of Ion-Selective Electrode to Determine Ion Concentrations in Solution
TWS-LBL-DP-06	Eh (Redox Potential) Measurements for the Yucca Mountain Waste Element Solubility Study

Enclosure 2